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<https://doi.org/10.1016/j.hydromet.2018.05.006>

O'Malley, G.P. and Nikoloski, A.N. (2018) The acidic ferric sulfate leaching of primary copper sulfides under recycle solution conditions observed in heap leaching. Part 1. Effect of standard conditions. Hydrometallurgy

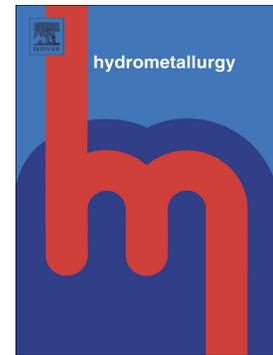
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## Accepted Manuscript

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PII: S0304-386X(17)30846-0  
DOI: doi:[10.1016/j.hydromet.2018.05.006](https://doi.org/10.1016/j.hydromet.2018.05.006)  
Reference: HYDROM 4812  
To appear in: *Hydrometallurgy*  
Received date: 10 October 2017  
Revised date: 12 March 2018  
Accepted date: 3 May 2018

Please cite this article as: Glen P. O'Malley, Aleksandar N. Nikoloski , The acidic ferric sulfate leaching of primary copper sulfides under recycle solution conditions observed in heap leaching. Part 1. Effect of standard conditions. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Hydrom(2017), doi:[10.1016/j.hydromet.2018.05.006](https://doi.org/10.1016/j.hydromet.2018.05.006)

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# **The Acidic Ferric Sulfate Leaching of Primary Copper Sulfides Under Recycle Solution Conditions Observed in Heap Leaching.**

## **Part 1. Effect of Standard Conditions.**

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## Abstract

Understanding the dissolution of copper from chalcopyrite is important as chalcopyrite is the most abundant copper mineral in the earth's crust. The main method for extraction of copper from chalcopyrite is by flotation concentration before being smelted and electro-refined. However, this process is not suitable for the treatment of the vast reserves of low grade chalcopyrite ores, where hydrometallurgical extraction through heap leaching is a better option. While pressure or high temperature leaching with the addition of sodium chloride or HCl have been proposed to extract copper from chalcopyrite concentrates, this process is too expensive to treat low grade copper ores. Currently the research focus to develop a treatment process involves the use of bacteria to oxidise the sulfide minerals and produce sulfuric acid. Given the slow extraction rates of this process it requires decades to extract all the copper from the mineral which would mean the leach solution would therefore be recycled during the process once the copper had been removed. While previous studies have reported the effect of leach temperature, pH (acid concentration) and  $E_h$  on copper extraction, these have only considered initial leaching conditions. Studies using recycle leach solution conditions have not been undertaken, and this is the focus of the study reported here. The recycle solution conditions were based on a simulated long term solution composition. This article is part of a series of papers that has investigated the effect on copper and iron extraction from chalcopyrite which has evaluated conditions, major species and additives under recycle leach concentrations. This article examines the effect of the conditions, specifically temperature, pH,  $E_h$  and solids density. It was determined that the temperature had the most significant effect on the copper and iron extraction while the pH,  $E_h$  or solids density had no appreciable effect on the extraction of either copper or iron under the recycle leach conditions tested. While the effect of temperature on chalcopyrite dissolution is known, the activation energy, the rate of dissolution and the degree of copper extraction is lower under these high solute or recycle concentrations. Similar observations were found when studying pyrite but this study attributed the lowering of these parameters under recycle conditions to the sulfate concentration causing a diffusion layer around the mineral particles which alters or slows the response of pH,  $E_h$  or temperature on the dissolution reaction.

## 1 Introduction

Copper has many uses and has been used for thousands of years due its malleable (ductile), anti-corrosive and conductive properties (Biswas and Davenport, 1994). Its main use today is in the electrical industry for the generation of power, transfer of electricity or in electronic components. It is also used for its heat transfer properties in refrigerators, air conditioners or steam condensers. It is used in plumbing and water desalination for its anti-corrosive properties, and as a building material or as a constituent of various metal alloys to improve their properties of hardness, ductility and corrosive resistance (Biswas and Davenport, 1994). Due to copper's versatility there is an ever increasing demand for it to be extracted from the earth's crust.

Copper in the earth's crust occurs as native copper or in minerals such as the copper sulfides, the copper carbonates, and the copper oxide minerals. Chalcopyrite is the most abundant of these copper minerals accounting for 70% of all copper-bearing minerals in the earth's crust. The copper is mainly recovered from these minerals through flotation followed by pyrometallurgical processing and this accounts for 80-85% of the world's copper production (Pradhan *et al.*, 2008). However, pyrometallurgical treatment is difficult and expensive for the low grade copper ores which are increasingly being mined. This has sparked increased research into developing a cost effective hydrometallurgical process to treat these ores.

The current focus of hydrometallurgical research is to extract the copper through heap leaching processes with the aid of bacteria. However, chalcopyrite is refractory, with slow leaching kinetics and poor overall extraction, so understanding the mechanism of how it leaches has generated considerable research over the past 50 years. The main problem identified is the passivating of the chalcopyrite surface in which a layer is formed which blocks the reaction interface or wetting of chalcopyrite. There is much debate as to how this layer is formed and what this layer consists of, which is why research is continuing to understand the mechanism and thereby enable heap leaching technology to be applied more effectively treat low grade chalcopyrite ore sources. If this process is utilised, given the slow dissolution it would mean the liquor will inevitably be recycled and from gangue dissolution particular species in solution will increase. Increase in these species especially iron are known to slow the extraction of copper from chalcopyrite (Muñoz *et al.*, 1979; Dutrizac, 1981; Qian *et al.*, 2014). Therefore it is important to investigate how chalcopyrite leaches under these conditions which was the basis for this study.

To understand how chalcopyrite leaches, the effect of temperature, pH and  $E_h$  have been investigated. Researchers have found typical activation energies of 71-88 kJ/mol (Dutrizac and MacDonald, 1974; Hirato *et al.*, 1987; Kaplun *et al.*, 2011; Lowe, 1970; Muñoz *et al.*, 1979; Sokić *et al.*, 2009; Yue and Asselin, 2014). Increasing the acid concentration (decreasing the pH) typically improves the extraction of copper from chalcopyrite (Dorado *et al.* 2012; Vilcañez *et al.*, 2009) as the additional acidity prevents formation of iron salt precipitates which are a possible retardant for copper extraction. The redox potential ( $E_h$ ) has been shown by several authors to significantly affect the leaching rate of copper from chalcopyrite (Córdoba *et al.*, 2008b; Kametani and Aoki, 1985; Koleini *et al.*, 2011; Viramontes-Gamboa *et al.*, 2006, 2007, 2010; Sandström *et al.*, 2005). They have identified a potential  $E_h$  window (610-640mV SHE) where they observed the highest recovery of copper from chalcopyrite. Electrochemical studies have shown that within this range of potentials, the chalcopyrite is in an active state while outside this range it either bistable or passive.

The temperature dependence of the leach rate is related to the dominant mechanism governing the rate of chalcopyrite dissolution (Kaplun *et al.*, 2011). For chemical reaction-controlled processes, the leaching rate can be expected to significantly improve with increasing temperature whereas for diffusion-controlled processes, the influence of temperature would be less noticeable. In many cases, it was found that an increase in the temperature had largely beneficial effects for chalcopyrite leaching. Sokić *et al.* (2009) found that chalcopyrite dissolution increased from 28% to 70% over a period of 4 hours in 1.5mol/L  $H_2SO_4$  when the temperature was increased from 70°C to 90°C, while

Córdoba *et al.* (2008a) found that the extracted copper increased from 3% to more than 80% when the temperature was increased from 35°C to 68°C. Padilla *et al.* (2008) reported improved dissolution of copper from chalcopyrite when the temperature was increased from 120°C to 150°C under high oxygen pressure conditions. These findings all support the proposition that increasing the temperature improves chalcopyrite leaching rates through chemical reaction-controlled processes up to a point where the passivating layer being formed on the chalcopyrite surface is sufficiently thick to cause diffusion to be the rate limiting process. Qiu *et al.* (2007) found in an investigation of oxidative leaching of chalcopyrite that during the first 0-10 min period, temperature significantly affected the oxidative leaching process, indicating a chemical reaction-controlled process, but beyond this period (10-60 min) the influence of temperature on the copper leaching rate became more complicated as diffusion through the passivating layer became the rate controlling step.

While increasing the temperature would be beneficial, in a system where oxygen is needed in the leaching reaction, increasing the temperature may be expected to result in decreased levels of dissolved oxygen or reduce reaction rate. An increase in temperature might also increase unwanted precipitation of iron that are believed to be one of the species known to passivate chalcopyrite. While additional  $H^+$  will help to prevent formation of iron salt precipitates, this iron precipitation may reduce the beneficial effects that an increase in temperature brings (Vilcaez *et al.*, 2009). Vilcaez *et al.* (2009) investigated the effect of temperature and found that an increase from 65°C to 80°C did not significantly improve the leaching rate of chalcopyrite because of iron precipitation at a given pH. But at a lower pH (or higher acidity) there was an improvement in the leaching rate, suggesting that increased acidity prevented the precipitation of iron and there was sufficient dissolved oxygen in the leach solution at 80°C to oxidise  $Fe^{2+}$  to  $Fe^{3+}$  to ensure the leaching of chalcopyrite.

Most of the studies of the effect of temperature report the activation energy, which is the least amount of energy needed for a chemical reaction to take place. Reported activation energies for the main sulfide minerals are listed in Tables 1 to 3.

Table 1: Activation Energies for Chalcopyrite in Sulfuric Acid

| Temperature (°C) | pH      | [SO <sub>4</sub> <sup>2-</sup> ] (g/L) | Activation energy (kJ/mol)            | Author                         |
|------------------|---------|--|---------------------------------------|--------------------------------|
| 38-68            | 0.3     | ~8                                     | 74.3                                  | Lowe, 1970                     |
| 27-94            | 1.0-1.8 | -                                      | 71-84                                 | Dutrizac & MacDonald, 1974     |
| 60-90            | -       | -                                      | 84                                    | Muñoz <i>et al.</i> , 1979     |
| 50-78            | -       | -                                      | 88                                    | Hirato <i>et al.</i> , 1987    |
| 70-90            | 0.2     | ~14                                    | 83                                    | Sokić <i>et al.</i> , 2009     |
| 25-150           | <2      | 20                                     | 85                                    | Yue and Asselin, 2014          |
| 55-85            | 1.0     | 10                                     | 80±10                                 | Kaplun <i>et al.</i> , 2011    |
| 55-85            | 1.0     | 11                                     | 21±5 (presence of Fe <sup>3+</sup> )* | Kaplun <i>et al.</i> , 2011    |
| 40-90            | 1.4-1.5 | ~2                                     | 76.5-101.9 (fresh/aged 0.42 V)        | Khoshkhoo <i>et al.</i> , 2017 |
| 30-80            | 1.4-1.5 | ~2                                     | 90.9-91.8 (fresh/aged 0.62 V)         | Khoshkhoo <i>et al.</i> , 2017 |

\*Initial rate (10 hrs)

Table 2: Activation Energies for Secondary Sulfides in Sulfuric Acid

| Temperature (°C) | pH  | [SO <sub>4</sub> <sup>2-</sup> ] (g/L) | Activation energy (kJ/mol)    | Author                       |
|------------------|-----|--|-------------------------------|------------------------------|
| 30-90            | -   | ~2                                     | 84 (CuS)                      | Mulak, 1969                  |
| 38-68            | 0.3 | ~8                                     | 59.4 (CuS)                    | Lowe, 1970                   |
| 20-90            | 1.0 | -                                      | 75-100 (CuS)                  | Dutrizac and MacDonald, 1974 |
| 25-50            | 2.0 | ~1                                     | 52-58 (CuS)                   | Walsh and Rimstidt, 1986     |
| 38-68            | 0.3 | ~8                                     | 28.2 (Cu <sub>2</sub> S)      | Lowe, 1970                   |
| 5-80             | 1.0 | -                                      | 20.9-29.3 (Cu <sub>2</sub> S) | Dutrizac and MacDonald, 1974 |

Table 3: Activation Energies for Pyrite/Pyrrhotite in Sulfuric Acid

| Temperature (°C) | pH    | [SO <sub>4</sub> <sup>2-</sup> ] (g/L) | Activation energy (kJ/mol) | Author                 |
|------------------|-------|--|----------------------------|------------------------|
| 38-68            | 0.3   | ~8                                     | 37.2*                      | Lowe, 1970             |
| 170-230          | 0.3   | ~5                                     | 33.2                       | Long, 2000             |
| 20-50            | 3     | ~5                                     | 50-55                      | Schoonen et al. 2000   |
| 25-37            | 5.5-6 | ~2                                     | 63-66                      | Kamei and Ohmoto, 2000 |

\*pyrrhotite

The reported covellite (CuS) activation energies are high (52-100 kJ/mol) while they are lower for chalcocite (Cu<sub>2</sub>S) (21-29 kJ/mol). The reported activation energies for pyrite (FeS<sub>2</sub>) are high (50-66 kJ/mol) but are lower for pyrrhotite (FeS). The reported activation energies for chalcopyrite are also high (71-102 kJ/mol) but were lower for the initial rate (21 kJ/mol) in the presence of Fe<sup>3+</sup> ions (Kaplun *et al.*, 2011). This would suggest that the type of mineral and the solution conditions influence the activation energies of leaching of the various minerals in the ore.

Vilcaèz *et al.* (2009) investigated the effect of pH at a temperature of 65°C in the absence of Fe<sup>3+</sup>, leaving O<sub>2</sub> as the sole oxidiser for chalcopyrite leaching (although through the dissolution of chalcopyrite ferric will be generated within the solution). The monitoring of the E<sub>h</sub> showed that low E<sub>h</sub> values below the critical potential (450 mV) occurred regardless of the solution pH. This suggested that the reduction of E<sub>h</sub> cannot be solely responsible for the enhanced chalcopyrite leach rates; otherwise the degree of copper extraction for all pH values would be similar. Viramontes-Gamboa *et al.* (2006) showed that the maximum critical current (that indicated the highest copper extraction) increased with decreased pH and increased temperature, which was consistent with Vilcaèz's results. Vilcaèz *et al.* (2009) proposed that acid was necessary for the generation of ferric ions which in turn were necessary to oxidize chalcopyrite. They proposed that the differences between the 0.5 and 1.5 pH tests were due to the formation of a passivating iron salt precipitate layer (such as jarosite) on the mineral surface at the higher pH of 1.5.

Dorado *et al.* (2012) studied the bioleaching of a chalcopyrite ore sample by a mixed culture of *Thiothrix spp.*, *Sulfurimonas denitrificans*, *Halothiobacillus neapolitanus*, *Thiobacillus denitrificans* and *Thiomonas intermedia* at various initial pH values and additional Fe<sup>3+</sup> concentrations at 30°C. They found leaching pH had a significant effect on copper extraction, with negligible extraction at pH 6.0, 20% at pH 4.0 and 50% at pH 1.5 in 50 days. Rodríguez *et al.* (2003) studied chalcopyrite bioleaching and attributed the observed initial decrease in the H<sup>+</sup> concentration (i.e. pH increased) to the consumption of acid during the protonic attack of the chalcopyrite. Later in the process, acidity increased (i.e. pH decreased) because of the oxidation of elemental sulfur by sulfur-oxidizing micro-organisms. The same pH isotherm was observed by Zhou *et al.* (2007) and this pH change is commonly observed during many bacterial leaching studies. While this has not been specifically explained earlier, it most likely is related to the speciation of iron in solution and the variation of Fe containing species likely in the leaching solution, such as Fe(SO<sub>4</sub>)<sub>2</sub><sup>-</sup>, FeSO<sub>4</sub><sup>+</sup> and FeHSO<sub>4</sub><sup>2+</sup> and others and whether it is there initially or not.

Nevertheless, it seems that the overall extraction of copper is not affected by this pH change if other conditions are ideal.

Several authors have reported the significant effects of redox potential ( $E_h$ ) on the leaching rate. The concept of a passivation potential ( $E_{pp}$ ) is employed to define the value of  $E_h$  below which the chalcopyrite mineral leaches and above which it does not leach as a result of the formation of the passivating layer. Viramontes-Gamboa *et al.* (2006, 2010), carried out a detailed study on the passivation of chalcopyrite over a range of  $E_h$ , with the findings summarised as follows:

- Below 685 mV - regardless of the impurity content, acidity and temperature chalcopyrite exhibits active behaviour in sulfuric acid solution;
- Between 685 mV to 755 mV - chalcopyrite exhibits bistable behaviour which means that it exhibits either active or passive behaviour depending on how it was brought to that potential. This bistable behaviour means that when the potential was increased from an active state at a temperature of 50°C to 755 mV, the chalcopyrite becomes passivated; on the other hand when the chalcopyrite was in a passivated state, a decrease in potential to approximately 685 mV brings about an activating effect; and
- Upwards of 755 mV - a passivating effect was observed within chalcopyrite which results in slow leaching rates.

Electrochemical studies on the passivating region of chalcopyrite were also undertaken by Sandström *et al.* (2005) over the potential range of 690-840 mV (SHE) at a temperature of 25°C, and at 840 mV at 65°C. These studies suggested that the temperature may have some influence on the optimum potential for the chalcopyrite leaching process. The potential which results in the greatest recovery of copper from chalcopyrite has been found to be in the range of 610-640 mV by many studies (Córdoba *et al.*, 2008b; Kametani, 1985; Koleini *et al.*, 2011; Viramontes-Gamboa *et al.*, 2007; Sandström *et al.*, 2005). However, the recent leaching study by Khoshkhoo *et al.* (2017) on fresh and aged chalcopyrite concentrates found atmospheric oxidation prior to leaching (ageing) had an effect on extraction of copper at different redox potentials. Copper recoveries in leaching of aged concentrates were higher at high redox potentials (420-710 mV, 14 to 55%) compared to little change due to the potential with freshly ground concentrate.

No studies have specifically studied the effect of  $E_h$ , pH, temperature and solids density on the leaching of chalcopyrite under high solute concentrations. Although some studies have conducted one or two test under high solute concentration under a given set of conditions (Muñoz *et al.*, 1979; Dutrizac, 1981; Qian *et al.*, 2014). A recent study have investigated the effect of potential and temperature on pyrite dissolution under high solute condition or sulfate concentrations (Nicol *et al.*, 2013a; Nicol *et al.*, 2013b; Basson *et al.*, 2013). Pyrite is commonly associate with chalcopyrite in ore and is commonly dissolved by bacteria where the iron is used the dissolution of chalcopyrite. These investigation found the anodic oxidation of pyrite decreases with increasing sulphate ion concentration and increases with increasing temperature. This decrease was attributed to the sulphate ions forming electrochemically less reactive iron sulphate complexes. This detrimental effect of high sulphate concentrations on the rate of dissolution was confirmed in leaching studies. Further work in the presence of bacteria showed the high sulfate concentration decreased the oxidation rate and growth of bacteria. But they found very similar dissolutions between abiotic and biotic leach testing and concluded an indirect mechanism applied where the mixed potential model could be used to quantitatively describe both abiotic dissolution and biotic dissolution of pyrite in acidic solutions.

What is least understood from these previous studies is how the leaching of copper from chalcopyrite is affected by these conditions under recycle solution conditions. This is potentially important as the leach solution exiting a heap is typically returned to irrigate the heap once the copper has been extracted from it. The purpose of the research reported in this paper was to develop an understanding of how a chalcopyrite ore leaches under recycle solution conditions. This article is part of a series of papers that report on how copper recovery from chalcopyrite is affected

by conditions, major species and additives (Nikoloski *et al.*, 2017; O'Malley and Nikoloski, 2017a,b,c). This article specifically examines the effect of temperature (25-70°C), pH (0.7-1.6),  $E_h$  (540-720 mV) and solids density (5-26%) on a low grade chalcopyrite-dominant ore source which was leached in acidic ferric sulfate media. This was undertaken by a tank leaching process where the ore was liberated and allowed to leach for 10 days. While chalcopyrite is known to be slow to leach a period of 10 days was deemed adequate to gauge an effect of a particular parameter. The recycle solution conditions were based on simulated long term heap recycle solution composition, namely, 25 g/L  $Fe^{3+/2+}$ , 10 g/L  $Al^{3+}$ , 1 g/L  $Mg^{2+}$ , 0.2 g/L  $Cu^{2+}$ , 125 g/L  $SO_4^{2-}$ , at a pH 1.20,  $E_h$  700 mV and temperature of 50°C.

## 2 Materials and Methods

### 2.1 Ore Sample

A chalcopyrite-dominant ore sample was supplied as -30 mm crushed rock for this test work. The ore characteristics, including the chemical composition and mineralogical analysis, are published in Nikoloski *et al.* (2017). The ore contained 0.85 % Cu with the copper mineral distribution being chalcopyrite (87.7%), enargite and bornite (5.3%), other copper minerals (malachite, azurite, etc.) (3.4 %), chalcocite (2.0%), covellite (1.0%), and copper oxide and copper clay/silicate minerals (0.6%).

### 2.2 Sample Preparation

The ore was stage crushed to -1.0 mm and split into 500 g charges before being rod milled to achieve a  $P_{80}$  size of 38  $\mu m$ . The sample preparation procedures are described in Nikoloski *et al.* (2017). All allotments and ground samples were stored in a refrigerator (5°C) until required.

### 2.3 Leaching Tests

Each leaching test was run for 10 days in a 1 L thermostatic baffled leaching vessel stirred at  $600 \pm 30$  rpm. The experimental setup and procedures, and procedures for analysing the leach samples are described in Nikoloski *et al.* (2017). All leach experiments were conducted with 5% solids, such that 42 g (dry basis) ore sample was added to 800 mL of lixiviant once the temperature had reached the set point. The  $E_h$  was monitored using a TPS ORP  $Ag^+/AgCl$  probe and only allowed to vary to within  $\pm 10$  mV, while pH only varied to within  $\pm 0.1$  of a unit. If required, adjustments were made by adding sodium metabisulfite or hydrogen peroxide to control the  $E_h$ , and by adding LiOH or  $H_2SO_4$  to control the pH. The lixiviant was prepared using deionised water and laboratory reagent (LR) grade purified salts of iron, magnesium, copper or aluminium. The temperature (25-70°C), pH (0.8-1.6),  $E_h$  (540-720 mV) and % solids (5-26%) were varied for the base condition of 25 g/L  $Fe^{3+/2+}$ , 10 g/L  $Al^{3+}$ , 1 g/L  $Mg^{2+}$ , 0.2 g/L  $Cu^{2+}$  and  $SO_4^{2-}$  concentration of 125 g/L. All potentials reported as  $E_h$  (i.e. have been converted to SHE). The error in extraction was calculated based on the average change in accountability and how that would alter the extraction.

## 3 Results

### 3.1 Effect of Temperature

Comparing the rates and extent of leaching at different temperatures but for the same pH,  $E_h$ , % solids and leach solution composition, it was clear that temperature had a major effect on both the initial rate of copper and iron extraction and on the final extraction of those elements from the chalcopyrite ore sample (Figures 1 and 2). The final copper extraction increased from 9% at 26°C to 32% at 70°C. The apparent final iron dissolution increased from negligible at 26°C to 57% at 40°C, but then decreased at higher temperatures due to iron precipitation as jarosite.

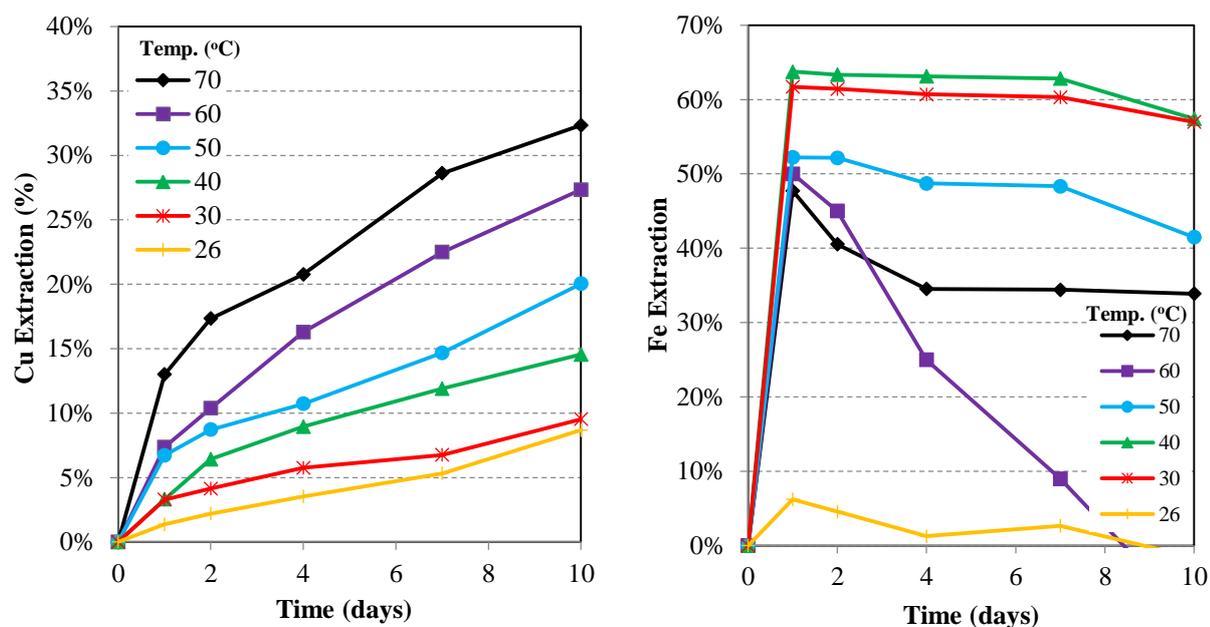


Figure 1: Copper and Iron Extraction in 25 g/L  $Fe^{3+/2+}$ , 10 g/L  $Al^{3+}$ , 1 g/L  $Mg^{2+}$ , 0.2 g/L  $Cu^{2+}$ , 125 g/L  $SO_4^{2-}$ , pH of 1.2,  $E_h$  of 700 mV and pH 1.2 at Varied Temperature.

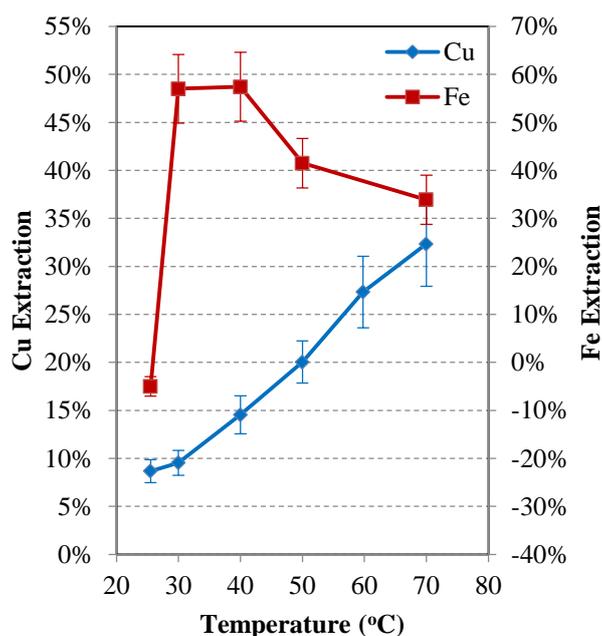


Figure 2: Final Copper and Iron Extraction Curves at Varied Temperature.

The ore sample was predominantly chalcopyrite but it also contained other copper minerals which will leach before the chalcopyrite, such as covellite and chalcocite. Therefore, the rate of leaching was first assessed for the first two days of leaching (“initial” rate) to determine leach rates for these secondary copper minerals that are easy to leach such as oxide and secondary copper sulfide minerals. The rate of leaching from day 4 to day 10 (“final” rate) was then assessed to determine the rate of chalcopyrite leaching. This initial rate was also contributed to pyrite dissolution while the final rate would be a combination of pyrite and chalcopyrite. These graphs are presented in Figure 3.

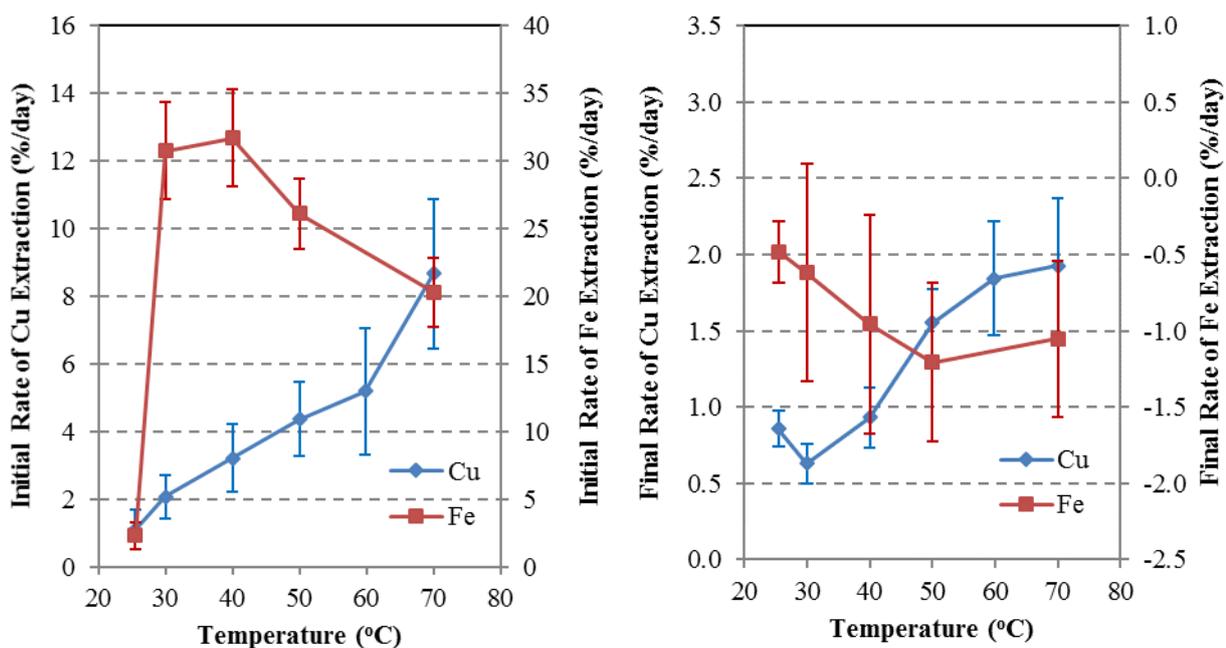


Figure 3: The Initial and Final Copper and Iron Extraction Rate Curves at Different Temperatures.

Both graphs show that temperature influences the initial and final rates of leaching, and suggest that leaching of all copper minerals would benefit from an increase in the leach temperature. The rate of initial iron extraction did not change significantly from 30°C to 50°C but at 70°C iron precipitation lowered the initial rate significantly. The final iron extraction rates show similar behaviour, with a gradual decrease in the rate due to iron precipitation from precipitating jarosite (confirmed by XRD analysis). However, the rate of extraction of iron was much slower in the final period than in the initial period.

This extraction rate information can be presented in an Arrhenius plot to determine the activation energies. This is depicted in Figure 4 and the activation energies are presented in Table 4. It is clear from the values of the activation energies that the extraction from the secondary copper minerals was more of a chemically-controlled process, while the lower activation energies for pyrite and chalcopyrite indicate extraction from these minerals is more likely a diffusion-controlled process. The final iron results represent jarosite precipitation, rather than extraction and so was not presented.

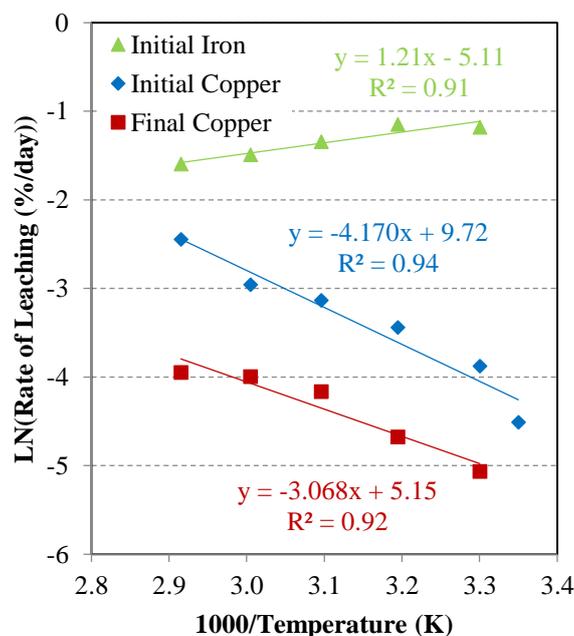


Figure 4: Arrhenius Plot for Copper and Iron at Different Temperatures.

Table 4: Determined Activation Energies.

| Mineral  | Activation Energy (kJ/mol) |
|--|----------------------------|
| Secondary Copper Minerals<br>(Chalcocite, Covellite, oxides, etc.) | 34.7                       |
| Chalcopyrite   | 25.5                       |
| Pyrite   | 10.1                       |

### 3.2 Effect of pH

The pH was varied from 0.7 to 1.6 for the same temperature,  $E_h$ , % solids and leach solution composition to understand how varying pH alters the extraction of copper and iron (Figure 5). Copper extraction did not change significantly over this pH range. The iron extraction curves show improved leaching below pH 1.03. Extraction decreases at higher pH values due to iron precipitation. These results are also presented in Figure 6 which shows higher dissolution at  $\text{pH} < 1.0$  than at  $\text{pH} > 1.0$  due to competing iron precipitation. The pH 1.6 iron curve was not presented due to excessive iron precipitation which showed no extraction. The copper extractions in Figure 6 showed a slight improvement in copper extraction at  $\text{pH} < 0.9$  but this result is not significant as it is within the experimental error.

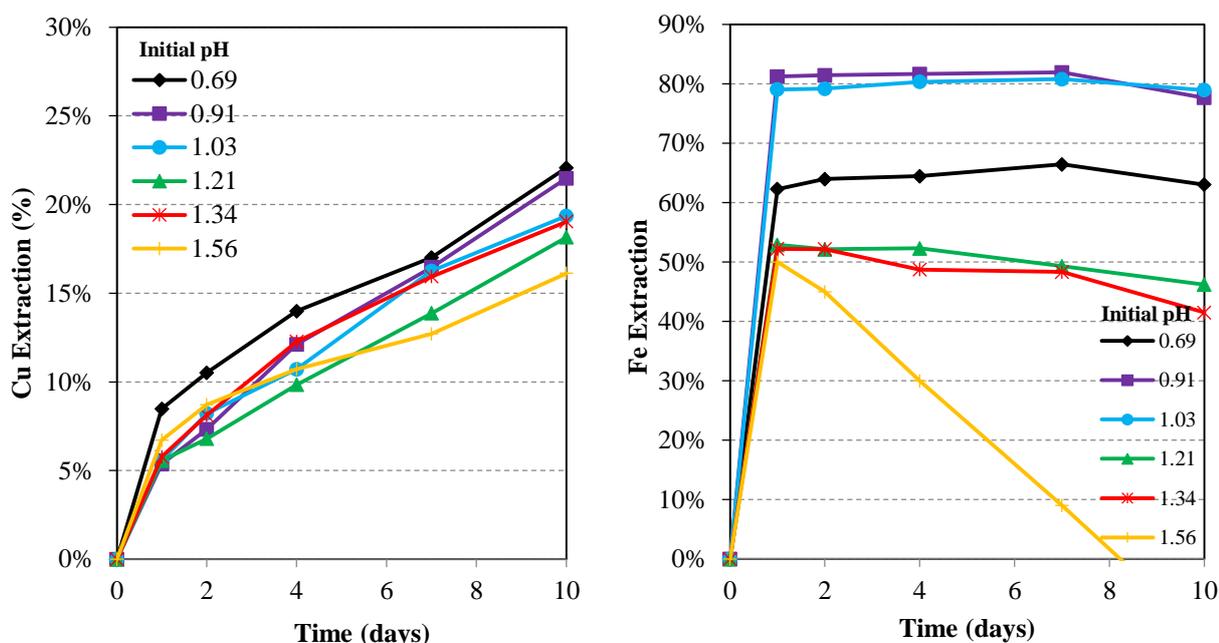


Figure 5: Copper and Iron Extraction in 25 g/L  $Fe^{3+/2+}$ , 10 g/L  $Al^{3+}$ , 1 g/L  $Mg^{2+}$ , 0.2 g/L  $Cu^{2+}$ , 125 g/L  $SO_4^{2-}$ , pH of 1.2,  $E_h$  of 700 mV and Temperature of 50°C at Different pH.

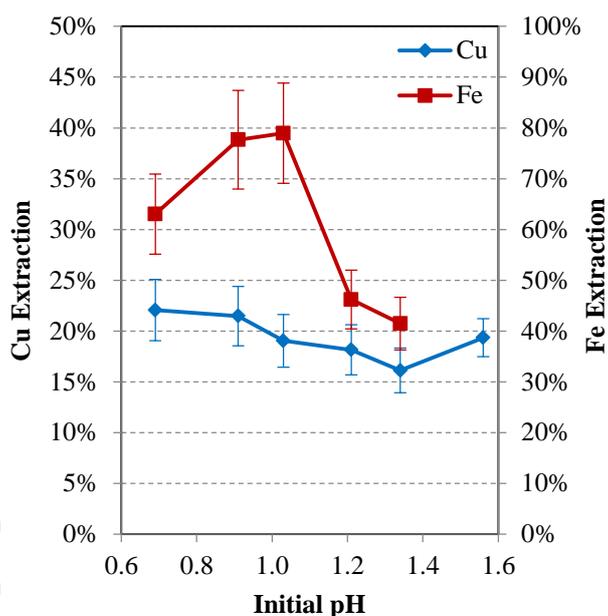


Figure 6: Final Copper and Iron Extraction Curves at Different Initial pH.

The initial and final rates of extraction of copper and iron extraction were very similar except that the iron initial and final extraction rates showed a general downwards trend above pH 1.0 (Figure 7).

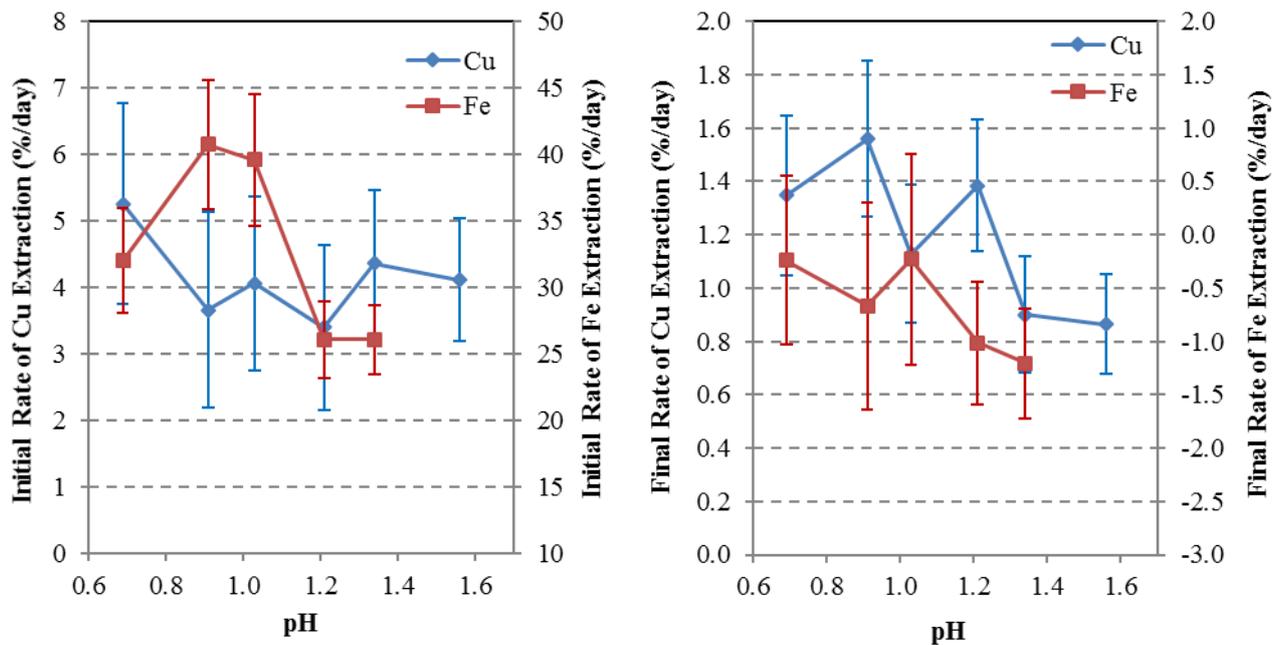


Figure 7: The Initial and Final Copper and Iron Extraction Rate Curves at Different pH.

### 3.3 Effect of $E_h$

The potential of the leach solution is related to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple, so varying the concentration of these two species will change the potential of the solution i.e. for high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios the potential will be high ( $>750$  mV SHE) while for low  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios the potential will be low ( $<600$  mV SHE). The effect of solution  $E_h$  on the extraction of copper and iron for the same temperature, pH, % solids and leach solution composition are presented in Figure 8. The copper and iron extractions over time show similar behaviour for all  $E_h$  values in the range tested.

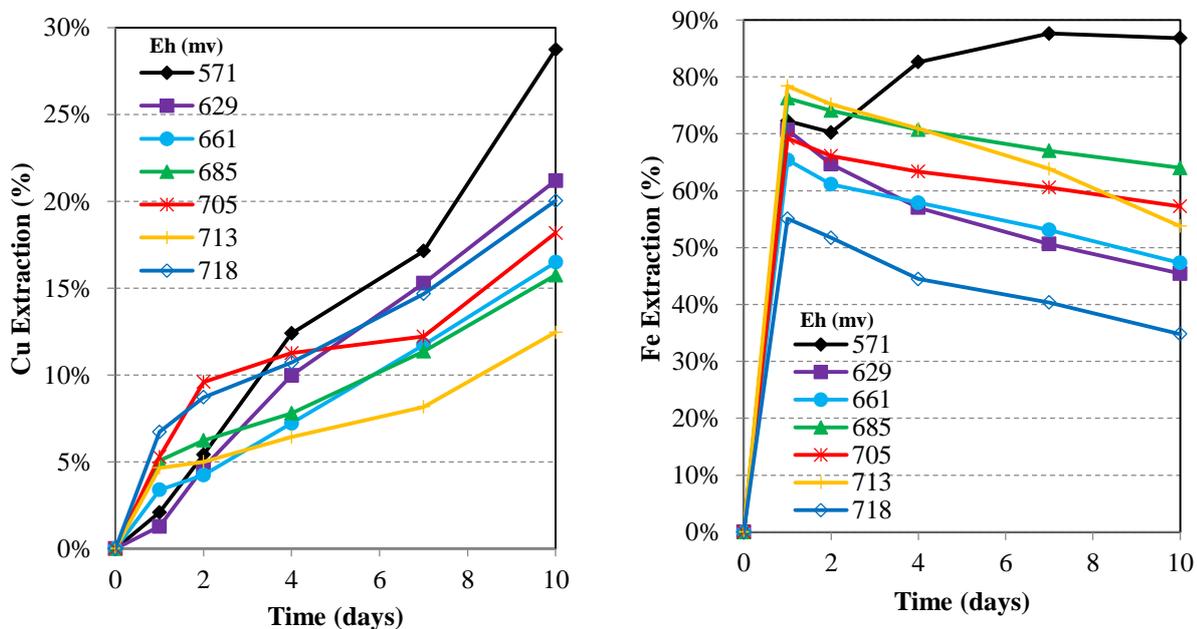


Figure 8: Copper and Iron Extraction in 25 g/L  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , 10 g/L  $\text{Al}^{3+}$ , 1 g/L  $\text{Mg}^{2+}$ , 0.2 g/L  $\text{Cu}^{2+}$ , 125 g/L  $\text{SO}_4^{2-}$ , pH of 1.2, and Temperature of  $50^\circ\text{C}$  at Different  $E_h$ .

The final extractions of copper and iron presented in Figure 9 show a similar extraction of copper for all  $E_h$  between 630-720 mV. Below this ( $E_h$  560 mV) there is a slight improvement in copper

extraction. The iron extraction shows a similar dependence on  $E_h$  except for the drop in extraction at  $E_h$  718 mV which is due to jarosite precipitation.

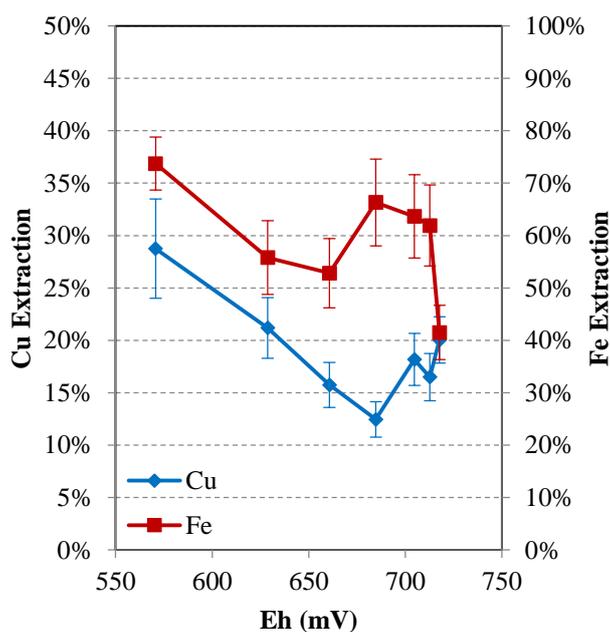


Figure 9: Final Copper and Iron Extraction Curves at Different  $E_h$ .

The initial and final rates of copper extraction are presented in Figure 10. While the initial copper rates of extraction were similar over the  $E_h$  range tested, the final rates for copper showed a gradual increase in the rate of copper extraction as the potential was lowered below 630 mV. The initial iron rates of extraction were similar over the  $E_h$  range tested, and the final iron extractions were also similar over the  $E_h$  range, and were negative indicating jarosite precipitation.

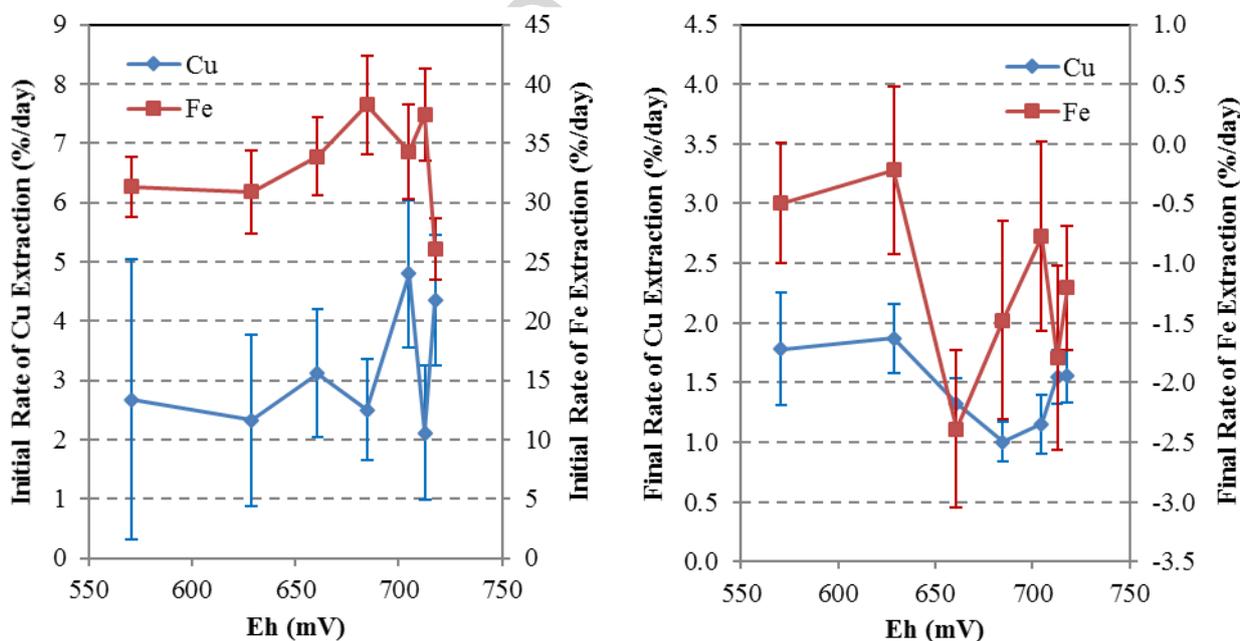


Figure 10: The Initial and Final Copper and Iron Extraction Rate Curves at Different  $E_h$ .

### 3.4 Effect of Solids Density

The effect of different solids densities was investigated for the same temperature, pH,  $E_h$  and leach solution composition (Figure 11). The results showed similar copper extractions for the different

solids densities tested. However, iron extraction was lower for higher solids densities due to jarosite precipitation.

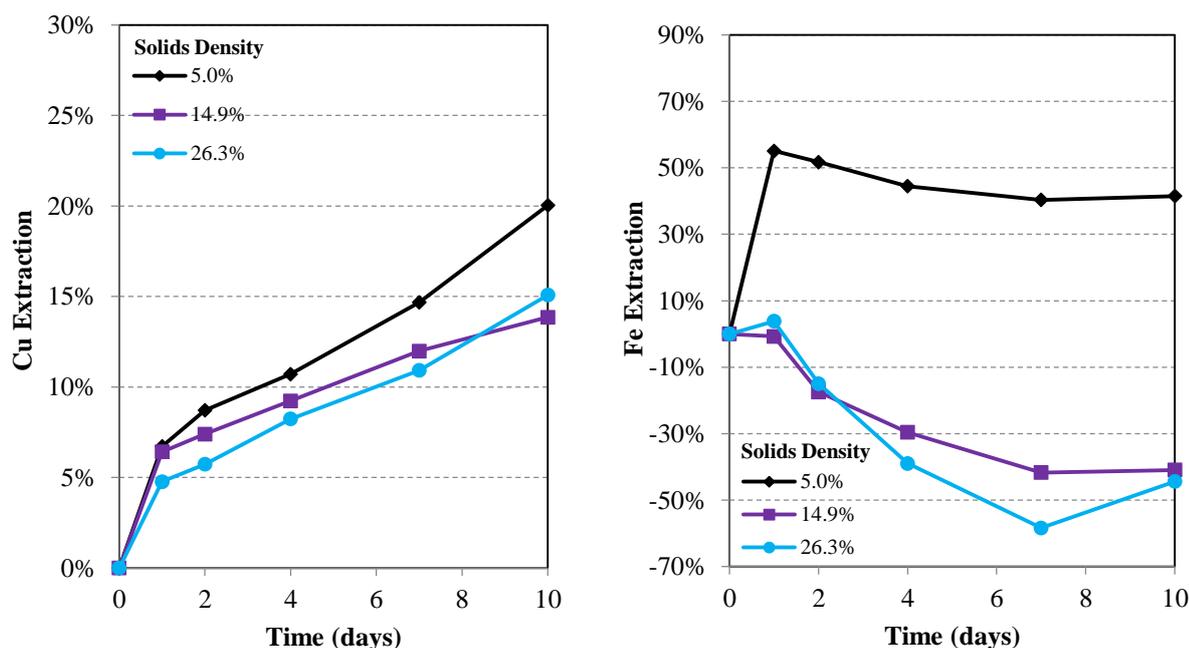


Figure 11: Copper and Iron Extraction in 25 g/L  $Fe^{3+/2+}$ , 10 g/L  $Al^{3+}$ , 1 g/L  $Mg^{2+}$ , 0.2 g/L  $Cu^{2+}$ , 125 g/L  $SO_4^{2-}$ , pH of 1.2,  $E_h$  of 700 mV, pH 1.2 and Temperature of 50°C at Different Solids Density.

Figure 12 represents the final extractions of copper and iron for different solids densities. The variation in copper extraction with solids density was within the experimental error. Iron extraction significantly decreased with increasing solids density due to jarosite precipitation.

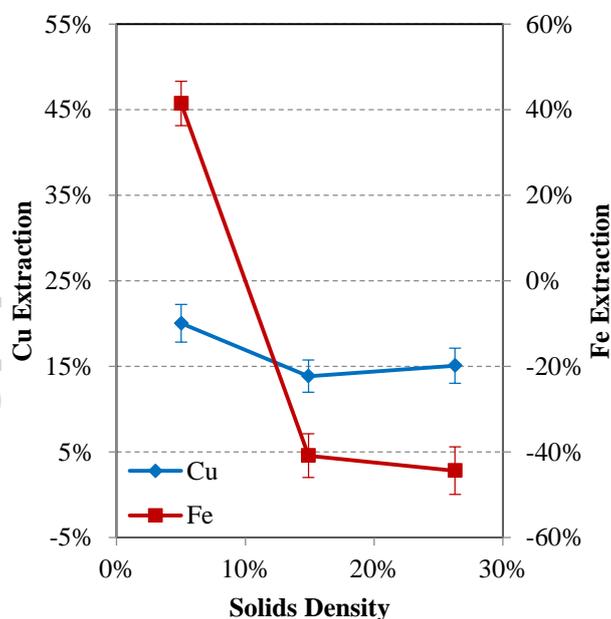


Figure 12: Final Copper and Iron Extraction Curves at Different Solids Density.

The initial rates of extraction of copper and iron showed a decrease with increasing solids density. However, the final rates of extraction were similar to within experimental error (Figure 13).

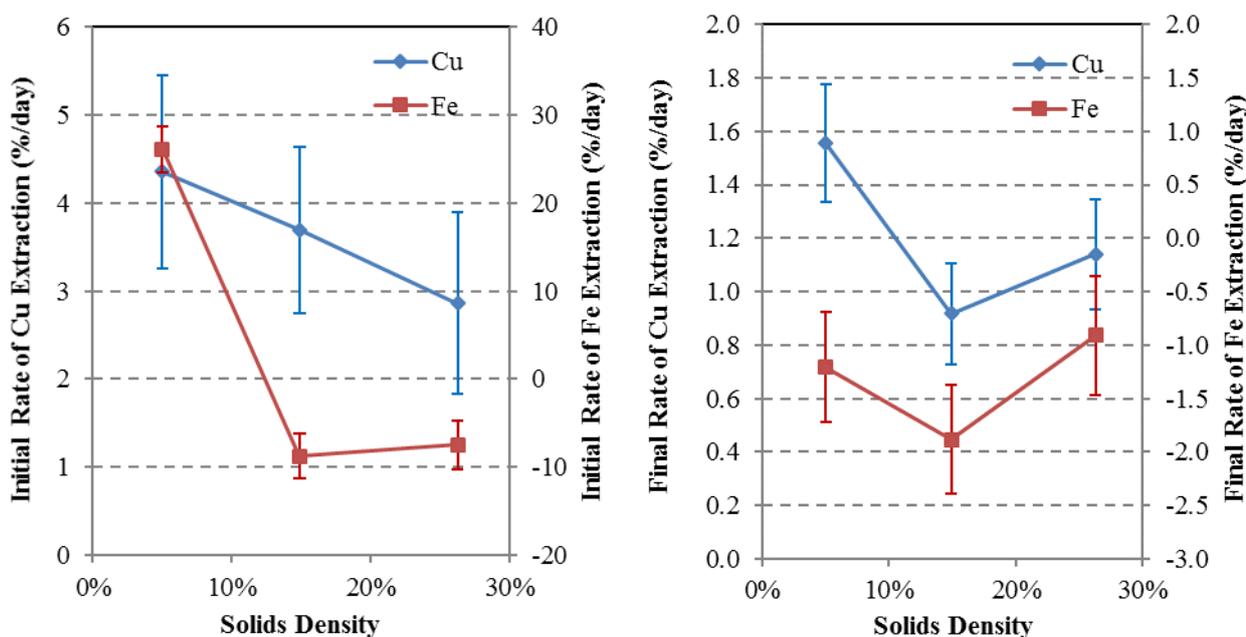


Figure 13: The Initial and Final Copper and Iron Extraction Rate Curves at Different Solids Density.

## 4 Discussion

Chalcopyrite leaching has been investigated since the 1960's with the vast majority of studies done using typical initial leach conditions of 1-5 g/L Fe, pH 1-3,  $E_h$  550-750 mV. Most studies used temperatures between 30-70°C and focused on pure chemical leaching or bioleaching with bacteria. While several studies have reported the effect of temperature,  $E_h$  and pH (acid concentration) on the extraction of copper from chalcopyrite (Kametani and Aoki, 1985; Sandström *et al.*, 2005; Viramontes-Gamboa *et al.*, 2007; Vilcaèz *et al.*, 2009), few if any studies have addressed copper and iron extraction under recycle leach conditions.

The study reported in this paper found that temperature influences the extraction of copper under recycle leach conditions. Increased temperature improved the initial rate of extraction of copper due to dissolution of secondary copper minerals in the predominantly chalcopyrite ore, and it also improved the final rate of extraction of copper due to chalcopyrite dissolution. The iron extraction was less influenced by temperature, although extraction was suppressed by iron precipitation above 50°C.

This study calculated an activation energy of 35 kJ/mol for the secondary copper sulfide minerals, which is similar to the reported chalcocite activation energy (21-29 kJ/mol) (Lowe, 1970; Dutrizac and MacDonald, 1974) but is lower than what has been reported for other copper minerals which could be related to the recycle concentration causing this inhibition. The activation energy calculated for chalcopyrite (26 kJ/mol) was also lower than activation energies reported elsewhere (71-88 kJ/mol) (Lowe, 1970; Dutrizac and MacDonald, 1974; Muñoz *et al.*, 1979; Hirato *et al.*, 1987; Kaplun *et al.*, 2011; Yue and Asselin, 2014). This is partially related to the small contribution from the dissolution of copper from the secondary copper minerals. However, Kaplun *et al.* (2011) has also reported a lower activation energy of 21 kJ/mol in the presence of  $Fe^{3+}$  ions for initial rate so a similar effect may have been the main cause of the low activation energy observed in the present study. The activation energy calculated for pyrite ( $FeS_2$ ) (10 kJ/mol) was also significantly lower than those reported elsewhere (50-66 kJ/mol) (Schoonen *et al.* 2000; Kamei and Ohmoto, 2000). While the investigation by Nicol *et al.* (2013b) did not report activation energies they did show a significant drop in the rate of pyrite leaching in the presence of increasing sulfate concentration and provide enough data to calculate activation energies. Their results showed in 20 g/L sulfate an activation energy of 49.4 kJ/mol was determined while in 120 g/L sulfate it had

fallen to 24.8 kJ/mol. Therefore it is possible that the sulfate concentration is producing varied diffusion layers around minerals, like pyrite and chalcopyrite, based on its concentration which ultimately lowers the rate and activation energies with increasing sulfate concentration. While this work could be also related to high sulfate concentration and the presence of high concentration of  $\text{Fe}^{3+}$  ions, this rate would also be influenced by the dissolution of iron from chalcopyrite and other iron bearing gangue minerals. However, the activation energy determined was similar to pyrrhotite ( $\text{FeS}$ ) under more oxidative conditions (Long, 2000). Further work is needed to answer this question.

This study found that redox potential did not influence the initial copper extraction rate, which has been attributed to leaching of secondary copper minerals, but did affect the final copper extraction rate due to dissolution of chalcopyrite. This suggests that chalcopyrite leaching is affected by redox potential, which is supported by other studies (Córdoba *et al.*, 2008b; Kametani, 1985; Koleini *et al.*, 2011; Viramontes-Gamboa *et al.*, 2007; Sandström *et al.*, 2005). However, the effect on copper extraction for redox potentials between 630-720 mV was not significant, and only at lower potentials (<630 mV) was there an observed improvement in the copper extraction. This suggests that solution composition and redox potential plays a significant role in determining the active and passive conditions for chalcopyrite leaching.

The solids density was not found to influence the extraction of copper, but did influence the precipitation of jarosite. This potentially suggests that the precipitation of jarosite does not affect the dissolution of copper from chalcopyrite.

The study found that there was a rapid initial dissolution of iron (mainly pyrite) before jarosite precipitation suppressed the iron extraction for all experimental conditions. In general, more jarosite formed at higher temperatures,  $\text{pH} > 1.6$  and higher solids densities. Excessive precipitation observed in some tests may have been due to effect of seeding of jarosite formed during other tests. Iron extraction did not vary significantly with redox potential between 630-720 mV but there was a slight increase below 630 mV, similar to what was observed for copper.

Overall it would appear that under these high solute concentration or recycle conditions that only temperature has any significant influence on the extraction of copper from chalcopyrite. Lower activations energies were determined which lead the researchers to a possible mechanism in that the sulfate concentration was influencing the passive boundaries of minerals like chalcopyrite and pyrite. This passivating layer may also be why very little change was observed with  $\text{pH}$  and  $E_h$  but further work was needed to confirm these predictions.

## 5 Conclusions

While many studies have investigated chalcopyrite leaching at initial leach conditions, few have investigated extraction rates from recycle leach conditions. This study investigated the leaching of a predominately chalcopyrite ore sample in a solution composition of 25 g/L  $\text{Fe}^{3+/2+}$ , 10 g/L  $\text{Al}^{3+}$ , 1 g/L  $\text{Mg}^{2+}$ , 0.2 g/L  $\text{Cu}^{2+}$ , 125 g/L  $\text{SO}_4^{2-}$ . The amount of copper and iron extraction, and extraction rates, were investigated over a range of temperatures (25-70°C),  $\text{pH}$  values (0.8-1.6),  $E_h$  values (540-720 mV) and solids densities (5-26%), for a period of 10 days. It was concluded that temperature was the only parameter that significantly improved the initial and final rate of copper extraction, and the overall extraction of copper. Solution potentials below 630 mV were also shown to improve the final rate and overall extraction of copper. The  $\text{pH}$  value and solids density had little if any effect on copper extraction or on the initial and final rates of copper extraction, although copper dissolution increased with decreasing  $\text{pH}$ . It was found that temperatures greater than 50°C,  $\text{pH}$  greater than 1.6 and % solids greater than 5% led to the precipitation of jarosite, although this did not affect the copper extraction over the 10 day leach period. The activation energy, the rate of dissolution and the degree of copper extraction is lower under these high solute or recycle concentrations. Similar observations were found when studying pyrite but this study attributed the

lowering of these parameters under recycle conditions to the sulfate concentration causing a diffusion layer around the mineral particles.

## 6 Acknowledgements

The authors would like to thank the Australian Research Council (ARC) and Rio Tinto's Growth and Innovation Group for the funding and direction provided by Rio Tinto personnel involved in the ARC-Linkage Project 'Advanced Studies on the Hydrometallurgy and Electrochemistry of Primary Copper Sulfide Ores' (LP130100991) during this study.

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**Highlights**

- Chalcopyrite ore leached in acidic ferric sulfate media under recycle leach conditions
- Studied were the effects of temperature, solids density, pH and  $E_h$
- The extraction of copper was strongly affected by temperature
- Solids density, pH and  $E_h$  had little effect on the leaching process.

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