# Copper leaching in chloride media with a view to using seawater for heap leaching of secondary sulfides

by

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## Abstract

Copper mines increasingly face the challenge of processing large amounts of low-grade sulfides of elevated concentrations of impurities. In most cases, the challenge is compounded by water scarcity. A potential strategy to address such challenge is to use seawater with elevated concentrations of chloride for heap leaching of secondary sulfides. To ensure success of such heap leach processes, we comprehensively investigated aqueous chloride solution properties at high ionic strength, kinetics of copper extraction from chalcocite in chloride media, and mechanisms by which various factors influence leaching rate, in both acidified ferric and cupric chloride media. The aqueous chloride solution properties were determined by thermodynamic calculations supported by laboratory ORP (oxidation-reduction potential) measurements. The leaching kinetics was quantified by conducting a series of reactor and column leaching tests under fully-controlled conditions. The mechanisms were uncovered using various surface characterization techniques, including SEM-EDX and XPS.

The thermodynamic calculation determined the speciation of iron and copper at increasing chloride concentration up to 3 M, based on which the actual cathodic and anodic reactions responsible for copper extraction were proposed. The kinetics study showed that the leaching reaction slowed down after 70 - 80% of copper was extracted in both ferric and cupric chloride media at ambient temperature. Kinetic models were first developed to satisfactorily describe copper extraction as a function of ORP, chloride concentration, and temperature in reactors, and then scaled up to describe copper leaching performance in columns. The surface characterization results showed that sulfur sequentially transformed from monosulfide to disulfide, and then to polysulfide and elemental sulfur. The slow decomposition of polysulfide was responsible for the

slow leaching at high ORPs, whereas a combination of polysulfide decomposition and diffusion barrier by elemental sulfur layer was the reason for the slow dissolution at low ORPs. The effect of chloride concentration on the reaction rate may only manifest itself at low ORPs where the level of the elemental sulfur crystallinity was lower. This body of knowledge would ultimately pinpoint possible options to optimize the leaching performance.

## Lay Summary

The use of seawater for copper extraction from sulfide minerals is a feasible alternative to freshwater for mining operations located in regions with limited freshwater supply. However, seawater contains high concentrations of chloride ions that may impact the extraction performance. The present study investigated the dissolution of chalcocite (a copper sulfide mineral) using ferric chloride and cupric chloride chemicals. The actual reactions responsible for the dissolution of copper from chalcocite in chloride media were proposed by identifying the speciation of iron and copper in chloride media. Moreover, the kinetics of the dissolution of chalcocite with ferric chloride and cupric chloride were investigated by performing a series of dissolution experiments. To interpret the kinetic data, the evolution of solid surface properties during the dissolution process, particularly morphology and the chemical states of the elements, and the responses of mineral surface properties to different test conditions were investigated.

## Preface

Firstly, the core idea of this research work was introduced by myself under the supervision of Dr. W. Liu. The objectives were discussed and identified by myself with the help of Dr. W. Liu. I was responsible for designing and executing the lab experiments, preparing and analyzing the results, and writing the manuscript. Dr. Liu extensively helped with all aspects of the research work. Professor D. G. Dixon helped with modeling the leaching kinetics and revising the papers published on the leaching kinetics of chalcocite in ferric chloride media.

The journal papers and conference presentations listed below have been prepared from the research work presented in the dissertation. The first article was published based on the experimental data in Chapter 6. The majority of the data presented in Chapter 7 was included in the second article. The third article which was accepted for publication at the time of submitting this thesis, was prepared using the experimental data in Chapter 5. The fourth article was published based on the experimental data presented in Chapter 9.

#### **Peer-Reviewed papers:**

- M. Hashemzadeh, D. G. Dixon, W. Liu, "Modelling the kinetics of chalcocite leaching in acidified ferric chloride media under fully controlled pH and potential", Hydrometallurgy, 186, June 2019, 275-283.
- M. Hashemzadeh, D. G. Dixon, W. Liu, "Modelling the kinetics of chalcocite leaching in acidified cupric chloride media under fully controlled pH and potential", Hydrometallurgy, 189, November 2019, Article 105114.

- M. Hashemzadeh, W. Liu, "Analysis of iron and copper speciation and activities in chloride leaching solutions of high ionic strength", Accepted for publication in Hydrometallurgy, 2020.
- M. Hashemzadeh, W. Liu, "Hashemzadeh, M., Liu, W., 2020. The response of sulfur chemical state to different leaching conditions in chloride leaching of chalcocite. Hydrometallurgy, 105245.

## **Conference** papers

- 1. **M. Hashemzadeh**, W. Liu, "Comparison of Chalcocite Leaching in Ferric Chloride and Cupric Chloride Media", Copper Conference, August 18-21, 2019, Vancouver, Canada
- M. Hashemzadeh, W. Liu, "Cupric chloride leaching of chalcocite under controlled pH and ORP", Proceedings of the 11th International Hydroprocess Conference, May 19-21, 2019, Santiago, Chile
- 3. **M. Hashemzadeh**, V. Concha, and W. Liu, "A New perspective on the kinetics of chalcocite leaching", The Conference of Metallurgists, 2017, Vancouver, Canada
- W. Liu, M. Hashemzadeh, "Modelling copper recovery, total iron concentration and acid balance in chalcocite heap bioleaching", Proceedings of Heap Leach Mining Solutions, 2016, October 18- 20, 2016, Lima, Peru

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3. **M. Hashemzadeh**, W. Liu, "Seawater in heap leaching of chalcocite", The Conference of Metallurgists, 2017, Vancouver, Canada, (Poster).

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# List of Symbols

Symbol	Meaning	Common Unit
K <sub>eq</sub>	Equilibrium constant	
$\alpha'_n$	Cumulative formation constants for Fe(II)	
α <sub>n</sub>	Cumulative formation constants for Fe(III)	
β'n	Cumulative formation constants for Cu(I)	
β <sub>n</sub>	Cumulative formation constants for Cu(II)	
a	Activity	_
С	Solution volume	L
с	Concentration of the interest element	g/L
$d_{\theta}$	Initial particle size	μm
$E^{\theta}$	Standard potential	V Pt. vs SHE
$E^{ heta \prime}$	Formal potential	V Pt. vs SHE
$E_a$	Activation energy	kJ/mol
F	Faraday's constant	C/mol
<i>F(C)</i>	Chemical composition function	_
h	Planck constant	J/s
k	Constant	_
R	Universal gas constant	J/mole/K
t	Time	h
Т	Temperature	Κ
Tref	Reference temperature	Κ
V	Frequency	hertz
x	Copper extraction	_
Χ	Total copper extraction	_
$X_{I}$	Copper extracted in the first leaching stage	_
$X_2$	Copper extracted in the second leaching stage	_
β	Fraction of leachable copper in the first leaching stage	_
γ	Activity coefficient	—
τ	Timescale	h
φ	Topological exponent	_

# List of Abbreviations

Auger electron spectrometry
Energy dispersive X-ray
X-ray Absorption Fine Structure
Full width at half maximum
Inductively coupled plasma optical emission spectrometry
near-edge X-ray Absorption Fluorescence
Oxidation/reduction potential
Pregnant leach solution
Polyvinyl chloride
Relative standard deviation
Shrinking core model
Secondary electron
Scanning Electron Microscopy
Standard hydrogen electron
Specific ion interaction theory
Solvent extraction/Electrowinning
Time-of-flight secondary ion mass spectrometry
X-ray photo-emission spectrometry
X-ray diffraction

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# Dedicated to my parents and my lovely wife Naeimeh

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## **Chapter 1: Introduction**

### **1.1** Research context and significance

The efficiency of water use has increasingly become a priority for the global minerals industry, especially in regions with limited freshwater supplies, such as northern Chile, southern Peru and Australia (Liu et al., 2013, 2011). In these arid regions, groundwater usage has reached its capacity limits, prompting mining companies to search for alternatives to freshwater (Philippe et al., 2010). This situation is compounded by depletion of oxide ores, which is traditionally processed by heap leaching, followed by solvent extraction for leaching solution purification and electrowinning for producing LME Grade copper cathode (Bobadilla-Fazzini et al., 2017). Mining companies increasingly access and process low-grade sulfide ores with elevated concentrations of impurities, such as arsenic. A potential strategy to address these challenges is to directly use seawater and water with elevated concentrations of chloride for heap leaching of secondary copper sulfides, in conjunction with existing solvent extraction and electrowinning facilities built for processing oxides. This is the general motivation of the present research.

Chalcocite leaching has been traditionally practiced using sulfate media with ferric ions as the surrogate oxidant. The leaching process occurs in two distinct stages. In the first stage, chalcocite is converted to a non-stoichiometric intermediate, which is further oxidized to cupric and elemental sulfur in the second stage. Assisted by iron- and sulfur-oxidizing bacteria, the regeneration of ferric ions from ferrous oxidation occurs with sufficiently fast kinetics. However, the challenge associated with a chloride system is that these bacteria do not tolerate chloride at concentrations found in seawater ( $\sim 0.5$  M) (Lawson et al., 1995). This means that fast

regeneration of ferric ions cannot be achieved. In reality, the chloride concentration of process water for heap leaching could be much higher than that of seawater due to evaporation and continuous recirculation of process water. It is very likely that the ionic strength of process water reaches as high as 3 M. Even though acclimatization of bacteria to higher chloride concentrations has been studied (Lo, 1996), tolerance of such high chloride concentrations, if possible, could be very challenging. Therefore, an oxidative chemical heap leach process must be developed for chloride media.

In an oxidative chemical chloride leach process, both cupric and ferric ions can be used as the oxidant. Given the slow oxidation of ferrous to ferric in such chemical leaching system, ferric ions can be regenerated chemically or biologically outside a heap. The use of cupric ions instead of ferric ions may address the problem of slow regeneration of ferric. The use of cupric chloride as the oxidant for copper sulfides leaching has been studied for many years (Herreros et al., 2006; Herreros and Viñals, 2007; Ruiz et al., 1998, 1997). Cuprous ions stabilize in the presence of chloride ions by forming chloro-complexes, which participate in the electrochemical oxidation of copper sulfides. The fast oxidation of cuprous to cupric by oxygen can offer an alternative to the bacterial assisted oxidation of ferrous to ferric (Parker et al., 1981).

Seawater has been used for mineral beneficiation and metal extraction processes (Hernández et al., 2015). Chloride, the major ion in seawater (0.56 M), has been shown to significantly affect the leaching kinetics of copper sulfide concentrates and ores (Watling et al., 2014). To ensure success of copper heap leach processes using seawater or process water with elevated concentrations of chloride (3 M), it is essential to obtain a comprehensive understanding of

chloride aqueous solution properties, factors controlling leaching kinetics, and mechanisms of chalcocite leaching in chloride media. Gaining such understanding is the general goal that drives the author of this thesis to conduct the present research.

### 1.2 Research aim and general methodology

This research aims to comprehensively investigate aqueous chloride solution properties (Chapter 5), kinetics of copper extraction from chalcocite in chloride media (Chapter 6, 7, and 8), and mechanisms by which various factors influence copper leaching reactions (Chapter 9), in both acidified ferric chloride media and cupric chloride media. The aqueous chloride solution properties were mainly determined by thermodyanic calculations in conjuction with some laboratory measurements to verify the results calculated. The leaching kinetics were quantified by carrying out a series of laboratory reactor and column leaching tests under fully-controlled leaching conditions. The leaching mechanisms were uncovered using various surface characterization techniques, including SEM-EDX and XPS. This body of knowledge would enhance the understanding of key factors that control the kinetics of chalcocite heap leaching in chloride media and pinpoint possible options to optimize the leaching performance.

#### 1.3 Thesis outline

This thesis is divided into ten chapters to show the current status of research and gaps in chloride leaching of copper secondary sulfides, the research objectives identified and research methods used, and the research findings obtained by the author on kinetics and mechanisms of copper secondary sulfides leaching in chloride media. Chapter 1 provides the general context of this research and the significance of studying chloride leaching to address the current challenges associated with water and decreasing ore grade.

Chapter 2 provides a detailed literature review of copper chloride leaching, including speciation of iron and copper in chloride media, the kinetics and mechanisms of chalcocite leaching in chloride media, and the solid surface characterization for chloride leaching.

After reviewing the current research and identify research gaps, the author states the general and specific research objectives in Chapter 3 and describes, in detail, the research methods applied to achieve the objectives in Chapter 4.

Chapter 5 reports thermodynamic calculations for determining the speciation of iron and copper in varied concentrations of chloride, the results of which were verified by laboratory ORP measurements. Based on the thermodynamics calculations, the cathodic reduction of ferric and cupric species and the anodic reaction of chalcocite leaching in chloride media were determined.

Chapter 6 and 7 investigate the kinetics of chalcocite leaching in both acidified ferric chloride and cupric chloride media by carrying out reactor leaching tests under fully controlled temperature, pH and ORP, the results of which were used to derive kinetic models and identify rate-limiting steps. The scale-up of the kinetic models to column leaching was reported in Chapter 8.

Chapter 9 deals with the characterization of solid surface properties during leaching and the response of solid surface properties to different leaching conditions using SEM-EDX and XPS techniques.

Chapter 10 provides a summary of the key findings of the present work and recommendations for future work.

## **Chapter 2: Literature review**

### 2.1 Introduction

This chapter reviews the literature of iron and copper speciation in chloride media, the kinetics of chalcocite leaching with ferric chloride and cupric chloride as the oxidants, and solid surface properties of chalcocite in response to chloride leaching. Section 2.2 presents the literature on the iron and copper speciation. The speciation of iron and copper have been studied by both analytical methods and thermodynamic calculations. The iron and copper speciation identified by the analytical methods may be used to confirm the speciation that is obtained through the thermodynamics calculations. For the thermodynamics calculations, an appropriate activity model for high ionic strength is explained in this Chapter. A general approach to calculate the concentration and activity of the leaching solution species is presented in Section 2.3. Section 2.4 shows the thermodynamics of the leaching solution by presenting the Eh-pH diagram of Cu-S-H<sub>2</sub>O and Cu-Cl-S-H<sub>2</sub>O systems.

Section 2.5 summarizes the reported studies on the kinetics of chalcocite leaching in chloride media. Research studies on the leaching kinetics of chalcocite with cupric chloride and ferric chloride are presented to identify the relevant research gaps. The findings in these studies, such as activation energies, reaction orders with respect to the leaching parameters, rate limiting steps, and dissolution models, shed light on the mechanisms of chalcocite leaching in chloride media.

Section 2.6 reviews the research studies on the solid surface properties of chalcocite in sulfate and chloride leaching environment. The surface analysis techniques used in the present study is briefly explained. In addition, a couple of research studies using these techniques on chalcopyrite mineral are presented here as the information from chalcopyrite surface analysis may provide valuable guidance in understanding the solid surface properties of chalcocite.

#### 2.2 Iron and copper speciation in chloride media

#### 2.2.1 Iron chloro-complexes

One of the distinctive features of transition metals is the formation of complexes with ligands. Ligands are molecules or anions containing one or more donor atoms, each of which donates a pair of electrons to form a covalent bond with metal ions. In complex formation, ligands act as Lewis base and metal ions act as Lewis acid. Examples of ligands can be Cl<sup>-</sup>, CN<sup>-</sup>, NH<sub>3</sub>, and H<sub>2</sub>O. The number of ligands (coordination number) bonded to the central metal ion is specific for a given metal ion. For instance, copper (II) has coordination numbers of 2, 4, or 6 in different complex ions.

The ferric and ferrous ions bind six water molecules in a regular octahedral arrangement in aqueous solution (Lundberg et al., 2007). The iron-chloride complex formation has been studied for many years. However, contradictory conclusions have been drawn by different authors, reporting different dominant chemical species (Persson, 2018; Zhao and Pan, 2001). This is due to using different analytical methods and activity models to identify the iron speciation. Ferric ion forms weak complexes with chloride in dilute solutions, while the complexation becomes stronger in hyper-saline solutions and at high temperatures (Tagirov et al., 2000). The complexes formed by ferric chloride include Fe<sup>3+</sup>, FeCl<sup>2+</sup>, FeCl<sub>2</sub><sup>+</sup>, FeCl<sub>3</sub>, and FeCl<sup>4-</sup> (Asakura et al., 1985; Lind, 1967; Magini et al., 2005; Murata et al., 2006; Pokrovski et al., 2003; Standley and Kruh,

1961; Stefansson et al., 2008; Wertz and Luter, 1981; Winand, 1991). FeCl<sub>4</sub><sup>-</sup> only occurs at high chloride concentrations and/or high temperatures (Böhm et al., 2015).

By means of extended X-ray absorption fine structure (EXAFS) technique, Persson (2018) showed that  $Fe^{3+}$  was the dominant chemical species in dilute acidic solution of ferric chloride of 1.0 mM, while  $FeCl_{2^+}$  became dominant when ferric chloride concentration increased to 1.0 M. Stefansson et al. (2008) employed Ultraviolet–visible spectroscopy (UV-Vis) and detected only  $Fe^{3+}$ ,  $FeCl^{2+}$ , and  $FeCl_{2^+}$  in acidified aqueous solution at 25 °C and 50 °C under the following conditions: total Fe concentrations ranged from  $6.184 \times 10^{-5}$  to  $1.652 \times 10^{-4}$  molal, HCl concentration was between  $1.260 \times 10^{-3}$  and 0.128 molal, NaCl concentration range was 0 - 1.805 molal, and HClO<sub>4</sub> concentration ranged from 0 to 0.398 molal.

In a survey of ferrous chloride complexes, Zhao (1997) summarized that over a wide range of temperature and chloride concentration, the predominant ferrous chloride complexes are in the form of octahedral complexes with chloride ligation number  $\leq 2$ ; FeCl<sup>+</sup> and FeCl<sub>2</sub>, and the formation of tetrahedral ferrous chloride complex, FeCl<sub>4</sub><sup>2+</sup>, occurred only at high temperature and chloride concentration. Zhao and Pan (2001) studied the ferrous chloride complexation using a UV-vis near-IR spectrophotometer over a chloride range 1 – 6 molal and temperature 10 – 100 °C. They showed that over the temperature range with chloride concentration less than 3 molal, Fe<sup>2+</sup> was the predominant species, while FeCl<sup>+</sup> became important in solutions with chloride concentrations higher than 1.0 molal. The FeCl<sub>2</sub> species was always less than 20% of the total ferrous concentration, and the concentration of FeCl<sub>4</sub><sup>2-</sup> complex started to contribute to the total ferrous concentration at temperatures higher than 80 °C and when the chloride concentration

exceeded 4 molal. They also showed that the hydrolysis of ferrous occurred only above natural pH over the tested temperature range. In another study, Heinrich and Seward (1990) investigated the ultraviolet absorption spectra of speciation of ferrous in a system with chloride concentrations ranging from 0.01 to 3.4 molal, Fe(II) concentrations ranging from 0.005 to 0.025 molal, and at 25, 50, 100, 150, and 200 °C. They showed that at temperatures lower than 100 °C, only Fe<sup>2+</sup> and FeCl<sup>+</sup> were detectable, whereas at higher temperatures a minor concentration of FeCl<sub>3</sub> started to emerge.

In summary, given that the concentration of ferric ion in a heap leaching process typically does not go above 0.1 molal (Schlesinger et al., 2011), ferric chloride speciation may include  $Fe^{3+}$ ,  $FeCl^{2+}$ , and  $FeCl_{2^+}$  depending on chloride concentration for such systems. The most likely speciation of ferrous ion in aqueous solutions containing chloride concentration less than 3 molal are  $FeCl^+$  and  $Fe^{2+}$ .

## 2.2.2 Copper chloro-complexes

A number of studies have been conducted on cuprous chloride complexation (Berger and Winand, 1984; Brugger et al., 2007; Carlsson and Wettermark, 1976; Fritz, 1984, 1981; Hikita et al., 1973; Sherman, 2007; Sugasaka and Fujii, 1976). It is generally believed that cuprouschloride species can be formed in chloride solutions in the form of CuCl, CuCl<sub>2</sub><sup>-</sup>, CuCl<sub>3</sub><sup>2-</sup>, CuCl<sub>4</sub><sup>3-</sup>, and even in polynuclear ones like Cu<sub>2</sub>Cl<sub>4</sub><sup>2-</sup> and Cu<sub>3</sub>Cl<sub>6</sub><sup>3-</sup>. Polynuclear complexes are probably not present in dilute Cu(I) solutions, as reported by Sharma and Millero (1990) who measured the ultraviolet absorption spectra of cuprous species and showed that no polynuclear complexes formed in copper concentration range 50-200 µM. Also, some studies concluded that
in solutions containing less than 6 M chloride and at room temperature, only  $CuCl_2^-$  and  $CuCl_3^{2-}$  were predominant (Ahrland and Rawsthorne, 1970; Fritz, 1981; Sharma and Millero, 1990; Sugasaka and Fujii, 1976). In addition, researchers showed that even in concentrated CuCl and high salinity,  $CuCl_4^{3-}$  was not observed. Examples are Brugger et al. (2007) who used XANES (X-ray absorption near edge structure) and EXAFS techniques and concluded that only  $CuCl_3^{2-}$  predominated at room temperature and high salinity (LiCl > 3 M) and Sherman (2007) who used Ab initio molecular dynamic simulation method, observed a stable  $CuCl_3^{2-}$  complex in 1 M CuCl and 4 M chloride solution at room temperature. However, a few authors have shown the presence of  $CuCl_4^{3-}$  in solutions containing chloride as low as 3 M (Ciavatta and Iuliano, 1998; Hikita et al., 1973).

The complexation of cupric ion with chloride is also controversial. For example, using EXAFS technique, Collings et al. (2000) observed no chloro-copper complex at temperatures up to 75 °C in solutions containing less than 2.2 M chloride. However, at a higher chloride concentration with 5 M NaCl, CuCl<sup>+</sup> was observed at temperature between 25 °C and 75 °C. This is in contrast with what Berger and Winand (1984) observed in their research. They stated that at low concentrations of chloride, copper (II) ions existed as Cu<sup>2+</sup>, whereas CuCl<sub>3</sub><sup>-</sup> and CuCl<sub>4</sub><sup>2-</sup> became dominant when the chloride concentration reached 2.5 and 5 M, respectively.

Overall, the speciation of Cu(I) and Cu(II) in chloride media depends on the concentration of copper and chloride and the reported speciation scatters in the literature. Generally, in aqueous solutions containing Cu(I), Cu(II), and chloride (< 6 M), Cu(I) ions are more likely to be present

in the form of  $CuCl_2^-$  and  $CuCl_3^{2-}$ . In these solutions, Cu(II) ions may exist as  $Cu^{2+}$ ,  $CuCl^+$ ,  $CuCl_3^-$  and  $CuCl_4^{2-}$  depending on the concentration of chloride.

## 2.2.3 Iron and copper speciation studies using thermodynamic calculations

Studies have been conducted to identify the speciation of copper and iron in chloride media using thermodynamic calculations (Hubli et al., 1997; Kim et al., 1986; Kimura et al., 1984). However, in these studies either the effect of ionic strength has been ignored, or the speciation studies were conducted using activity models suitable only for low ionic strength (< 0.5 M). For example, Kim et al. (1986) investigated the speciation of iron in chloride concentration range 1 – 5 M using the Davies model, which is suitable for low ionic strength (< 0.5 M). According to their results, hydrated ferric was dominant at chloride concentrations up to almost 3 M, above which FeCl<sub>3</sub> became dominant. Hydrated ferrous dominated in solution at chloride concentrations up to almost 2.2 M, beyond which FeCl<sub>2</sub> appeared to be dominant. Kimura et al. (1984) also employed Davies model to study the speciation in the FeCl<sub>3</sub>–FeCl<sub>2</sub>–CuCl<sub>2</sub>–CuCl–NaCl–HCl–H<sub>2</sub>O system in the ionic strength range 0.1 - 7 molal. They showed that when the concentration of all components added to solution was 0.01 molal, the dominant species were Fe<sup>3+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, CuCl<sub>2</sub><sup>-</sup>, while FeCl<sub>3</sub>, FeCl<sub>2</sub>, CuCl<sub>2</sub>, and CuCl<sub>3</sub><sup>2-</sup> became dominant when the concentrations of all components increased to 3 molal.

### 2.2.4 Activity models

Developing a hydrometallurgical process depends upon a profound knowledge of the physical properties of metal ions and salts in solution to understand the interactions of ions in solution and their impact on ion activity, complexation, ion speciation, solubility, and reduction potential 11

(Muir and Senanayake, 1985). The activity of any species in a solution is equal to its concentration at infinite dilution. However, at higher ionic strength the ion activity alters. This change is represented by activity coefficient, which is obtained by dividing the ion activity of the ith species,  $a_i$ , by its concentration,  $C_i$  (Robinson and Stokes, 1959).

$$\gamma_i = \frac{a_i}{c_i} \tag{2-1}$$

A number of models have been developed to predict the activity of species in aqueous electrolyte solutions. These models include Debye-Huckel, Davies, B-dot, Brønsted–Guggenheim-Scatchard Specific Interaction Model (SIT), Bromley–Zaemaitis, Electrolyte NRTL, Mixed Solvent Electrolyte (MSE), Meissner, Three-Characteristic-Parameter Correlation (TCPC), Binding Mean Spherical Approximation (BIMSA), and Pitzer model (Ge et al., 2008; Kusik and Meissner, 1975; Lin et al., 1998; Meissner and Tester, 1972; Pitzer and Silvester, 1977; Renon, 1986; Scatchard, 1976).

The Pitzer model is the most comprehensive model to describe the non-ideal behavior of ionic solutions. The Pitzer equations calculate both the long-range forces between ionic species and the short-range forces between all species. However, the model generally requires a large number of coefficients, and the complete set of the Pitzer coefficients is only available for simple salt-water systems. Such data are usually scarce for complex systems, especially systems containing complexes such as copper and iron chloro-complexes (Wang et al., 1997; Yue et al., 2014). Meissner model can also be applied to solutions with high ionic strength (up to 20 molal). However, this model is suitable for salt activity calculation in aqueous solutions when the ion pairing and complex formation are negligible (Renon, 1986).

The SIT model is a simplified version of the Pitzer model, ignoring the triple interactions, which become important only in very concentrated solutions, and the interactions between ions of the same charge, which are very small (Wang et al., 1997). The SIT activity model has been successfully applied for ionic strength up to 4 M and for NaCl solutions up to the saturation concentration at 25 °C (Xiong, 2006). Eq. (2–2) represents the SIT model.

$$log\gamma_i = -\frac{AZ_i^2 I^{0.5}}{1+1.5I^{0.5}} + \sum_j \in (i,j)m_j$$
(2-2)

where A is the Debye-Huckel parameter (at 25 °C and 1 atm, A = 0.51),  $m_j$  is the concentration of ion j in mol/kg,  $\in$ (i,j) is the SIT coefficient, and the summation covers the interactions of all ions of opposite charge and neutral species. The first term in SIT model calculates the long-range electrostatic interactions of ions, and the second term represents the short-range interactions of ion-ion, ion-neutral, and neutral-neutral. The  $\in$ (i,j) has a value of zero if the charge of ions are identical. For completely dissociated electrolytes, the accuracy is believed to be above 90% for ionic strength as high as 6-10 molal (Wang et al., 1997). In Eq. (2–2), *I* is the ionic strength which was first introduced by Gilbert Newton Lewis and Merle Randall in 1921 (Pilson, 1998). Ionic strength is calculated by Eq. (2–3) in which  $C_i$  and  $Z_i$  are, respectively, the ionic concentration and ionic charge of the *i*th species present in the solution. In the present work, the SIT model was applied to calculate the activity coefficients of iron and copper species in chloride media.

$$\mathbf{I} = \frac{1}{2} \sum C_i \cdot Z_i^2 \tag{2-3}$$

## 2.3 Copper and iron species activity calculation approach

In this Section, the general procedure to calculate the activity of the species present in a leaching solution is described. According to Eq. (2-1), the concentration and activity coefficient of each species are required to obtain the activity of each species. To calculate the concentration of a species, an equation system involving stability constants equations, mass balance equations, and electrical charge neutrality equations, is used (Anderson and Crerar, 1994). Table 2.1 shows all the required equations and thermodynamic data for a leaching solution containing HCl-NaCl-CuCl<sub>2</sub>-FeCl<sub>3</sub>-FeCl<sub>2</sub>-H<sub>2</sub>O. In Table 2.1, Eqs. (2-4) to (2-8) are the stability constants equations for iron and copper, Eqs. (2-9) to (2-15) are the mass balance equations, and Eq. (2-16) is the electrical charge neutrality equation.

In Table 2.1,  $\beta_n$  and  $\beta'_n$  are the cumulative formation constants for Cu(II) and Cu(I) complexes, respectively,  $\alpha_n$  and  $\alpha'_n$  are the cumulative formation constants for, respectively, Fe(III) and Fe(II) complexes, m is concentration in molal, K<sub>eq</sub> is the equilibrium constant for the reaction (Eq. (2.8)) involving Fe<sup>3+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, and Cu<sup>+</sup>, and  $\gamma$  is the activity coefficient. The thermodynamic data for all copper and iron species are available in the literature (Kimura et al., 1984).

In the equation system, the concentrations of total copper, total iron, and total chloride are known, so the concentrations of other species must be calculated. In a system consisting of HCl, NaCl, CuCl<sub>2</sub>, FeCl<sub>3</sub>, and FeCl<sub>2</sub>, the following procedure is applied. At first, the values of activity coefficients in Eqs. (2-4) to (2-8) are assigned unity and the concentrations of all species are calculated through Eqs. (2-9) to (2-16). Then, the ionic strength of the solution is calculated

using Eq. (2-3) (Pilson, 1998). After obtaining the solution ionic strength, the activity coefficients of all species are calculated using Eq. (2-2) and the corresponding activities are calculated using Eq. (2-1). In the next step, the newly calculated activities are placed in Eqs. (2-4) to (2-8) and again new concentrations and activities are obtained through Eqs. (2-9) to (2-16) and Eqs. (2-2) to (2-3). If activity correction is required, this method will be iterated until successive concentrations and activities stop changing within some acceptable limits. The equation system may be solved using Excel VBA (Visual Basic for Application) programming language or by any commercial software.

Eq.#	Copper	Eq.#	Iron			
(2-4)	$\beta_{n} = \frac{\gamma_{CuCl_{n}^{(2-n)}}m_{CuCl_{n}^{(2-n)}}}{\gamma_{Cu^{2}}+m_{Cu^{2}}+\gamma_{Cl}}m_{Cl}}$	(2-6)	$\alpha_{n} = \frac{\gamma_{FeCl_{n}^{(3-n)}}m_{FeCl_{n}^{(3-n)}}}{\gamma_{Fe^{3}}+m_{Fe^{3}}+\gamma_{Cl}}m_{Cl}}$			
(2-5)	$\beta'_{n} = \frac{\gamma_{CuCl_{n}^{(1-n)}}m_{CuCl_{n}^{(1-n)}}}{\gamma_{Cu}+m_{Cu}+\gamma_{Cl}{}^{n}m_{Cl}{}^{n}}$	(2-7)	$\alpha'_{n} = \frac{\gamma_{FeCl_{n}^{(2-n)}}m_{FeCl_{n}^{(2-n)}}}{\gamma_{Fe^{2}}+m_{Fe^{2}}+\gamma_{Cl}{}^{n}m_{Cl}{}^{n}}$			
(2-8)	$Fe^{3+} + Cu^+ = Fe^{2+} + Cu^+$	$Fe^{3+} + Cu^{+} = Fe^{2+} + Cu^{2+} \qquad K_{eq} = \frac{\gamma_{Fe^{2+}m_{Fe^{2+}}\gamma_{Cu^{2+}}m_{Cu^{2+}}}}{\gamma_{Fe^{3+}m_{Fe^{3+}}\gamma_{Cu^{+}}m_{Cu^{+}}}}$				
(2-9)	$m_{Cu(I)} = \sum_{n=0}^{3} m_{CuCl_{n}^{(1-n)}}$	(2-12)	$m_{Fe(III)} = \sum_{n=0}^{3} m_{FeCl_n^{(3-n)}}$			
(2-10)	$m_{Cu(II)} = \sum_{n=0}^{3} m_{CuCl_{n}^{(2-n)}}$	(2-13)	$m_{Fe(II)} = \sum_{n=0}^{2} m_{FeCl_n^{(2-n)}}$			
(2-11)	$m_{Cu_{Total}} = m_{Cu(II)} + m_{Cu(I)}$	(2-14)	$m_{Fe_{Total}} = m_{Fe(III)} + m_{Fe(II)}$			
(2-15)	$m_{Cl_{Total}} = m_{Cl_{free}} + \sum_{n=1}^{3} n \times m_{CuCl_{n}^{(2-n)}} + \sum_{n=1}^{3} n \times m_{CuCl_{n}^{(1-n)}} + \sum_{n=0}^{3} m_{FeCl_{n}^{(3-n)}} + \sum_{n=0}^{2} m_{FeCl_{n}^{(2-n)}}$					
(2-16)	$m_{H^{+}} + m_{Cu^{+}} + 2m_{Cu^{2+}} + m_{CuCl^{+}} + m_{Na^{+}} + \sum_{n=1}^{2} (3-n)m_{FeCl_{n}^{(3-n)}} + FeCl^{+} = m_{Cl_{free}^{-}} \sum_{n=2}^{3} (n-1)m_{CuCl_{n}^{(1-n)}} + m_{CuCl_{3}^{-}}$					

Table 2.1 The required equations for calculation the activity of leaching species in HCl-NaCl-CuCl<sub>2</sub>-FeCl<sub>3</sub>-FeCl<sub>2</sub>-H<sub>2</sub>O system

### 2.4 Thermodynamics of chalcocite leaching

The thermodynamics of a leaching solution can be described by a Pourbaix diagram. Figure 2.1 shows the Eh–pH diagram of the Cu-S-H<sub>2</sub>O system at 25 °C, which was plotted using the STABCAL software (Gow et al., 2016; Huang et al., 2005; Huang and Young, 1996). According to Figure 2.1, the leaching of chalcocite requires a pH value lower than 6 and an ORP higher than approximately 0.4 V vs SHE. Sulfuric acid is typically used to lower the pH of the leaching solution and ferric, cupric, and dissolved oxygen are the common oxidants to dissolve chalcocite. It is noteworthy that the pH value must be lower than 2 in the case that ferric ion is used as the oxidant due to hydrolysis of ferric ion. Figure 2.2 shows the Pourbaix diagram of the Cu–S–Cl–H<sub>2</sub>O system at 1 M chloride concentration. In Figure 2.2, Cu(I) species appears in the Eh–pH diagram, which is attributed to the stabilization of cuprous ions by chloride via complexation. More detailed information is provided in Chapter 5.



Figure 2.1 Eh-pH diagram of the Cu–S–H<sub>2</sub>O system drawn using the STABCAL software at 25 °C, 0.01 M [Cu], and 0.01 M [S]



Figure 2.2 Eh-pH diagram of the Cu–S–Cl–H<sub>2</sub>O system drawn using the STABCAL software at 25 °C, 0.01 M [Cu], 0.01 M [S], and 1 M [Cl]

#### 2.5 Chalcocite leaching in chloride media

Chalcocite with the formula Cu<sub>2</sub>S is the most common secondary copper sulfide mineral on the earth. Copper extraction from secondary copper sulfide minerals is generally carried out via heap bioleaching in which iron- and sulfur- oxidizing bacteria, in acidified sulfate media, assist the leaching process. The rate of chalcocite leaching is more rapid than that of primary copper sulfides, such as chalcopyrite. However, it is still substantially slower than those of copper oxidized minerals, such as malachite and azurite. As a result, many research studies have been conducted to increase the copper extraction rate. Different leaching media, such as ferric ion, cupric ion, oxygen, cyanide, ammonium, and chlorine have been examined to enhance the extraction rate. Another alternative to the acidified ferric sulfate leaching is chloride leaching process, which has recently gained intense interest due to pressure to reduce freshwater withdrawal in regions where copper mines are mostly located.

As opposed to the understanding of copper leaching kinetics and pathways in sulfate media, there is not as much understanding in chloride media. The knowledge gained with the sulfate system provides valuable guidance in understanding the chloride system. Sullivan (1930) showed that the leaching of chalcocite in an acidified ferric sulfate solution occurred in two distinct stages. In the first stage, chalcocite is converted to secondary covellite mineral by Eq. (2–17), which is further oxidized to cupric and elemental sulfur in the second stage by Eq. (2–18). The first stage has been shown to form a series of reaction intermediates, including djurleite  $Cu_{1.94}S$ , digenite  $Cu_{1.8}S$ , anilite ( $Cu_{1.75}S$ ), and blue-remaining covellite, which is composed of geerite

(Cu<sub>1.6</sub>S), spionkopite (Cu<sub>1.4</sub>S) and yarrowite (Cu<sub>1.12</sub>S) (Cavallotti and Salvago, 1969; Thomas et al., 1967; Whiteside and Goble, 1986).

The completion of the first stage of chalcocite leaching has become a matter of controversy. Some researchers believed that the first stage was completed as chalcocite was converted to blue remaining covellite (Cu<sub>1.2</sub>S) (Bolorunduro, 1999; Petersen and Dixon, 2007; Whiteside and Goble, 1986). Hashemzadeh et al. (2017) showed that the completion of the first stage depended on the leaching conditions, such as ferric concentration and temperature. They proposed Eqs. (2–19) and (2–20) to describe the two stages of chalcocite leaching in sulfate media. In Eqs. (2–19) and (2–20), *x* is the fraction of leachable copper in the first stage of chalcocite leaching, which depends on ferric concentration and temperature.

$$Cu_2S + 2Fe^{3+} \rightarrow CuS + Cu^{2+} + 2Fe^{2+}$$
 (2-17)

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^0$$
 (2-18)

$$Cu_2S + 4xFe^{3+} \rightarrow Cu_{2(1-x)}S + 2xCu^{2+} + 4xFe^{2+}$$
(2-19)

$$Cu_{2(1-x)}S + 4(1-x)Fe^{3+} \rightarrow 2(1-x)Cu^{2+} + 4(1-x)Fe^{2+} + S^{0}$$
(2-20)

Two-stage leaching has been proposed in acidic chloride media (Cheng and Lawson, 1991a; Herreros et al., 2006; King et al., 1975). The formation of non-stoichiometric compounds in chloride media has also been explored. Herreros et al. (2006) detected spionkopite and geerite in an investigation on the leaching of djurleite in acidic chloride media.

### 2.5.1 Leaching kinetics and mechanisms in ferric chloride media

The kinetics of chalcocite and covellite leaching in chloride media have been investigated using chemical and electrochemical techniques, with different oxidants in the leaching system, 20

including oxygen, ferric, and cupric ions (Cheng and Lawson, 1991a, 1991b; Fisher, 1994; Herreros et al., 2006; King, 1966; Miki et al., 2011; Nicol and Basson, 2017; Nicol, 1984; Ruiz et al., 1997; Vracar et al., 2000). In the leaching kinetics studies, the effect of leaching parameters, such as ferric ion, ferrous ion, ORP, chloride concentration, particle size, and temperature, are investigated. Based on the kinetics results, the reaction order with respect to the leaching parameters and the activation energy are obtained. The activation energy is treated as an indicator of the rate limiting mechanism in the leaching process. According to Crundwell (2013), an activation energy below 20 kJ/mol indicates a diffusion controlled leaching process, whereas the activation energy of a chemical reaction controlled process is above 40 kJ/mol. The reaction orders with respect to the leaching parameters also assist to identify the rate limiting steps. The reaction order of one usually supports a diffusion controlled process (Crundwell, 2013).

The dissolution mechanism of the first and second stages of chalcocite leaching with ferric chloride have been reported in the literature (Hirato et al., 1989; King, 1966; Miki et al., 2011). King (1966) obtained a low activation energy of 3.4 kJ/mol for the first stage of chalcocite leaching and 101–122 kJ/mol for the second stage of leaching. The author thus concluded that in ferric chloride media, the diffusion of cupric ions through the sulfide lattice was limiting the dissolution rate of chalcocite in the first stage and the chemical reaction controlled the dissolution rate in the second stage. Miki et al. (2011) calculated an activation energy of 71.5 kJ/mol for the dissolution of covellite mineral in ferric chloride media. They proposed the chemical reaction as the rate controlling step. Hirato et al. (1989) showed that the dissolution rate of covellite media was controlled by an electrochemical mechanism. Studies on chalcocite in chloride media with other oxidants, such as oxygen and cupric ions, have shown a

mixed kinetics mechanism for the second stages of chalcocite leaching (Cheng and Lawson, 1991a, 1991b; Ruiz et al., 1997).

#### 2.5.2 Leaching kinetics and mechanisms in cupric chloride media

Secondary copper sulfides, specifically chalcocite, is typically processed via heap bioleaching in sulfate media, where iron- and sulfur-oxidizing bacteria assist the regeneration of ferric from ferrous oxidation (Weston, 1995). The growth of these bacteria in chloride concentration of more than 7 g/L is inhibited (Lawson et al., 1995). Nevertheless, in the presence of chloride ions cupric (II) and cuprous (I) ions form chloro-complexes, which could act as an electrochemical couple that oxidizes chalcocite (Wilson and Fisher, 1981). In addition, Cu(I) ion is oxidized by atmospheric oxygen to regenerate Cu(II) with fast kinetics, thereby offering an alternative to bacteria-assisted oxidation of Fe(II) to Fe(III) in sulfate media (Parker et al., 1981). The fast oxidation of cuprous ion by oxygen has prompted researchers to study the kinetics and the mechanism of chalcocite leaching in cupric chloride media as an alternative to the acidified ferric sulfate system. Hence, a brief literature of the dissolution of chalcocite in cupric chloride is presented here.

A comparison of chalcocite dissolution in the sulfate, perchlorate, nitrate, chloride, ammonia, and cyanide systems (using oxygen as the oxidant) was carried out by Fisher (1994). The author showed that in systems with no ligand (sulfate, perchlorate, and nitrate solutions) the dissolution proceeded in two steps and the rate of the first step was very slow. In contrast, when ligands such as chloride, ammonium, or cyanide exist, the dissolution occurred in two steps, and the rate of

the first step was 60 to 90 times faster than that in non-complexing systems depending on the ligand type.

The mechanism of chalcocite leaching in cupric chloride media has been proposed by researchers based on the kinetics experimental data, such as reaction orders and activation energies. Cheng and Lawson (1991) conducted a comprehensive study on the kinetics of chalcocite leaching in acidic oxygenated sulfate-chloride solutions. They proposed that the kinetics of the first stage was controlled by the diffusion of oxygen through the boundary layer around the chalcocite particles. For the second stage, it was proposed that the leaching kinetics in the early second stage was described by the chemical reaction controlled shrinking core model and in the late second stage, by both the surface chemical reaction and pore diffusion processes. The activation energies of 33.5 kJ/mol and 69 kJ/mol were obtained in the first and second stages, respectively. They ignored the participation of cupric ion in the chalcocite dissolution, and they believed that chalcocite was only attacked by oxygen and acid (Cheng and Lawson, 1991a).

Cheng and Lawson (1991b) also studied the dissolution kinetics of a synthetic covellite mineral in oxygenated acidic sulfate-chloride solutions. They described the kinetics using the shrinking core model and concluded that the covellite leaching was controlled by a chemical reaction process in the initial stages and by both chemical reaction and pore diffusion in the late stages. They also found that in the absence of chloride, no covellite dissolution occurred, for which they concluded that it was most likely due to the formation of a cryptocrystalline or amorphous passivating sulfur layer. However, it is noteworthy to mention that in the absence of chloride ion, the electrochemical couple of Cu(II)/Cu(I) is not formed, and therefore the dissolution does not commence. Hence, their hypothesis of forming cryptocrystalline or amorphous passivating sulfur layer in the absence of sulfur could be inaccurate.

Ruiz et al. (1998) studied the digenite (Cu<sub>1.8</sub>S) dissolution kinetics in the CuCl<sub>2</sub>-HCl-NaCl-O<sub>2</sub> system. They showed that in the first stage of leaching, the fraction of the extracted copper ( $\alpha$ ) was linearly proportional to time, whereas in the second stage, the leaching of covellite was represented by a shrinking core diffusion-controlled model. They calculated the activation energies of 15.8 and 80.0 kJ/mol for the first and second stages, respectively. Contradicting with Cheng and Lawson (1991a), they proposed that the leaching reaction of digenite with oxygen occurred by the attack of cupric ions on the copper sulfides to produce cuprous ions.

Vracar et al. (2000) evaluated the atmospheric leaching of copper (I) sulfide in calcium chloride solution with HCl and oxygen. They also found that the chalcocite leaching rate was diffusion-controlled and of second order with respect to the concentration of total chloride ions. For the total leaching reaction, an activation energy equivalent to  $66 \pm 0.8$  kJ/mole was calculated. They proposed the role of chloride ions in chalcocite dissolution to be the disruption of the passivating sulfur layer on the copper sulfide surfaces. Chloride ions were thought to be associated with the formation of crystalline sulfur rather than a crypto-crystalline or amorphous product. However, they provided no evidence to support their conclusion.

The leaching kinetics of djurleite was studied by Herreros et al. (2006) with copper sulfate as the oxidant in the presence of sodium chloride. The leaching conditions were: copper concentration 0.02-0.23 M, chloride concentration 0.6-1.3 M, and temperature 20-80 °C. They concluded that

the kinetics was governed by chemical reaction with an activation energy of 35 kJ/mol and the reaction orders were 0.23 and 0.53 with respect to the total Cu(II) and total Cl<sup>-</sup>, respectively.

The leaching kinetics of synthetic covellite, chalcocite and digenite were also studied in dilute HCl solutions containing copper(II) and iron(III) at controlled potentials and low temperatures (Miki et al., 2011). The authors found that the dissolution rate of covellite was independent of the concentration of Cl<sup>-</sup> and HCl in the range 0.2 to 2.5 M and 0.1 to 1 M, respectively and an activation energy of 72 kJ/mol was obtained showing that the dissolution reaction was controlled by the chemical reaction. It was also shown that covellite dissolution at 600 mV and 650 mV was similar but lower at potential 550 mV. For chalcocite and digenite, at 500 mV, the relatively rapid initial dissolution did not proceed beyond about 50% and 45% copper dissolution, respectively, supporting the formation of secondary covellite phase, which cannot be leached at a potential of 500 mV. However, increasing the potential led to the quick dissolution of secondary covellite relative to primary covellite.

An electrochemical study was recently conducted by Nicol and Basson (2017) on the anodic behavior of covellite in chloride solution. They showed an active but slow dissolution at potentials below about 0.65 V, a passivation in the potential range 0.7-1.4 V, and a rapid transpassive dissolution above 1.4 V. This behavior has also been observed for chalcopyrite under similar conditions. They proposed a dissolution mechanism in which the formation of polysulfides (typically CuS<sub>2</sub>) is responsible for the passivation, Eq. (2–21).

$$Cu_2S_2 = CuS_2 + Cu(I) + e^-$$
 (2-21)

#### 2.5.3 Chalcocite dissolution model and leaching pathway

The information from kinetics study and surface characterization enables researchers to propose a mineral dissolution model and reaction pathways. Cheng and Lawson (1991a) explained the dissolution of chalcocite in an oxygenated chloride solution based on the information from SEM analysis and kinetics data. They believed that cuprous chloride complexes are only stable in slurries with very high pulp density where the reaction solution is oxygen starved. Hence, they concluded that chalcocite was only attacked by dissolved oxygen and, therefore, the first stage of chalcocite leaching was controlled by the diffusion of oxygen through the liquid film around the solid particles. The half anodic and cathodic reactions for the first stage of chalcocite leaching was proposed as Eq. (2-22) and (2-123). The overall leaching reaction is shown in Eq. (2-24).

$$Cu_2S = Cu^{2+} + CuS + 2e^{-}$$
(2-22)

$$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O$$
 (2–23)

$$Cu_2S + \frac{1}{2}O_2 + 2H^+ = Cu^{2+} + CuS + H_2O$$
(2-24)

For the second stage of chalcocite leaching, Eqs. (2-25) and (2-26) were proposed as the anodic half reaction and the overall leaching reaction. The half cathodic reaction is the same as in the first stage, Eq. (2-23).

$$CuS = Cu^{2+} + S^0 + 2e^-$$
(2-25)

$$CuS + \frac{1}{2}O_2 + 2H^+ = Cu^{2+} + S^0 + H_2O$$
(2-26)

The second stage was assumed to occur in parallel to the first stage but at much lower reaction rate. In the second stage, covellite dissolves and leaves behind a shell of elemental sulphur around the unreacted covellite. The role of chloride ion was deemed to disrupt the sulfur passivating layer, forming a more crystalline sulfur layer rather than a cryptocrystalline or amorphous one in absence of chloride. This porous crystalline sulphur layer enhances the reaction rate by increasing the diffusion of the reactants.

Fisher et al. (1992) proposed a leaching model for each stage of chalcocite leaching in chloride media. Figure 2.3 shows the sequential leaching of chalcocite in the first leaching stage in which cuprous ions diffuse from the interior layers towards the surface and form complexes with chloride ions. In parallel, oxygen is adsorbed on the surfaces of the particles and reduced by the electrons from the oxidation of  $S^{2-}$  to  $S_2^{2-}$ . The cuprous chloride complexes may also be oxidized by the dissolved oxygen to hydrated cupric ion or cupric chloride complexes. The second leaching stage model of chalcocite leaching was depicted in Figure 2.4. Oxygen was reduced on the solid surfaces through Eqs. (2-27) to (2-30) and the electrons were supplied by the oxidation of blue-remaining covellite.

$$O_2 + H^+ + e^- = HO_2$$
 (2-27)

$$HO_2 + H^+ + e^- = H_2O_2$$
(2-28)

$$H_2O_2 + H^+ + e^- = H_2O + OH$$
 (2-29)

$$OH + H^+ + e^- = H_2O$$
 (2-30)

Ruiz et al. (1998) studied the leaching of digenite in an oxygenated chloride solution. They proposed Eqs. (2-31) and (2-32) as the anodic half reactions for the first and second stage of digenite leaching in chloride media and Eq. (2-33) as the cathodic half reaction.

 $Cu_{1.8}S = Cu^+ + 0.8CuS + 0.8e^-$ (2-31)

$$CuS = Cu^{+} + S^{0} + e^{-}$$
(2-32)

$$Cu^{2+} + e^{-} = Cu^{+}$$
 (2-33)

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Figure 2.3 Physico-chemical model for the first stage of chalcocite dissolution in the chloride system (Fisher et

al., 1992)



Figure 2.4 Electrochemical model of second stage chalcocite dissolution in the chloride system (Fisher et al.,

The authors provided Figure 2.5 as a schematic diagram of the dissolution of digenite in the oxygenated chloride media in the first stage (a) and second stage (b). According to Figure 2.5, in the first leaching stage, the anodic half reaction occurs at the interface I,  $Cu_{1.8}S - CuS$ . The cathodic reaction occurs at the interface II, CuS - solution given that covellite is capable of electron conduction; this means that the first stage acts as a galvanic couple. They also showed that the reaction rate in the first stage was a linear function of time. Based on this finding, they proposed that the two stages of leaching occurred in sequence. In a sequential dissolution, the external surface of the mineral particle should remain essentially constant until all the digenite is converted to covellite. Therefore, if the kinetics is controlled by the diffusion of  $Cu^{2+}$  through the liquid film toward the external surface of the particle, the reaction rate will be constant, which was in accordance with their finding of the linear dependency.

For the second stage of chalcocite leaching, they proposed that a sulfur layer formed over the surface of the covellite particles and the anodic and cathodic reactions occur at the interface III,  $CuS-S^0$ . This is due to the non-conductivity of the sulfur layer. Therefore, the  $Cu^{2+}$  ions must diffuse toward the shrinking core of unreacted CuS and therefore, the rate limiting process was concluded to be the diffusion of the oxidant through a growing layer of sulfur. However, they did not provide any surface characterization information to support their assumption that sulfur was the product layer on the surface.



Figure 2.5 Schematic diagram of electrochemical dissolution of digenite in oxygenated chloride media: (a) first-stage galvanic couple and (b) second- stage corrosion couple (Ruiz et al., 1998)

## 2.6 Surface characterization of chalcocite

In general, the slow dissolution of copper sulfides at ambient temperature is believed to be associated with the formation of a passivating layer, such as metal-deficient sulfide, jarosite, polysulfides, and sulfur (Dutrizac, 1990; Ghahremaninezhad et al., 2013; Klauber et al., 2001; Yang et al., 2015). Various surface analysis techniques have been utilized to characterize surface properties, such as composition and morphology. A significant amount of work has been conducted on the formation of the passivating layer in the leaching of chalcopyrite, but little information is available on the behavior of the product layer in chalcocite leaching process (Niu et al., 2015). The knowledge obtained on chalcopyrite provides valuable guidance in understanding the surface analysis of chalcocite surface.

The formation of a sulfur layer in acidic chloride leaching of chalcocite has been hypothesized to be the cause of the slow dissolution. Cheng and Lawson (1991) examined the sulfur formation on the surface of chalcocite by pausing the leaching test and washing the chalcocite leaching residue by xylene to dissolve the sulfur layer. The leaching test was conducted under the following conditions: particle size 42µm, 85 °C, 0.5 M H<sub>2</sub>SO<sub>4</sub>, and 0.5 M NaCl. The leaching residue after washing with xylene was placed back in the leaching reactor and the leaching was resumed. The results showed an increase by around 10% in the copper extraction compared with the case without xylene washing. Fisher et al. (1992) used SEM to analyze the morphology of chalcocite leaching residues in chloride media. They showed the presence of a product layer on the solid surface, but no information was provided on the characteristics of the product layer. The surface analysis of chalcocite leaching in chloride media has not been well studied.

### 2.6.1 Surface characterization by Scanning Electron Microscopy (SEM)

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) has been widely applied to study the solid surface properties in the leaching of copper sulfide minerals (Niu et al., 2015; Qian et al., 2014; Sokić et al., 2009; Vela, 2000). A scanning electron microscope uses a focused beam of electrons to produce images of a sample. The electrons from the focused beam interact with the atoms of a sample and produce various signals containing information about the sample surface and its composition. These signals include secondary electrons providing topographic information, backscattered electrons producing compositional information, and characteristic X-rays which provides elemental information (O'Connor et al., 2003).

Several research studies have employed SEM or SEM-EDX analyses to investigate the morphological and elemental composition changes of chalcocite in acidified sulfate and chloride leaching solutions. These studies mainly attempted to show the development of cracks and pores

on solid surface as a result of the leaching reaction, but no attempt was made to investigate the impact of the leaching parameters, such as ORP and chloride concentration, on the morphology of particle surfaces. The effect of increasing temperature as a key leaching parameter on the solid surface morphology has been shown to be positive by enhancing the porosity of the solid surfaces (Bolorunduro, 1999; Niu et al., 2015).

Fisher et al. (1992) applied SEM analysis to characterize chalcocite surfaces in response to chloride leaching. The authors showed that a network of parallel cracks was developed on solid surfaces when chalcocite transferred to blue-remaining covellite. The reason for this behavior was claimed to be a molar volume decrease of 26.9% when chalcocite was converted to blue-remaining covellite and the crystal structure changed from orthorhombic to hexagonal. It was also shown that the cracks extended into the particle interior. They believed that the parallel nature of the cracks was attributed to the tendency of covellite mineral to cleave in sheets in a manner similar to mica.

Elsherief et al. (1995) evaluated the morphology of chalcocite surfaces in a study of anodic leaching of chalcocite in acidic sulfate media. The authors analyzed an anodically polarized natural chalcocite electrode using SEM technique. They observed cracks and pores on the dark blue surface of the electrode and associated that to the decrease in the molar volume when chalcocite transferred to a copper deficient sulfide. As copper released from chalcocite, honeycomb-shape entities with cracks and corrosion pits were created.

Bolorunduro (1999) used SEM-EDX to analyze the morphology and the elemental composition of chalcocite in an acidic sulfate media. Using the SEM backscattered images, the author showed

that cracks were developed on solid surfaces in response to the leaching process. The size of some particles remained unchanged, whereas some particles were disintegrated into smaller particles. The author believed that sponge-like solid surfaces enhanced the reaction. In spite of observing cracks and pores at low and high temperatures, the author concluded that the higher reaction rate at higher temperatures could not just be attributed to the morphological changes on the solid surfaces.

Niu et al. (2015) conducted a detailed study on the kinetics of chalcocite dissolution in acidic ferric sulfate media. In their study, they utilized SEM–EDX to study the formation of sulfur product layer on secondary covellite particles. The analytical results confirmed the presence of a sulfur layer and also supported the hypothesis that high temperature leads to a more porous sulfur layer. They supported the formation of elemental sulfur using Raman analysis. Based on the Raman results, they concluded that polysulfide was not formed on particle surfaces.

# 2.6.2 Surface characterization by X-Ray Photoelectron Spectrometry (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a surface analysis technique that has been used as a tool to study the surface of copper sulfide minerals by researchers (Fantauzzi et al., 2015; Ghahremaninezhad et al., 2013; McCarron et al., 1990; Qian et al., 2014; Yang et al., 2015; Zhao et al., 2016). XPS irradiates the sample surface with a low energy X-ray. This X-ray excites the electrons of the sample atoms. If their binding energy is lower than the X-ray energy, they will be emitted from the parent atom as a photoelectron. Only the photoelectrons at the extreme outer surface (1-8 nm) can escape the sample surface, making XPS a surface analysis technique (Vickermann and Gilmore, 2009). The XPS analysis can reveal valuable information about the

sample surface composition, including the concentration of the available elements and the chemical bonding information.

As opposed to the research studies on identification of the solid product layer in the leaching of chalcocite, the passivation layer formed in the leaching of chalcopyrite has been widely investigated by XPS analysis technique. The XPS information obtained in the studies on chalcopyrite mineral may shed light on the mechanism by which the second stage of chalcocite leaching slows down. In this Section, a brief review of the literature on the use of XPS technique to understand the passivation layer of chalcopyrite is presented.

Hackl et al. (1995) applied Auger electron spectrometry (AES) and XPS to analyze the passivation layer formed on the surface of chalcopyrite leached under a pressure of 1.38 MPa and 110 - 220 °C. The AES analysis showed that copper to iron atomic ratio of solid surface increased in response to leaching, which implied that iron leached preferentially to copper to form an iron-deficient sulfide phase on the surface of chalcopyrite. The AES results also showed a low concentration of oxygen on the surface of the leaching residues. Based on this result, it was concluded that possible iron hydrolysis products, such as ferric hydroxide, hematite or basic ferric sulfate, were only slightly formed on the solid surface, which ruled out these iron compounds being responsible for the slow reaction rate.

The authors also applied XPS analysis to analyze the chemical state of sulfur and iron. They obtained broad Fe  $2p_{3/2}$  peaks for the untreated chalcopyrite sample, which indicated the presence of possible iron oxides, such as Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, and FeOOH, due to the brief exposure of the chalcopyrite sample to the air and the fast oxidation of iron. However, the Fe  $2p_{3/2}$  peaks for

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the leached samples were narrow indicating less iron oxide on solid surfaces and more soluble iron into the leaching solution. The deconvolution of the S 2p spectrum of the leaching residue showed the presence of four sulfur species, including monosulfide S<sup>2–</sup>, disulfide S<sub>2</sub><sup>2–</sup>, polysulfide S<sub>n</sub><sup>2–</sup>, and elemental sulfur S<sup>0</sup>. The authors believed that the decomposition of polysulfide to cuprous ion and elemental sulfur was the rate limiting step for the dissolution of chalcopyrite.

Klauber et al. (2001) studied the speciation of sulfur formed on the surface of chalcopyrite residues using XPS technique. The authors pointed out that neither metal deficient sulfides nor polysulfides were identified as the major surface layer compounds. They concluded that elemental sulfur was responsible for the passivation of chalcopyrite mineral. The second major solid product layer was identified as disulfide  $S_2^{2-}$ . However, the associated cation with disulfide was unidentified, though CuS<sub>2</sub> was excluded as the candidate due to the oxidation status of copper, Cu<sup>+</sup>, identified by XPS analysis.

Ghahremaninezhad et al. (2013) studied the passivation layer formed on the surface of chalcopyrite during the electrodissolution process in sulfuric acid solution at ambient temperature using XPS analysis technique. The authors analyzed the survey XPS spectra of chalcopyrite and also the high-resolution spectra of copper, iron and sulfur species at potential range 450 - 1000 mV vs SHE. It was shown that chalcopyrite was passivated at potentials below 900 mV, above which chalcopyrite was actively dissolvable. As opposed to the results obtained by Hackl et al. (1995), they showed that the passivation layer was composed of copper, iron, and sulfur and therefore, concluded that a metal-deficient sulfide layer (Cu<sub>1-x</sub>Fe<sub>1-y</sub>S<sub>2-z</sub>) was the most

plausible compound passivating the surface of chalcopyrite. This metal-deficient sulfide layer consisted of cuprous sulfide (Cu–S) and iron sulfide (Fe–S) bonds.

At potentials above 900 mV, the surface concentration of sulfur significantly decreased, and no elemental sulfur and polysulfide were observed on the solid surface. From this observation, it was concluded that the transpassive oxidation of chalcopyrite was mainly associated with the oxidation of sulfur. In addition, a comparison was made between the XPS sulfur spectra of chalcopyrite with those of iron sulfides (pyrite and pyrrhotite) and copper sulfides (chalcocite and covellite). The results showed that the high energy feature in sulfur species spectra (~ 163.3 eV) was most probably linked to the S  $3p \rightarrow Fe 3d$  interband excitation and did not originate from polysulfide.

Yang et al (2015) investigated the oxidation of chalcopyrite electrode at three potentials, 530, 600, and 650 mV vs SHE using XPS analysis. It was shown that increasing the potential made the solid surface increasingly metal deficient, which is in agreement with the results obtained by Ghahremaninezhad et al (2013). The authors also showed a moderate increase in  $S_n^{2-}/S^0$  at 530 mV, an increase in  $S_2^{2-}$  at 600 mV, and a dramatic decrease in  $S_2^{2-}$  at 650 mV. This observation was explained by a reaction pathway of chalcopyrite leaching in sulfate media, in which chalcopyrite was converted to  $Cu_{1-x}Fe_{1-y}S_{2-z}$  and then to  $Cu_{1-x-z}S_2$ , and eventually to copper and elemental sulfur.

#### 2.7 Summary

The literature review revealed that the studies on the speciation of copper and iron in chloride media at high solution ionic strength either ignored the effect of ionic strength or applied activity 36

models which are suitable only for low ionic strength. Therefore, it is essential that the speciation calculations be performed by a suitable activity model for high solution ionic strength. These calculations must be conducted under conditions that could be encountered in heap leaching of chalcocite using seawater as the process water.

Most of the existing studies on the kinetics of chalcocite were carried out at temperatures higher than ambient temperature and under uncontrolled redox potentials (ORP). Temperature and redox potential have been shown to considerably affect chalcocite leaching, particularly the second stage of leaching that may convert secondary covellite to elemental sulfur (Miki et al., 2011; Nicol and Basson, 2017). However, heap leaching of secondary copper sulfide minerals is generally operated under ambient temperature and under relatively constant potential (~700 mV vs SHE) due to the continuous oxidation of ferrous to ferric as assisted by microorganisms (Petersen and Dixon, 2007). Therefore, it is essential to evaluate chalcocite leaching kinetics in chloride media under temperature and redox conditions relevant to heap leach operations.

A few studies investigated surface morphology and chemical composition in the leaching of chalcocite. These studies mainly showed the presence of cracks and pores on the solid surface after leaching. The surface evolution of chalcocite and the response of chalcocite surface to the leaching parameters in chloride media has not been investigated. The evolution of chalcocite surface in the course of leaching should be studied by surface analysis techniques such as SEM-EDX and XPS to provide a sound basis for the interpretation of the leaching mechanism and kinetics of chalcocite in chloride media.

## **Chapter 3: Research gaps and objectives**

The following research gaps were identified from the literature review regarding copper leaching from chalcocite in chloride media:

## The speciation of copper and iron in chloride media at high ionic strength (up to 3 M)

Many studies have been conducted to determine the speciation of copper and iron in chloride media (Hubli et al., 1997; Kim et al., 1986; Kimura et al., 1984). However, those studies either ignored the effect of ionic strength or used activity models suitable only for low ionic strength (< 0.5 M). Determining speciation was essential for estimating the redox potential of chloride leaching solutions and pinpointing measures of achieving sufficiently high ORPs for the second stage of chalcocite leaching.

#### Leaching kinetics in ferric chloride and cupric chloride media

Temperature and redox potential have been shown to considerably affect chalcocite leaching, particularly the much slower second stage of leaching that may convert secondary covellite to elemental sulfur (Miki et al., 2011; Nicol and Basson, 2017). Most of the existing studies were carried out at temperatures higher than ambient temperature and under uncontrolled redox potentials (ORP). However, practical heap leaching is generally operated under ambient temperature and under relatively constant potential (~700 mV vs SHE) due to the continuous bio-oxidation of ferrous to ferric (Petersen and Dixon, 2007). To improve and optimize process performance, it is essential to evaluate kinetics under temperature and redox potential relevant to practical heap leach operations.

## Mechanisms of chalcocite leaching in chloride media

The major causes of the slow dissolution of copper sulfides have been proposed to be associated with sulfur layer, jarosite precipitation, metal-deficient sulfide, and polysulfide layer (Niu et al., 2015). In the case of chalcocite leaching, the nature of this product layer has not been thoroughly studied in chloride media. The formation of a sulfur layer has been hypothesized to be the cause of the slow reaction rate of the second stage of chalcocite leaching (Cheng and Lawson, 1991). Therefore, analysis of the evolution of solid surface properties will help elucidate the reasons for the slow reaction rate.

To address the research gaps outlined above, the overarching objective of the present study was to quantify the leaching kinetics and uncovering mechanisms by which chalcocite is leached in chloride media, in efforts to eventually facilitate the application of seawater in copper heap leaching. The overarching objective was broken down into three specific objectives:

• **Objective I**: To determine the speciation of copper and iron in chloride media at high ionic strength by experimental ORP measurements and thermodynamic calculations (results reported in Chapter 5)

• **Objective II:** To quantify and scale up the kinetics of chalcocite leaching in ferric chloride and cupric chloride leaching media under fully controlled leaching conditions (results reported in Chapter 6, 7 and 8)

• **Objective III:** To examine solid surface properties and characterize sulfur chemical state in chloride leaching of chalcocite by various surface characterization techniques (Chapter 9)

## **Chapter 4: Research methods**

## 4.1 Introduction

This chapter outlines the research methods applied to achieve the objectives. For Objective I, to determine the speciation of copper and iron in chloride media at high ionic strength by experimental ORP measurements and thermodynamic calculations, the detailed research method was described in Section 4.2. For objective II, to quantify and scale up the kinetics of chalcocite leaching in ferric chloride and cupric chloride leaching media under fully controlled leaching conditions, the research methodology was explained in Section 4.3. For Objective III, to examine solid surface properties and characterize sulfur chemical state in chloride leaching of chalcocite by various surface characterization techniques, the research method was described in Section 4.4.

#### 4.2 Research methods for Objective I

**Objective I:** To determine the speciation of copper and iron in chloride media at high ionic strength by experimental ORP measurements and thermodynamic calculations

### 4.2.1 Experimental design

The experimental objective was to measure the ORP at varied ferric/ferrous ratio and chloride concentration, the results of which were used to verify the ORP values calculated by the STABCAL software. Table 4.1 shows the list of the tests carried out at different nominal ferric/ferrous ratio and chloride concentration at constant pH (1.5) and temperature (25 °C). Nominal [Fe(III)]/[Fe(II)] ratio was defined as the ratio of total Fe(III) to total Fe(II) added to the reactor. The nominal [Fe(III)]/[Fe(II)] ratios were chosen in reference to the practical ORP 40

values for heap leaching (Schlesinger et al., 2011). The total chloride concentration was varied in the range of 0.5 to 3 M. This range was chosen in an attempt to cover all possible concentrations that may be relevant to a heap leaching process, from lower than in a typical seawater (0.5 M) to 3 M that represents concentrated leaching solutions due to evaporation and recirculation of process water. The total chloride concentration was calculated as the summation of the chloride from the hydrochloric acid used for pH adjustment, ferric chloride, ferrous chloride, and sodium chloride.

Table 4.2 shows the list of the tests carried out for measuring solution ORP at different nominal cupric/cuprous ratio and chloride concentration at constant pH (1.5) and temperature (25 °C). The nominal [Cu(II)]/[Cu(I)] ratios were selected based on the practical heap leaching ORP values (Schlesinger et al., 2011). The total chloride concentration was calculated as the sum of the chloride from the hydrochloric acid, cupric chloride, cuprous chloride, and sodium chloride.

Test #	[Fe(III)]/[Fe(II)]	[Fe(II)], mM	[Fe(III)], mM	[Cl <sup>_</sup> ], M	
1	0.33	75.0	25.0	0.5	
2	1.00	50.0	50.0	0.5	
3	4.00	20.0	80.0	0.5	
4	9.10	9.9	90.1	0.5	
5	0.33	75.0	25.0	1.0	
6	1.00	50.0	50.0	1.0	
7	4.00	20.0	80.0	1.0	
8	9.10	9.9	90.1	1.0	
9	0.33	75.0	25.0	2.0	
10	1.00	50.0	50.0	2.0	
11	4.00	20.0	80.0	2.0	
12	9.10	9.9	90.1	2.0	
13	0.33	75.0	25.0	3.0	
14	1.00	50.0	50.0	3.0	
15	4.00	20.0	80.0	3.0	
16	9.10	9.9	90.1	3.0	

Table 4.1 The experimental design for ORP measurements in ferric/ferrous chloride media at pH 1.5, total iron concentration of 0.1 M, and 25 °C

Test #	[Cu(II)]/[Cu(I)]	[Cu(II)], mM	[Cu(I)], mM	[Cl-], M
1	1000	31.44	0.03	0.5
2	100	31.16	0.31	0.5
3	10	28.61	2.86	0.5
4	1	15.74	15.74	0.5
5	1000	31.44	0.03	1.0
6	100	31.16	0.31	1.0
7	10	28.61	2.86	1.0
8	1	15.74	15.74	1.0
9	1000	31.44	0.03	2.0
10	100	31.16	0.31	2.0
11	10	28.61	2.86	2.0
12	1	15.74	15.74	2.0
13	1000	31.44	0.03	3.0
14	100	31.16	0.31	3.0
15	10	28.61	2.86	3.0
16	1	15.74	15.74	3.0

Table 4.2 The experimental design for the ORP measurements in cupric/cuprous media at pH 1.5, total copper concentration of 32 mM, and 25 °C

### 4.2.2 Materials

The reagent grade chemicals used in the ORP measurement experiments include ferrous chloride (FeCl<sub>2</sub>.4H<sub>2</sub>O, 98%, Alfa Aesar), hydrochloric acid (HCl, 36.5-38%, VWR) for pH adjustment, ferric chloride (FeCl<sub>3</sub>, 97%, Acros) as the oxidant, cupric chloride (CuCl<sub>2</sub>, 99%, Acros), cuprous chloride (CuCl, 97%, Sigma-Aldrich), saturated potassium chloride (KCl, LabChem) for refilling pH electrodes, 4M potassium chloride saturated with silver chloride (KCl, Fisher Scientific) for refilling the ORP electrodes, and sodium chloride (NaCl, Ward's Science) for adjusting chloride concentration.

# 4.2.3 ORP measurement procedure

The ORP measurements were carried out in 500 mL jacketed reactors, where the stirring was provided by means of a magnetic stirrer and temperature was maintained constant using a water 42

bath to circulate water through the jacket of the reactor (Figure 4.1). The procedure to prepare the chemical solutions involved introducing hydrochloric acid to deionized water to reach pH around 1.8, adding desired amounts of ferric ions, and making up the leaching solution to 250 mL by adding deionized water. After adding ferric chloride salt, the pH value dropped to 1.6 due to the hydrolysis of ferric ions.

The reactor was then sealed using a rubber stopper. An ultra-purity nitrogen gas was sparged into the reactor through a glass gas sparger for 1 h and throughout the experiment. Ferrous chloride was then added through a syringe to avoid air leakage into the reactor. Solution ORP was measured using an Accumet Platinum ORP Electrode from Fisher Scientific. The Accumet Platinum ORP electrodes were manufactured with double junctions to prevent the contamination of the internal electrolyte solution. The high concentration of the electrolyte solution, 4 M KCl saturated with AgCl, also prevented the junction potential from developing due to higher mobility of chloride ions than that of sodium. Oxygen content was randomly measured in some experiments to ensure that the solution contained no oxygen. In the case of cupric/cuprous solution, the procedure was the same except that the initial pH was adjusted at 1.6 instead of 1.8 due to the insignificant hydrolysis of cupric ions.

The ORP reading was stable in the ORP measurement experiments, especially in the case of ferric/ferrous system. After adding ferrous chloride or cuprous chloride into the solution, the ORP change was monitored until the rate of ORP change was less than 0.5 mV/10 min, after which the ORP value was recorded. The ORP reading took approximately 15 min to stabilize in ferric/ferrous system and 25 min in cupric/cuprous system. The ORP measurement tests were

replicated for 3 times and the average values were reported. The potential of a silver/silver chloride reference electrode with respect to standard hydrogen electrode (SHE) depends on the electrolyte concentration. In our experiments, 4 M KCl solution saturated with silver chloride was used as the filling solution, which gave +200 mV potential of Ag/AgCl against SHE (McDermand, 2015). Therefore, 200 mV was added to the measured ORP values to convert them to the SHE scale. All redox potentials were reported with respect to the SHE at 25°C in the present study unless otherwise stated.

It is noteworthy that the activity of proton is sensitive to chloride concentration of the solution. Proton activity increases with increasing chloride concentration (Muir, 2002). Therefore, at a lower chloride concentration, a higher amount of HCl was added to adjust the pH value to 1.5 than the case of higher chloride concentrations. When chloride concentration was increased from 0.5 M to 3 M, the HCl concentration decreased by 0.01 M. Consequently, the difference in the concentration of chloride resulting from the different amount of HCl added for pH adjustment was negligible.



Figure 4.1 A schematic of the ORP measurement apparatus

## 4.2.4 Computer program

STABCAL (hereafter also referred to as "the software") is a computer program developed to perform thermodynamic calculations for constructing different types of stability diagrams, such as speciation diagram, Eh-pH diagram, and Eh-Ligand diagram (Gow et al., 2016; Huang et al., 2005; Huang and Young, 1996). In the software, one can choose Gibbs free energies of formation for chemical species from different databases, including NBS, MINTEQ, Naumov, NIST, LLNL, HSC, Woods, WatEq4F, and Helgeson. The program applies the Extended Debye-Huckel equation for ionic strength <0.1, the Davies model for ionic strength <0.5, and the SIT model for ionic strength in the range of 0.5 to 5.0. In the present study, STABCAL was applied
to calculate the speciation and activities of iron and copper species possibly present in chloride leaching system. The SIT model was selected for calculating the activity coefficients.

Figure 4.2 shows the main window of STABCAL where one can use various functions for constructing diagrams, e.g., Eh-pH, ligand-Eh, and ligand-pH, calculating activity, accessing the databases, and more. In the present study, STABCAL was used mainly to identify the speciation of iron and copper in chloride media. Therefore, the procedure to use the software to calculate the activity of iron and copper species are described here.

Figure 4.3 depicts the speciation worksheet of STABCAL where the species of interest and their activities can be identified. According to Figure 4.3, the number of components must be first inserted in the worksheet and subsequently the elements, their concentrations, and their valence must be added. The other inputs include temperature, pH value, Eh value, database, and activity model. If Eh value is left empty or zero, the software will calculate the Eh value based on the available electrochemical couples. As explained above, one can choose an activity model among the Extended Debye-Huckel (I <0.1), Davies (I <0.5), and SIT (0.5 < I < 5.0). When the worksheet is filled with the required information, the software will calculate the activities of the species of interest once the "Save then(Calculate)" box was clicked.

🔏 Windows STABCAL Start Menu and Program Layout - Hsin-Hsiung Huang, Montana Tech 1985 to January-2017 🦳 🛛 🗙								
Aqueous System Non-Aqueous Demo/Tutor	Stabcal Settings/Edi	itings Windows Ut	tilities Copy dBases	s/files Quit	Help/Info			
Major Functions in Stabcal	Documents an	d Descriptions	) Ba	ckup and Re	estore			
Click Button Below for Major Function Click Checked Box below to See its Representative Example								
A. Normal Aqueous Systems	Predominant D	iagrams Point-bu-Point	Distribution Diag	rams 3D Iubilitu do 1	Solubility Chermal Calc			
A1. Construct diagrams and Perform Thermal Calculations for Reactions or Species <b>Redox</b>	EhpH	EhpHm	DEh		3DE			
Diagrams and Reactions	CpxCpx			v V	SpecRex			
A2. Speciation. Titration (chem/Tem), and	🗹 СрхрН	CpxpHm	DTC	More.	List them all	1		
Mixing Simulation. Redox and nonRedox	Speciation & Ana	alysis 🔽 Chemical T	itration 🔽 Tem Varia	bles 🔲 Mix w	ith Solutions			
Speciation and Titration A3 dBases and Utilities for Aqueous System Databases and Utilities	<ul> <li>✓ View/Edit Dbase</li> <li>✓ Size Distrbt Anay</li> <li>NBS</li> <li>Non-Critical</li> <li>✓ WatEq4F</li> </ul>	es Create d0 vlsys Energy(T) Naumov User1(HSC) LLNL (PhreeQC)	i(T) Dbases Cor I to Cp Org MINTEQA2 User2(HKF)	nvert dG <> logt anic ligand (NIS Critical (NI User and F	(/Eh )T) ST) Personal			
B. NON-Aqueous Systems B1 Thermal-Calculation: Diagrams, Simulation, Reactions, and Read/Plot Existent Graph HiTemBex Calculations	<ul> <li>Ellingham</li> <li>Energies of Rea</li> <li>Potential vs p0(2)</li> </ul>	pGas-pGas ction/species 2-) for molten salt bath	<ul> <li>✓ (AQ) Ion-Ion</li> <li>✓ Speciation and M</li> <li>✓ pGas-Main</li> </ul>	pGas-Tem lass distribution	p dZ byLine			
Plots: Read chart. Add Existence. StabStype	🔲 Read X-Y plot	🔲 Read Ternary	🔲 Plot stabcal Style	🔲 Add Text/	line to Chart			
Using dGmin SGM-PV Stable Phases Diagram B2 View/Edit Non-AQ databases	<ul> <li>✓ pG1-pG2 Multiple</li> <li>✓ BinaryMetalsMultiple</li> <li>✓ 3D X, Y and Z b</li> </ul>	e phases 🔽 Const tiple phase 🗹 Binary by point 🔽 3D Me	pG1-pG2 Distribution phase Liquid/Solid etal ratio, X, and Y	☑ Gas1-Tem ☑ 3D Tem,≻	Multiple phase ( and Y	1		
Non Aqueous Databases	<ul> <li>Ellingham</li> <li>Naumov</li> </ul>	Reed Robie(usgs)	HSC Kubaschewski	User Creat	ed n Elsewhere			
Personalized-display of Current Monitor is Small. Small is recommended to Cover all Stabcal Menus User's directory: c:\users\lisa\documents\stabcal W32-Stabcal SN: 02-25-2017. Setup in: c:\program files\stabcal. OS: Win8 or higher. Language: English (Canadian). C drive NonRestricted. Licensed Users: Dreisinger UBC								

Figure 4.2 The main window of STABCAL to run various tasks such as speciation calculation and

construction of diagrams



Figure 4.3 The speciation worksheet of STABCAL

#### 4.3 **Research methods for Objective II**

Objective II: To quantify and scale up the kinetics of chalcocite leaching in ferric chloride and cupric chloride leaching media under fully controlled leaching conditions

 $\times$ 

# 4.3.1 Experimental design

To evaluate the effect of different parameters on the kinetics of chalcocite leaching in ferric chloride media, leaching tests were designed as shown in Table 4.3. The key parameters investigated include the concentrations of chloride, ferric, and ferrous, the ferric-to-ferrous ratio, temperature, and particle size. In the case of cupric chloride system, the leaching tests were performed according to Table 4.4. The total chloride concentration was calculated as the summation of the chloride from the hydrochloric acid used for pH adjustment, ferrous chloride, ferric chloride, and sodium chloride.

For the column leaching tests, a mixture of a copper ore and a pure chalcocite sample was used. The purpose of performing the column leaching tests was to scale up the kinetic models obtained from the reactor leaching tests. It was expected that the copper ore react with the leaching solution and some copper release from the copper ore into the leaching solution in the course of the column leaching test. Therefore, it necessitated to know the copper extraction from the copper ore to minimize the experimental error. For this purpose, in each leaching system, a column leaching test was carried out without the addition of the pure chalcocite sample to evaluate the copper extraction from the copper ore. The leaching conditions for these tests are shown in Table 4.5 and Table 4.6 (Test 1).

The column leaching tests on the mixture samples were conducted in both ferric chloride and cupric chloride systems under the condition shown in Table 4.5 and Table 4.6 (Test 2). The effect of irrigation rate on the copper extraction from chalcocite was also evaluate. Test 3 in Table 4.5 and Table 4.6 shows the conditions under which column leaching tests were performed

at higher irrigation rate  $(10.6 \text{ L/m}^2/\text{h})$  for each leaching system. To validate the scaled-up kinetics models for each leaching system, one column leaching test was performed under randomly chosen leaching conditions. The validation column leaching tests were performed under conditions shown as Test 4 in Table 4.5 and Table 4.6.

Table 4.3 Design of the leaching experiments for investigation of the effect of various parameters on chalcocite leaching kinetics in acidified ferric chloride media

Variable	[Cl <sup>-</sup> ], M	[Fe(III)], M	[Fe(II)], M	ORP, mV vs SHE	Temperature, °C	Particle size, µm
	0.172	0.05	0.001	810	25	-75+53
[Cl <sup>-</sup> ]	0.522	0.05	0.001	810	25	-75+53
	1.522	0.05	0.001	810	25	-75+53
	3.022	0.05	0.001	810	25	-75+53
	0.322	0.1	0.001	820	25	-75+53
	0.172	0.05	0.001	810	25	-75+53
[Fe(III)]	0.112	0.03	0.001	800	25	-75+53
	0.052	0.01	0.001	760	25	-75+53
	0.037	0.005	0.001	740	25	-75+53
	0.37	0.05	0.1	690	25	-75+53
	0.27	0.05	0.05	700	25	-75+53
[Fe(II)]	0.19	0.05	0.01	740	25	-75+53
	0.18	0.05	0.005	760	25	-75+53
	0.172	0.05	0.001	810	25	-75+53
	0.245	0.025	0.075	660	25	-75+53
[Fe(III)]/[Fe(II)]	0.27	0.05	0.05	700	25	-75+53
	0.3	0.08	0.02	760	25	-75+53
	0.3368	0.099	0.00099	820	25	-75+53
	0.172	0.05	0.001	810	25	-75+53
Temperature	0.172	0.05	0.001	810	35	-75+53
1	0.172	0.05	0.001	810	45	-75+53
	0.172	0.05	0.001	810	55	-75+53
	0.172	0.05	0.001	810	25	-212+180
Particle size	0.172	0.05	0.001	810	25	-150+125
	0.172	0.05	0.001	810	25	-125+106
	0.172	0.05	0.001	810	25	-75+53

Variable	Salt	[Cl <sup>-</sup> ], M	[Cu(II)], M	Particle size, µm	Temperature, °C
	NaCl	3.062	0.016	-75+53	25
[C]-]	NaCl	1.562	0.016	-70+53	25
	NaCl	1.062	0.016	-70+53	25
	NaCl	0.562	0.016	-70+53	25
	NaCl	1.562	0.128	-75+53	25
$[C_{1}/II)]$	NaCl	1.562	0.064	-75+53	25
[Cu(II)]	NaCl	1.562	0.032	-75+53	25
	NaCl	1.562	0.008	-75+53	25
	NaCl	1.062	0.016	-150+125	25
Doutialo aire	NaCl	1.062	0.016	-125+106	25
Particle size	NaCl	1.062	0.016	-106+75	25
	NaCl	1.062	0.016	-75+53	25
Temperature	NaCl	1.562	0.016	-75+53	55
	NaCl	1.562	0.016	-75+53	45
	NaCl	1.562	0.016	-75+53	35
	NaCl	1.562	0.016	-75+53	25

Table 4.4 Design of the leaching experiments for investigation of the effect of various parameters on chalcocite leaching kinetics in acidified cupric chloride media

Table 4.5 Design of the leaching experiments to scale up and validate the leaching kinetics model in ferric chloride media at 25 °C and pH 1.5

Test #	[Cl-], M	[Fe(III)], M	[Fe(II)], M	ORP, mV vs SHE	Irrigation rate, L/m <sup>2</sup> /h	Particle size, µm
1	0.27	0.05	0.05	700	5.3	
2	0.27	0.05	0.05	700	5.3	-150+125
3	0.27	0.05	0.05	700	10.6	-150+125
4	0.34	0.0909	0.00909	810	5.3	-180 + 150

Table 4.6 Design of the leaching experiments to scale up and validate the leaching kinetics model in cupric chloride media at 25 °C and pH 1.5

Test #	[Cl <sup>-</sup> ], M	[Cu(II)], M	ORP, mV vs SHE	Irrigation rate, L/m <sup>2</sup> /h	Particle size, µm
1	2	0.004	670	5.3	
2	2	0.004	670	5.3	-150+125
3	2	0.004	670	10.6	-150+125
4	1.0	0.004	630	5.3	-180+150

#### 4.3.2 Materials

Natural chalcocite purchased from Ward's Science was ground by a Spex sample prep ball mill and then sieved to varied particle size fractions including -212+180, -180+150, -150+125, -125+106, -106+75, and  $-75+53 \mu m$ . The wet sieving was conducted by means of Taylor sieves and a Rotap shaker to provide various narrow-sized fractions. A copper ore sample received from Quebrada Blanca mine in Chile was used to run the column leaching tests. 30 kg copper ore sample with the biggest particle size of 5 cm was crushed using a jaw crusher and two cone crushers. The crushed sample after each crusher was screened by a sieve with an opening size of 2.83 mm and the over-screen portion was crushed with the next crusher. The crushed ore sample was then sieved to provide a narrow-particle size feed for the column leaching tests. The particle size fraction -2.83 + 1.00 mm was selected to charge the leaching columns. The selected fraction was split into subsamples of 1.5 kg using a riffle splitter for the column leaching tests. One sample from the selected particle size fraction was ground by a ball mill to particle size with d<sub>80</sub> of 53 µm for chemical and mineral characterization.

The reagent grade chemicals used in the experiments included ferrous chloride (FeCl<sub>2</sub>.4H<sub>2</sub>O, Alfa Aesar), hydrochloric acid (HCl, 36.5-38%, VWR) for pH adjustment, ferric chloride (FeCl<sub>3</sub>, Acros) as the oxidant, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 30%, VWR), sodium cyanide (NaCN, Sigma-Aldrich), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%, Anachemia), nitric acid (HNO<sub>3</sub>, 68-70%, VWR), saturated potassium chloride (KCl, LabChem) for refilling pH electrodes, 4M potassium chloride saturated with silver chloride (KCl, Fisher Scientific) for refilling the ORP electrodes, and sodium chloride (NaCl, Ward's Science) for adjusting chloride concentration. Diluted hydrogen peroxide (3% by

volume) was used to maintain the ORP of the leaching solutions in the ferric chloride media. Sodium cyanide was used in the diagnostic sequential leaching test to dissolve the secondary copper sulfide minerals in the copper ore. Nitric acid was mixed with hydrochloric acid to provide aqua regia solution to digest the copper ore sample. Sulfuric acid was used in the acid washing of chalcocite sample prior to the leaching experiments and also in the first step of diagnostic sequential leaching test to dissolve the oxide mineral in the copper ore. The diagnostic sequential leaching test was explained in Section 4.3.4.

### 4.3.3 Chalcocite sample characterization

The chalcocite sample was ground to an optimum grain size range for quantitative X-ray analysis (<10  $\mu$ m) by milling under ethanol in a vibratory McCrone Micronizing Mill for 10 minutes. XRD analysis was performed using a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye-XE detector. Step-scan X-ray powder-diffraction data were collected over a range 3-80 °20 with CoKa radiation. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. The X-ray diffractogram was analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. X-ray powder-diffraction data of the sample were refined with Rietveld program Topas 4.2 (Bruker AXS).

### 4.3.4 Copper ore characterization

The ground copper ore sample ( $d_{80} = 53 \ \mu m$ ) was subjected for X-ray diffraction and diagnostic sequential leaching test to determine the mineral contents. A representative sample was prepared 53

by coning and quartering sampling method. The procedure to perform the XRD analysis was the same as that for chalcocite sample which was described in Section 4.3.3. Beside the XRD analysis, the copper ore sample was analyzed by the diagnostic sequential leaching method to determine the proportion of oxide copper mineral, secondary copper sulfide minerals, and primary copper sulfide minerals. A representative sample was first leached in sulfuric acid solution under nitrogen gas for 2 h. The solid/liquid ratio was 40% and the pH value was 1.1 during the leaching test. The high solid/liquid ratio was chosen as in the column leaching test, a small amount of acidic liquid is in contact with ore particles meaning that the solid/liquid ratio in the column leaching test is high. The pH value slightly increased (from 1.1 to 1.25) in the course of leaching process, indicating a low content of copper oxide mineral or acid consuming minerals in the copper ore sample. The leaching residue was filtered and rinsed with deionized water and then, dried at 60 °C and weighted for the next sequential test step. The filtrate solution was collected for copper content analysis with ICP- OES.

In the second step, the sulfuric acid leaching residue was leached by NaCN to leach the secondary copper sulfide minerals. In the cyanidation test, 1 g of the leaching residue from the previous step was added into 250 ml of the cyanide solution containing 1 g/L CN<sup>-</sup>. The pH value was adjusted to 10.5 to avoid the formation of HCN gas. The leaching solution was open to air to supply oxygen for the cyanidation process. After 24 h, the cyanidation test was stopped, and the solid phase was collected after filtration and the filtrate was kept for copper analysis by ICP-OES. In the final step of the sequential leaching test, 1 g of the cyanidation residue was leached by aqua regia. The digestion solution contained 6 mL of concentrated HCl acid and 3 ml of

HNO<sub>3</sub> acid and 1 mL of deionized water. The digestion test was conducted using Ethos Up Microwave Digestion System instrument.

#### 4.3.5 Reactor leaching test procedure

Prior to leaching, chalcocite mineral was acid washed in 5% sulfuric acid under nitrogen for 1 h to remove any copper oxide mineral. Leaching experiments were conducted in 500 mL jacketed reactors. Figure 4.4 shows the experimental apparatus in which temperature was kept constant using a water bath to circulate water through the jacket. Stirring was provided using Cole-Parmer Compact Digital Mixer overhead stirrers and maintained at 500 rpm. At 500 rpm, the solid particles were thoroughly suspended in the leaching solution. The pH and ORP electrodes were inserted through a rubber stopper into the reactor to minimize the evaporation of the leaching solution. pH and ORP were monitored and controlled using a pH/ORP controller (HACH SC200 Universal Controller) attached to metering pumps (Iwaki, Hi-Resolution Pump). The controller received ORP and pH signals from an ORP electrode (Accumet Platinum ORP Electrode from Fisher Scientific) and a pH electrode (Accumet pH/ATC Electrode from Fisher Scientific) immersed in the leaching solution. The controller then compared the signals to the desired values (set points) and sent output signals to the metering pump to add hydrogen peroxide (3% v/v) for ORP adjustment or hydrochloric acid (10% w/w) for pH adjustment when needed.

The procedure to prepare the leaching solution involved introducing hydrochloric acid to deionized water to reach pH around 1.8, adding desired amounts of ferric and ferrous ions, making up the leaching solution to 250 mL by adding deionized water, and adjusting the final pH to 1.5. The pH of the leaching system was maintained at 1.5 during the course of leaching for all

leaching tests. In the leaching experiments where sodium chloride was used to evaluate the effect of chloride concentration on the reaction rate, sodium chloride was added into the deionized water prior to adding hydrochloric acid. The addition of sodium chloride reduced solution pH due to the increase in chloride concentration. Ferric chloride dissolution in water generated heat, which slightly increased the leaching solution temperature. Therefore, prior to adding chalcocite sample into the leaching solution, approximately 30 min was given for the leaching solution to cool down to 25 °C, after which 1 g chalcocite was added into the leaching solution.

In the case of the cupric chloride system, the leaching solution was prepared by adding sodium chloride into deionized water, adjusting the solution pH to 1.6 by introducing hydrochloric acid, adding desired amounts of cupric chloride, making up the leaching solution to 250 mL by adding deionized water, and adjusting the final pH to 1.5. The pH of the leaching system was maintained at 1.5 during the course of leaching for all leaching tests. Hydrogen peroxide was not added into the leaching solution to maintain the ORP of the leaching solutions constant. It was due to the contribution of hydrogen peroxide to the dissolution of chalcocite in the first stage, though diluted hydrogen peroxide (3% by volume) was used.



Figure 4.4 A schematic of the leaching setup under fully controlled pH and ORP

Aliquots of 0.5 mL of the leachate samples were taken more frequently during the first hour and less frequently over the next nine hours and then on a daily basis. The samples were analyzed for copper content by inductively coupled plasma optical emission spectroscopy (ICP-OES Agilent 5100). The feed sample and the leaching residues were washed four times with deionized water and dried at 60°C, digested in aqua regia solution using the Ethos Up Microwave Digestion System, and then analyzed for copper content by ICP-OES. After finishing each leaching test, the internal electrolyte solution of the ORP electrodes was replaced with fresh 4 M KCl saturated with silver chloride solution and that of the pH electrodes was replaced with fresh saturated KCl solution. Prior to starting new leaching tests, the pH and ORP electrodes were calibrated.

As was explained in Section 4.2.3, due to enhanced proton activity by increased chloride concentration, at a higher chloride concentration, a lower amount of HCl was added to adjust the pH value to 1.5. However, the small variation by 0.01 M in the amount of HCl added meant that the difference in chloride concentration associated with HCl addition was insignificant.

# 4.3.6 Kinetic modelling

The shrinking core models (SCMs) are the established kinetic models that are most commonly used to describe the rate of leaching reactions (Sohn and Wadsworth, 1979). However, these models are not always suitable to describe leaching data. Dixon and Hendrix (1993) developed a variable-order kinetic model as an alternative to SCMs, which has been successfully applied to study leaching rates (Bouffard and Dixon, 2007; Dixon and Hendrix, 1993). This model, shown in Eq. (4.1) in a differential form, is referred to as the "general model" in this study. The general model assumes that the copper grade of the chalcocite ore and the degree of mineral liberation have no effect on the leaching rate. Another assumption for applying the general model is that the concentration of the reactants is constant in the course of leaching. In the present work, chalcocite samples of high purity were used in all leaching tests to ensure a constant cupric to cuprous ratio in the course of leaching. The advantage of using this general model is that its integral form can simply be obtained as Eq. (4.2).

$$\frac{dx}{dt} = \frac{(1-x)^{\varphi}}{\tau} \tag{4.1}$$

$$1 - x = \begin{cases} \exp\left(\frac{-t}{\tau}\right) & @ \varphi = 1\\ \left(1 - (1 - \varphi)\frac{t}{\tau}\right)^{\frac{1}{1 - \varphi}} & @ \varphi \neq 1 \end{cases}$$

$$(4.2)$$

$$\frac{1}{\tau} = \frac{k_{(T_{ref})}}{d_0^q} \exp\left(\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) f(c)$$
(4.3)

$$X = \beta X_1 + (1 - \beta) X_2 \tag{4.4}$$

In Eqs. (4.1) and (4.2), x is the copper extraction, t (h) is the leaching time,  $\tau$  is the reaction timescale (h), and  $\varphi$  is a topological exponent. In Eq. (4.3), f(c) (c in mol/L) is the concentration term reflecting the reaction orders with respect to the concentrations of ferric, ferrous, cupric, and chloride (more information is provided in Chapters 6 and 7),  $T_{ref}$  (K) is the reference temperature,  $E_a$  (J/mol) is the activation energy, and  $d_0$  (µm) is the initial particle diameter.

The overall copper extraction (X) from both stages is defined as Eq. (4.4).  $\beta$  is the fraction of leachable copper in the first stage, and 1- $\beta$  is the fraction of leachable copper in the second stage. X<sub>1</sub> and X<sub>2</sub> represent the modelled copper extraction for the first and the second stage, ranging from 0 to 1, with 1 indicating the completion of the stage. Both X<sub>1</sub> and X<sub>2</sub> were obtained by Eq. (4.2). The kinetic equation was parameterized by the method of least squares, i.e., minimizing the sum of the squared difference between an observed extraction value and the fitted value provided by the general model, Eq. (4.4). The least squares method finds the optimal set of parameters by minimizing the sum. More detailed explanation was provided in Appendix B.

For the sake of kinetics study and to maintain an identical condition for all tests, in the ferric chloride system, the first stage completion was assumed to be at 50% copper extraction and

hence,  $\beta$  in Eq. (4.4) was assumed to be 0.5. In cupric chloride system,  $\beta$  was assumed to be 0.4. This assumption was based on the leaching experimental data in cupric chloride, where they showed that the completion of the first stage was approximately 40% copper extraction.

#### 4.3.7 Procedure for the column leaching tests

A transparent PVC column of 10-cm diameter and 20-cm length was used for the column leaching tests. Two meshes and a thin layer of glass wool were placed at the bottom of the column to prevent the exit of particles from the column. A thin layer of glass wool was also placed on top of the ore in the column to help the distribution of leaching solutions through the top surface (Figure 4.5). In each column leaching test, 1.5 kg of the mixed sample was charged into the column. The sample was a mixture of 7.5 g of pure chalcocite and 1492.5 g of copper ore to avoid the interference of incomplete mineral liberation. To ensure thorough mixing, the copper ore was split into three 497.5 g subsamples, in each of which 2.5 g of the pure chalcocite sample was added. The mixed subsamples were then charged into the column.

The leaching solution was prepared by introducing hydrochloric acid to 9 L of deionized water until pH reached around 1.8, followed by the addition of desired amounts of ferric and ferrous ions. The leaching solution was made up to 10 L by adding deionized water, the final pH of which was adjusted to 1.5. To remove the heat generated from ferric chloride dissolution, prior to irrigation, approximately 2 h was given for the leaching solution to cool down to 25 °C. In the case of cupric chloride solution, the leaching solution was prepared by adding sodium chloride into 9 L of deionized water, adjusting pH to 1.6 by introducing hydrochloric acid, adding cupric chloride, making up the leaching solution to 10 L by adding deionized water, and adjusting the final pH to 1.5. Fresh leaching solution was prepared every 10 days for the column leaching tests.

A peristaltic pump was used to provide leaching solutions for irrigating the columns. The irrigation rate was set at 1 L/day, which corresponds to 5.3 L/h/m<sup>2</sup>. The column leaching tests were conducted in an open circuit, meaning that the pregnant leaching solution (PLS) was not recycled. The PLS was collected in a small bucket underneath the column. The volume, ORP, and pH of the PLS was measured and recorded on a daily basis. One sample of 1 mL PLS solution was taken each day for subsequent analysis of copper concentration by ICP-OES. The column leaching test was performed approximately 500 h and 900 h for ferric chloride and cupric chloride systems, respectively. An air flow controller was used to control and maintain a constant air flow rate at 0.8 m<sup>3</sup>/m<sup>2</sup>/h. Air was provided at the bottom of the column. The columns were capped to avoid the evaporation of the leaching solution irrigated on top of the sample. The column cap had a small hole to let the aerated air leave the column.



Figure 4.5 A schematic of the column leaching apparatus

### 4.4 Research methods for Objective III

Objective III. To examine solid surface properties and characterize sulfur chemical state in chloride leaching of chalcocite by various surface characterization techniques

# 4.4.1 Experimental design

The experimental objectives were to explore the evolution of solid surface properties in the course of leaching and to examine the responses of surface properties to varying leaching conditions. To evaluate the evolution of solid surface properties, the surfaces of the leaching residues collected at different leaching times corresponding to increasing levels of copper

extraction was characterized by SEM-EDX and XPS techniques. To examine the responses of surface properties to different leaching conditions, the leaching residues corresponding to 80% copper extraction were collected under different ORP, chloride concentration, and temperature, and analyzed by SEM-EDX. Table 4.7 shows the experimental design to evaluate the evolution of solid surface properties and the responses of the surface properties to ORP and temperature. Because the effect of chloride concentration on the reaction rate was only observed with cupric as the oxidant, the leaching residues collected from the cupric chloride leaching were used to evaluate the effect of chloride concentration on surface properties (

Table 4.8).

To evaluate the role of elemental sulfur as a product layer in the slow second-stage leaching, leaching tests with and without sulfur removal were performed at either 600 mV or 800 mV (vs SHE), as shown in Table 4.9.

Variable	Cu	[Cl <sup>-</sup> ],	[Fe(III)],	[Fe(II)],	ORP, mV	Leaching	Temperature, °C
	Extraction, %	Μ	Μ	Μ	vs SHE	time	-
	10	0.172	0.05	0.001	810	30 s	25
	20	0.172	0.05	0.001	810	1 min	25
Cu Extraction	49	0.172	0.05	0.001	810	10 min	25
	55	0.172	0.05	0.001	810	6 h	25
	80	0.172	0.05	0.001	810	144 h	25
	80	0.245	0.025	0.075	660	240 h	25
	80	0.27	0.05	0.05	700	192 h	25
[Fe(III)]/[Fe(II)]	80	0.3	0.08	0.02	760	168 h	25
	80	0.172	0.05	0.001	810	144 h	25
	80	0.337	0.099	0.00099	820	120 h	25
	80	0.172	0.05	0.001	810	144 h	25
Temperature	80	0.172	0.05	0.001	810	24 h	35
	80	0.172	0.05	0.001	810	7 h	45
	80	0.172	0.05	0.001	810	3 h	55

Table 4.7 The experimental design for the leaching tests in ferric chloride media at pH 1.5

Variable	Cu Extraction, %	[Cl-], M	[Cu(II)],	ORP, mV vs SHE	Leaching time	Temperature, °C
			М			
[Cl-]	80	0.562	0.016	600	384 h	25
	80	1.062	0.016	635	288 h	25
	80	1.562	0.016	670	240 h	25
	80	3.062	0.016	705	240 h	25

Table 4.8 The experimental design for the leaching tests in cupric chloride media at pH 1.5

Table 4.9 The experimental design for the CS<sub>2</sub> washing tests in ferric chloride media at pH 1.5

Variable	[Cl <sup>-</sup> ], M	[Fe(III)], M	[Fe(II)], M	ORP, mV vs SHE	Temperature, °C
With CS <sub>2</sub> washing	0.2	0.00118	0.0988	600	25
Without CS2 washing	0.2	0.00118	0.0988	600	25
With CS2 washing	0.3	0.0966	0.0034	800	25
Without CS2 washing	0.3	0.0966	0.0034	800	25

### 4.4.2 Materials

The same chalcocite sample and chemicals described in Section 4.3.2 plus carbon disulfide ( $CS_2$ , 99.9%, Sigma-Aldrich) were used in the leaching tests to prepare the leaching residues for the surface characterization tests.

#### 4.4.3 Experimental procedure

To prepare the leaching residue for the surface analysis by SEM-EDX and XPS analyses, leaching tests were performed in the 500 mL jacketed reactors at varied leaching conditions described in Table 4.7 and

Table 4.8. The leaching experiments were terminated at 80% copper extraction to provide consistent solid surfaces for the surface characterization tests. Two leaching tests were conducted at either 600 or 800 mV to study the role of sulfur on copper extraction kinetics. The leaching procedure was the same as described in Section 4.3.5. At 600 mV, when copper extraction

reached 74%, one leaching test was paused and the leaching residue was collected, washed by CS<sub>2</sub> for 1 h at room temperature to remove sulfur, filtered, and washed with acetone. The dried residue was then placed back in the reactor and the leaching was resumed. Then the extraction without and with CS<sub>2</sub> washing was compared. For the test at 800 mV, the same procedure was repeated except that the test was paused after 80% of copper was extracted.

To study the surface of chalcocite leaching residues by SEM-EDX, dried powder samples were placed on pin-type stubs with double-sided carbon adhesive. The samples were then coated with carbon by means of a high-vacuum thermal evaporation technique to make the surface conductive and minimize surface charging. The images were taken using the secondary electron (SE) imaging mode with a FEI Quanta 650 SEM-EDX. The equipment was operated at 20 kV to obtain sufficient secondary electrons for imaging and the working distance was maintained at 10 mm.

Leybold Max2000 spectrometer was used for the XPS analyses of the untreated chalcocite sample and the leaching residues. X-ray photoelectron spectra were generated using the Mg Ka (hv = 1253.6 eV) irradiation source. Binding energy calibration was based on C 1s at 284.6 eV. The XPS spectra were analyzed using XPSPeak 4.1 software to fit the XPS peaks. The background of the spectrum was first subtracted using the Shirley method (Shirley, 1972). To keep the fitting process consistent for all S 2p spectra, the following conditions were applied: peak area ratio of 2:1 for S  $2p_{3/2}$  to S  $2p_{1/2}$ , FWHM 0.6 for S<sup>2–</sup> and S<sub>2</sub><sup>2–</sup> and 1.2 for S<sub>n</sub><sup>2–</sup> and S<sup>0</sup>, and 1.18 eV splitting. The S 2p spectra peak fitting was conducted using the Gaussian– Lorentzian function to describe the combined Gaussian–Lorentzian line shapes of the peaks, for which the weighting used was 80% Gaussian and 20% Lorentzian (Shirley, 1972). The peaks were assigned using the reported peak positions in the literature.

# Chapter 5: Iron and copper speciation in chloride solution with high ionic strength

#### 5.1 Introduction

The second stage of leaching, i.e., the leaching of a covellite-like material produced in the first stage, is particularly sensitive to the ORP of leaching solution. Miki et al. (2011) reported that the covellite-like phase cannot be leached at a potential of 500 mV or less. To control potential in a desired range, it is essential to determine the predominant species participating in the redox reactions and their activities at varied leaching conditions. In this Chapter, we analyzed the speciation and activities of iron and copper in chloride media, with a focus on chalcocite leaching. Compared with other published work, the present study carried out such analysis at high solution ionic strength up to 3 M. For this purpose, the SIT activity model was used in the thermodynamic calculations performed by the STABCAL software.

The speciation results obtained from the software were validated by the experimental ORP measurements, which were performed in a sealed jacketed reactor under an ultra-high purity nitrogen environment. Based on the speciation and activities results, we proposed the actual cathodic and anodic half reactions responsible for copper leaching from chalcocite in chloride media. The proposed cathodic half reactions pinpoint ways of manipulating solution redox potentials, which is vital for determining the kinetics of the second stage of chalcocite leaching. This Chapter was submitted for publication in Hydrometallurgy.

#### 5.2 Ferric/ferrous chloride system

# 5.2.1 Verification of the STABCAL reliability

Prior to applying the software to calculate the speciation of iron in chloride media, the reliability of the software was evaluated by comparing the ORP values calculated by the software with those measured experimentally. The ORP measurements were conducted at varied nominal [Fe(III)]/[Fe(II)] ratios and varied chloride concentrations according to Table 4.1. Figure 5.1 show the ORP values measured experimentally at varied chloride concentrations and varied nominal [Fe(III)]/[Fe(II)] ratios. Each data point in Figure 5.1 represents the mean ORP value of three replicated ORP measurements. The error bars are the standard error at 95% confidence level with a maximum variability of  $\pm 3.62$  mV. All available databases in the software were tested to calculate the ORP values and the best values were obtained by applying the Woods database, which gave an average error of 0.56% between the calculated and the measured ORP values. Figure 5.1 shows that using this database, the software was capable of satisfactorily calculating the ORP of the acidic ferric/ferrous solutions at varied nominal [Fe(III)]/[Fe(II)] ratio and varied chloride concentration. The equation the software uses to calculate ORP is shown as Eq. (5.1), where  $E^0$  is the standard reduction potential and  $a_{Fe^{3+}}$  and  $a_{Fe^{2+}}$  are the activities for free ferric and free ferrous ions. The value of the standard reduction potential for the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple (0.770 V) was calculated from the free Gibbs energies in the Woods database (Table A.1, Appendix A).

$$E = E^{0} + \frac{2.303RT}{F} \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} = 0.770 + 0.059 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$
(5.1)

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Figure 5.1 Comparison of the ORP values calculated by STABCAL with those measured experimentally under the following conditions: pH 1.5, total iron of 0.1 M, and 25 °C, the squares denote the measured values and triangles denote the calculated values

Because we generally only know the total concentration of an element, the activity terms in Eq. (5.1) were expressed as the total ferric and ferrous concentration multiplied by their respective activity coefficient in Eq. (5.2). Due to iron complexation with chloride, the two activity coefficients in Eq. (5.2),  $\gamma_{Fe(III)}$  and  $\gamma_{Fe(II)}$ , should be called the total activity coefficient of ferric and ferrous, each representing the product of the percent free ions and the free ion activity coefficient. [Fe(III)] and [Fe(II)] are the total (nominal) concentration of ferric and ferrous. Eq. (5.2) was further rearranged as Eq. (5.3), in which the total activity coefficients were combined with the standard reduction potential  $E^{0}$  into a new standard potential  $E^{0'}$ , termed the formal

potential.  $E^{0'}$  can be obtained by measuring the ORP of the solutions with varied nominal [Fe(III)]/[Fe(II)] ratio and chloride concentration (Hiroyoshi et al., 2000).

$$E = E^{0} + \frac{2.303RT}{F} \log \frac{\gamma_{Fe(III)}[Fe(III)]}{\gamma_{Fe(II)}[Fe(II)]}$$
(5.2)

$$E = E^{0} + \frac{2.303RT}{F} \log \frac{\gamma_{Fe(III)}}{\gamma_{Fe(II)}} + \frac{2.303RT}{F} \log \frac{[Fe(III)]}{[Fe(II)]} = E^{0'} + \frac{2.303RT}{F} \log \frac{[Fe(III)]}{[Fe(II)]}$$
(5.3)

In Figure 5.1, the intercept of the straight lines with the y axis represents the formal potential  $(E^{0'})$  for that specific solution composition. Straight lines implied that  $E^{0'}$  value was not affected by the nominal [Fe(III)]/[Fe(II)] ratio. However, the  $E^{0'}$  values decreased by approximately 16 mV when chloride was increased from 0.5 M to 3 M. The slope of the linear lines was approximately 59 mV/decade, which is in agreement with the theoretical value calculated by the Nernst equation at 25 °C.

To more clearly show the effect of chloride on the formal potential, Figure 5.2 plotted the formal potential  $E^{0'}$  as a function of logarithmic chloride concentration. The linear line with a negative slope represents a negative correlation between the two variables, suggesting that increasing chloride concentrations decreased the formal potential. Because -20.4 log [Cl<sup>-</sup>] is related to  $\frac{2.303RT}{F}\log\frac{\gamma_{Fe(III)}}{\gamma_{Fe(II)}}$ , mathematically, the negative slope means that the ratio of the total activity coefficient for ferric to that for ferrous is less than 1, i.e.,  $\frac{\gamma_{Fe(III)}}{\gamma_{Fe(II)}} < 1$ , suggesting that ferric has a higher tendency to complex with chloride than ferrous, which agrees with the results published by other researchers (Miki et al., 2011; Muir, 2002). Although Miki et al. (2011) used a different database (NIST database) and did not provide information on the activity model used in their

calculations, their results were similar to the results obtained in the present study. The ratio decreases with increasing chloride concentration in a power-law relationship with an exponent of -0.345 (-20.4/59.2). Combining results presented in Figure 5.1 and Figure 5.2, we derived Eq. (5.4), which calculates ORP when the two easily measurable parameters, the nominal [Fe(III)]/[Fe(II) ratio and chloride concentration, are given. Compared with Eq. (5.1) that involves activity terms, the experimentally derived Eq. (5.4) is a straightforward empirical equation for calculating ORP without resorting to a seemingly complicated software.

$$E = 0.708 - 0.02 \log[Cl^{-}] + 0.059 \log \frac{[Fe(III)]}{[Fe(II)]}$$
(5.4)



Figure 5.2 Formal potential versus logarithmic chloride concentration under the following conditions: pH 1.5, total iron of 0.1 M, and 25  $^\circ C$ 

#### 5.2.2 Concentrations and activities of iron species in chloride media

In order to determine the actual cathodic reaction responsible for chalcocite leaching in ferric chloride media, the species possibly present in the system were identified using the software for the conditions shown in Table 4.1. The distribution of various iron species was constructed using the Dist-Ligand feature in the Diagrams and Reactions section of STABCAL as shown in Figure

4.2. Figure 5.3 shows the distribution of ferric species at ferric concentration of 0.05 M and varied chloride concentrations. The hydrated Fe<sup>3+</sup> dominated in an acidic chloride solution containing up to 3 M of chloride. By increasing the concentration of chloride from 0.5 M to 3 M, the percentage of hydrated  $Fe^{3+}$  decreased from 92% to 66%. The decrease in hydrated  $Fe^{3+}$  was due to the increase in the formation of FeCl<sup>2+</sup> by increasing the concentration of chloride. The percentage of FeCl<sup>2+</sup> increased from 8% at 0.5 M chloride concentration to 34% at 3 M chloride concentration. In the case of ferrous species, the hydrated  $Fe^{2+}$  was the only dominant species of ferrous at all chloride concentrations up to 3 M, which is in agreement with the literature. Zhao and Pan (2001) conducted a spectrophotometric study on the chloro-complexes of Fe(II) in the temperature range 10 - 100 °C and at chloride concentrations less than 3 molal. They used Pitzer and Helgeson activity models for the thermodynamic calculations. The authors showed that Fe<sup>2+</sup> was the predominant species, while FeCl<sup>+</sup> accounted for less than 40%. In another spectrophotometric study, Heinrich and Seward (1990) investigated the speciation of ferrous in a system with 0.01 to 3.4 molal of chloride, 0.005 to 0.025 molal of Fe(II), and at different temperatures. Using the Helgeson activity model, the authors showed that at temperatures lower than 100 °C, only Fe<sup>2+</sup> and FeCl<sup>+</sup> were dominant, whereas at higher temperatures a minor concentration of FeCl<sub>2</sub> started to emerge.



Figure 5.3 Ferric speciation in chloride media at increasing chloride concentration under conditions: [Fe(III)] 0.05 M, pH 1.5, 25 °C

Ashurst and Hancock (1977) studied the sulphato-complexes of the transition-metal ions and showed that FeSO<sub>4</sub><sup>+</sup> was an inner-sphere complex, while FeSO<sub>4</sub>, FeHSO<sub>4</sub><sup>+</sup>, and FeHSO<sub>4</sub><sup>2+</sup> were outer-sphere iron complexes. Taking this finding into consideration, Crundwell pointed out the dependence of the sphalerite leaching rate on iron complexes in sulfate media (Crundwell, 1987). The author explained that in the leaching of sphalerite in sulfate media, charge transfer to FeSO<sub>4</sub><sup>+</sup> would need to break the Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> bond in the inner coordination sphere to form the FeSO<sub>4</sub> outer-sphere complex. Accordingly, the different bonding in the FeSO<sub>4</sub><sup>+</sup> and FeSO<sub>4</sub> complexes would stop the charge transfer to FeSO<sub>4</sub><sup>+</sup> and therefore, the outer-sphere couples including FeHSO<sub>4</sub><sup>2+</sup>/FeHSO<sub>4</sub><sup>+</sup> and Fe<sup>3+</sup>/Fe<sup>2+</sup> would be the electro-active species. However, the author suggested that the reaction rate was independent of a particular iron complex in chloride media. The author supported his conclusion by using data presented in a study by Dutrizac and MacDonald (1978) and calculating the reaction order with respect to FeCl<sup>2+</sup> and FeCl<sub>2</sub><sup>+</sup>, respectively, which gave an overall reaction order of 0.36. This value was equal to the reaction

order with respect to Fe(III) obtained by Dutrizac and MacDonald (1978). Crundwell also reported that the reaction order with respect to Fe(III) was obtained to be 0.5 in a research study by Jin and Warren (1985), and the reaction order with respect to both  $FeCl^{2+}$  and  $FeCl^{2+}$  was 0.5.

Based on Crundwell's suggestion, all iron species in chloride media could be electro-active complexes. Therefore, in the present study, iron complexes with the highest activity were chosen to be the dominant electro-active species. The activity of iron species was calculated using the Speciation and Titration feature of STABCAL as shown in Figure 4.2 and Figure 4.3. Figure 5.4 shows the activities of Fe(III) species as a function of chloride concentration at varied nominal [Fe(III)]/[Fe(II) ratios. FeCl<sup>2+</sup> has a higher activity than hydrated Fe<sup>3+</sup> and FeCl<sub>2</sub><sup>+</sup> at all nominal [Fe(III)]/[Fe(II) ratios. This suggests that the Fe(III) species responsible for chalcocite dissolution is most likely to be FeCl<sup>2+</sup>. According to Figure 5.4, the activity of FeCl<sup>2+</sup> increased approximately 5 times as chloride concentration increased from 0.5 M to 3 M, whereas  $FeCl_2^+$ increased 25 times and FeCl<sub>3</sub> increased 130 - 150 times when chloride concentration changed from 0.5 M to 3 M. The activity of hydrated ferric remained almost constant as chloride concentration increased. In the case of Fe(II) species, as shown in Figure 5.5, hydrated Fe<sup>2+</sup> was the dominant ferrous species. The activity of hydrated Fe<sup>2+</sup> and FeCl<sup>+</sup> was approximately constant as chloride concentration increased from 0.5 M to 3 M. The concentration, activity, and activity coefficient of all iron species at varied chloride concentrations are shown in Table A.3 to Table A.6 in Appendix A.

Because  $FeCl^{2+}$  and  $Fe^{2+}$  were identified as the Fe(III) and Fe(II) species of the highest activities in the chloride concentration range of 0.5 M to 3 M, the actual cathodic reaction occurring in the leaching system and the corresponding Nernst equation were proposed as Eqs. (5.5) and (5.6). To derive Eq. (5.6), the free Gibbs energies from Woods database was used (Appendix A, Table A.1). By using Eq. (5.6), we calculated the solution redox potentials with relevant thermodynamic data obtained from the software. The calculated values were compared with those measured experimentally to validate the proposed cathodic reaction. Figure 5.6 shows that the difference between the calculated and the experimentally measured values was rather small, with the largest difference being 8.7 mV and the average error being 0.21%. More importantly, this average error was lower than the value of 0.56%, which represents the average error between what the software calculated using Eq. (5.1) and the experimentally measured values (shown in Figure 5.1). Therefore, it is concluded that Eq. (5.5) is likely to be the actual cathodic reaction responsible for chalcocite leaching.

$$FeCl^{2+} + e^{-} = Fe^{2+} + Cl^{-}$$
(5.5)

$$E_{FeCl^{2+}/Fe^{2+}} = 0.704 - 0.059 \log a_{Cl^{-}} + 0.059 \log \frac{a_{FeCl^{2+}}}{a_{Fe^{2+}}}$$
(5.6)



Figure 5.4 The activities of Fe(III) species calculated by the STABCAL software under the following conditions: total iron of 0.1 M, pH 1.5 and 25 °C



Figure 5.5. The activities of Fe(II) species calculated by the STABCAL software under the following conditions: total iron of 0.1 M, pH 1.5 and 25 °C



Figure 5.6 Comparison between the ORP values calculated by Eq. (5.6) and those measured experimentally under the following conditions: total iron of 0.1 M, pH 1.5 and 25 °C

### 5.3 Cupric/cuprous chloride system

# 5.3.1 Verification of the STABCAL reliability

The reliability of the software was assessed by comparing the ORP values calculated by the software with those measured experimentally (Table 4.2). Figure 5.7 show the ORP values measured experimentally at varied chloride concentrations and varied nominal [Cu(II)]/[Cu(I)] ratios. Each data point in Figure 5.7 represents the mean ORP value of three replicated ORP measurements. The error bars are the standard error at 95% confidence level with a maximum variability of  $\pm 15.7$  mV. The error was higher at 3 M chloride concentration, most likely due to the junction potential, which is higher at higher chloride concentration because of high mobility of chloride ions compared with sodium ions. Among the databases available in the software, the 77

HSC database provided the lowest average error, 1.61%, between the calculated and the measured values. Figure 5.7 shows that using the HSC database, the software was able to calculate the ORP of the acidic cupric/cuprous solutions at varied nominal [Cu(II)]/[Cu(I)] ratio and varied chloride concentration, but the discrepancy between the calculated and the measured values became larger at higher chloride concentration. The software uses Eq. (5.7) to calculate the ORP, where  $E^0$  is the standard reduction potential and  $a_{Cu^{2+}}$  and  $a_{Cu^+}$  are the activities for free cupric and cuprous ions. The value of the standard reduction potential for the Cu<sup>2+</sup>/Cu<sup>+</sup> couple (0.156 V) was calculated from the free Gibbs energies in the HSC database (Table A.2, Appendix A).

$$E = E^{0} + \frac{2.303RT}{F} \log \frac{a_{Cu^{2+}}}{a_{Cu^{+}}} = 0.156 + 0.059 \log \frac{a_{Cu^{2+}}}{a_{Cu^{+}}}$$
(5.7)

Eq. (5.8) is the Nernst equation for the Cu(II)/Cu(I) couple that converts the activity terms to their respective total concentration multiplying the total activity coefficient. Eq. (5.8) was further rewritten as Eq. (5.9), in which the total activity coefficients of cupric and cuprous ions were combined with the standard reduction potential  $E^0$  into the formal potential  $E^{0'}$ .

$$E = E^{0} + \frac{2.303RT}{F} \log \frac{\gamma_{Cu(II)}[Cu(II)]}{\gamma_{Cu(I)}[Cu(I)]}$$
(5.8)

$$E = E^{0} + \frac{2.303RT}{F} \log \frac{\gamma_{Cu(II)}}{\gamma_{Cu(I)}} + \frac{2.303RT}{F} \log \frac{[Cu(II)]}{[Cu(I)]} = E^{0'} + \frac{2.303RT}{F} \log \frac{[Cu(II)]}{[Cu(I)]}$$
(5.9)

In Figure 5.7, the formal potential  $(E^{0'})$  for any specific solution composition is obtained as the intercept of the straight lines with the y axis. Straight lines implied that  $E^{0'}$  value was not affected by the nominal [Cu(II)]/[Cu(I)] ratio. However, the  $E^{0'}$  values increased by approximately 120

mV when chloride was increased from 0.5 M to 3 M. The slope of the linear lines in Figure 5.7 is 55 mV/decade on average, which is lower than 59 mV/decade according to the Nernst equation. This may be attributed to the rapid oxidation of cuprous ions by oxygen in the process of transferring it into the reactors, though measures were strictly taken to prevent oxidation. This might have affected the nominal [Cu(II)]/[Cu(I)] ratio and thereby developed discrepancy between the ORP values measured experimentally and those calculated by the software.



Figure 5.7 Comparison of the ORP values calculated by STABCAL with those measured experimentally under the following conditions: pH 1.5 and 25 °C, total copper of 32 mM, the squares denote the measured values and triangles denote the calculated ORP values by the software

To more clearly show the effect of chloride on the formal potential, Figure 5.8 plotted the formal potential as a function of logarithmic chloride concentration. The linear line with a positive slope

represents a positive correlation between the two variables, suggesting that increasing chloride concentrations raised the formal potential. As opposed to the ferric/ferrous system, the positive slope means that cupric has a lower tendency to complex with chloride than cuprous (Colton and Canterford, 1969; Muir, 2002). Based on the experimental results shown in Figure 5.8, an empirical equation for estimating ORP for cupric/cuprous system was shown as Eq. (5.10).

$$E = 0.468 + 0.132 \log[Cl^{-}] + 0.059 \log \frac{[Cu(II)]}{[Cu(I)]}$$
(5.10)



Figure 5.8 Formal potential versus logarithmic chloride concentration under the following conditions: pH 1.5, total copper of 32 mM, and 25  $^{\circ}$ C

#### 5.3.2 Concentrations and activities of copper species in chloride media

In order to determine the actual cathodic and anodic reactions for chalcocite leaching in cupric chloride media, the speciation and activities of copper species in chloride media were determined using the software for the conditions shown in Table 4.2. The distribution of copper species was constructed using the Dist-Ligand feature in the Diagrams and Reactions section of STABCAL as shown in Figure 4.2. Figure 5.9A shows that the dominant Cu(II) species at all chloride

concentration is the hydrated  $Cu^{2+}$ . The percentage of hydrated  $Cu^{2+}$  dropped from 88% at 0.5 M chloride concentration to 49% at 3 M chloride concentration. The drop in Cu<sup>2+</sup> concentration was attributed to the increase in the formation of CuCl<sup>+</sup> and CuCl<sub>2</sub>. The percentage of CuCl<sup>+</sup> increased from 12% at 0.5 M chloride concentration to 43% at 3 M chloride concentration, while CuCl<sub>2</sub> increased from 0 to 8% as chloride concentration increased from 0.5 M to 3 M. Using Extended X-ray Absorption Fine Structure (EXAFS), Collings et al. (2000) showed that below 75 °C, only hydrated Cu<sup>2+</sup> was present in solutions with lower than 2.2 M chloride and CuCl<sup>+</sup> species was predominant at higher chloride concentration (5 M NaCl) between 25 °C and 75 °C. In the case of cuprous species, the dominant cuprous chloride species at chloride concentration up to 3 M, according to Figure 5.9B, was CuCl<sub>3</sub><sup>2-</sup>. It accounted for 71% at 0.5 M chloride concentration and increased to 95% at 3 M chloride concentration. The percentage of CuCl<sup>2-</sup> was 29% at 0.5 M chloride concentration and dropped to 5% at 3 M chloride concentration. These results agree with those reported in the literature that in solutions containing less than 6 M chloride and at room temperature only CuCl<sub>2</sub><sup>-</sup> and CuCl<sub>3</sub><sup>2-</sup> were predominant (Ahrland and Rawsthorne, 1970; Fritz, 1981; Sharma and Millero, 1990; Sugasaka and Fujii, 1976). Brugger et al. (2007) concluded that only CuCl<sub>3</sub><sup>2-</sup> predominated at room temperature and high salinity (LiCl > 3 M) and Sherman (2007) observed a stable CuCl<sub>3</sub><sup>2-</sup> complex in 1 M CuCl and 4 M chloride solution at room temperature.


Figure 5.9 The speciation of A) Cu(II) and B) Cu(I) in chloride media at the following conditions: pH 1.5, [Cu(II]] 31.44 mM, [Cu(I)] 31.10×10<sup>-3</sup> mM, 25 °C

The activity of iron species was calculated using the Speciation and Titration feature of the software as shown in Figure 4.2 and Figure 4.3. Figure 5.10 shows that the activity of CuCl<sup>+</sup> is higher than that of hydrated Cu<sup>2+</sup>, except at low chloride concentrations (<0.5 M), where the hydrated  $Cu^{2+}$  has a higher activity. The activity of hydrated  $Cu^{2+}$  decreased by a factor of approximately 0.6, while the activity of CuCl<sup>+</sup> increased approximately 3 times. The decrease in the activity of hydrated Cu<sup>2+</sup> and the increase in the activity of CuCl<sup>+</sup> was because of the change in the concentration of these species as was shown in Figure 5.9A. In the case of Cu(I) speciation, Figure 5.11 shows that CuCl<sub>3</sub><sup>2-</sup> had a higher activity at chloride concentrations higher than 0.5 M, but at chloride concentrations lower than 0.5 M,  $CuCl_2^-$  had a higher activity than CuCl<sub>3</sub><sup>2-</sup>. The activity of CuCl<sub>3</sub><sup>2-</sup> increased 1.7 times (on average) as chloride concentration increased from 0.5 M to 3 M, while the activity of CuCl<sub>2</sub><sup>-</sup> decreased by a factor of approximately 0.3. The trend in the activities of Cu(I) species at varied chloride concentrations is similar to that in the concentration of Cu(I) species as shown in Figure 5.9B. The concentration, activity, and activity coefficient of all copper species at varied chloride concentrations are shown in Table A.7 to Table A.10 in the Appendix.



Figure 5.10 The activities of Cu(II) species calculated by the STABCAL software under the following conditions: total copper 32 mM, pH 1.5, 25 °C



Figure 5.11 The activities of Cu(I) species calculated by the STABCAL software under the following conditions: total copper 32 mM, pH 1.5, 25 °C

According to the speciation results, the cathodic reaction and the corresponding Nernst equation were proposed as Eqs. (5.11) and (5.12) for chloride concentrations lower than 0.5 M and as Eqs. (5.13) and (5.14) for chloride concentrations in the range of 0.5 M - 3 M. The standard reduction potentials were calculated from the Gibbs free energies obtained from the HSC database. Similar equations were proposed by Muir (Muir, 2002). The appropriateness of these two equations in describing the cathodic process was tested by comparing the ORP values calculated by these two equations with those measured experimentally. Figure 5.12 shows that the proposed equations can satisfactorily describe the reduction of cupric species in the chloride concentration range investigated.

$$Cu^{2+} + 2Cl^{-} + e^{-} = CuCl_{2}^{-}$$
 [Cl<sup>-</sup>] < 0.5 (5.11)

$$E_{Cu^{2+}/CuCl_{2}^{-}} = 0.469 + 0.118 \log a_{Cl^{-}} + 0.059 \log \frac{a_{Cu^{2+}}}{a_{CuCl_{2}^{-}}}$$
(5.12)

$$CuCl^{+} + 2Cl^{-} + e^{-} = CuCl_{3}^{2-}$$
  $0.5 < [Cl^{-}] < 3$  (5.13)

$$E_{CuCl^+/CuCl_3^{2-}} = 0.468 + 0.118 \log a_{Cl^-} + 0.059 \log \frac{a_{CuCl^+}}{a_{CuCl_3^{2-}}}$$
(5.14)



Figure 5.12 Comparison between the ORP values calculated by Eqs. (5.12) and (5.14) and those measured experimentally under the following conditions: total copper 32 mM, pH 1.5, 25 °C, the squares denote the measured values and triangles denote the calculated ORP values by the software

# 5.4 Integration of the ferric/ferrous and cupric/cuprous couple in chalcocite chloride leaching

To better understand the effect of chloride concentration on chalcocite leaching, the anodic reactions and the corresponding Nernst Equations are shown in Table 5.1. The standard reduction potentials were calculated from the Gibbs free energies of all species obtained from the HSC database (Appendix A, Table A.2). The anodic reaction omits the intermediate products that could be formed in the first stage of leaching, because the thermodynamic data for these intermediates is unavailable (Miki et al., 2011). Figure 5.13 shows that increasing chloride concentration reduces the redox potentials of the anodic half reaction for both stages of

chalcocite dissolution. More importantly, the difference between the cathodic and anodic potentials represents the thermodynamic driving force for chalcocite leaching to occur. Overall, increasing chloride concentration leads to a greater difference, thereby rendering chalcocite leaching thermodynamically more favorable.

[CI⁻] 0.5 M				
	$Cu_2S + 2Cl^- = CuCl_2^- + CuS + e^-$	(5.15)		
1 <sup>st</sup> stage	$E_{Cu_2S/CuCl_2^-} = 0.563 + 0.059 \log a_{CuCl_2^-} - 0.118 \log a_{Cl^-}$	(5.16)		
2 <sup>nd</sup> stage	$CuS + 2Cl^- = CuCl_2^- + S^0 + e^-$	(5.17)		
	$E_{CuS/CuCl_{2}^{-}} = 0.758 + 0.059 log a_{CuCl_{2}^{-}} - 0.118 log a_{Cl^{-}}$	(5.18)		
	0.5 M < [CI <sup>-</sup> ] < 3 M			
1 <sup>st</sup> stage	$Cu_2S + 3Cl^- = CuCl_3^{2-} + CuS + e^-$	(5.19)		
	$E_{Cu_2S/CuCl_3^{2-}} = 0.540 + 0.059 \log a_{CuCl_3^{2-}} - 0.177 \log a_{Cl^{-}}$	(5.20)		
	$CuS + 3Cl^{-} = CuCl_{3}{}^{2-} + S^{0} + e^{-}$	(5.21)		
2 <sup>nd</sup> stage	$E_{CuS/CuCl_3^{2-}} = 0.735 + 0.059 log a_{CuCl_3^{2-}} - 0.177 log a_{Cl^{-}}$	(5.22)		

Table 5.1 The anodic half reactions and the corresponding Nernst equations for chalcocite leaching under the following conditions: varied chloride concentrations, total copper of 32 mM, pH 1.5, 25°C

In the case of using cupric as the oxidant, Figure 5.13 shows that when chloride concentration is lower than 0.5 M, it is likely that the second stage of chalcocite leaching cannot be initiated due to insufficient potential difference between the cathodic and anodic processes. Miki et al. (2011) showed that above 20 g/L chloride, the reduction potential of Cu(II)/Cu(I) was higher than that of the second stage of chalcocite leaching. However, they did not provide sufficient information about the activity model and the ionic strength range they used in their thermodynamic calculations.



Figure 5.13 Comparison of reduction potentials of cathodic and anodic reaction of the first and second stage of chalcocite leaching under the following conditions: [Cu(II)] 31.44 mM, [Cu(I)] 31.10×10<sup>-3</sup> mM, [Fe(III)] 0.05 M, [Fe(II]] 0.05 M, pH 1.5, 25 °C, the symbols denote the experimentally measured ORP and the dashed lines denote the calculated ORP

Figure 5.13 also shows that in the chloride concentration range investigated, the predominant oxidizing couple is ferric/ferrous species. However, when chloride concentration is elevated beyond a certain level, the reduction potential of cupric/cuprous couple may exceed that of the ferric/ferrous couple, especially when ferric/ferrous ratio is low. In this case, the oxidation of ferrous species by cupric species becomes thermodynamically possible and cupric species may become increasingly important as the oxidants. This hypothesis requires further experimental proof.

# 5.5 Conclusions

Determination of iron and copper speciation and activities of various species in chloride media is essential for estimating ORP, which is a key factor determining the kinetics of copper sulfide leaching. In this study, using the STABCAL software, we determined the speciation of iron and copper in chloride media at high solution ionic strength (< 3 M) that might be encountered in heap leaching using seawater as process water. The SIT activity model, which is appropriate for high solution ionic strength (up to 3 M), was applied to calculate the activity coefficients of various iron and copper species. To verify the reliability of the software, we measured ORP at various nominal ferric/ferrous and cupric/cuprous ratio and different chloride concentration and then compared the measured values with those calculated by the software. After verification of its reliability, the software was used to determine the speciation and activities of various iron and copper species. Then the actual cathodic and anodic reactions responsible for chalcocite leaching in chloride media were proposed.

In general, the potentials calculated by the software matched those measured experimentally, even though discrepancies were observed in the cupric/cuprous system. As chloride concentration was increased, the potential of the ferric/ferrous couple slightly decreased, while the potential of the cupric/cuprous couple markedly increased. Empirical equations (Eqs. (5.4) and (5.10)) were derived from the experimental data that allow the calculation of ORP without resorting to a thermodynamic software package.

The speciation results show that the dominant species of ferric and ferrous were FeCl<sup>2+</sup> and hydrated Fe<sup>2+</sup>. At [Cl<sup>-</sup>] < 0.5 M, hydrated Cu<sup>2+</sup> and CuCl<sub>2</sub><sup>+</sup> were the predominant cupric and cuprous species. At 0.5 M < [Cl<sup>-</sup>] < 3 M, CuCl<sup>+</sup> and CuCl<sub>3</sub><sup>2-</sup> were the dominant species of cupric and cuprous ions. Based on the speciation results, the cathodic reaction of ferric and cupric reduction and the anodic reaction of chalcocite leaching were proposed. According to the

proposed anodic reaction, increasing the chloride concentration reduces the redox potential of chalcocite dissolution. Overall, increasing chloride concentration increases the potential difference between the cathodic and anodic processes, thereby rendering chalcocite leaching thermodynamically more favorable.

# Chapter 6: Chalcocite leaching kinetics in ferric chloride media

# 6.1 Introduction

This chapter aims to investigate and model the kinetics of chalcocite leaching in acidified ferric chloride media. Reactor leaching experiments were carried out at fully controlled temperature, pH and ORP. The effect of chloride concentration, ferric concentration, ferrous concentration, ORP, particle size, and temperature on the copper extraction rate was studied. Two individual kinetics models were developed to simulate the rate of copper extraction from chalcocite in the first and second stage of leaching. This body of knowledge would enhance the understanding of the key factors that control the kinetics of chalcocite leaching in ferric chloride media, which will provide insights on the application of seawater in heap leaching. This Chapter was published as a journal paper in Hydrometallurgy.

#### 6.2 Chalcocite sample characterization

The results of quantitative phase analysis by Rietveld refinements are given in Table 6.1. The values represent the relative percentages of crystalline phases normalized to 100%. The Rietveld refinement plot is shown in Figure 6.1. This figure shows that the mineral consists of djurleite and chalcocite low and chalcocite Q which are the polymorphs of chalcocite depending on crystallography and composition (Evans, 1981; Fuentes et al., 2008; Posfal and Buseck, 1994). Table 6.2 shows the chemical composition of the chalcocite sample. The results are the average of four replicated analyses. The relative standard deviation (RSD) for copper and sulfur were negligible. The RSD for iron was slightly higher due to low content of iron leading to low

accuracy in ICP analysis. Chemical composition shows that the copper content is slightly lower than a pure chalcocite mineral, confirming the XRD results and the presence of djurleite mineral.



Figure 6.1 X-ray diffraction pattern of chalcocite mineral, blue line - observed intensity at each step; red line - calculated pattern; solid grey line below - difference between observed and calculated intensities; vertical bars - positions of all Bragg reflections. Colored lines are individual diffraction patterns of all phases.

Table 6.1 Qualitative analysis of chalcocite by XRD				
Mineral	Ideal formula	Percentage of a phase, %		
Chalcocite low	$Cu_2S$	41		
Chalcocite-Q	$Cu_2S$	23		
Djurleite	Cu <sub>31</sub> S <sub>16</sub>	36		

_	Mineral	Ideal formula	Percentage of a phase, %
	Chalcocite low	$Cu_2S$	41
	Chalcocite-Q	$Cu_2S$	23
	Djurleite	$Cu_{31}S_{16}$	36

Table 6.2. Chemical composition of the chalcocite sample analyzed by ICP-OES					
	Element	Symbol	Test sample, %	RSD, %	Pure chalcocite, %
	Copper	Cu	79.1	0.47	79.85
	Sulfur	S	20.7	1.63	20.15
	Iron	Fe	0.1	8.8	0

# 6.3 Effect of leaching parameters on chalcocite leaching in ferric chloride media

# 6.3.1 Reproducibility of the leaching tests and maintaining constant pH and ORP

Prior to performing the designed tests to study the kinetics of chalcocite leaching, the reproducibility of the experimental results was evaluated by conducting the same leaching test in four replicates, from which standard errors were calculated. Figure 6.2 shows the average copper extraction over time in the first and second stages of leaching with the standard error bars. The standard error was obtained by calculating the standard deviation of four replicates divided by the square root of the number of repeats performed. The average standard error from all data points was obtained to be 0.46%, which was used as the benchmark for assessing whether an observed difference in copper extraction is statistically significant. Only values higher than 0.46% were considered statistically significant. Figure 6.3 illustrates an example of controlling pH and ORP in the course of leaching, which shows that both parameters could be well maintained at constant values during leaching.



Figure 6.2 Chalcocite leaching in ferric chloride media under the following conditions: [Fe(II)] 0.001 M, [Fe(III)] 0.05 M, pH 1.5, 25 °C, particle size -75+53 µm. A: the first stage; B: the second stage. The error bars represent standard errors calculated from four replicates



Figure 6.3 An example of ORP and pH control in the course of chalcocite leaching. The leaching conditions were [Fe(III)] 0.05 M, [Fe(II)] 0.01 M, [Cl<sup>-</sup>] 0.19, pH 1.5, 25 °C, particle size –75+53 μm

# 6.3.2 Effect of controlled potential

In order to avoid the participation of hydrogen peroxide in the leaching of chalcocite, diluted hydrogen peroxide (3% by volume) was used in the leaching tests. Figure 6.4 shows the effect of controlled potential by using diluted hydrogen peroxide on the first and second leaching stage of chalcocite. It shows that the reaction rate was slightly higher in the presence of hydrogen peroxide in both leaching stages. Hydrogen peroxide maintains the ferric concentration constant which, in turn, enhances the reaction rate because the kinetics rate is sensitive to the ferric concentration as is shown in Section 6.1.3. Figure 6.4 also shows copper extraction from chalcocite by hydrogen peroxide (3% by volume) without the presence of ferric and ferrous in the solution. It shows that the reaction rate of chalcocite leaching with hydrogen peroxide is very slow, therefore, the contribution of hydrogen peroxide is negligible. In addition, since the reduction of hydrogen peroxide by ferrous is faster than that by chalcocite, ferrous ions immediately consume hydrogen peroxide leaving no hydrogen peroxide to oxidize chalcocite.



Figure 6.4 Effect of controlled potential on the first and second stage of chalcocite leaching in ferric chloride media under the following conditions: [Fe(III)] 0.05 M, [Fe(II)] 0.01 M, [CΓ] 0.19, pH 1.5, 25 °C, particle size -75+53 μm

#### 6.3.3 Concentration terms

The chloride concentrations of 0.172, 0.522, 1.522, and 3.022 M were generated by adding sodium chloride to the leaching solution. For reference, the concentration of chloride ions in seawater is around 0.5 M. The leaching solution ORP was maintained constant at 810 mV in all leaching tests. Figure 6.5 shows that increasing chloride concentration had an insignificant effect on the copper extraction rate in both stages. This result suggests that chloride concentration is not a rate-controlling parameter in chalcocite leaching with ferric as the oxidant.

Despite the insignificant effect of chloride concentration, the beneficial role of chloride ions compared with sulfate media on copper sulfide leaching has been postulated to be twofold. First, chloride ions may accelerate copper dissolution by forming copper chloro-complexes, which contribute to the oxidization of copper sulfide minerals (Cheng and Lawson, 1991a; Fisher et al., 1992). Second, chloride ions could lead to the formation of porous crystalline sulfur as the sulfide dissolution product instead of a cryptocrystalline or amorphous sulfur layer in the sulfate system. This porous crystalline sulfur layer helps enhance the dissolution rate by increasing the

oxidant diffusion through the product layer (Cheng and Lawson, 1991a; Rauld Faine et al., 2005).

The subsequent surface analysis by SEM-EDX (details available in Chapter 9) showed the formation of a sulfur layer as the product layer. In addition, the effect of chloride concentration and ORP on the sulfur layer formation was evaluated. On one hand, increasing chloride concentration improved the crystallinity of the sulfur layer. On the other hand, increasing ORP to around 800 mV rendered the sulfur layer thinner and more crystalline. In the present study, the leaching tests at varied chloride concentrations were conducted at a high ORP, 810 mV. As a result, the sulfur layer was considered to be already thin and crystalline and therefore, the effect of chloride concentration on the leaching reaction rate would be more likely to be seen at lower ORPs, at which sulfur layers were considered to be thicker and more amorphous.



Figure 6.5 Copper extraction versus leaching time at varied chloride concentrations under the following conditions: [Fe(III)] 0.05 M, [Fe(II)] 0.001 M, 25 °C, pH 1.5, particle size -75+53 µm. A: the first stage; B: the second stage

The ferric concentrations studied were chosen based on the iron concentration range typically encountered in heap leaching. A typical ferric concentration range in heap bioleaching of chalcocite is 0.02–0.1 M (Schlesinger et al., 2011). The effect of ferric concentration on chalcocite dissolution kinetics is shown in Figure 6.6. Similarly, the entire leaching cycle was divided into a faster first stage (Figure 6.6A) and a slower second stage (Figure 6.6B). For the first stage, when the ferric concentration was at or above 0.05 M, chalcocite oxidation rate only marginally changed. In contrast, when the ferric concentration. The effect of ferric concentration on the second stage was less significant than that on the first stage. Even though an increase in the ferric concentration increased the reaction rate of the second stage, the second stage of leaching became insensitive to ferric concentration above 0.05 M.



Figure 6.6 Copper extraction versus leaching time at varied ferric concentrations under the following conditions: [Fe(II)] 0.001 M, 25 °C, pH 1.5, particle size –75+53 µm. A: the first stage; B: the second stage

The effect of ferrous concentration on copper extraction is shown in Figure 6.7. Ferrous concentration had an insignificant effect on the reaction rate in the first stage, but an increase in the ferrous concentration slightly lowered the copper extraction rate in the second stage. This might be attributed to the drop in the redox potential due to the ferrous addition. According to Figure 6.7B, the ferrous concentration must be maintained as low as possible in heap leaching of chalcocite. In other words, the re-oxidation of ferrous to ferric should proceed sufficiently

rapidly. In a well-aerated heap, the chemical composition of the leaching solution, including ferrous, ferric, chloride, and cupric concentrations, plays a vital role in enhancing the oxidation of ferrous by oxygen. Many researchers have shown that increasing chloride concentration has a positive effect, while increasing ferric concentration is detrimental and cupric ions act as a catalyst (Colborn and Nicol, 1973; Miki and Nicol, 2008).

It is important to note that the copper extraction rate, in the second stage, slowed down after 70 - 80% of copper was extracted. Increasing ferric concentration and reducing the ferrous concentration improved the reaction rate, but it was still slow at 70 - 80% copper extraction. The subsequent surface analysis study, discussed in Chapter 9, shed light on the mechanism by which the reaction slowed down. The results from the surface analysis study showed that, in the second stage of chalcocite leaching, elemental sulfur and polysulfide formed on the surface of the particles. At low ORPs, both elemental sulfur and polysulfide were present on the solid surface and contributed to the slow reaction rate. At higher ORPs (>800 mV), the sulfur layer was thinner and more crystalline and therefore, the main contributor to the slow reaction rate was proposed to be the decomposition of polysulfide.



Figure 6.7 Copper extraction versus leaching time at varied ferrous concentrations under the following conditions: [Fe(III)] 0.05 M, 25 °C, pH 1.5, particle size –75+53 µm. A: the first stage; B: the second stage

The effect of ferric/ferrous ratio on the second stage was also investigated by conducting leaching experiments at varied ferric/ferrous ratios while the total iron concentration was maintained constant at 0.1 M. Eh-pH diagram of chalcocite in chloride media shown in Figure 2.2 indicates that at low pH values (~1.5), chalcocite could be oxidized to copper at ORP values higher than approximately 400 mV vs SHE. Therefore, the ferric/ferrous ratios of 0.33, 1, 4, 100 were selected, which corresponded to redox potentials of 660 mV, 700, 760, and 820 mV, respectively. Figure 6.8 shows the copper extraction over time at different redox potentials. The rate of copper extraction was slightly enhanced by increasing redox potential.

The effect of redox potential on the second stage of chalcocite leaching and on covellite leaching have been reported in both sulfate and chloride media (Bolorunduro, 1999; Miki et al., 2011; Nicol and Basson, 2017). Miki et al. showed that covellite dissolution at 600 mV and 650 mV was similar but was lower at 550 mV. At 500 mV, chalcocite and digenite underwent rapid first stage dissolution, but the extraction did not reach beyond 50% and 45%, respectively, suggesting that the secondary covellite phase formed could not be leached at a potential of 500 mV or lower. However, increasing the potential led to a quick dissolution of the secondary covellite formed 98

relative to primary covellite (Miki et al., 2011). The minimum potential tested in the present study was 660 mV, higher than the 550 mV reported in the literature, below which a significant slowdown in the second stage kinetics was reported. The higher potentials used in the present study may explain the observed slight increase in kinetics with increasing redox potential in the second stage.



Figure 6.8 Copper extraction versus leaching time at varied ferric/ferrous ratios in the second stage, 25 °C, pH 1.5, particle size –75+53 μm

#### 6.3.4 Temperature

The effect of temperature on the copper extraction from chalcocite is shown in Figure 6.9. The ORP for all tests were maintained at 810 mV. In the first stage, increasing temperature slightly increased the copper extraction. In contrast, temperature had a significant effect on the copper extraction rate in the second stage. Based on the subsequent surface analysis results (Chapter 9), increasing temperature, in the second leaching stage, rendered the solid surface more porous and the surface sulfur layer thinner and more crystalline. This may, in turn, enhance the reaction rate by improving the reduction of ferric ions on the solid surface, but direct experimental evidence

was not available. It might also assist the leaching reaction by enhancing the decomposition of polysulfide, which was formed as the intermediate reaction product. The improved reaction rate by increasing temperature implies that, similar to heap bioleaching of chalcocite in ferric sulfate media, increasing heap temperature, especially in the second stage, would significantly enhance copper extraction rate in chloride media. Various heat management and temperature control techniques in heap leaching have been evaluated, such as controlling raffinate temperature, adjusting the ratio of irrigation to aeration, and applying a thermal cover (Dixon, 2000; Liu and Granata, 2018). These techniques would be equally applicable to chalcocite heap leaching using seawater.



Figure 6.9 Copper extraction versus leaching time at varied temperatures under the following conditions: [Fe(II)] 0.001 M, [Fe(III)] 0.05 M, pH 1.5, particle size -75+53 µm. A: the first stage; B: the second stage

#### 6.3.5 Particle size

Particle size fractions of -75+53, -125+106, -150+125, and -212+180 µm were selected to investigate the effect of particle size distribution on chalcocite leaching kinetics. Figure 6.10 shows that copper extraction over time at different particle size fractions in the first and second stages. The first stage of chalcocite leaching was more sensitive to the particle size than the second stage. An increase in the initial particle size was associated with a marked decrease in the 100

reaction kinetics in the first stage but a slight decrease in the second stage. It has been shown by the surface analysis results that upon completion of the first stage, the mineral particles had been broken down into finer ones with many cracks and pores, whose actual sizes were unknown. These finer particles with cracks and pores within a narrower size range continued to be leached in the second stage. Therefore, the data shown in Figure 6.10B only reflected the effect of initial particle size, not the real effect of particle size on the second stage leaching kinetics.



Figure 6.10 Copper extraction versus leaching time at varied particle sizes under the following conditions: [Fe(III)]: 0.05 M, [Fe(II)]: 0.001 M, 25 °C, pH: 1.5. A: the first stage; B: the second stage

#### 6.4 Development of the leaching kinetics models in acidified FeCl<sub>3</sub> media

Considering the electrochemical polarization curves and the Tafel equation, Nicol (1993) categorized the leaching reactions into three types, Type I, Type II, and Type III. Dixon (1999) reclassified them and provided more calculations. According to Dixon, in Type I leaching (Figure B.1), the exchange current densities of both half cells are similar in magnitude, but the reversible potentials of the half cells are far apart. The fractional reaction order with respect to ferric concentration is 0.5. In Type II leaching (Figure B.2), the exchange current density of the oxidant couple is much higher than that of mineral dissolution and thus the mixed potential

corresponds to the reversible potential of the oxidant. Therefore, the dissolution rate is proportional to the square root of the ratio of the concentrations of the oxidized and reduced forms of the oxidant. In Type III leaching (Figure B.3), reactions are quite fast, and the reaction rate is limited by mass transfer of oxidants to mineral surfaces. The reversible potentials of the half reactions are far apart, and the leaching reaction proceeds at the limiting current density of the oxidant couple. The leaching rate is proportional to the oxidant concentration (Bolorunduro, 1999; Bouffard et al., 2006; Dixon, 1999).

Bouffard et al. (2006) tabulated various forms of the compositional function f(c), shown as Eq. (4.4), for pyrite dissolution. Considering the electrochemical kinetics, the authors derived a single chemical composition equation, shown as Eq. (6.1). In Eq. (6.1), *K* is a constant,  $C_{Fe^{3+}}$  is ferric concentration, and  $C_{Fe^{2+}}$  is ferrous concentration.

$$f(c) = \left(\frac{C_{Fe^{3+}}}{K + C_{Fe^{2+}}}\right)^{0.5}$$
(6.1)

From this equation, two types of leaching kinetics can be obtained:

Type I: 
$$K \gg C_{Fe^{2+}} \therefore f(C) \approx (C_{Fe^{3+}})^{0.5}$$
  
Type II:  $K \ll C_{Fe^{2+}} \therefore f(C) \approx \left(\frac{C_{Fe^{3+}}}{C_{Fe^{2+}}}\right)^{0.5}$ 

In Type I leaching, ferric reduction is slow, and therefore irreversible and far from equilibrium. Consequently, the reverse cathodic reaction can be safely ignored. In contrast, in Type II leaching, ferric reduction is rapid and at equilibrium and the mixed potential corresponds to the reversible potential of the ferric/ferrous electrochemical couple. Nicol's leaching type classification has been used to explain leaching kinetics in several studies (Bolorunduro, 1999; Bouffard et al., 2006; Crundwell, 2013; Yue and Asselin, 2014). This theory was applied in this study to describe the leaching mechanism of chalcocite leaching in ferric chloride media.

#### 6.4.1 First-stage kinetic equation derivation

The kinetic equation for the first stage of chalcocite leaching in ferric chloride was derived as Eq. (6.2). In Eq. (6.2).  $d_0$  is in  $\mu$ m, t in h, T in kelvin, and  $C_{Fe^{3+}}$  in mole/L. The kinetic model parameters are shown in Table 6.3. Chloride and ferrous concentrations were not included in the reaction kinetic equation due to their insignificant effect on the reaction rate in the ranges tested. An activation energy of 24.04 kJ/mol was calculated for the first stage of chalcocite leaching. This activation energy lies in the range for diffusion-controlled reactions, meaning that the first stage of chalcocite leaching was limited by the diffusion of ferric ions towards the mineral surface, which is in agreement with the literature (Crundwell, 2013). However, the value is higher than that reported by King (1966), who calculated a very low activation energy of 3.4 kJ/mol for the first stage of chalcocite leaching in ferric chloride media in temperature range 20-80 °C. The reason for such a low activation energy was due to the procedure used to calculate the activation energy. The author used the Arrhenius method and plotted the natural logarithm of the rate constants versus the reverse temperature. However, the rate constants were obtained from the amount of copper extracted at a given leaching time (2 minutes) instead of a given copper extraction (like 50% copper extraction).

$$x = 1 - \left(1 - \frac{11.68 \times 10^4 t(h)}{d_0^{1.07}(\mu m)} \exp\left(2891.98\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Fe^{3+}})^{1.05}\right)^{55.55}$$
(6.2)

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The second				
Leaching stage	φ	Ea, kJ/mol	k <sub>ref</sub>	
1 <sup>st</sup>	0.982	24.04	$6.49 \times 10^4$	

Table 6.3 The kinetic model parameters for the 1st stage of chalcocite in ferric chloride media

The reaction order with respect to ferric concentration was found to be 1.05. This value is very close to unity, which supports the hypothesis that the first stage reaction was a Type III leaching reaction, i.e., the mass transfer of the oxidant towards the mineral surface limits the reaction. King (1966) showed that the first stage of chalcocite leaching was insensitive to ferric concentration in the concentration range of 0.004-0.018 M. It must be noted that King conducted the leaching experiments under uncontrolled pH and ORP. However, the dependence of the first stage of chalcocite leaching on ferric concentration has been reported to be unity in sulfate media (Bolorunduro, 1999; Marcantonio, 1976; Thomas et al., 1967). The experimental leaching data was plotted against the fitted data provided by Eq. (6.2), as shown in Figure 6.11. The rate equation is reasonably capable of predicting copper extraction.



Figure 6.11 Application of the general kinetics model to the first stage of chalcocite leaching data under various conditions, A: ferric concentration; B: temperature; C: particle size. Scatter plots represent experimental data and solid lines represent model fitted data

#### 6.4.2 Second-stage kinetic equation derivation

Eq. (6.3) represents the kinetic equation for the second stage of chalcocite leaching in ferric chloride media. In Eq. (6.3),  $d_0$  is in  $\mu$ m, t in h, T in kelvin, and  $C_{Fe^{3+}}$  and  $C_{Fe^{2+}}$  in mole/L. Table 6.4 shows the kinetic model parameters for the second stage of chalcocite leaching. The activation energy was obtained as 104.8 kJ/mol, suggesting that chemical reaction controls the kinetics of the second stage of chalcocite leaching. On the other hand, the best fit was obtained when the compositional function given in Eq. (6.1) was applied. This reveals that the second stage is a mix of Type I and Type II leaching. In other words, the rate limiting step is a combination of mineral decomposition and ferric reduction. It is noteworthy that both mineral decomposition and ferric reduction in nature, meaning that the leaching 105

mechanism is still chemical reaction. This conclusion is consistent with the findings of Dixon in research on the second stage of chalcocite leaching in acidic ferric sulfate media (Dixon, 1999). It is noteworthy that the actual exponent for the compositional function was obtained to be 0.5, which is equal to the theoretical value.

$$x = 1 - \left(1 + \frac{0.69t(h)}{d_0^{0.272}(\mu m)} \exp\left(12607.53\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) \left(\frac{C_{Fe^{3+}}}{0.044 + C_{Fe^{2+}}}\right)^{0.5}\right)^{-0.66}$$
(6.3)

 Table 6.4 The kinetic model parameters for the second stage of chalcocite leaching in ferric chloride media

Leaching stage	φ	Ea, kJ/mol	k <sub>ref</sub>
2 <sup>nd</sup>	2.5	104.82	0.46

The leaching kinetics mechanism, proposed based on the kinetics data, is in agreement with the subsequent surface analysis results, which showed that elemental sulfur and polysulfide accounted for the main components of the solid surface. Based on this information, it was proposed that the slow reaction rate of the second stage of chalcocite was attributed to the presence of elemental sulfur and the decomposition of polysulfide. This hypothesis was confirmed by our proposed kinetics model, a combination of ferric reduction and mineral decomposition. Sulfur layer as a non-conductive layer may slow down the reduction of ferric on the solid surface and the slow decomposition of polysulfide could contribute to the slow reaction rate.

King (1966) obtained an activation energy range of 101–122 kJ/mol for the second stage of chalcocite leaching with ferric chloride. In a research on the ferric chloride leaching of a synthetic covellite mineral, Miki and his co-workers obtained an activation energy of 71.5 kJ/mol (Miki et al., 2011). Figure 6.12 shows the experimental data plotted against the fit

provided by Eq. (6.3), which reasonably predicted the copper extractions under various conditions.



Figure 6.12 Application of the general kinetics model to the second stage of chalcocite leaching data under various conditions, A: ferric concentration; B: ferrous concentration; C: temperature; D: particle size. Scatter plots represent experimental data and solid lines represent model fitted data

Two individual kinetic equations were derived to describe the kinetics of chalcocite leaching in the first and second stages. The first stage of chalcocite leaching with ferric chloride was fast and controlled by the diffusion of ferric ion towards the mineral surface. This hypothesis was supported by the low activation energy and the first order dependence of the dissolution rate on the ferric concentration. The rate of the second stage was slow and limited by a mixed kinetics; a combination of anodic mineral decomposition and ferric reduction in the second stage. It was confirmed by the high activation energy and the chemical composition equation used in the kinetic equation to fit the experimental data.

#### 6.5 Conclusions

The kinetics of chalcocite leaching in ferric chloride media were comprehensively studied, with the ultimate purpose of using seawater for heap leaching. We quantified the effects of chloride concentration, ferric concentration, ferrous concentration, ferric/ferrous ratio, temperature, and particle size on chalcocite leaching using jacketed reactors under fully controlled pH, ORP, and temperature. Using the experimental data obtained, we derived two distinct kinetic models for the two stages of chalcocite leaching. The modelling results suggested that the rate limiting step was diffusion of ferric ions through the reaction product layer in the first stage and a combination of mineral decomposition reaction and ferric reduction in the second stage. The present kinetic models recommended managing heap heat to keep the heap temperature as high as possible and maintaining a high ORP.

The surface analysis data, which was discussed in detail in Chapter 9, could explain the kinetics results presented in this Chapter. In summary, the surface analysis results showed that the solid surface, in the second stage, was mainly composed of elemental sulfur and polysulfide. The elemental sulfur layer became thinner at higher ORP and higher chloride concentrations. The insensitivity of the reaction rate to the chloride concentration was explained by the high ORP at which the leaching tests were conducted. In addition, the slow reaction rate in the second stage of chalcocite leaching was attributed to the slow ferric reduction on the solid surfaces, which were covered by elemental sulfur, and also the slow decomposition of polysulfide.

# Chapter 7: Chalcocite leaching kinetics in cupric chloride media

# 7.1 Introduction

The main objective of this chapter is to derive the kinetic equations for chalcocite leaching in acidified cupric chloride media. Derivation of such equations is essential for identifying key factors that control the leaching performance and for predicting copper production under various leaching conditions. The objective was achieved by carrying out a series of chalcocite leaching experiments at controlled temperature and pH. The effects of chloride concentration, cupric concentration, particle size, and temperature on copper extraction rate were quantified and individual kinetic equations were derived for the first and second stage of chalcocite leaching. The experimental results obtained in Chapter 9 was used to elucidate the kinetics results and propose the leaching mechanism. A version of this Chapter was published in Hydrometallurgy.

#### 7.2 Effect of leaching parameters on chalcocite leaching in cupric chloride media

#### 7.2.1 Effect of controlled potential

Figure 7.1 shows the effect of hydrogen peroxide on the copper extraction rate from chalcocite. It is obvious that hydrogen peroxide significantly affected the copper extraction rate in the first leaching stage by participating in the dissolution of chalcocite. Based on the kinetics results in Section 7.3.1, the first stage of chalcocite leaching was limited by a mix-controlled kinetics of diffusion process and chemical reaction. It seems that hydrogen peroxide enhanced the reaction rate by contributing to the dissolution of chalcocite and hence, enhancing the chemical reaction. The first stage of chalcocite leaching in the ferric chloride media was very fast and limited by the

diffusion of ferric ion towards the mineral surface. This means that hydrogen peroxide did not affect the reaction rate of the first stage of chalcocite leaching in ferric chloride media as the results showed in Section 6.3.2. Figure 7.1B shows that the second stage of chalcocite leaching was not affected by the presence of hydrogen peroxide. It implies that ferric chloride system was stronger than the diluted hydrogen peroxide to oxidize the secondary covellite mineral.



Figure 7.1 Effect of hydrogen peroxide on the copper extraction rate in A) the first and B) second stage of chalcocite in cupric chloride media under the following conditions: [Cu(II)] 64 mM, [Cl<sup>-</sup>] 1.562 M, 25 °C, pH 1.5, particle size -75+53 μm

Figure 7.2 shows the ORP and pH values changes in the course of a leaching test. It shows that the ORP values increased significantly in the first leaching stage of chalcocite, while the rate of change slows down in the second leaching stage of chalcocite. The ORP increase was due to the oxidation of cuprous ions, as the leaching product, to cupric by the dissolved oxygen. The ORP value was very low at the beginning of the first leaching stage, around 450 mV vs SHE, whereas it increased to almost 640 mV at the end of the second stage. The ORP value in the entire of the second stage was in the range of 550 - 640 mV which was high enough for the dissolution of secondary covellite mineral (Miki et al., 2011). Figure 7.2 also illustrates an example of

controlling pH in the course of leaching, which shows that pH could be well maintained at constant value during leaching.



Figure 7.2 An example of ORP and pH control in the course of chalcocite leaching. The leaching conditions were [Cu(II)] 16 mM, [CI<sup>-</sup>] 1.62 M, pH 1.5, 25 °C, particle size -75+53 µm

# 7.2.2 Effect of initial cupric concentration

Figure 7.3 shows the effect of initial cupric ion concentration on the chalcocite leaching in the first and second stage. The range of cupric concentration was chosen based on the copper concentration in a typical raffinate solution after SX/EW (solvent extraction and electrowinning) process and the increase in copper concentration due to the dissolution of chalcocite. The initial cupric concentration had a noticeable effect on the copper extraction in the first stage. However, at copper concentration above 64 mM, copper extraction rate became insensitive to the initial copper concentration. The effect of copper concentration on the copper extraction rate in the second stage was small. Based on these results, initial copper concentration of 64 mM was chosen for the next leaching experiments. Figure 7.3A also reveals two important things about

the copper concentration range. First, above copper concentration of 64 mM, the reaction rate did not respond to the copper concentration. This means that the chalcocite reaction will not be limited by the mass transfer of copper ion to the particle surface when we choose copper concentration of 64 mM. The second is that, since cuprous ions is produced from the dissolution of chalcocite and converted to cupric ion, the increase of copper concentration during the leaching process will not affect the kinetics rate.



Figure 7.3 Copper extraction versus leaching time at varied initial cupric chloride concentrations under the following conditions: [Cl<sup>-</sup>] 1.562 M, 25 °C, pH 1.5, particle size -75+53 µm. A: first stage; B: second stage

#### 7.2.3 Effect of total chloride concentration

The leaching tests were conducted to evaluate the effect of total chloride concentration by adding sodium chloride to the leaching solution at various concentrations as shown in Table 4.4. The sodium chloride concentration range was chosen in an attempt to cover all possible concentrations that may be relevant to a heap leaching process, from lower than in a typical seawater to 3 M that represents concentrated leaching solutions due to evaporation and recirculation of process water. The ORP of the leaching solution changed in response to the addition of sodium chloride. The ORP increased from 600 mV in 0.5 M NaCl to 705 mV in 3 M

NaCl. The effect of chloride concentration on ORP has been reported in the literature. The higher tendency of cuprous ions to form cuprous chloro-complexes than that of cupric ions led to an increase in ORP in response to an increase in the chloride concentration (Muir, 2002; Senanayake, 2009).

Figure 7.4 shows that increasing chloride concentration had a pronounced positive effect on copper extraction rate in both stages. However, the effect of chloride concentration on the second stage copper extraction was only noticeable up to 1.5 M, after which the effect was insignificant. Based on the effect of chloride on the first stage rate, it is concluded that chloride ions diffuse through the liquid film surrounding the particle surface and form chloro-complexes with the released cuprous ions from the chalcocite dissolution. The electrochemical couple from the chloro-complex formation contributes to the chalcocite leaching and enhances the reaction rate.



Figure 7.4 Copper extraction versus leaching time at varied chloride concentrations under the following conditions: [Cu(II)] 0.016 M, 25 °C, pH 1.5, particle size -75+53 µm. A: first stage; B: second stage

#### 7.2.4 Effect of particle size

The effect of initial particle size on chalcocite leaching was investigated by conducting leaching tests at various particle size fractions. Figure 7.5 shows that copper extraction over time at

different particle size fractions in the first and second stage. An increase in the initial particle size was associated with a marked decrease in the reaction kinetics in the first stage but a slight decrease in the second stage. According to the surface characterization results, which was discussed in detail in Chapter 9, the mineral particles underwent decrepitation as leaching progressed, leading to an enlargement on surface area. Consequently, the results presented in Figure 7.5B only show the effect of initial particle size, while the real effect of particle size on the second stage leaching kinetics is unclear.



Figure 7.5 Copper extraction versus leaching time at varied initial particle sizes under the following conditions: [Cu(II)]: 0.016 M, [CI<sup>-</sup>] 1.562 M, 25 °C, pH 1.5, particle size -75+53 µm. A: the first stage; B: the second stage

#### 7.2.5 Effect of temperature

The effect of temperature on the copper extraction from chalcocite is shown in Figure 7.6. In the first stage, increasing temperature considerably increased the copper extraction. However, temperature had a more significant effect on the copper extraction rate in the second stage, suggesting that the second stage is a chemical reaction process. Based on the surface characterization of leaching residues corresponding to 70 - 80% copper extraction (detailed results explained in Chapter 9), at higher temperatures, the surface of chalcocite residue was 114

more crystalline and less sulfur was present on the solid surface. This could improve the reduction of Cu(II) ions on the solid surface and also the decomposition of polysulfide formed on the surface and therefore, enhance the leaching reaction rate. The improved leaching rate by increasing temperature implied that increasing heap temperature, especially in the second stage, would enhance copper extraction rate in cupric chloride media. Controlling raffinate temperature, adjusting the ratio of irrigation to aeration, and applying a thermal cover are among the various heat management and temperature control techniques in heap leaching (Dixon, 2000; Liu and Granata, 2018).



Figure 7.6 Copper extraction versus leaching time at varied temperatures under the following conditions: [Cu(II)] 0.016 M, [Cl<sup>-</sup>] 1.562 M, pH 1.5, particle size -75+53 µm. A: first stage; B: second stage

#### 7.3 Development of the leaching kinetics models in acidified CuCl<sub>2</sub> media

# 7.3.1 First-stage kinetic equation derivation

Eq. (7.1) shows the kinetic equation for the first stage of chalcocite leaching in cupric chloride media. In Eq. (7.1),  $d_0$  is in  $\mu$ m, t in h, T in kelvin, and (C<sub>CI</sub><sup>-</sup>) in mol/L. The kinetic model parameters are shown in Table 7.1. As copper extraction rate was only sensitive to copper concentration up to 64 mM, Eq. (7.1) is only valid for copper concentrations up to 64 mM. An

activation energy of 38.08 kJ/mol was calculated for the first stage of chalcocite leaching. The reaction order with respect to chloride concentration and initial copper concentration was obtained as 1.1 and 0.53, respectively.

$$x = 1 - \left(1 + \frac{188.75t(h)}{d_0^{1.23}(\mu m)} \exp\left(4580.22\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Cu^2+})^{0.53} (C_{Cl^-})^{1.10}\right)^{0.461}$$
(7.1)

Table 7.1 The kinetic model parameters in the first stage of chalcocite leaching in cupric chloride media			
Leaching stage	φ	Ea, kJ/mol	k <sub>ref</sub>
1 <sup>st</sup>	3.17	38.08	86.98

The activation energy and reaction orders with respect to chloride and cupric concentrations reported in the literature for chalcocite leaching in cupric chloride media are scattered and therefore, different leaching mechanisms have been proposed accordingly. For example, Fisher et al. (1992) calculated the reaction order with respect to chloride concentration to be 1.01 in a study on chalcocite leaching in an oxygenated acidic solution. They proposed the diffusion of chloride ions through the liquid film around the mineral particles as the rate limiting step for the first stage of chalcocite leaching, supported by an activation energy of 22.6 kJ/mol. In a study of djurleite leaching in cupric chloride, Herreros et al. (2006) obtained an activation energy of 35 kJ/mol for the first stage and suggested a chemical reaction control kinetics. They reported the reaction order with respect to cupric and chloride to be 0.23 and 0.53, respectively.

Based on the first order dependence on the chloride concentration, half order on the initial copper concentration, and the activation energy observed in the present study, we propose a mixed kinetics for the first stage of chalcocite leaching in cupric chloride media. The rate limiting step is a combination of the diffusion of chloride ions through the liquid film and the chemical reaction which is the reaction between the chloro-complexes and chalcocite. The chloride ions diffuse through the liquid film and form cuprous-chloride complexes which as a result, create the electrochemical couple with cupric-chloride complexes for chalcocite oxidation. The experimental leaching data was plotted against the fitted data provided by Eq. (7.1), as shown in Figure 7.7. The rate equation was reasonably capable of describing copper extraction under varying chloride concentration, particle size, and temperature.



Figure 7.7 Application of the general kinetics model to the first stage of chalcocite leaching data under various conditions: A: initial copper concentration; B: chloride concentration; C: particle size; D: temperature. Scatter plots represent experimental data and solid lines represent model fit
## 7.3.2 Second-stage kinetic equation derivation

The kinetic equation for the second stage of chalcocite leaching in cupric chloride media is presented as Eq. (7.2) with the parameters shown in Table 7.2. In Eq. (7.2),  $d_0$  is in  $\mu$ m, t in h, T in kelvin, and  $(C_{Cl})$  in mol/L. The reaction order with respect to the chloride concentration was 0.34, which was lower than that in the first stage. According to the surface characterization results (detailed discussion in Chapter 9), increasing chloride concentration, especially at low ORP, improved the crystallinity of the elemental sulfur layer. This suggests that the second stage of chalcocite leaching could be limited by a combination of anodic mineral decomposition and the reduction of Cu(II) ions on the solid surface. At higher chloride concentrations, the more crystalline and thinner sulfur layer on the particle surface assisted the reduction of Cu(II) ions on the solid surface. In addition, higher chloride concentrations provided higher ORP, which might help the decomposition of polysulfide. The activation energy was obtained as 91.24 kJ/mol, which supports a chemical reaction-controlled leaching for the second stage of chalcocite leaching. Researchers have reported different activation energies for the second stage of chalcocite leaching in cupric chloride media, though the surface chemical reaction was mostly reported as the rate limiting step. The difference originates from the different materials, approaches, leaching apparatus, and chemicals used in different studies. For example, to study the leaching behavior one may apply the chemical leaching or electrochemical techniques, leaching reactor or rotating disk, controlled or uncontrolled (pH, temperature, and ORP) conditions, and chemicals of different purity. Even a specific pure mineral obtained from different sources may show different leaching behavior (Prosser, 1996).

$$x = 1 - \left(1 + \frac{0.069t(h)}{d_0^{0.34}(\mu m)} \exp\left(10974.26\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Cu^{2+}})^{0.09} (C_{Cl^{-}})^{0.34})^{0.575}$$
(7.2)

Table 7.2 The kinetic model parameters for the second stage of chalcocite leaching in cupric chloride media

Leaching stage	φ	Ea, kJ/mol	kref
2 <sup>nd</sup>	2.74	91.24	0.04

Fisher et al. (1992) obtained an activation energy of 34.6 kJ/mol for the second stage of chalcocite leaching in an acidic oxygenated leaching solution. They proposed the surface chemical reaction as the rate limiting step. Miki et al. (2011) studied the dissolution of synthetic covellite in oxygenated chloride leaching solution. They obtained an activation energy of 71.5 kJ/mol and suggested that the second stage was limited by the chemical reaction. The predicted copper extraction data obtained by Eq. (7.2) was plotted against the experimental data in Figure 7.8. It shows that the kinetic model was able to confidently predict the copper extraction at varied conditions, except at 55 °C which deviated at high copper extractions.

In summary, a distinct kinetic equation was derived for each stage of chalcocite leaching in cupric chloride media. The equations describe the copper extraction kinetics reasonably well. Activation energies of 38.08 kJ/mol for the first stage and 91.24 kJ/mol for the second stage were obtained. It is proposed that the first stage was limited by a mixed kinetics; a combination of diffusion of chloride ion towards the mineral surface and the chemical reaction, which is supported by the first order dependence on the chloride concentration, half order dependence on initial copper concentration, and the activation energy. The high activation energy obtained in the second stage implied that the second stage reaction was most likely to be limited by the combination of Cu(II) ions on the solid surface and anodic mineral

decomposition. The effect of stirring speed was not investigated in the present study due the limitation of the leaching apparatus. The importance of the stirring speed is to ensure that the leaching reaction was not limited by the mass transfer of the oxidant to the particle surface which in turn may affect the activation energy and reaction orders.



Figure 7.8 Application of the general kinetics model to the second stage of chalcocite leaching data under various conditions, A: chloride concentration; B: particle size; C: temperature. Scatter plots represent experimental data and solid lines represent model fit

#### 7.4 Conclusions

The present chapter developed kinetic models to describe chalcocite leaching in acidified cupric chloride media using leaching data collected under controlled temperature and pH. Leaching tests were carried out to quantify the effects of total chloride concentration, initial cupric concentration, particle size, and temperature on the copper extraction from chalcocite. Increases 120

in chloride concentration and temperature resulted in faster kinetics of the first and the second stage of chalcocite leaching. The first stage of chalcocite leaching kinetics was sensitive to the initial cupric chloride concentration. An increase in the initial particle size was associated with a marked decrease in the reaction kinetics in the first stage but a slight decrease in the second stage.

The leaching data collected were used for derivation of the individual kinetic models for the first and the second stage of chalcocite leaching in cupric chloride media. The leaching mechanism of the first leaching stage was proposed as a combination of chloride diffusion towards the particle surface and chemical reaction. In the second leaching stage, a combination of reduction of Cu(II) ions on the solid surface and anodic mineral decomposition was proposed as the leaching mechanism. The kinetic models could reasonably describe the experimental data. However, caution should be exercised for direct application of these models to predict copper extraction from heap leach pads. The reason is that hydrodynamic factors, specifically, the movement of leaching solution and air through packed ore beds, do not exist in reactor leaching. In other words, the kinetic models developed in the present study did not incorporate the effect of hydrodynamic factors. Therefore, column leaching tests were conducted to scale up the kinetics models from the reactor leaching tests. In the next chapter, the results of the column leaching tests are presented. Assuming optimum hydrodynamic conditions, the present study suggests that higher total chloride concentration and higher heap temperature would be conducive to faster extraction kinetics. Overall, with the advantage of rapid oxidation of cuprous chloride complexes to cupric ions, heap leaching of chalcocite with cupric chloride could be a viable alternative to

heap bioleaching with ferric chloride, making the application of seawater to heap leaching more practical.

# Chapter 8: Scale-up of the kinetic models for column leaching

## 8.1 Introduction

The kinetic models derived from the reactor leaching provided such key information as reaction orders and activation energy. However, they could not be directly applied to predict copper extraction in heap leaching of chalcocite in chloride media, because the hydrodynamic factor, specifically, the movement of leaching solution and air through packed ore beds, was not considered in the reactor leaching. In this Chapter, column leaching tests were performed, the results of which were used to scale up the kinetic models obtained in Chapter 6 and Chapter 7.

#### 8.2 Copper sulfide ore characteristics

The X-ray diffractogram was analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. The X-ray powder-diffraction data of the sample was refined with the Rietveld program Topas 4.2 (Bruker AXS). The results of quantitative phase analysis by Rietveld refinements are given in Table 2. These values represented the relative amounts of crystalline phases normalized to 100%. The Rietveld refinement plot is shown in Figure 8.1. The small broad calculated peak indicated by a vertical line at about 7.5°20 in Figure 8.1 was used to better fit the X-ray patterns and was the result of the presence of a small amount of an unknown clay mineral which could not be analyzed.

The XRD results showed that the only copper mineral in the copper ore sample was chalcopyrite, accounting for 0.6%. Therefore, a sequential diagnostic leaching test was performed to validate the XRD results and determine the availability of other forms of copper minerals, such as oxides

and secondary sulfides. The diagnostic leaching test showed that the copper ore had 0.259% copper, of which 0.004% was from copper oxides, 0.031% from secondary copper sulfides, and the rest (0.224%) from primary copper sulfides. Assuming that the secondary copper mineral was chalcocite and the primary copper ore was chalcopyrite, the diagnostic test results suggested that the copper ore contained 0.038% chalcocite and 0.65% chalcopyrite. The diagnostic test results were consistent with the XRD analysis results.

Mineral	Ideal Formula	Test sample, %
Biotite 1M	K(Mg,Fe) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	2.7
Chalcopyrite	CuFeS <sub>2</sub>	0.6
Clinochlore	(Mg,Fe <sup>2+</sup> )5Al(Si3Al)O10(OH)8	1.6
Illite/Muscovite 2M1	K0.65Al2.0Al0.65Si3.35O10(OH)2/KAl2AlSi3O10(OH)2	17.0
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	1.3
K-feldspar	KAlSi <sub>3</sub> O <sub>8</sub>	10.1
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	0.3
Plagioclase	$NaAlSi_3O_8 - CaAl_2Si_2O_8$	29.2
Pyrite	$FeS_2$	2.7
Quartz	$SiO_2$	34.5
Total		100.0

Table 8.1 Results of the quantitative phase analysis (wt.%), XRD-Rietveld



Figure 8.1 Rietveld refinement plot of the copper ore sample, blue line - observed intensity at each step; red line - calculated pattern; solid grey line - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases

## 8.3 Scale-up of the kinetic models in ferric chloride system

## 8.3.1 Column leaching tests

The sequential leaching test showed that 86% of copper in the copper ore used in the column leaching tests was from primary copper sulfides. To evaluate copper extraction from the copper ore, a column leaching test was first performed using the original ore without the addition of pure chalcocite. The column leaching test was performed under the conditions shown as Test 1 in Table 4.5.

Figure 8.2 shows the copper extraction from the original copper ore. Only 4.12% of copper contained in the copper ore was extracted after 500 h. To minimize the error from the copper

extracted from the copper ore in the column leaching test, we applied the general model (Eq. 4.2) to model the copper extraction data from the column leaching of the copper ore. The kinetics model is shown as Eq. (8.1). Using Eq. (8.1), the copper extracted from copper ore was calculated and then subtracted from the copper extracted from the mixture sample for each data point. In Eq. (8.1), *X* is the copper extraction and *t* is the leaching time (h).

$$X = 4.2[1 - (1 - 0.0082(1 - 1.185)t(h))^{-5.4}]$$
(8.1)



Figure 8.2 Copper extraction from the original copper ore without addition of pure chalcocite under the following conditions: pH 1.5, [Fe(III)] 0.0909 M, [Fe(II)] 0.0909 M, [Cl<sup>-</sup>] 0.29 M, 25 °C

The column leaching tests were conducted according to the leaching conditions shown in Table 4.5. Figure 8.3 shows the cumulative copper extraction from the chalcocite sample in column leaching in ferric chloride media. Compared with the leaching time in the reactor under the same leaching conditions, the times required to complete the first and second stage of leaching in the column were much longer. Specifically, the first stage was completed within 10 min in the reactor, as opposed to 120 h in the column. In the second stage, the copper extraction reached 73% after 96 h in the reactor, whereas the same extraction required 400 h in the column. This comparison suggested that the mass transfer of ferric ions towards the chalcocite mineral surface 126

was slower in the column. Therefore, increasing the irrigation rate was likely to enhance the reaction rate.



Figure 8.3 Copper extraction from column leaching of chalcocite under the following leaching conditions: pH 1.5, particle size -150+125µm, [Fe(III)] 0.05 M, [Fe(II]] 0.05 M, 25 °C

To evaluate the effect of irrigation rate on the copper extraction rate, one column leaching test was conducted at a double irrigation flowrate (10.6  $L/m^2/h$ ). Figure 8.4 shows the first and second stage of copper leaching from chalcocite and the comparison between the low and high irrigation rates. The slope of the copper extraction curve at higher irrigation rate in the first stage was higher than that at lower irrigation rate. This supports that the first stage of chalcocite column leaching was limited by the mass transfer of ferric ions towards the mineral surface. The slopes of the copper extraction curves in the second stage at both irrigation rates were similar, meaning that the second stage was not controlled by the mass transfer of ferric ions.

Figure 8.5A shows that the pH value was below 2 during the column leaching of chalcocite and, except at the initial stage, it was constant. The increase in pH value in the initial stage may be attributed to the presence of oxide minerals and the acid consuming minerals. It could not be related to the fast reaction rate of the first stage of chalcocite leaching as the first stage of

chalcocite does not consume proton and the oxidation of ferrous to ferric is extremely slow (Akilan and Nicol, 2016). Figure 8.5B shows the trend of ORP in the course of column leaching of chalcocite sample. ORP dropped markedly in the first stage of leaching, which was attributed to the fast consumption of ferric ions by chalcocite oxidation. The ORP value was relatively constant in the second stage. This was important because the second stage of chalcocite leaching was responsive to the ORP.



Figure 8.4 Copper extraction in A: the first stage and B: the second stage of chalcocite column leaching at two irrigation rates under the following leaching conditions: pH 1.5, particle size -150+125µm, [Fe(III)] 0.05 M, [Fe(III)] 0.05 M, 25 °C



Figure 8.5 A: The pH changes and B: the ORP changes and the copper extraction during the column leaching of chalcocite under the following leaching conditions: pH 1.5, particle size -150+125µm, [Fe(III)] 0.05 M, [Fe(III)] 0.05 M, 25 °C

#### 8.3.2 Scale-up of the kinetics model

To scale up the kinetic model, the least squares method was applied and the reaction rate constants,  $k_{ref}$  in Eqs. (5.2) and (5.3) were subjected to vary. Eqs. (8.2) and (8.3) were obtained as the scaled-up kinetic models for the first and second stage of chalcocite leaching in columns. The kinetic model parameters are shown in Table 8.2. Figure 8.6 shows a satisfactory fitting of the scaled-up models to the experimental data points. In the next step, another column leaching test was carried out under randomly chosen conditions as [Fe(III)] 0.0909 M, [Fe(II)] 0.00909, [Cl<sup>-</sup>] 0.29 M, pH 1.5, 25 °C. The experimental results were used to validate the scaled-up models. Figure 8.7 shows that the scaled-up kinetic models, Eqs. (8.2) and (8.3), were able to satisfactory describe the reaction rate of chalcocite in the column leaching tests.



Figure 8.6 Application of the scaled-up models on the copper extraction data in ferric chloride media in A: the first stage and B: the second stage under the following leaching conditions: pH 1.5, particle size – 150+125µm, [Fe(III)] 0.05 M, [Fe(II]] 0.05 M, 25 °C

$$x = 1 - \left(1 - \frac{1.054t(h)}{d_0^{1.07}(\mu m)} \exp\left(2891.98\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Fe^{3+}})^{1.05}\right)^{55.55}$$
(8.2)

$$x = 1 - \left(1 + \frac{0.019t(h)}{d_0^{0.272}(\mu m)} \exp\left(12607.53\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) \left(\frac{C_{Fe^{3+}}}{0.044 + C_{Fe^{2+}}}\right)^{0.5}\right)^{-0.66}$$
(8.3)

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Table 8.2 The kinetics parameters for the scaled-up models

Figure 8.7 Copper extraction from column leaching of chalcocite under the following leaching conditions: pH 1.5, particle size –180+150µm, [Fe(III)] 0.0909 M, [Fe(II)] 0.00909 M, 25 °C

## 8.4 Scale-up of the kinetics model in cupric chloride media

## 8.4.1 Column leaching tests

First, a column leaching test was carried out on the copper ore without the addition of chalcocite sample to examine the copper extraction from the copper ore. The copper extraction from the copper ore after 900 h was only 1.67%. Therefore, the experimental error associated with the copper extraction from the copper ore was small and ignored in the column leaching tests on the mixed samples.

The column leaching test was conducted according to the leaching conditions shown in Table 4.6. Figure 8.8 shows the column leaching results for the first and second stage of chalcocite leaching in cupric chloride media. It shows that at low initial copper concentration (4 mM) and a chloride concentration of 2 M, a satisfactory copper extraction was obtained compared with the

copper extraction in ferric chloride media as shown in Figure 8.6. The copper extraction rate in ferric chloride media was approximately 2-3 times faster than that in cupric chloride media.



Figure 8.8 Copper extraction in A: the first stage and B: the second stage of chalcocite column leaching under the following leaching conditions: pH 1.5, particle size –150+125µm, [Cu(II)] 4 mM, [Cl<sup>-</sup>] 2 M, 25 °C

The effect of irrigation rate on the copper extraction rate was investigated by conducting a column leaching test at a double irrigation rate  $(10.6 \text{ L/m}^2/\text{h})$ . Figure 8.9 shows the results for the first and second stage of chalcocite leaching at both irrigation rates. It shows that the slope of the copper extraction curve at higher irrigation rate in the first stage was slightly higher than that at lower irrigation rate. This may support the hypothesis that the first stage of chalcocite leaching was limited by a mixed kinetics; the mass transfer of cupric ion towards the mineral surface and the chemical reaction. The reaction rate in the second stage at both irrigation rates was similar, meaning that the second stage was not controlled by the mass transfer of ferric ions.



Figure 8.9 Copper extraction in A: the first stage and B: the second stage of chalcocite column leaching under the following leaching conditions: pH 1.5, particle size -150+125µm, [Cu(II)] 4 mM, [Cl<sup>-</sup>] 2 M, 25 °C, C: Comparison of copper extraction at two irrigation flowrates

Figure 8.10A shows the ORP of the leaching solution against the leaching time. The copper extraction curve was also added in the graph to evaluate the ORP changes at the corresponding copper extraction. It shows that after approximately 30% of copper was extracted, the ORP became plateau, meaning that the second stage of chalcocite leaching happened at constant ORP. According to the experimental data obtained in the reactor leaching tests in Chapter 7, the second stage of chalcocite leaching in cupric chloride media is controlled by a mixed kinetics, a combination of the reduction of Cu(II) ions and anodic mineral decomposition, therefore sensitive to the ORP. According to the kinetics study in Chapter 7, the first stage of chalcocite leaching in cupric chloride media was controlled by a combination of diffusion of cupric ion towards the mineral surface and the chemical reaction. However, in column leaching test, the ORP was not constant in the first stage, according to Figure 8.10A. Therefore, the reaction rate in the first stage is believed that would be faster if the ORP was constant in the course of the column leaching test. Figure 8.10B shows the trend of the pH changes in the course of column leaching of chalcocite. It shows that the pH value was initially above 2 for a few hours but dropped to below 2 after approximately 6 h. It is noteworthy that dissolved copper is not 132

precipitated at pH values less than 8 according to the Eh-pH diagram presented in Figure 2.2. The increase in pH value was mainly due to the fast dissolution of chalcocite in the first leaching stage and the presence of acid consuming gangue minerals. The leaching of chalcocite does not consume proton but the cuprous ion which is a product of the first leaching stage requires proton to get oxidized to cupric ion by oxygen. It is noteworthy to mention that the oxidation of cuprous ion to cupric by oxygen is extremely fast (Nicol, 1984).



Figure 8.10 A: The ORP and copper extraction and B: pH changes during the column leaching of chalcocite under the following leaching conditions: pH 1.5, particle size –150+125µm, [Cu(II)] 4 mM, [CI<sup>-</sup>] 2 M, 25 °C

## 8.4.2 Scale-up of the kinetic models

To scale up the kinetic model, the least squares method was employed and the reaction rate constants,  $k_{ref}$  in Eqs. (6.2) and (6.3) were subjected to vary. Eqs. (8.4) and (8.5) were obtained as the scaled-up kinetic models for the first and second stage of chalcocite leaching in columns. The kinetic model parameters are shown in Table 8.3. Figure 8.11 shows a satisfactory fitting of the scaled-up models to the experimental data points. In the next step, another column leaching test was carried out under randomly chosen conditions as [Cu(II)] 4 mM, [Cl<sup>-</sup>] 1 M, pH 1.5, particle size -180+150 µm, and 25 °C. The experimental results were used to validate the scaled-up

models. Figure 8.12 shows that the scaled-up kinetic models, Eqs. (8.4) and (8.5), were able to satisfactory describe the reaction rate of chalcocite in the column leaching tests.



Figure 8.11 Application of the scaled-up models on the copper extraction data in ferric chloride media in A: the first stage and B: the second stage under the following leaching conditions: pH 1.5, particle size – 150+125µm, [Cu(II)] 4 mM, [Cl<sup>-</sup>] 2 M, 25 °C

$$x = 1 - \left(1 + \frac{0.95t(h)}{d_0^{1.23}(\mu m)} \exp\left(4580.2\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Cu^{2+}})^{0.53} (C_{Cl^{-}})^{1.10})^{-0.461}$$
(8.4)

$$x = 1 - \left(1 + \frac{0.029t(h)}{d_0^{0.34}(\mu m)} \exp\left(10974.26\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Cu^{2+}})^{0.09} (C_{Cl^{-}})^{0.34})^{-0.575}$$
(8.5)

Table 8.3 The kinetics parameters for the scaled-up models in cupric chloride media



Figure 8.12 Copper extraction from column leaching of chalcocite under the following leaching conditions: pH 1.5, particle size −180+150µm, [Cu(II)] 4 mM, [CΓ] 1 M, 25 °C

#### 8.5 Applicability of the scaled-up kinetic models

The kinetic models for the leaching of chalcocite were derived and scaled up for both ferric chloride and cupric chloride media. The applicability of the proposed models could be evaluated by emphasizing the strength and limitations of the kinetics models. The merits of the proposed kinetics models were described as:

- The effect of key leaching parameters was studied in both ferric chloride and cupric chloride systems. In ferric chloride media, the effect of chloride concentration, ferric concentration, ferrous concentration, ORP, particle size, and temperature were evaluated. Likewise, in cupric chloride media, the effect of cupric concentration, chloride concentration, particle size, and temperature on the reaction rate were studied. These were the key leaching parameters that were incorporated in the proposed kinetics models, which were more comprehensive than the available models (Cheng and Lawson, 1991a; Fisher, 1994; Herreros et al., 2006; King, 1966; Ruiz et al., 1997).
- The proposed models were derived under controlled leaching conditions and at 25 °C, which better mimic the leaching conditions in a practical heap leaching process (Petersen and Dixon, 2007). Chalcocite heap leaching is generally operated under ambient temperature and under relatively constant potential (Petersen and Dixon, 2007). Moreover, temperature and redox potential have been shown to greatly affect the second stage of chalcocite leaching (Miki et al., 2011; Nicol and Basson, 2017). However, most of the existing studies were conducted at temperatures higher than 25 °C and under uncontrolled redox potentials (ORP).

- The levels of the key parameters were selected in an attempt to cover the ranges of the leaching conditions that may be encountered in a practical heap leaching process using seawater.
- The general kinetics model, Eq. (4-1), was applied to model the leaching kinetics of chalcocite. This model can easily be integrated as Eq. (4-2), which makes it convenient to predict copper extraction.

The main limitations regarding the applicability of the proposed models can be listed as follows:

- In the present study, pure chalcocite sample was mixed with real copper ore and used in the leaching experiments. This was done mainly to eliminate the interference of incomplete particle liberation. Therefore, these models are required to be further optimized by carrying out leaching tests with real chalcocite ore. In those leaching tests the galvanic effect, which has been shown to improve the leaching rate by facilitating the electron transfer on the particle surface (Elsherief, 1994; Wu et al., 2013), is suggested to be studied.
- Chloride ion is the main anion in seawater. Seawater also contains other cations and anions, such as potassium, calcium, magnesium, and sulfate, though their concentrations are very low compared with chloride ion (Kennish, 2000). Their presence may affect chalcocite leaching reaction, especially considering the possible accumulation of these ions from evaporation and recirculation of process water
- Heap leaching of chalcocite is a complicated process that involves many other parameters that could affect the leaching reaction rate. One important column leaching parameter

that was not investigated in the present study is the column height. Heap height plays an important role in the leaching of copper ore (Petersen and Dixon, 2007). In addition, the column leaching tests were operated in an open circuit, i.e., fresh leaching solution was used for irrigation without solution recycling. For a practical heap leaching process, raffinate solution recycled from the solvent extraction process is irrigated back on the heap surface.

## 8.6 Conclusions

The present study performed column leaching tests to scale up the kinetic models obtained in the reactor leaching tests in both ferric chloride and cupric chloride systems. The copper extraction rates in the column leaching tests were slower than those in the reactor leaching tests conducted in Chapter 6 and Chapter 7. The mass transfer of oxidant towards the mineral surface was thought to be responsible for the slower copper extraction rates in the column leaching tests. Therefore, the effect of irrigation rate was investigated on the copper extraction rate in both leaching systems. In ferric chloride system, increasing irrigation rate enhanced the copper extraction rate in the first stage, while the rate of the second leaching stage was only slightly improved. This confirms that the mass transfer of ferric to the mineral surface was insufficient in first stage of chalcocite leaching in the column leaching test.

In cupric chloride column leaching test, irrigation rate slightly improved the copper extraction rate in the first stage, while the second leaching stage was insensitive to the irrigation rate. The small improvement in the reaction rate in the first stage may be attributed to the mix-controlled kinetics of the first stage, a combination of diffusion control and chemical reaction control. The

kinetic models obtained in ferric chloride and cupric chloride leaching systems were scaled up and validated through the column leaching experiments. The scaled-up models could be further improved using chalcocite ore to include the effect of chalcocite particle liberation in the kinetic models.

# Chapter 9: Characterization of solid surfaces in chloride leaching

## 9.1 Introduction

In this Chapter, we investigated the evolution of chalcocite surface properties in the course of chloride leaching and the changes in mineral surface properties in response to different leaching parameters using SEM-EDX and XPS techniques. The results of mineral surface characterization were used to interpret the leaching kinetics and reveal the reasons for the slow kinetics in the second stage of leaching. A version of this Chapter was submitted for publication in Hydrometallurgy.

## 9.2 Evolution of mineral surface properties during chalcocite leaching

## 9.2.1 Characterization of surface morphological change by SEM

The morphological changes of chalcocite surfaces during leaching were characterized by scanning electron microscopy. For comparison, Figure 9.1 shows the secondary electron images of the chalcocite sample prior to leaching at increasing magnification. The sample surfaces were smooth with no initial pores or cracks. At the highest magnification, the crystals of chalcocite mineral were clearly shown.

Figure 9.2 and Figure 9.3 show the low- and high- magnification secondary electron images of chalcocite surfaces corresponding to increasing levels of copper extraction during leaching. Even at 10% copper extraction, cracks appeared on the surfaces of the solid particles. More and larger cracks were developed with increasing copper extraction in the course of leaching. These cracks appeared most likely due to a decrease in the molar volume when chalcocite was converted to the

non-stoichiometric reaction intermediates (Elsherief et al., 1995; Fisher et al., 1992). Fisher et al. (1992) attributed the appearance of cracks to a molar volume decrease by 26.9% and the crystal structure change from orthorhombic to hexagonal when chalcocite was converted to blue-remaining covellite.

Upon completion of the first stage (49% copper extraction), the chalcocite particles might have disintegrated into finer particles of a narrow particle size distribution, which continued to be leached in the second stage. Such particle disintegration could explain the previous experimental observation that particle size did not significantly affect the copper extraction in the second stage of chalcocite leaching (Chapter 6 and Chapter 7). These surface morphological changes might reflect the concomitant formation of a series of non-stoichiometric intermediates during leaching, as stated by Cheng and Lawson (1991). Further analyses of the surface elemental composition and chemical state were subsequently carried out and reported in the following sections.



Figure 9.1 The secondary electron images of chalcocite sample prior to leaching at increasing magnification



Figure 9.2. The secondary electron images of chalcocite leaching residues at varied leaching time corresponding to increasing copper extraction under the following conditions: [Fe(III)] 0.05 M, [Fe(II)] 0.001 M, [Cl<sup>-</sup>] 0.172 M, pH 1.5, 25 °C



Figure 9.3. The secondary electron images of chalcocite leaching residues at varied leaching time corresponding to increasing copper extraction at higher magnification under the following conditions: [Fe(III)] 0.05 M, [Fe(II)] 0.001 M, [Cl<sup>-</sup>] 0.172 M, pH 1.5, 25 °C

## 9.2.2 Quantification of surface elemental composition (Cu/S ratio) by EDX analysis

To identify changes in the surface elemental composition during leaching, EDX analysis was performed with a general resolution of about  $1 - 2 \mu m$  in depth. Figure 9.4 shows the EDX results of the chalcocite sample and the leaching residues at increasing levels of copper extraction. As the leaching progressed, the concentration of copper on the solid surfaces decreased, while the surface concentration of sulfur increased. This result supported the hypothesis proposed by Cheng and Lawson (1991) that in the first stage of chalcocite leaching in chloride media, cuprous ions diffused through the solid towards the surfaces and into the solution, resulting in the formation of a series of copper deficient non-stoichiometric solid intermediates.

Table 9.1 summarizes the Cu/S ratios corresponding to different copper extraction, which were calculated using the integrated peak area. Each value in Table 9.1 was the average of three Cu/S ratios that were analyzed at three different points on each sample surfaces. Even though the surface composition might vary at different depth, the Cu/S ratio approximately correlated with the percentage of copper extracted in the leaching process. As leaching progressed with higher copper extraction, the Cu/S ratio decreased. Whiteside and Goble (1986) studied the mineralogy of digenite (Cu<sub>1.8</sub>S) leaching intermediates in sulfate media using X-ray diffraction (XRD) to detect structural changes at 23°C. The author showed the structural change from digenite to anilite (Cu<sub>1.75</sub>S) and then to geerite (Cu<sub>1.6</sub>S), spionkopite (Cu<sub>1.4</sub>S), and yarrowite (Cu<sub>1.12</sub>S). EDX analysis had not been used to detect reaction intermediates of chalcocite leaching in chloride media.



Figure 9.4. The EDX results of chalcocite sample and the leaching residues at varied leaching time corresponding to increasing copper extraction under the following conditions: [Fe(III)] 0.05 M, [Fe(II)] 0.001, [Cl] 0.172, pH 1.5, 25 °C

Table 9.1 The Cu/S ratios of the chalcocite surface and the leaching residues surface at varied leaching time

Copper extraction, %		10%	20%	49%	55%	80%
Cu/S ratio	2.06	1.7	1.37	1	0.96	0.46
Corresponding reaction intermediate (approximately)		$Cu_{1.8}S$	$Cu_{1.6}S$	CuS	CuS	$CuS_2$

## 9.2.3 Determination of sulfur chemical bonding on solid surfaces by XPS analysis

We investigated the survey XPS spectra of chalcocite and the high-resolution spectra of copper and sulfur species. The high-resolution spectra of Cu 2p and copper auger spectrum  $Cu_{L3M45M45}$ were used to characterize the composition of the solid surface. In addition, the high-resolution spectra of S 2p and S 2s were studied to identify the chemical state of sulfur on the surfaces of the chalcocite sample and the leaching residues corresponding to increasing levels of copper extraction. To ensure the validity of the results, the obtained spectra results were compared with those available in the literature.

#### (1) Chalcocite sample

The XPS analysis of the chalcocite sample before its exposure to a leaching solution was conducted to obtain a baseline for comparison. To study the surface composition of chalcocite, the survey XPS spectrum of chalcocite and the high-resolution spectra of copper and sulfur species were obtained (Figure 9.5). Figure 9.5A presents the survey XPS spectrum of the chalcocite sample, which showed the peaks of Cu, O, C, and S. The C1s peak with binding energy of 284.8 eV was for aromatic/aliphatic carbons. The presence of O1s peak could be due to air contamination of the sample and/or surface oxidation of the sample.

Figure 9.5B shows the high-resolution spectrum of Cu 2p obtained from the chalcocite sample, which was further analyzed by the XPSPeak 4.1, an XPS peak fitting program. The analysis showed that Cu 2p<sub>1/2</sub> was positioned at 952.7 and Cu 2p<sub>3/2</sub> at 932.9 eV. The values reported in the literature vary from 952.4 – 952.9 eV for Cu 2p<sub>1/2</sub> peak and from 932.4 – 932.9 eV for Cu 2p<sub>3/2</sub> peak (Klein et al., 1983; Krylova and Andrulevi<sup>×</sup>, 2009; Kuhn and Rodriguez, 1994; Nakai 146

et al., 1978; Naumkin et al., 2012). The satellite peak associated with the divalent copper Cu<sup>2+</sup> was not present, suggesting that only monovalent copper atom exists in chalcocite structure. The satellite peak may appear when the outgoing photoelectron simultaneously shakes a valence electron up to a higher-energy level. As a result, the kinetic energy of the core electron is slightly reduced, resulting in a satellite structure a few eV below the core level position (Watts and Wolstenholme, 2003). The absence of the satellite peak in the S 2p spectra of chalcopyrite has been reported in the literature, suggesting that chalcopyrite is composed of monovalent copper atoms (Ghahremaninezhad et al., 2013; Hackl et al., 1995). Figure 9.5C shows that the high-resolution peak of copper auger spectrum Cu LMM was centered at 569.7 eV, which was consistent with those (569.5 eV) reported in the literature (Ghahremaninezhad et al., 2011; Krylova and Andrulevi<sup>×</sup>, 2009).

The high-resolution peak of S 2p of chalcocite sample was also studied. The S 2p exists as doublets of S  $2p_{1/2}$  and S  $2p_{3/2}$  because of spin-orbit splitting. Figure 9.5D shows the high-resolution peak of S 2p of chalcocite sample with the fitted peaks analyzed by the XPSPeak 4.1. Integrated peak areas were analyzed to determine the percentages of the different sulfur species on chalcocite surface. The analyses showed that chalcocite consisted of three sulfur species, namely, monosulfide S<sup>2–</sup>, disulfide S<sub>2</sub><sup>2–</sup>, and polysulfide S<sub>n</sub><sup>2–</sup>. Monosulfide accounted for 84%, disulfide 11%, and polysulfide 5% of the total sulfur. The S  $2p_{3/2}$  peak was positioned at 161.8 eV for monosulfide, at 162.3 eV for disulfide, and at 163 eV for polysulfide. These values were consistent with those reported in the literature, specifically, 161.7 eV for S<sup>2–</sup> (Folmer and

Jellinek, 1980; Nava et al., 2008; Wang et al., 2009), 162.5 eV for  $S_2^{2-}$  (Ghahremaninezhad et al., 2013), and 163.0-163.9 eV for  $S_n^{2-}$  (Harmer et al., 2006).



Figure 9.5. The XPS analyses of chalcocite sample, A: survey XPS spectrum, B: high-resolution spectrum of Cu 2p, C: high-resolution peak of copper auger spectrum Cu LMM, D: high-resolution peaks of S 2p

The presence of sulfur in various chemical states has also been shown in chalcopyrite. Hackl et al. (1995) used XPS technique to analyze the surface composition of chalcopyrite. By the deconvolution of the S 2p spectrum of the untreated chalcopyrite, the authors showed the presence of four sulfur species, including monosulfide S<sup>2–</sup>, disulfide S<sub>2</sub><sup>2–</sup>, polysulfide S<sub>n</sub><sup>2–</sup>, and elemental sulfur S<sup>0</sup>. The monosulfide was assigned to unaltered CuFeS<sub>2</sub>, the disulfide to an irondeficient sulfide with the composition of Cu<sub>1-x</sub>Fe<sub>1-y</sub>S<sub>2</sub> where y >> x and x + y  $\approx$  1, and the polysulfide to  $CuS_n$ , with n > 2. The proportion of the sulfur species in the untreated chalcopyrite were calculated as 68% monosulfide, 18% disulfide, 10% polysulfide (10%) and 4% S°. The authors claimed that the brief air exposure caused the alteration in the original monosulfide component of chalcopyrite.

To avoid the surface oxidation of chalcopyrite due to the air exposure, Ghahremaninezhad et al. (2013) studied the XPS analysis of chalcopyrite after ion etching the solid surface. The authors showed that S 2p spectrum consisted of two main doublets representing monosulfide and disulfide and one broad peak at 163.7, which was attributed to the S  $3p \rightarrow Fe$  3d interband excitation, not to polysulfide. To support this hypothesis, the authors compared the S 2p peaks obtained from Fe-S minerals including pyrite, pyrrhotite, and Cu-S minerals including chalcocite and covellite. They showed that the high-energy peak at 163.5 was only observed in Fe-S minerals, which proved that the broad peak was originated from the S  $3p \rightarrow Fe$  3d excitation.

Figure 9.6 shows the analysis of the S 2s peak of the chalcocite sample. The binding energy of S 2s peak was centered at 226.8 eV, which was consistent with that reported by Wang et al. (2009), who showed that the binding energy of the S 2s level of chalcocite was 226.6 eV. The binding energy of the S 2s level of elemental sulfur is 228.4 eV. The difference in the S 2s binding energy between elemental sulfur and chalcocite can be used as an indicator to differentiate elemental sulfur from sulfur atoms of chalcocite. This was used in this study to confirm sulfur formation on the surfaces of chalcocite leaching residues.



Figure 9.6. High resolution peak of S 2s of the chalcocite sample

# (2) Leaching residues

Figure 9.7A shows the Cu 2p peaks of the chalcocite sample and the leaching residues corresponding to increasing levels of copper extraction. The Cu 2p peaks of the leaching residues remained centered at the same position at varied copper extractions. The Cu  $2p_{3/2}$  peak of the leaching residues was positioned at 932.3 as opposed to 932.9 eV for the chalcocite sample and the Cu  $2p_{1/2}$  peak of the leaching residues was centered at 952.3 eV as opposed to 952.7 eV for the chalcocite sample. In other words, the differences in the binding energies between the leaching residues and the chalcocite sample were 0.6 eV for Cu  $2p_{3/2}$  and 0.4 eV for Cu  $2p_{1/2}$ . In reference to the value of 0.6 eV difference between covellite and chalcocite reported in the literature (Klein et al., 1983; Nakai et al., 1978), the present analysis showed that even with 10% copper extraction, a thin layer of covellite could have formed on chalcocite particle surfaces. Moreover, because the satellite peak resulting from the divalent copper Cu<sup>2+</sup> was not observed on the leaching residue surfaces, the oxidation state of copper on solid surfaces remained monovalent during leaching.



Figure 9.7. High-resolution XPS spectra of chalcocite sample and leaching residues corresponding to increasing levels of copper extraction, A: Cu 2p, B: copper auger spectrum Cu<sub>L3M45M45</sub>, C: S 2p, D: S 2s

The copper auger spectra shown in Figure 9.7B indicated that the binding energy of the Cu LMM was shifted from 569.7 eV for the chalcocite sample to 568.7 eV for the leaching residues at 10% and 20% copper extraction. Compared with the suggested Cu LMM peak positions of 569.5 for Cu<sub>2</sub>S and 568.5 eV for CuS (Krylova and Andrulevi<sup>\*</sup>, 2009), these results supported that covellite layers could have formed on chalcocite particle surfaces even at the very early stage of leaching (10% copper extraction). At higher copper extraction (> 20%), the Cu LMM peaks were slightly shifted towards the lower binding energies. Because no binding energy was found for the Cu LMM peaks of polysulfide, we were unable to assign these binding energies to polysulfide. Using Cu 2p and copper augur Cu LMM, Ghahremaninezhad et al. (2013)

confirmed the formation of covellite on the surface of chalcopyrite after 6 h of potentiostatic polarization at 450 - 1000 mV vs SHE in 0.5 M sulfuric acid.

Figure 9.7C shows the S 2p peaks of the chalcocite sample and the leaching residues. The S 2p peaks of the leaching residues widened and shifted towards higher binding energies as the copper extraction increased. Given that polysulfide and elemental sulfur have higher FWHM and binding energies than monosulfide and disulfide, these results implied that the chemical state of sulfur transformed from monosulfide/disulfide to polysulfide/elemental sulfur in the course of chalcocite leaching. To further support the formation of elemental sulfur during leaching, the S 2s peaks were investigated.

Figure 9.7D shows that similar to S 2p spectra shown in Figure 9.7C, the S 2s spectra of the leaching residues at 10% and 20% copper extraction were centered at approximately the same binding energy, whereas the S 2s spectra of the leaching residues at higher copper extractions were widened and centered at higher binding energies at increasing copper extraction. The shifting of the binding energy toward higher values as leaching progressed was indicative of elemental sulfur formation, given that the S 2s binding energy of elemental sulfur was 1.6 eV higher than that of the sulfur atoms in chalcocite.

To elaborate the alteration of sulfur chemical state during leaching, peak fitting of the S 2p spectra corresponding to increasing levels of copper extraction was performed using the XPSPeak 4.1 program. The binding energies of the various sulfur chemical states were shown in Figure 9.8. The S 2p doublets of the chalcocite leaching residues after 10% and 20% copper extraction are shown in Figure 9.8A and in Figure 9.8B. The leaching residues were mainly

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composed of disulfide, with a small amount of monosulfide and polysulfide. Figure 9.8C shows that at the beginning of the second stage (49% copper extraction), the proportion of disulfide drastically declined, and the peaks of the elemental sulfur appeared. This implied that at the beginning of the second stage, the outer layer of the particle surface was mainly composed of polysulfide and sulfur. Figure 9.8D and Figure 9.8E show the S 2p doublets of the leaching residues after 55% and 80% copper extraction, respectively. It seemed that the surface composition of the two residues was almost similar. This might be due to the possible evaporation of the elemental sulfur layer under the ultra-vacuum chamber of XPS.

The possibility of the evaporation of elemental sulfur layer under ultra-vacuum condition of XPS instrument has been mentioned by the researchers (Buckley and Woods, 1984; Kaplun et al., 2011). Consequently, the portion of sulfur and polysulfide, especially in the second stage of chalcocite leaching, may be higher than what was observed. However, Klauber et al. (2001) believed that there was a significant difference between the evaporation of multilayers of elemental sulfur attached to other sulfur molecules and that of a monolayer of elemental sulfur attached to the surface of a mineral. They claimed that the adsorption energy of sulfur atoms interacting with a sulfur mono (or multi) layer is less than that of adsorbed sulfur on the surface of a leached mineral because of the more polar nature of mineral surfaces. It was supported by detecting adsorbed water, which has a much higher vapor pressure than sulfur, on the surface of a material with XPS. Therefore, XPS is capable of detecting monolayer sulfur on mineral surfaces.

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Figure 9.8. The high-resolution spectra of S 2p of the chalcocite leaching residues at varied Cu extractions; A: 10%, B: 20%, C: 49%, D: 55%, E: 80%. S 2p doublets of S<sup>2-</sup> in red dashed lines, S 2p doublets of S<sup>2-</sup> in blue dashed lines, and CuS<sub>n</sub> in green dashed lines.

The integrated spectra areas were used to determine the proportion of each sulfur species in the course of leaching, the results of which are shown in Figure 9.9. Figure 9.9 illustrates the progressive alteration of sulfur as leaching proceeded. For the chalcocite sample, as high as 84%

of total sulfur existed as monosulfide, with much smaller proportions of disulfide and polysulfide. As leaching progressed to 10% and 20% of copper extraction, the proportion of disulfide drastically increased to 66% and 69%, respectively and became dominant, confirming the formation of covellite in the early stage of chalcocite leaching. Progressively, the proportion of disulfide decreased.

As leaching transitioned to the second stage, the proportion of disulfide markedly decreased to 19%, which was converted mainly to polysulfide and elemental sulfur, accounting for 43% and 25%, respectively. Concomitantly, the proportion of polysulfide and elemental sulfur became larger. Hackl et al (1995) showed a similar trend in the sulfur chemical state change during the acidic ferric sulfate leaching. Monosulfide and disulfide proportions reduced from 68% and 18% in the fresh chalcopyrite to 54% and 8% in the leached chalcopyrite, whereas polysulfide increased from 10% in the untreated chalcopyrite to 35% in the leached sample. The minor reduction from 4% to 3% in the proportion of elemental sulfur was attributed to its rapid evaporation under ultra-high vacuum.



Figure 9.9. The distribution of sulfur species on the surface of the chalcocite sample and leaching residues at increasing copper extraction

In summary, the XPS analyses showed that copper existed as  $Cu^+$  and sulfur mainly as  $S^{2-}$  in chalcocite sample. The oxidation state of copper remained unchanged as  $Cu^+$  during leaching, while sulfur was transformed from monosulfide  $S^{2-}$  to mainly disulfide  $S_2^{2-}$  in the first stage of leaching and to polysulfide  $S_n^{2-}$  and elemental sulfur  $S^0$  in the second stage of leaching. The XPS spectra of Cu 2p, copper augur, and S 2p supported the hypothesis that a thin layer of covellite was formed at the very early stage of chalcocite leaching and the surface was transformed to a mixture of covellite, polysulfide, and elemental sulfur in the second stage.

### 9.3 Effect of ORP on solid particle surface properties

ORP had a positive effect on the copper extraction rate in the second stage of chalcocite leaching (Chapter 6). To investigate whether ORP affects mineral surface properties, the leaching residues collected at the same copper extraction under different ORP were characterized by SEM and EDX. The influence of sulfur on the leaching behavior was evaluated using CS<sub>2</sub> extraction for sulfur removal.

## 9.3.1 Characterization of surface morphology by SEM

Figure 9.10 shows the secondary electron images of the surfaces of the leaching residues at increasing ORP. When ORP was < 800 mV, the surfaces of the leaching residues seemed to be covered by a thin amorphous product layer, on top of which abundant nodules were visible. In contrast, at ORP values > 800 mV, the surfaces appeared to be more crystalline and nodules were almost absent on the surfaces. To identify the chemical composition of this amorphous layer and the nodules, EDX analysis was applied, the results of which were shown in the next section.



Figure 9.10 The secondary electron images of the leaching residues at increasing ORP under the following conditions: pH 1.5, 25 °C, and 80% copper extraction

### 9.3.2 Quantification of surface elemental composition by EDX analysis

EDX analyses were conducted on two main areas on the surfaces of the leaching residues, namely, nodules (shown as A on the SEM images) and the bulk surfaces (shown as B on the SEM images). Figure 9.11 shows the secondary electron images at increasing ORP and the corresponding EDX analyses of the nodules and the bulk surfaces. Table 9.2 summarizes the quantitative Cu/S ratios of the nodules and the bulk surfaces.

At potential values < 800 mV, the nodules had very low Cu/S ratios, indicating that the nodules were solid elemental sulfur; the low Cu/S ratios on the bulk surfaces indicated that the surfaces were mainly covered by a layer of sulfur. As the ORP was increased, the Cu/S ratio of the bulk surfaces increased, suggesting that the sulfur layer became thinner. When the ORP reached > 800 mV, the nodules were absent and the bulk surface Cu/S ratio increased to as high as 0.46. It may imply that at higher ORPs, the crystallinity level of the elemental sulfur layer was higher. This finding could explain the kinetics results obtained in Chapter 6 and Chapter 7. According to the kinetics results, ORP had a positive effect on the leaching rate of chalcocite in chloride media and the second leaching stage was limited by a mix kinetics mechanism, i.e., a combination of anodic decomposition of minerals and the reduction of oxidant ions (ferric ions or cupric ions) on the solid surface. The high crystallinity level of the sulfur layer could improve the reduction of ferric/cupric ions on the particle surface. In the following sections, this was further elaborated. Note that the Cu/S ratios must be treated as approximate values, because the composition of the surfaces may slightly alter at different depth.





Figure 9.11 The secondary electron images and the EDX spectra of the leaching residues at increasing ORP under the following conditions: pH 1.5, 25 °C, and 80% copper extraction

Table 9.2. The Cu/S ratios of the leaching residue surfaces at increasing ORP under the following conditions:pH 1.5, 25°C, and 80% copper extraction

		P	,	· ··· PP··· ····			
	ORP, mV	600	660	700	760	810	820
Cu/S	Nodules (A)	0.05	0.07	0.02	0.05		
-	Bulk surface (B)	0.12	0.13	0.22	0.33	0.46	0.45

To evaluate the influence of the sulfur layer on the leaching behavior at low and high potentials, the sulfur layer was removed from the leaching residues corresponding to 74% and 80% copper extraction at 600 and 800 mV, respectively. After CS<sub>2</sub> washing to remove any possible sulfur layer, the washed leaching residues were placed back to the reactors for resumed leaching. Another two baseline tests without CS<sub>2</sub> washing were conducted for comparison. Figure 9.12 presents only the experimental data of the second stage of chalcocite leaching for clarity. The leaching times at which the leaching tests were paused for sulfur removal by CS<sub>2</sub> are shown by a vertical dashed line in Figure 9.12. The removal of the sulfur layer by CS<sub>2</sub> washing had no effect on the copper extraction rate by approximately 4% at 600 mV. However, CS<sub>2</sub> washing had no effect on the copper extraction rate at 800 mV. These results showed that at low ORPs, elemental sulfur layer could contribute to the slow reaction rate in the second stage of chalcocite leaching by limiting the reduction of ferric/cupric ions on the particle surface. However, at high ORPs, sulfur

layer was not the reason for the slow leaching kinetics, which were supported by the previous SEM – EDX analysis that the sulfur layer was thin and more crystalline at high ORPs.



Figure 9.12. The effect of sulfur layer removal by CS<sub>2</sub> washing on leaching behavior at ORPs 600 mV and 800 mV

## 9.4 Effect of chloride concentration on solid surface properties

It is believed that the beneficial role of chloride ions compared with sulfate on copper sulfide leaching is twofold. Chloride ions may accelerate copper dissolution by forming Cu(II)/Cu(I) chloro-complexes, which act as the redox couple for oxidization of copper sulfide minerals (Cheng and Lawson, 1991a; Fisher et al., 1992). The second postulation is that chloride ions could lead to the formation of porous crystalline sulfur as the sulfide dissolution product instead of a cryptocrystalline or amorphous sulfur layer formed in the sulfate system. Porous crystalline sulfur layers enhance the dissolution rate by increasing the oxidant diffusion through the product layer (Cheng and Lawson, 1991a; Rauld Faine et al., 2005). In Chapter 7, it was shown that chloride concentration had a significant effect on copper extraction rate with cupric as the oxidant. Therefore, the leaching residues used for studying the effect of chloride concentration on solid surface properties were collected from the leaching tests with cupric as the oxidant.

#### 9.4.1 Characterization of surface morphology by SEM

To examine the effect of chloride ion on solid surface morphology, SEM images were taken on the surfaces of the leaching residues collected at 80% copper extraction. Figure 9.13 shows that the surfaces of the leaching residues seemed to be covered by a thin amorphous layer and some spherical nodules. These images were similar to those obtained at low ORPs in ferric chloride media (Figure 9.10). Therefore, the presence of the thin sulfur layer and the nodules observed in the cupric chloride leaching media were attributed to the ORPs being lower than 800 mV (values shown in Table 4.4). To show the effect of increasing chloride concentration on the porosity and morphology of the solid surfaces, images of higher magnification are shown in Figure 9.14. The porosity and crystallinity of the surfaces appeared to increase with increasing chloride concentration, which supported the hypothesis made by Cheng and Lawson (1991) and Faine et al. (2005), who reported that increasing chloride concentration enhanced the copper extraction by increasing the porosity and crystallinity of the solid surfaces. However, SEM images or other evidence were not available to show that increasing chloride concentration increased the porosity of the solid surface. The effect of chloride on the rate of chalcopyrite leaching in sulfate media has been studied (Carneiro and Leão, 2007; Lu et al., 2000). Lu et al. (2000) believed that chloride ions improved the crystallinity and porosity of the particle surface and linked this improvement to the increase in the leaching rate in the presence of chloride. The authors provided two SEM images showing that the leaching residue in the presence of chloride ion was more porous and crystalline compared with the one in the absence of chloride ion. Carneiro and Leão (2007) also showed that the presence of chloride changed the sulfur layer on the chalcopyrite leaching residues from amorphous to crystalline.

Kinetics results showed that copper extraction was insensitive to chloride concentration in ferric chloride media when potential was set at 810 mV. A possible explanation was that at this high potential, sulfur layer was thinner and therefore the effect of increasing chloride on sulfur morphology was negligible. In other words, the effect of chloride concentration on the reaction rate may only manifest itself at lower potentials where the level of elemental sulfur crystallinity is lower. However, in cupric chloride system, chloride concentration had a positive effect on the reaction rate in the second stage of leaching. The positive effect could result from two phenomena. First, increasing chloride concentration improved the crystallinity of the sulfur layer and therefore, enhanced the reaction rate by facilitating the reduction of cupric ions on the particle surface. Second, increasing chloride concentration increased the ORP that improved the decomposition of polysulfide.



Figure 9.13. The secondary electron images of chalcocite leaching residues collected at 80% copper extraction at increasing chloride concentrations under the following conditions: [Cu(II)] 0.016 M, pH 1.5, 25 °C, 500

rpm



Figure 9.14. The surface of chalcocite leaching residues at varied chloride concentrations at high magnification under the following conditions: [Cu(II)] 0.016 M, pH 1.5, 25 °C

## 9.4.2 Quantification of surface elemental composition by EDX analysis

The SEM images taken at varied chloride concentrations in cupric chloride media showed thin amorphous layers and some nodules on the surfaces of the leaching residues (Figure 9.14). EDX analysis was performed to examine the chemical composition of these layers and nodules observed. Figure 9.15 shows the EDX spectra obtained on both the nodules (shown as A on the SEM images) and the bulk surfaces of the particles (shown as B on the SEM images). The nodules were solid elemental sulfur and the bulk surfaces were mainly covered by a thin layer of amorphous sulfur. Table 9.3 shows the ratios of Cu/S of the nodules and the bulk surfaces, calculated as the average of three points on the solid surfaces. The Cu/S ratio of the nodules did not respond to variations in chloride concentration. In contrast, increasing the chloride concentration was associated with increased Cu/S ratio of the bulk surfaces, suggesting that the solid surfaces were covered, to a lesser extent, by a sulfur layer.





Figure 9.15. The EDX analyses of the surfaces of the leaching residues at increasing chloride concentrations in cupric chloride media under the following conditions: [Cu(II)] 0.016 M, pH 1.5, 25 °C, 500 rpm, 80% copper extraction

 Table 9.3. The Cu/S ratios of the surfaces of the leaching residues at increasing chloride concentrations in cupric chloride media

		1			
Chl	oride concentration, M	0.562	1.062	1.562	3.062
Cu/S	Spherical nodules (A)	0	0.06	0.05	0.07
-	Bulk body (B)	0.2	0.28	0.28	0.38

## 9.5 Effect of temperature on solid surface morphology

In Chapter 6 and 7, it was shown that temperature significantly enhanced the copper extraction rate from chalcocite in chloride media. Temperature has been reported to cause the surface of the minerals more porous (Bolorunduro, 1999; Niu et al., 2015). Therefore, in this study, the surfaces of chalcocite leaching residues at varied temperatures were analyzed by SEM to evaluate the changes in the surface morphology. Figure 9.16 presents the SEM images of the leaching residues at different temperatures at 80% of copper extraction. These images showed that parallel cracks developed on the solid surfaces, which became increasingly porous when temperature was elevated. At 55 °C, abundant pits were observed on the solid surfaces, which might offer less resistance to oxidant diffusion to mineral surfaces. A similar network of cracks were observed in chloride media by Fisher et al. (1992), and in sulfate media by Niu et al. (2015). It is well known that temperature enhances the leaching rate when the leaching kinetics is

limited by the chemical reaction itself. However, in the chloride leaching of chalcocite, temperature not only accelerated the anodic decomposition of mineral, but also rendered the particle surface more crystalline. The more crystalline sulfur layer at higher temperature may facilitate the reduction of the oxidant ions (Fe(III) in ferric chloride media and Cu(II) ions in cupric chloride media) on the surface of the solid particles. It should be remembered that the kinetics of chalcocite leaching in the second stage was limited by a combination of chemical reaction and the reduction of oxidant on the solid particles.



Figure 9.16. Secondary electron images of chalcocite residues at varied temperatures under the following conditions: [Fe(III)] 0.05 M, [Fe(II)] 0.05, [Cl<sup>-</sup>] 0.27, pH 1.5

#### 9.6 Interpretation of the kinetics results using the solid surface analysis data

Chapter 6 showed that increasing the ORP enhanced the leaching rate, but the reaction was still slow at ORPs as high as 800 mV. Based on the kinetics data, we concluded that the second stage of chalcocite leaching in ferric chloride media was controlled by a combination of mineral decomposition and ferric reduction on the mineral surfaces. Here, we attempted to interpret those kinetics results with the surface analysis data to elaborate the mechanisms of chalcocite leaching in chloride media. In the above sections, it was attempted to elucidate the kinetics results using the surface analysis data obtained in this Chapter. In this section, the interpretation of the kinetics results by the surface characterization data is summarized.

The XPS analyses identified both polysulfide and sulfur as the main reaction products on the surfaces of the second-stage leaching residues. However, the formation of a sulfur product layer occurred to a lesser extent on the solid surfaces at higher chloride concentrations and higher ORPs, as suggested by the SEM-EDX results. Therefore, we attributed the higher copper extraction rates obtained under those leaching conditions to either less resistance to oxidant diffusion towards the mineral surfaces or faster electron transfer from the mineral surfaces to the oxidant.

Despite the formation of thinner sulfur layers at higher ORPs, the leaching rate was still slow in the second stage. The removal of sulfur layer slightly improved copper extraction at 600 mV, but did not improve the leaching performance at 800 mV (Figure 9.12). Hence, it led us to conclude that sulfur layer was not the sole contributor to the slow reaction rate. It seemed that a combination of sulfur layer and polysulfide  $CuS_n$  was responsible for the slow reaction in the

second stage. The latter played an increasingly important role with increasing ORP. Even though an ORP as high as 800 mV was used in our leaching tests, at which the effect of sulfur layer was thinner, the value was still not high enough to leach polysulfides with fast kinetics. Hackl et al. (1995) showed the formation of polysulfide on the surface of chalcopyrite leaching residue and believed that the decomposition of polysulfide to cuprous ion and elemental sulfur was the rate limiting step for the dissolution of chalcopyrite in sulfate media.

#### 9.7 Leaching pathway

Given the difference in the analysis depth of XPS (<10 nm) and SEM-EDX (1-3  $\mu$ m), the Cu/S ratios obtained by these two techniques were compared to shed light on the progressive conversion of chalcocite particles to various reaction products during leaching. Table 9.4 showed that at the same copper extraction, lower Cu/S ratios were obtained by XPS (Figure 9.9) than by EDX (Table 9.4), except for the unreacted chalcocite sample. Because XPS analyzed the topmost layer typically up to 10 nm and EDX penetrated much deeper into a sample, these results indicated that the deeper towards the solid interior, the higher the Cu/S ratio.

Copper extraction, %	0%	10%	20%	49%	55%	80%
XPS (<10 nm) - Cu/S ratio	1.98	1.07	0.96	0.45	0.46	0.44
EDX (1-3 µm) - Cu/S ratio	2.06	1.7	1.37	1	0.96	0.46

Table 9.4. The Cu/S ratio of the chalcocite leaching residues at varied Cu extractions

The comparison in Table 9.4 led us to propose a progressive conversion model for the dissolution of chalcocite in chloride media, as shown in Figure 9.17. This model illustrated that once chalcocite leaching was initiated (10% and 20% copper extraction), a thin layer of covellite covered the surface of the mineral (Cu/S ratio close to 1); Meanwhile, the deeper layers towards

the interior were converted to a series of intermediate reaction products with decreasing Cu/S ratio. As leaching transitioned to the second stage (49% and 55% copper extraction), covellite on the surfaces was converted to a mixture of polysulfide and sulfur (Cu/S ratio close to 0.45), while the deeper layers towards the interior remained as covellite (Cu/S ratio close to 1). As the leaching continued, the covellite towards the interior was progressively converted to sulfur and polysulfide (decreasing Cu/S ratio). The dissolution of polysulfide at ambient temperature was slow, but the reaction could be accelerated at high temperatures (> 45 °C), as was shown in Chapter 6.



Figure 9.17 Model for the dissolution of chalcocite in the first and second leaching stage

This progressive conversion model was supported by the XPS results. Consistent with the literature (Biesinger et al., 2007; Folmer and Jellinek, 1980; Ghahremaninezhad et al., 2013; Liu et al., 2003; Wang et al., 2018), the XPS results in the present study showed that the copper atom in chalcocite and covellite was in the form of monovalent Cu<sup>+</sup> and sulfur in monosulfide S<sup>2–</sup> and disulfide S<sup>2–</sup>. The composition of chalcocite can be regarded as a combination of Cu<sup>+</sup> with monosulfide (S<sup>2–</sup>) and disulfide (S<sup>2–</sup>). Muir et al. (1976) proposed a chemical formula for

chalcocite as a combination of Cu<sup>+</sup>, monosulfide (S<sup>2–</sup>), disulfide (S<sub>2</sub><sup>2–</sup>), and polysulfide (S<sub>n</sub><sup>2–</sup>). One chemical formula for covellite is Cu<sub>2</sub>S<sub>2</sub>, although CuS is commonly used (Marcantonio, 1976). Another one proposed for covellite is Cu<sub>3</sub>+S<sub>2</sub><sup>2–</sup>S<sup>–</sup> (Folmer and Jellinek, 1980; Goh et al., 2006).

In the progressive leaching of chalcocite in an acidified cupric/ferric chloride solution, the cathodic reactions involved are the reduction of Cu(II) by Eq. (9.1) and the reduction of Fe(III) by Eq. (9.2) on solid particle surfaces (Table 9.5). The anodic half-cell reaction is the oxidation of sulfur, which was proposed to occur in a sequential manner, as supported by the XPS results (Figure 9.9). The sequential oxidation refers to the conversion of sulfide sulfur (S<sup>2–</sup>) to disulfide (S<sub>2</sub><sup>2–</sup>), then to polysulfides (S<sub>n</sub><sup>2–</sup>), and eventually to elemental sulfur (S<sup>0</sup>) by Eq. (9.3), (9.4), and (9.5). Meanwhile, Cu<sup>+</sup> diffuses from the particle interior to the solid surfaces, part of which participates in the formation of cuprous chloride complexes by Eq. (9.6), and part of which reacts with S<sub>2</sub><sup>2–</sup> to produce secondary covellite (CuS) by Eq. (9.7). Cu(II) and Fe(III) ions are regenerated by continuous supply of oxygen to the leaching system.

Cathodic	$CuCl^+ + 2Cl^- + e^- \rightarrow CuCl_3^{2-}$	(1)
	$FeCl^{2+} + e^- \rightarrow Fe^{2+} + Cl^-$	(2)
Anodic	$2S^{2-} \to S_2^{2-} + 2e^-$	(3)
	$nS_2^{2-} \to 2S_n^{2-} + (2n-4)e^{-}$	(4)
	$S_n^{2-} \to nS^0 + 2e^-$	(5)
$Cu^+$ ions	$Cu^+ + 3Cl^- \rightarrow CuCl_3^{2-}$	(6)
	$2Cu^{+} + S_2^{2-} = Cu_2S_2 \ (covellite)$	(7)

Table 9.5. The cathodic and anodic reactions for the leaching of chalcocite in chloride media

#### 9.8 Conclusions

To uncover the reasons that copper leaching from chalcocite in chloride media slowed down after 70 - 80% copper extraction, we investigated the evolution of solid surface properties during leaching and changes in surface properties in response to different leaching conditions. The SEM images showed the development of cracks on solid surfaces and the disintegration of solid particles as leaching progressed. Using the XPS analysis, we concluded that during leaching copper in the solid phase remained unchanged as Cu<sup>+</sup>, whereas sulfur in the solid phase underwent a sequential transformation, from monosulfide S<sup>2–</sup> to disulfide S<sup>2–</sup>, and then to polysulfide Sn<sup>2–</sup> and elemental sulfur S<sup>0</sup>. This transformation resulted in a mixture consisting mainly of polysulfide Sn<sup>2–</sup> and elemental sulfur S<sup>0</sup> covering the solid surfaces at 80% copper extraction. Both were proposed as the candidates responsible for the slow rate of dissolution after 70% – 80% copper extraction.

The SEM-EDX analysis of Cu/S ratio confirmed the formation of elemental sulfur layer on solid surfaces, which appeared to be thinner at higher ORPs. To understand the role of the sulfur layer on leaching kinetics, elemental sulfur was removed from the solids under leach by  $CS_2$  washing. The experimental results showed that sulfur removal slightly enhanced the reaction rate at a low ORP (600 mV), but did not improve it at a high ORP (800 mV). The results suggested that the sulfur layer was only partially responsible for the slow reaction at low potentials, but had no impact on the reaction rate at high potentials. Given the presence of polysulfides on the surfaces and its known slow reaction rate (Hackl et al., 1995), a combination of elemental sulfur layer and polysulfide  $CuS_n$  were concluded to be responsible for the slow reaction in the second stage. The

latter played an increasingly important role with increasing ORP. The effect of chloride concentration on the reaction rate may only manifest itself at low potentials where the level of the elemental sulfur crystallinity was lower.

# **Chapter 10: Conclusions and recommendations**

Due to the depletion of copper oxide ores, mining companies increasingly access and process low-grade sulfide ores with increasing levels of impurities. This challenge is compounded by water shortage in regions with limited access to freshwater. Direct use of seawater and water with elevated concentrations of chloride for heap leaching of secondary copper sulfides is one potential option to address this challenge. To thoroughly understand chloride leaching of copper from chalcocite, this research comprehensively investigated aqueous chloride solution properties (Objective I), kinetics of copper extraction from chalcocite in chloride media (Objective II), and mechanisms by which various factors influence copper leaching reactions (Objective III), in both acidified ferric chloride media and cupric chloride media. The key conclusions of the present study and recommendations for further study are presented here.

## **10.1 Conclusions**

The speciation study revealed the dominant species of ferric, ferrous, cupric, and cuprous ions in chloride media. Based on the speciation results, the cathodic reaction of ferric and cupric reduction and the anodic reaction of chalcocite leaching were proposed. On the one hand, increasing chloride concentration slightly lowered the potential of the ferric/ferrous couple, whereas markedly increased the potential of the cupric/cuprous couple. On the other hand, according to the proposed anodic reaction, increasing chloride concentration reduced the redox potential of chalcocite dissolution. Overall, increasing chloride concentration increased the potential difference between the cathodic and anodic processes, thereby rendering chalcocite leaching thermodynamically more favorable. The speciation results also revealed that at chloride

concentration lower than 0.5 M, it is likely that the second stage of chalcocite leaching in cupric chloride media cannot be initiated due to insufficient potential difference between the cathodic and anodic processes. After analysis of the thermodynamics of the leaching of chalcocite in ferric and cupric chloride media, the kinetics of the leaching reaction were studied.

Two individual kinetic equations derived in the first and second leaching stages could describe the kinetics of chalcocite leaching in ferric and cupric chloride media. These kinetics models were scaled up and then validated by performing the column leaching tests. The comparison of the column leaching results in ferric chloride and cupric chloride systems showed that chalcocite reaction rate was 2-3 times faster in ferric chloride than that in cupric chloride media. The first stage of chalcocite leaching with ferric chloride was fast and controlled by the diffusion of ferric ion towards the mineral surface, whereas, in cupric chloride media, it was limited by a mixed mechanism, i.e., a combination of chloride diffusion towards the particle surface and the chemical reaction. The rate of the second stage was slow in both ferric chloride and cupric chloride media and limited by a mixed kinetics, i.e., a combination of anodic mineral decomposition and ferric/cupric reduction in the second stage. The kinetics results were well interpreted by the subsequent surface analysis results.

According to the XPS analysis, in the course of chloride leaching of chalcocite, sulfur in the solid phase underwent a sequential transformation, from monosulfide  $S^{2-}$  to disulfide  $S_2^{2-}$  to polysulfide  $S_n^{2-}$  and elemental sulfur  $S^0$ , resulting in a mixture consisting mainly of polysulfide  $S_n^{2-}$  and elemental sulfur  $S^0$  covering the solid surfaces at 80% copper extraction. The SEM-EDX analysis of chalcocite and the leaching residues confirmed the formation of elemental

sulfur layer on solid surfaces, which appeared to be thinner at higher ORPs, higher chloride concentrations, and higher temperatures.

The role of the sulfur layer on leaching kinetics was uncovered by removing the elemental sulfur from the leaching residues using  $CS_2$  washing. The leaching results showed that sulfur removal marginally enhanced the reaction rate at the low ORP (600 mV), but did not improve it at the high ORP (800 mV). The results implied that the sulfur layer was partially responsible for the slow reaction rate at the low potential but had no impact on reaction rate at the high potential. Given the presence of polysulfides on the surfaces and its known slow reaction rate (Hackl et al., 1995), a combination of elemental sulfur layer and polysulfide  $CuS_n$  were responsible for the slow reaction in the second stage. The latter played an increasingly important role with increasing ORP.

The thinner sulfur layer at high ORP also explained the insensitivity of the leaching reaction rate to the chloride concentration in ferric chloride system at high ORPs. The effect of chloride concentration on the reaction rate may only manifest itself at low potentials where the level of the elemental sulfur crystallinity was lower. In cupric chloride media, chloride ion improved the second stage of chalcocite leaching at low ORPs through two phenomena: first by improving the crystallinity of the sulfur layer formed on the surface and therefore, enhancing the reduction of cupric ions on the solid surface, and second by increasing the ORPs through the formation of the Cu(II)/Cu(I) chloro-complexes and therefore, improving the decomposition of polysulfide.

### **10.2** Contributions to knowledge

The main contributions of the present study to knowledge are as follow:

- The speciation of iron and copper in chloride media was determined at high ionic strength. As opposed to the available studies in the literature, the SIT activity model was used in the thermodynamic calculations performed by the STABCAL software. For completely dissociated electrolytes, the accuracy is believed to be above 90% for ionic strength as high as 6 10 molal (Wang et al., 1997). From the speciation results, the cathodic and anodic reactions of chalcocite leaching in both ferric chloride and cupric chloride were proposed.
- The kinetics of chalcocite leaching with ferric chloride and cupric chloride was studied and the kinetics models were derived. The kinetics models were derived at ambient temperature and under fully controlled leaching conditions. These conditions are more relevant to actual heap leaching of secondary copper sulfide minerals, which is generally operated under ambient temperature and under relatively constant potential (~700 mV vs SHE) due to the continuous bacterial oxidation of ferrous to ferric (Petersen and Dixon, 2007). In contrast, most of the existing kinetics models on the leaching of chalcocite were obtained at temperatures higher than ambient temperature and under uncontrolled leaching conditions.
- The surface properties of chalcocite mineral before and after leaching in chloride media were investigated using SEM-EDX and XPS techniques. In this investigation, the formation of the non-stoichiometric intermediates, sulfur, and polysulfide was confirmed and the response of solid surface properties to different leaching conditions were explained. The leaching conditions that were considered were chloride concentration,

ORP, and temperature. The information obtained from the analysis of the surface characterization could reasonably explain the results from the leaching kinetics study. This information has not been reported in the literature for the leaching of chalcocite in chloride media.

- The surface characterization results also provided some interesting information with regard to the first and second stages of chalcocite leaching in chloride media. The results showed that covellite was formed at the very beginning of the first stage (after 10% copper extraction). But its dissolution was slow and would not occur until the potential increased to a sufficiently high level in the second stage. The other observation was that sulfur and polysulfide were formed at the early stage of the second leaching stage. This information led us to propose a progressive leaching model.

## **10.3** The practical implications

The ultimate purpose of the present study was to assist chalcocite heap leaching operations located in regions with limited access to freshwater to replace freshwater with seawater as process water. The presence of elevated concentrations of chloride inhibits or eliminates activities of iron- and sulfur oxidizing bacteria, which are essential to the regeneration of ferric ions by ferrous oxidation. In contrast, in the presence of chloride ions Cu(II)/Cu(I) electrochemical couple could oxidize chalcocite (Wilson and Fisher, 1981). In addition, Cu(I) ion is oxidized by atmospheric oxygen to regenerate Cu(II) with fast kinetics, thereby offering an alternative to bacteria-assisted oxidation of Fe(II) to Fe(III) in sulfate media (Parker et al., 1981).

One important finding in the present study was that chalcocite reaction rate was 2-3 times faster in ferric chloride than that in cupric chloride media. To take advantage of this faster kinetics, one practical chloride heap leach process could be proposed that uses ferric as the direct oxidant for chalcocite leaching. In such a system, ferric will be regenerated inside a heap, instead of a separate reactor or heap, from ferrous oxidation by cupric ions. In order for this process to occur, a sufficiently high chloride concentration must be provided. Oxygen provided by aeration will be the ultimate electron acceptor, which oxidizes cuprous to cupric with fast kinetics in chloride media.

In addition, the present study investigated the aqueous chloride solution properties and derived empirical Nernst equations for calculating ORPs for both the ferric chloride and cupric chloride system, without resorting to a thermodynamic software package. Furthermore, a kinetic equation was developed for each leaching system for the first and second stages of leaching, which were subsequently scaled up to describe kinetics for column leaching. Given the limitations of these models, they should be further optimized using real chalcocite ore before being applied to describe copper extraction from industrial scale heap leach pads. The findings of this research strengthen the understanding of the key factors that determine the copper extraction rate, which would help pinpoint options to optimize the leaching performance.

## **10.4 Recommendations**

The effect of pH and temperature on the ORP of ferric/ferrous and cupric/cuprous systems was not studied. They may have an impact on the ORP, especially in ferric/ferrous system due to the hydrolysis of ferric at higher pH values and higher temperature. Temperature and pH terms may be included in the empirical equations obtained in this study, Eqs. (5–4) and (5–10), to more accurately describe the ORP.

The effect of stirring speed was not investigated in the present study due to the limitation of the leaching apparatus. Providing sufficient stirring is important to ensure that the leaching reaction is not limited by mass transfer of oxidants to particle surfaces, which in turn may affect the activation energy and reaction orders.

It is suggested that further leaching kinetic studies should be carried out in a sulfate-chloride system, which is more approximate to the actual conditions encountered in chalcocite heap leach environment. The positive effect of chloride in such hybrid systems has been pointed out by various researchers (Cheng and Lawson, 1991a, 1991b; Senanayake, 2007).

The presence of other minerals such as pyrite may affect the leaching performance through the galvanic phenomenon. Therefore, it is suggested to analyze the impact of the presence of pyrite on chalcocite leaching rate in chloride media. In this study, natural chalcocite mineral was used in the leaching experiments to avoid the effect of impurities on the leaching reaction rate. For further studies, it is suggested to use real chalcocite ore sample to scale up the leaching kinetic equations obtained in the present study.

Apart from sodium and chloride ions, seawater contains other cations and anions, such as potassium, calcium, magnesium, and sulfate (Kennish, 2000). Although the concentrations of these ions were much lower than sodium and chloride, they may affect chalcocite leaching reaction, especially at high concentrations due to evaporation and recirculation of the process

water. Hence, it is recommended to examine the effect of these ions on chalcocite leaching kinetics.

An efficient re-oxidation of ferrous to ferric is crucial to maintaining the ORP. Many investigations have been carried out on the atmospheric oxidation of ferrous by oxygen in acidic chloride environment (Bouboukas et al., 1987; Colborn and Nicol, 1973; Posner, 1952a; Posner, 1952b; George, 1954). In addition, the effect of copper ion as a catalyst on the oxidation of ferrous ion has been identified in some atmospheric and pressurized experiments (Akilan and Nicol, 2016; Chmielewski and Charewicz, 1984; Colborn and Nicol, 1973; Dreisinger and Peters, 1989; George, 1954; Huffman and Davidson, 1956; Littlejohn, 2008; Ruiz et al., 2016). It is recommended to study the kinetics of ferrous oxidation by oxygen in conditions that could be encountered in heap leaching of chalcocite using seawater as the process water.

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# Appendices

## Appendix A

Species	Phase	∆G⁰, kJ/mol
Fe <sup>2+</sup>	Aqueous	-87.4625
Fe <sup>3+</sup>	Aqueous	-13.15
FeO4 <sup>2-</sup>	Aqueous	-467.3
FeOH <sup>+</sup>	Aqueous	-279.25
FeOH <sup>2+</sup>	Aqueous	-237.5
Fe(OH)2 <sup>+</sup>	Aqueous	-448.275
Fe(OH)2	Aqueous	-458.15
Fe(OH)3 <sup>-</sup>	Aqueous	-617.925
Fe(OH)4 <sup>2-</sup>	Aqueous	-773.3
Fe(OH) <sub>3</sub>	Aqueous	-669.133
Fe(OH)4 <sup>-</sup>	Aqueous	-842.85
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	Aqueous	-467.3
FeCl <sup>2+</sup>	Aqueous	-150.567
Fe	Solid	0
Fe0.95O, Wustite	Solid	-245.017
FeO, Wustite	Solid	-244.3
FeO	Solid	-251.567
Fe <sub>2</sub> O <sub>3</sub> , Hematite	Solid	-742.633
Fe <sub>3</sub> O <sub>4</sub> , Magnetite	Solid	-1014.26
Fe(OH)2, Amakinite	Solid	-489.167
Fe(OH)2	Solid	-486.5
Fe(OH)3	Solid	-705.55
Fe(OH)3	Solid	-696.5
FeOOH, Goethite	Solid	-489.7
FeOOH, Lepidocrocite	Solid	-471.4
FeCl <sub>2</sub> , Lawrencite	Solid	-302.5
FeCl <sub>3</sub> , Molysite	Solid	-334

Table A.1 Standard Gibbs free energies of iron species from Woods database

Species	Phase	ΔG <sup>0</sup> , kJ/mol	Species	Phase	∆G <sup>0</sup> , kJ/mol
Cu <sup>2+</sup>	Aqueous	65.04028	Cu	Gas	298.3066
Cu <sup>+</sup>	Aqueous	49.98206	Cu	Solid	0.012552
CuCl	Aqueous	-94.5793	Cu <sub>2</sub>	Gas	433.0273
CuCl <sub>2</sub>	Aqueous	-193.025	CuCl	Solid	-119.558
CuCl <sup>+</sup>	Aqueous	-68.4168	CuCl	Gas	63.54659
CuCl <sub>2</sub> <sup>-</sup>	Aqueous	-242.781	CuCl <sub>2</sub>	Solid	-174.925
CuCl <sub>3</sub> -	Aqueous	-315.172	CuCl <sub>2</sub>	Gas	-43.2249
CuCl <sup>32–</sup>	Aqueous	-376.317	Cu <sub>2</sub> Cl <sub>2</sub>	Gas	-55.1451
CuCl4 <sup>2–</sup>	Aqueous	-433.266	Cu <sub>2</sub> Cl <sub>4</sub>	Gas	-191.514
CuClO <sub>4</sub>	Aqueous	46.68507	Cu <sub>3</sub> Cl <sub>3</sub>	Gas	-245.086
Cu(ClO <sub>3</sub> ) <sub>2</sub>	Aqueous	65.30806	Cu <sub>4</sub> Cl <sub>4</sub>	Gas	-371.096
CuO	Aqueous	-87.1569	Cu5Cl5	Gas	-459.173
CuO <sub>2</sub> <sup>2–</sup>	Aqueous	-172.46	CuCl <sub>2</sub> :3Cu(OH) <sub>2</sub>	Solid	-1340.07
CuOH	Aqueous	-107.278	CuCl <sub>2</sub> :2H <sub>2</sub> O	Solid	-663.729
CuOH <sup>+</sup>	Aqueous	-126.399	Cu2Cl(OH)3, Atacamite	Solid	-669.599
Cu(OH)₃ <sup>−</sup>	Aqueous	-501.515	CuH	Gas	260.0482
Cu(OH)4 <sup>2–</sup>	Aqueous	-656.758	CuO	Gas	-129.595
Cu <sub>2</sub> OH <sup>3+</sup>	Aqueous	-68.718	CuO	Gas	276.8134
Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	Aqueous	-283.78	CuO, Tenorite	Solid	-127.876
Cu <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	Aqueous	-633.558	Cu <sub>2</sub> O	Solid	-145.858
HCuO <sub>2</sub> -	Aqueous	-251.442	Cu <sub>2</sub> O	Liquid	-108.612
Cl <sub>2</sub> Cu <sub>2</sub>	Gas	-55.1451	CuOH	Gas	103.8887
Cu	Solid	0	Cu(OH) <sub>2</sub>	Solid	-372.715
Cu	Liquid	7.706928			

Table A.2 Standard Gibbs free energies of copper species from HSC database

$[Fe^{3+}]/[Fe^{2+}]$	0.0	25/0.075			0.05/0.05			0.08/0.02			0.09/0.01		
Aqueous	Conc,Moles/L	Activity	Act	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act	
-		•	Coeff	Moles/L	-	Coeff	Moles/L	•	Coeff	Moles/L		Coeff	
$\mathbf{H}^{+}$	1.25E-04	3.16E-02	252.45	1.32E-04	3.16E-02	240.01	1.40E-04	3.16E-02	226.15	1.43E-04	3.16E-02	221.77	
OH-	2.52E-15	3.20E-13	126.61	2.51E-15	3.20E-13	127.35	2.49E-15	3.20E-13	128.18	2.49E-15	3.20E-13	128.44	
H <sub>2</sub> O	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	
Na <sup>+</sup>	2.30E+00	1.57E+00	0.68	2.31E+00	1.57E+00	0.68	2.31E+00	1.57E+00	0.68	2.31E+00	1.57E+00	0.68	
NaOH	7.64E-14	7.64E-14	1.00	7.64E-14	7.64E-14	1.00	7.64E-14	7.64E-14	1.00	7.63E-14	7.63E-14	1.00	
Cl⁻	2.52E+00	1.76E+00	0.70	2.50E+00	1.75E+00	0.70	2.48E+00	1.74E+00	0.70	2.47E+00	1.74E+00	0.70	
HCl	2.80E-08	2.80E-08	1.00	2.79E-08	2.79E-08	1.00	2.77E-08	2.77E-08	1.00	2.77E-08	2.77E-08	1.00	
NaCl	4.46E-01	4.46E-01	1.00	4.44E-01	4.44E-01	1.00	4.41E-01	4.41E-01	1.00	4.40E-01	4.40E-01	1.00	
Fe <sup>2+</sup>	7.31E-02	1.90E-02	0.26	4.87E-02	1.26E-02	0.26	1.95E-02	4.98E-03	0.26	9.76E-03	2.49E-03	0.25	
FeOH <sup>+</sup>	1.17E-08	6.73E-09	0.57	7.76E-09	4.46E-09	0.57	3.08E-09	1.77E-09	0.57	1.54E-09	8.82E-10	0.57	
Fe(OH)2	1.32E-17	1.32E-17	1.00	8.73E-18	8.73E-18	1.00	3.46E-18	3.46E-18	1.00	1.73E-18	1.73E-18	1.00	
Fe(OH)3 <sup>-</sup>	2.01E-29	1.15E-29	0.57	1.33E-29	7.63E-30	0.57	5.27E-30	3.03E-30	0.57	2.63E-30	1.51E-30	0.57	
Fe(OH)4 <sup>2-</sup>	1.57E-41	1.71E-42	0.11	1.04E-41	1.13E-42	0.11	4.13E-42	4.49E-43	0.11	2.06E-42	2.24E-43	0.11	
FeCl <sup>+</sup>	1.26E-03	7.24E-04	0.57	8.30E-04	4.77E-04	0.57	3.28E-04	1.88E-04	0.57	1.63E-04	9.36E-05	0.57	
FeCl <sub>2</sub>	6.42E-06	6.42E-06	1.00	4.21E-06	4.21E-06	1.00	1.65E-06	1.65E-06	1.00	8.20E-07	8.20E-07	1.00	
FeCl4 <sup>2–</sup>	6.46E-04	7.01E-05	0.11	4.19E-04	4.55E-05	0.11	1.62E-04	1.76E-05	0.11	8.03E-05	8.73E-06	0.11	
Fe <sup>3+</sup>	8.87E-03	4.58E-04	0.05	1.80E-02	9.13E-04	0.05	2.91E-02	1.45E-03	0.05	3.29E-02	1.63E-03	0.05	
FeOH <sup>2+</sup>	2.57E-04	8.24E-05	0.32	5.17E-04	1.64E-04	0.32	8.32E-04	2.61E-04	0.31	9.38E-04	2.93E-04	0.31	
Fe(OH)2 <sup>+</sup>	1.08E-07	6.20E-08	0.57	2.15E-07	1.23E-07	0.57	3.42E-07	1.96E-07	0.57	3.84E-07	2.20E-07	0.57	
Fe(OH)3	2.72E-09	2.72E-09	1.00	5.42E-09	5.42E-09	1.00	8.63E-09	8.63E-09	1.00	9.69E-09	9.69E-09	1.00	
Fe(OH) <sub>4</sub> -	1.15E-18	6.59E-19	0.57	2.29E-18	1.31E-18	0.57	3.64E-18	2.09E-18	0.57	4.09E-18	2.35E-18	0.57	
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	2.14E-07	3.04E-10	0.00	8.65E-07	1.20E-09	0.00	2.24E-06	3.05E-09	0.00	2.84E-06	3.84E-09	0.00	
Fe3(OH)4 <sup>5+</sup>	1.64E-09	1.54E-15	0.00	1.29E-08	1.22E-14	0.00	5.19E-08	4.90E-14	0.00	7.33E-08	6.93E-14	0.00	
FeO	3.80E-19	3.80E-19	1.00	2.52E-19	2.52E-19	1.00	9.99E-20	9.99E-20	1.00	4.98E-20	4.98E-20	1.00	
Fe(OH) <sup>2+</sup>	2.07E-03	6.63E-04	0.32	4.17E-03	1.32E-03	0.32	6.70E-03	2.10E-03	0.31	7.55E-03	2.36E-03	0.31	
FeO <sub>2</sub> <sup>-</sup>	2.55E-15	1.46E-15	0.57	5.07E-15	2.91E-15	0.57	8.07E-15	4.63E-15	0.57	9.06E-15	5.20E-15	0.57	
HFeO <sub>2</sub>	1.72E-07	1.72E-07	1.00	3.43E-07	3.43E-07	1.00	5.46E-07	5.46E-07	1.00	6.13E-07	6.13E-07	1.00	
FeCl <sup>2+</sup>	2.17E-03	9.71E-03	4.47	4.44E-03	1.92E-02	4.33	7.30E-03	3.04E-02	4.17	8.28E-03	3.41E-02	4.12	
<b>FeCl</b> <sub>3</sub>	9.51E-04	9.51E-04	1.00	1.87E-03	1.87E-03	1.00	2.92E-03	2.92E-03	1.00	3.26E-03	3.26E-03	1.00	
FeCl <sub>2</sub> <sup>+</sup>	1.06E-02	6.10E-03	0.57	2.10E-02	1.20E-02	0.57	3.30E-02	1.89E-02	0.57	3.69E-02	2.12E-02	0.57	
FeCl <sub>4</sub> -	3.89E-05	2.23E-05	0.57	7.59E-05	4.36E-05	0.57	1.18E-04	6.77E-05	0.57	1.31E-04	7.55E-05	0.57	

Table A.3 Iron species in 3 M chloride solution at pH 1.5 and 25 °C

$[Fe^{3+}]/[Fe^{2+}]$		0.025/0.075			0.05/0.05			0.08/0.02		0.09/0.01		
Aqueous	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act
-	Moles/L	-	Coeff	Moles/L	-	Coeff	Moles/L	-	Coeff	Moles/L	-	Coeff
$\mathbf{H}^{+}$	1.15E-03	3.16E-02	27.55	1.18E-03	3.16E-02	26.77	1.22E-03	3.16E-02	25.87	1.24E-03	3.16E-02	25.58
OH-	2.40E-14	3.20E-13	13.29	2.41E-14	3.20E-13	13.27	2.41E-14	3.20E-13	13.26	2.41E-14	3.20E-13	13.25
H <sub>2</sub> O	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00
Na <sup>+</sup>	1.31E+00	8.68E-01	0.66	1.31E+00	8.66E-01	0.66	1.31E+00	8.64E-01	0.66	1.31E+00	8.64E-01	0.66
NaOH	3.33E-13	3.33E-13	1.00	3.33E-13	3.33E-13	1.00	3.32E-13	3.32E-13	1.00	3.32E-13	3.32E-13	1.00
Cl⁻	1.54E+00	1.05E+00	0.68	1.53E+00	1.06E+00	0.69	1.52E+00	1.06E+00	0.70	1.51E+00	1.06E+00	0.70
HCl	1.68E-08	1.68E-08	1.00	1.68E-08	1.68E-08	1.00	1.69E-08	1.69E-08	1.00	1.69E-08	1.69E-08	1.00
NaCl	4.42E-01	4.42E-01	1.00	4.42E-01	4.42E-01	1.00	4.42E-01	4.42E-01	1.00	4.42E-01	4.42E-01	1.00
Fe <sup>2+</sup>	7.43E-02	1.61E-02	0.22	4.96E-02	1.06E-02	0.21	1.98E-02	4.20E-03	0.21	9.91E-03	2.09E-03	0.21
FeOH <sup>+</sup>	9.55E-09	5.70E-09	0.60	6.32E-09	3.77E-09	0.60	2.50E-09	1.49E-09	0.60	1.25E-09	7.43E-10	0.59
Fe(OH) <sub>2</sub>	1.12E-17	1.12E-17	1.00	7.38E-18	7.38E-18	1.00	2.92E-18	2.92E-18	1.00	1.46E-18	1.46E-18	1.00
Fe(OH)3 <sup>-</sup>	1.64E-29	9.76E-30	0.60	1.08E-29	6.45E-30	0.60	4.29E-30	2.55E-30	0.60	2.14E-30	1.27E-30	0.59
Fe(OH)4 <sup>2-</sup>	1.14E-41	1.45E-42	0.13	7.57E-42	9.56E-43	0.13	3.02E-42	3.78E-43	0.13	1.51E-42	1.88E-43	0.13
FeCl <sup>+</sup>	6.05E-04	3.61E-04	0.60	4.01E-04	2.39E-04	0.60	1.59E-04	9.48E-05	0.60	7.94E-05	4.72E-05	0.59
FeCl <sub>2</sub>	1.95E-06	1.95E-06	1.00	1.29E-06	1.29E-06	1.00	5.14E-07	5.14E-07	1.00	2.57E-07	2.57E-07	1.00
FeCl4 <sup>2–</sup>	6.02E-05	7.63E-06	0.13	4.02E-05	5.08E-06	0.13	1.62E-05	2.03E-06	0.13	8.09E-06	1.01E-06	0.13
Fe <sup>3+</sup>	1.35E-02	4.51E-04	0.03	2.72E-02	8.87E-04	0.03	4.36E-02	1.39E-03	0.03	4.91E-02	1.55E-03	0.03
FeOH <sup>2+</sup>	3.30E-04	8.11E-05	0.25	6.55E-04	1.59E-04	0.24	1.04E-03	2.50E-04	0.24	1.17E-03	2.79E-04	0.24
Fe(OH)2 <sup>+</sup>	1.02E-07	6.10E-08	0.60	2.01E-07	1.20E-07	0.60	3.16E-07	1.88E-07	0.60	3.53E-07	2.10E-07	0.59
Fe(OH)3	2.68E-09	2.68E-09	1.00	5.27E-09	5.27E-09	1.00	8.25E-09	8.25E-09	1.00	9.22E-09	9.22E-09	1.00
Fe(OH) <sub>4</sub> <sup>-</sup>	1.09E-18	6.49E-19	0.60	2.14E-18	1.28E-18	0.60	3.36E-18	2.00E-18	0.60	3.75E-18	2.23E-18	0.59
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	2.75E-07	2.94E-10	0.00	1.09E-06	1.14E-09	0.00	2.78E-06	2.79E-09	0.00	3.52E-06	3.48E-09	0.00
Fe <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>	6.49E-10	1.61E-15	0.00	5.08E-09	1.22E-14	0.00	2.02E-08	4.70E-14	0.00	2.86E-08	6.55E-14	0.00
FeO	8.76E-06	5.23E-06	0.60	1.72E-05	1.03E-05	0.60	2.70E-05	1.61E-05	0.60	3.02E-05	1.80E-05	0.59
Fe(OH) <sup>2+</sup>	2.66E-03	6.53E-04	0.25	5.28E-03	1.28E-03	0.24	8.37E-03	2.01E-03	0.24	9.38E-03	2.25E-03	0.24
FeO <sub>2</sub> <sup>-</sup>	2.41E-15	1.44E-15	0.60	4.74E-15	2.83E-15	0.60	7.44E-15	4.43E-15	0.60	8.32E-15	4.95E-15	0.59
HFeO <sub>2</sub>	1.70E-07	1.70E-07	1.00	3.33E-07	3.33E-07	1.00	5.22E-07	5.22E-07	1.00	5.84E-07	5.84E-07	1.00
FeCl <sup>2+</sup>	4.64E-03	5.73E-03	1.23	9.34E-03	1.13E-02	1.21	1.51E-02	1.77E-02	1.18	1.70E-02	1.98E-02	1.16
FeCl3	2.01E-04	2.01E-04	1.00	3.97E-04	3.97E-04	1.00	6.26E-04	6.26E-04	1.00	7.01E-04	7.01E-04	1.00
FeCl <sub>2</sub> <sup>+</sup>	3.61E-03	2.15E-03	0.60	7.13E-03	4.25E-03	0.60	1.12E-02	6.68E-03	0.60	1.26E-02	7.48E-03	0.59
FeCl <sub>4</sub> -	4.74E-06	2.83E-06	0.60	9.38E-06	5.59E-06	0.60	1.48E-05	8.84E-06	0.60	1.66E-05	9.90E-06	0.59

Table A.4 Iron species in 2 M chloride solution at pH 1.5 and 25 °C

$[Fe^{3+}]/[Fe^{2+}]$	0	.025/0.075			0.05/0.05			0.08/0.02		0.09/0.01		
Aqueous	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act
$\mathbf{H}^{+}$	5.16E-03	3.16E-02	6.13	5.27E-03	3.16E-02	6.00	5.40E-03	3.16E-02	5.86	5.44E-03	3.16E-02	5.81
OH-	1.09E-13	3.20E-13	2.92	1.10E-13	3.20E-13	2.91	1.10E-13	3.20E-13	2.91	1.10E-13	3.20E-13	2.90
H <sub>2</sub> O	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00
Na <sup>+</sup>	6.29E-01	4.18E-01	0.66	6.30E-01	4.17E-01	0.66	6.30E-01	4.15E-01	0.66	6.30E-01	4.15E-01	0.66
NaOH	1.60E-13	1.60E-13	1.00	1.60E-13	1.60E-13	1.00	1.59E-13	1.59E-13	1.00	1.59E-13	1.59E-13	1.00
Cl⁻	8.71E-01	5.97E-01	0.69	8.64E-01	5.98E-01	0.69	8.55E-01	5.99E-01	0.70	8.52E-01	5.99E-01	0.70
HCl	9.50E-09	9.50E-09	1.00	9.51E-09	9.51E-09	1.00	9.53E-09	9.53E-09	1.00	9.54E-09	9.54E-09	1.00
NaCl	0.120564	0.120564	1.00	1.20E-01	1.20E-01	1.00	1.20E-01	1.20E-01	1.00	1.20E-01	1.20E-01	1.00
Fe <sup>2+</sup>	7.47E-02	1.54E-02	0.21	4.98E-02	1.01E-02	0.20	1.99E-02	3.99E-03	0.20	9.96E-03	1.98E-03	0.20
FeOH <sup>+</sup>	8.76E-09	5.48E-09	0.63	5.77E-09	3.60E-09	0.62	2.28E-09	1.41E-09	0.62	1.13E-09	7.03E-10	0.62
Fe(OH) <sub>2</sub>	1.07E-17	1.07E-17	1.00	7.05E-18	7.05E-18	1.00	2.77E-18	2.77E-18	1.00	1.38E-18	1.38E-18	1.00
Fe(OH)3 <sup>-</sup>	1.50E-29	9.38E-30	0.63	9.89E-30	6.16E-30	0.62	3.90E-30	2.42E-30	0.62	1.94E-30	1.20E-30	0.62
Fe(OH)4 <sup>2-</sup>	9.08E-42	1.39E-42	0.15	6.04E-42	9.13E-43	0.15	2.41E-42	3.59E-43	0.15	1.20E-42	1.78E-43	0.15
FeCl <sup>+</sup>	3.14E-04	1.96E-04	0.63	2.07E-04	1.29E-04	0.62	8.19E-05	5.09E-05	0.62	4.08E-05	2.53E-05	0.62
FeCl <sub>2</sub>	6.01E-07	6.01E-07	1.00	3.96E-07	3.96E-07	1.00	1.56E-07	1.56E-07	1.00	7.78E-08	7.78E-08	1.00
FeCl4 <sup>2–</sup>	4.91E-06	7.52E-07	0.15	3.29E-06	4.97E-07	0.15	1.32E-06	1.97E-07	0.15	6.62E-07	9.83E-08	0.15
Fe <sup>3+</sup>	1.49E-02	4.41E-04	0.03	3.00E-02	8.58E-04	0.03	4.83E-02	1.33E-03	0.03	5.44E-02	1.48E-03	0.03
FeOH <sup>2+</sup>	3.57E-04	7.93E-05	0.22	7.04E-04	1.54E-04	0.22	1.11E-03	2.39E-04	0.21	1.24E-03	2.66E-04	0.21
Fe(OH)2 <sup>+</sup>	9.53E-08	5.96E-08	0.63	1.86E-07	1.16E-07	0.62	2.89E-07	1.80E-07	0.62	3.22E-07	2.00E-07	0.62
Fe(OH)3	2.62E-09	2.62E-09	1.00	5.10E-09	5.10E-09	1.00	7.89E-09	7.89E-09	1.00	8.78E-09	8.78E-09	1.00
Fe(OH) <sub>4</sub> <sup>-</sup>	1.01E-18	6.35E-19	0.63	1.98E-18	1.23E-18	0.62	3.07E-18	1.91E-18	0.62	3.42E-18	2.13E-18	0.62
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	2.30E-07	2.81E-10	0.00	9.19E-07	1.06E-09	0.00	2.35E-06	2.55E-09	0.00	2.97E-06	3.16E-09	0.00
Fe <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>	1.87E-10	1.50E-15	0.00	1.48E-09	1.11E-14	0.00	6.02E-09	4.10E-14	0.00	8.54E-09	5.65E-14	0.00
FeO	8.17E-06	5.11E-06	0.63	1.59E-05	9.94E-06	0.62	2.48E-05	1.54E-05	0.62	2.76E-05	1.71E-05	0.62
Fe(OH) <sup>2+</sup>	2.87E-03	6.39E-04	0.22	5.67E-03	1.24E-03	0.22	8.94E-03	1.92E-03	0.21	1.00E-02	2.14E-03	0.21
FeO <sub>2</sub> <sup>-</sup>	2.25E-15	1.41E-15	0.63	4.39E-15	2.74E-15	0.62	6.81E-15	4.23E-15	0.62	7.59E-15	4.71E-15	0.62
HFeO <sub>2</sub>	1.66E-07	1.66E-07	1.00	3.23E-07	3.23E-07	1.00	4.99E-07	4.99E-07	1.00	5.56E-07	5.56E-07	1.00
FeCl <sup>2+</sup>	5.73E-03	3.17E-03	0.55	1.14E-02	6.17E-03	0.54	1.82E-02	9.57E-03	0.53	2.05E-02	1.07E-02	0.52
<b>FeCl</b> <sub>3</sub>	3.56E-05	3.56E-05	1.00	6.96E-05	6.96E-05	1.00	1.08E-04	1.08E-04	1.00	1.21E-04	1.21E-04	1.00
FeCl <sub>2</sub> <sup>+</sup>	1.08E-03	6.74E-04	0.63	2.11E-03	1.32E-03	0.62	3.29E-03	2.04E-03	0.62	3.67E-03	2.28E-03	0.62
FeCl <sub>4</sub> -	4.53E-07	2.83E-07	0.63	8.89E-07	5.54E-07	0.62	1.39E-06	8.65E-07	0.62	1.56E-06	9.66E-07	0.62

Table A.5 Iron species in 1 M chloride solution at pH 1.5 and 25 °C

[Fe <sup>3+</sup> ]/[Fe <sup>2+</sup> ]	0	.025/0.075			0.05/0.05			0.08/0.02		0.09/0.01		
Aqueous	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act	Conc	Activity	Act
1	Moles/L		Coeff	Moles/L		Coeff	Moles/L		Coeff	Moles/L		Coeff
<u>H</u> <sup>+</sup>	1.24E-02	3.16E-02	2.55	1.26E-02	3.16E-02	2.50	1.29E-02	3.16E-02	2.45	1.30E-02	3.16E-02	2.43
OH-	2.64E-13	3.20E-13	1.21	2.65E-13	3.20E-13	1.21	2.67E-13	3.20E-13	1.20	2.67E-13	3.20E-13	1.20
H <sub>2</sub> O	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00	5.55E+01	1.00E+00	1.00
Na <sup>+</sup>	2.26E-01	1.53E-01	0.68	2.26E-01	1.52E-01	0.67	2.26E-01	1.51E-01	0.67	2.26E-01	1.51E-01	0.67
NaOH	5.88E-14	5.88E-14	1.00	5.85E-14	5.85E-14	1.00	5.81E-14	5.81E-14	1.00	5.80E-14	5.80E-14	1.00
Cl-	4.69E-01	3.29E-01	0.70	4.64E-01	3.27E-01	0.71	4.57E-01	3.26E-01	0.71	4.55E-01	3.25E-01	0.71
HCl	5.23E-09	5.23E-09	1.00	5.21E-09	5.21E-09	1.00	5.18E-09	5.18E-09	1.00	5.17E-09	5.17E-09	1.00
NaCl	2.43E-02	2.43E-02	1.00	2.41E-02	2.41E-02	1.00	2.38E-02	2.38E-02	1.00	2.37E-02	2.37E-02	1.00
Fe <sup>2+</sup>	7.48E-02	1.64E-02	0.22	4.99E-02	1.07E-02	0.21	2.00E-02	4.14E-03	0.21	9.98E-03	2.05E-03	0.21
FeOH <sup>+</sup>	8.86E-09	5.82E-09	0.66	5.79E-09	3.78E-09	0.65	2.26E-09	1.47E-09	0.65	1.12E-09	7.28E-10	0.65
Fe(OH)2	1.14E-17	1.14E-17	1.00	7.41E-18	7.41E-18	1.00	2.88E-18	2.88E-18	1.00	1.43E-18	1.43E-18	1.00
Fe(OH)3 <sup>-</sup>	1.52E-29	9.97E-30	0.66	9.92E-30	6.48E-30	0.65	3.88E-30	2.52E-30	0.65	1.93E-30	1.25E-30	0.65
Fe(OH)4 <sup>2-</sup>	7.92E-42	1.48E-42	0.19	5.27E-42	9.60E-43	0.18	2.10E-42	3.73E-43	0.18	1.05E-42	1.85E-43	0.18
FeCl <sup>+</sup>	1.75E-04	1.15E-04	0.66	1.14E-04	7.43E-05	0.65	4.43E-05	2.87E-05	0.65	2.19E-05	1.42E-05	0.65
FeCl <sub>2</sub>	1.93E-07	1.93E-07	1.00	1.25E-07	1.25E-07	1.00	4.79E-08	4.79E-08	1.00	2.37E-08	2.37E-08	1.00
FeCl4 <sup>2-</sup>	3.94E-07	7.34E-08	0.19	2.57E-07	4.69E-08	0.18	1.01E-07	1.79E-08	0.18	5.01E-08	8.80E-09	0.18
Fe <sup>3+</sup>	1.55E-02	5.15E-04	0.03	3.13E-02	9.85E-04	0.03	5.08E-02	1.50E-03	0.03	5.73E-02	1.65E-03	0.03
FeOH <sup>2+</sup>	4.06E-04	9.26E-05	0.23	7.97E-04	1.77E-04	0.22	1.25E-03	2.69E-04	0.22	1.39E-03	2.97E-04	0.21
Fe(OH)2 <sup>+</sup>	1.06E-07	6.97E-08	0.66	2.04E-07	1.33E-07	0.65	3.12E-07	2.02E-07	0.65	3.45E-07	2.24E-07	0.65
Fe(OH) <sub>3</sub>	3.06E-09	3.06E-09	1.00	5.85E-09	5.85E-09	1.00	8.89E-09	8.89E-09	1.00	9.83E-09	9.83E-09	1.00
Fe(OH) <sub>4</sub> <sup>-</sup>	1.13E-18	7.42E-19	0.66	2.17E-18	1.42E-18	0.65	3.32E-18	2.15E-18	0.65	3.68E-18	2.38E-18	0.65
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	2.07E-07	3.84E-10	0.00	8.33E-07	1.40E-09	0.00	2.15E-06	3.24E-09	0.00	2.73E-06	3.96E-09	0.00
Fe3(OH)4 <sup>5+</sup>	8.70E-11	2.40E-15	0.00	7.03E-10	1.68E-14	0.00	2.91E-09	5.86E-14	0.00	4.16E-09	7.93E-14	0.00
FeO	9.09E-06	5.97E-06	0.66	1.75E-05	1.14E-05	0.65	2.67E-05	1.73E-05	0.65	2.96E-05	1.92E-05	0.65
Fe(OH) <sup>2+</sup>	3.27E-03	7.46E-04	0.23	6.42E-03	1.43E-03	0.22	1.00E-02	2.17E-03	0.22	1.12E-02	2.40E-03	0.21
FeO <sub>2</sub> <sup>-</sup>	2.50E-15	1.64E-15	0.66	4.81E-15	3.14E-15	0.65	7.35E-15	4.77E-15	0.65	8.15E-15	5.28E-15	0.65
HFeO <sub>2</sub>	1.94E-07	1.94E-07	1.00	3.71E-07	3.71E-07	1.00	5.63E-07	5.63E-07	1.00	6.22E-07	6.22E-07	1.00
FeCl <sup>2+</sup>	5.47E-03	2.04E-03	0.37	1.08E-02	3.88E-03	0.36	1.69E-02	5.86E-03	0.35	1.88E-02	6.47E-03	0.34
FeCl <sub>3</sub>	6.95E-06	6.95E-06	1.00	1.31E-05	1.31E-05	1.00	1.96E-05	1.96E-05	1.00	2.16E-05	2.16E-05	1.00
FeCl <sub>2</sub> <sup>+</sup>	3.64E-04	2.39E-04	0.66	6.93E-04	4.53E-04	0.65	1.05E-03	6.80E-04	0.65	1.16E-03	7.50E-04	0.65
FeCl <sub>4</sub> -	4.63E-08	3.04E-08	0.66	8.74E-08	5.71E-08	0.65	1.31E-07	8.50E-08	0.65	1.44E-07	9.35E-08	0.65

#### Table A.6 Iron species in 0.5 M chloride solution at pH 1.5 and 25 °C

$[Cu^{2+}]/[Cu^{+}]$		1		10				100		1000		
Aqueous	Conc Moles/L	Activity	Act Coeff									
$\mathbf{H}^{+}$	4.78E-05	3.16E-02	661.97	4.62E-05	3.16E-02	684.77	4.59E-05	3.16E-02	689.28	4.58E-05	3.16E-02	689.79
OH-	1.81E-15	3.24E-13	178.57	1.83E-15	3.24E-13	176.79	1.83E-15	3.24E-13	176.43	1.83E-15	3.24E-13	176.39
H <sub>2</sub> O	55.51	1	1.00	5.55E+01	1.00E+00	1.00	55.51	1	1.00	5.55E+01	1.00E+00	1.00
Na <sup>+</sup>	2.45E+00	1.68E+00	0.69	2.45E+00	1.68E+00	0.68	2.45E+00	1.67E+00	0.68	2.45E+00	1.67E+00	0.68
NaOH	3.17E-13	3.17E-13	1.00	3.16E-13	3.16E-13	1.00	3.16E-13	3.16E-13	1.00	3.16E-13	3.16E-13	1.00
Cl⁻	2.47E+00	1.69E+00	0.68	2.49E+00	1.71E+00	0.69	2.50E+00	1.71E+00	0.69	2.50E+00	1.72E+00	0.69
HCl	1.04E-02	1.04E-02	1.00	1.06E-02	1.06E-02	1.00	1.06E-02	1.06E-02	1.00	1.06E-02	1.06E-02	1.00
NaCl	4.71E-01	4.71E-01	1.00	4.76E-01	4.76E-01	1.00	4.77E-01	4.77E-01	1.00	4.77E-01	4.77E-01	1.00
Cu <sup>+</sup>	1.91E-09	1.23E-09	0.65	3.87E-10	2.50E-10	0.65	4.40E-11	2.84E-11	0.65	4.33E-12	2.80E-12	0.65
CuCl	4.45E-07	4.45E-07	1.00	9.14E-08	9.14E-08	1.00	1.04E-08	1.04E-08	1.00	1.03E-09	1.03E-09	1.00
CuCl <sub>2</sub> -	8.17E-04	6.98E-04	0.86	1.70E-04	1.45E-04	0.85	1.95E-05	1.66E-05	0.85	1.92E-06	1.64E-06	0.85
CuCl <sub>3</sub> <sup>2–</sup>	1.22E-02	2.95E-03	0.24	2.57E-03	6.22E-04	0.24	2.95E-04	7.14E-05	0.24	2.91E-05	7.03E-06	0.24
CuOH	3.94E-22	3.94E-22	1.00	8.00E-23	8.00E-23	1.00	9.11E-24	9.11E-24	1.00	8.97E-25	8.97E-25	1.00
Cu <sub>2</sub> Cl <sub>4</sub> <sup>2–</sup>	1.37E-03	1.51E-04	0.11	5.93E-05	6.52E-06	0.11	7.76E-07	8.53E-08	0.11	7.53E-09	8.28E-10	0.11
Cu <sup>2+</sup>	9.57E-03	1.66E-03	0.17	1.73E-02	3.01E-03	0.17	1.88E-02	3.28E-03	0.17	1.90E-02	3.31E-03	0.17
CuCl <sub>2</sub>	7.84E-04	7.84E-04	1.00	1.46E-03	1.46E-03	1.00	1.60E-03	1.60E-03	1.00	1.61E-03	1.61E-03	1.00
CuCl <sup>+</sup>	5.33E-03	6.80E-03	1.28	9.72E-03	1.25E-02	1.29	1.06E-02	1.36E-02	1.29	1.07E-02	1.38E-02	1.29
CuCl <sub>3</sub> -	5.83E-05	3.36E-05	0.58	1.10E-04	6.33E-05	0.58	1.21E-04	6.94E-05	0.58	1.22E-04	7.01E-05	0.58
CuCl <sub>4</sub> <sup>2–</sup>	2.54E-06	2.80E-07	0.11	4.86E-06	5.34E-07	0.11	5.34E-06	5.88E-07	0.11	5.40E-06	5.94E-07	0.11
CuO	2.18E-15	2.18E-15	1.00	3.96E-15	3.96E-15	1.00	4.31E-15	4.31E-15	1.00	4.35E-15	4.35E-15	1.00
$CuO_2^{2-}$	4.97E-38	5.47E-39	0.11	9.03E-38	9.93E-39	0.11	9.83E-38	1.08E-38	0.11	9.92E-38	1.09E-38	0.11
CuOH <sup>+</sup>	1.88E-09	5.17E-10	0.28	3.44E-09	9.38E-10	0.27	3.75E-09	1.02E-09	0.27	3.78E-09	1.03E-09	0.27
Cu(OH) <sub>3</sub> <sup>-</sup>	1.16E-24	2.19E-24	1.88	2.11E-24	3.98E-24	1.88	2.30E-24	4.33E-24	1.88	2.32E-24	4.37E-24	1.88
Cu(OH)4 <sup>2–</sup>	9.66E-37	3.11E-37	0.32	1.76E-36	5.64E-37	0.32	1.92E-36	6.15E-37	0.32	1.93E-36	6.20E-37	0.32
Cu <sub>2</sub> OH <sub>3</sub> <sup>+</sup>	7.25E-10	1.67E-11	0.02	2.37E-09	5.51E-11	0.02	2.80E-09	6.53E-11	0.02	2.85E-09	6.65E-11	0.02
Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	2.34E-13	7.15E-14	0.31	7.64E-13	2.36E-13	0.31	9.04E-13	2.80E-13	0.31	9.20E-13	2.85E-13	0.31
Cu <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	4.12E-23	4.53E-24	0.11	2.47E-22	2.72E-23	0.11	3.19E-22	3.51E-23	0.11	3.28E-22	3.61E-23	0.11
HCuO <sub>2</sub> <sup>-</sup>	2.06E-26	1.19E-26	0.58	3.75E-26	2.16E-26	0.58	4.08E-26	2.35E-26	0.58	4.12E-26	2.37E-26	0.58
Cu(OH) <sub>2</sub>	1.22E-16	1.22E-16	1.00	2.22E-16	2.22E-16	1.00	2.41E-16	2.41E-16	1.00	2.44E-16	2.44E-16	1.00

Table A.7 Copper species in 3 M chloride solution at pH 1.5 and 25  $^{\rm o}{\rm C}$ 

$[Cu^{2+}]/[Cu^{+}]$		1			10			100			1000	
Aqueous	Conc Moles/L	Activity	Act Coeff	Conc Moles/L	Activity	Act Coeff	Conc Moles/L	Activity	Act Coeff	Conc Moles/L	Activity	Act Coeff
$\mathbf{H}^{+}$	2.45E-04	3.16E-02	129.16	2.45E-04	3.16E-02	129.06	2.47E-04	3.16E-02	128.10	2.57E-04	3.16E-02	123.26
OH-	9.93E-15	3.24E-13	32.57	9.93E-15	3.24E-13	32.58	9.92E-15	3.24E-13	32.63	9.84E-15	3.24E-13	32.87
H <sub>2</sub> O	55.51	1	1.00	55.51	1	1.00	55.51	1	1.00	55.51	1	1.00
Na <sup>+</sup>	1.70E+00	1.14E+00	0.67	1.70E+00	1.14E+00	0.67	1.70E+00	1.14E+00	0.67	1.70E+00	1.14E+00	0.67
NaOH	2.15E-13	2.15E-13	1.00	2.15E-13	2.15E-13	1.00	2.15E-13	2.15E-13	1.00	2.16E-13	2.16E-13	1.00
Cl⁻	1.76E+00	1.18E+00	0.67	1.76E+00	1.18E+00	0.67	1.75E+00	1.175853491	0.67	1.73E+00	1.16E+00	0.67
HCl	7.29E-03	7.29E-03	1.00	7.28E-03	7.28E-03	1.00	7.26E-03	7.26E-03	1.00	7.13E-03	7.13E-03	1.00
NaCl	2.23E-01	2.23E-01	1.00	2.23E-01	2.23E-01	1.00	2.22E-01	2.22E-01	1.00	2.19E-01	2.19E-01	1.00
Cu <sup>+</sup>	1.15E-11	7.40E-12	0.64	1.15E-10	7.37E-11	0.64	1.02E-09	6.53E-10	0.64	4.88E-09	3.14E-09	0.64
CuCl	1.87E-09	1.87E-09	1.00	1.86E-08	1.86E-08	1.00	1.64E-07	1.64E-07	1.00	7.75E-07	7.75E-07	1.00
CuCl <sub>2</sub> -	2.63E-06	2.05E-06	0.78	2.61E-05	2.04E-05	0.78	2.30E-04	1.79E-04	0.78	1.07E-03	8.32E-04	0.78
CuCl <sub>3</sub> <sup>2–</sup>	2.83E-05	6.06E-06	0.21	2.82E-04	6.03E-05	0.21	2.47E-03	5.28E-04	0.21	1.12E-02	2.41E-03	0.21
CuOH	2.37E-24	2.37E-24	1.00	2.36E-23	2.36E-23	1.00	2.09E-22	2.09E-22	1.00	1.00E-21	1.00E-21	1.00
Cu <sub>2</sub> Cl <sub>4</sub> <sup>2–</sup>	1.05E-08	1.30E-09	0.12	1.04E-06	1.29E-07	0.12	8.04E-05	9.95E-06	0.12	1.73E-03	2.14E-04	0.12
Cu <sup>2+</sup>	2.08E-02	3.56E-03	0.17	2.06E-02	3.53E-03	0.17	1.90E-02	3.24E-03	0.17	1.05E-02	1.79E-03	0.17
CuCl <sub>2</sub>	8.22E-04	8.22E-04	1.00	8.14E-04	8.14E-04	1.00	7.42E-04	7.42E-04	1.00	3.95E-04	3.95E-04	1.00
CuCl <sup>+</sup>	9.75E-03	1.02E-02	1.05	9.67E-03	1.01E-02	1.04	8.86E-03	9.24E-03	1.04	4.84E-03	5.01E-03	1.03
CuCl <sub>3</sub> <sup>-</sup>	4.15E-05	2.46E-05	0.59	4.10E-05	2.43E-05	0.59	3.73E-05	2.21E-05	0.59	1.95E-05	1.16E-05	0.59
CuCl <sub>4</sub> <sup>2–</sup>	1.16E-06	1.43E-07	0.12	1.15E-06	1.42E-07	0.12	1.04E-06	1.28E-07	0.12	5.32E-07	6.59E-08	0.12
CuO	4.68E-15	4.68E-15	1.00	4.64E-15	4.64E-15	1.00	4.26E-15	4.26E-15	1.00	2.35E-15	2.35E-15	1.00
CuO <sub>2</sub> <sup>2–</sup>	9.48E-38	1.17E-38	0.12	9.40E-38	1.16E-38	0.12	8.63E-38	1.07E-38	0.12	4.75E-38	5.88E-39	0.12
CuOH <sup>+</sup>	3.16E-09	1.11E-09	0.35	3.14E-09	1.10E-09	0.35	2.87E-09	1.01E-09	0.35	1.57E-09	5.56E-10	0.35
Cu(OH) <sub>3</sub> <sup>-</sup>	3.48E-24	4.70E-24	1.35	3.45E-24	4.66E-24	1.35	3.17E-24	4.28E-24	1.35	1.74E-24	2.36E-24	1.35
Cu(OH)4 <sup>2–</sup>	2.56E-36	6.67E-37	0.26	2.54E-36	6.61E-37	0.26	2.33E-36	6.07E-37	0.26	1.28E-36	3.35E-37	0.26
Cu <sub>2</sub> OH <sub>3</sub> <sup>+</sup>	3.62E-09	7.68E-11	0.02	3.56E-09	7.55E-11	0.02	3.01E-09	6.37E-11	0.02	9.21E-10	1.93E-11	0.02
$Cu_2(OH)_2^{2+}$	1.28E-12	3.29E-13	0.26	1.26E-12	3.23E-13	0.26	1.07E-12	2.73E-13	0.26	3.27E-13	8.29E-14	0.25
Cu <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	3.62E-22	4.48E-23	0.12	3.53E-22	4.36E-23	0.12	2.73E-22	3.38E-23	0.12	4.57E-23	5.66E-24	0.12
HCuO <sub>2</sub> <sup>-</sup>	4.30E-26	2.55E-26	0.59	4.26E-26	2.53E-26	0.59	3.91E-26	2.32E-26	0.59	2.15E-26	1.28E-26	0.59
Cu(OH) <sub>2</sub>	2.62E-16	2.62E-16	1.00	2.60E-16	2.60E-16	1.00	2.38E-16	2.38E-16	1.00	1.31E-16	1.31E-16	1.00

Table A.8 Copper species in 2 M chloride solution at pH 1.5 and 25  $^{\circ}\mathrm{C}$ 

$[Cu^{2+}]/[Cu^{+}]$		1			10			100		1000			
Aqueous	Conc Moles/L	Activity	Act Coeff										
$\mathbf{H}^{+}$	1.56E-03	3.16E-02	20.23	1.56E-03	3.16E-02	20.21	1.58E-03	3.16E-02	20.05	1.65E-03	3.16E-02	19.20	
OH-	6.44E-14	3.24E-13	5.02	6.44E-14	3.24E-13	5.02	6.43E-14	3.24E-13	5.03	6.40E-14	3.24E-13	5.06	
H <sub>2</sub> O	55.51	1	1.00	55.51	1	1.00	55.51	1	1.00	55.51	1	1.00	
Na <sup>+</sup>	8.63E-01	5.78E-01	0.67	8.63E-01	5.78E-01	0.67	8.63E-01	5.78E-01	0.67	8.65E-01	5.81E-01	0.67	
NaOH	1.09E-13	1.09E-13	1.00	1.09E-13	1.09E-13	1.00	1.09E-13	1.09E-13	1.00	1.10E-13	1.10E-13	1.00	
Cl⁻	9.28E-01	6.23E-01	0.67	9.27E-01	6.22E-01	0.67	9.21E-01	6.18E-01	0.67	8.94E-01	5.99E-01	0.67	
HCl	3.84E-03	3.84E-03	1.00	3.84E-03	3.84E-03	1.00	3.82E-03	3.82E-03	1.00	3.70E-03	3.70E-03	1.00	
NaCl	5.97E-02	5.97E-02	1.00	5.97E-02	5.97E-02	1.00	5.94E-02	5.94E-02	1.00	5.78E-02	5.78E-02	1.00	
Cu <sup>+</sup>	6.82E-11	4.47E-11	0.66	6.75E-10	4.42E-10	0.66	5.72E-09	3.75E-09	0.66	2.53E-08	1.66E-08	0.66	
CuCl	5.96E-09	5.96E-09	1.00	5.89E-08	5.89E-08	1.00	4.96E-07	4.96E-07	1.00	2.13E-06	2.13E-06	1.00	
CuCl <sub>2</sub> -	4.78E-06	3.45E-06	0.72	4.71E-05	3.40E-05	0.72	3.94E-04	2.85E-04	0.72	1.64E-03	1.18E-03	0.72	
CuCl <sub>3</sub> <sup>2–</sup>	2.62E-05	5.38E-06	0.21	2.58E-04	5.30E-05	0.21	2.14E-03	4.41E-04	0.21	8.58E-03	1.78E-03	0.21	
CuOH	1.43E-23	1.43E-23	1.00	1.42E-22	1.42E-22	1.00	1.20E-21	1.20E-21	1.00	5.31E-21	5.31E-21	1.00	
Cu <sub>2</sub> Cl <sub>4</sub> <sup>2–</sup>	2.36E-08	3.67E-09	0.16	2.30E-06	3.58E-07	0.16	1.61E-04	2.50E-05	0.16	2.76E-03	4.33E-04	0.16	
Cu <sup>2+</sup>	2.34E-02	4.33E-03	0.18	2.32E-02	4.29E-03	0.18	2.14E-02	3.94E-03	0.18	1.18E-02	2.18E-03	0.18	
CuCl <sub>2</sub>	2.78E-04	2.78E-04	1.00	2.75E-04	2.75E-04	1.00	2.50E-04	2.50E-04	1.00	1.30E-04	1.30E-04	1.00	
CuCl <sup>+</sup>	7.71E-03	6.53E-03	0.85	7.64E-03	6.47E-03	0.85	6.99E-03	5.91E-03	0.85	3.78E-03	3.17E-03	0.84	
CuCl <sub>3</sub> -	6.98E-06	4.38E-06	0.63	6.91E-06	4.34E-06	0.63	6.22E-06	3.91E-06	0.63	3.14E-06	1.97E-06	0.63	
CuCl4 <sup>2–</sup>	8.66E-08	1.35E-08	0.16	8.56E-08	1.33E-08	0.16	7.66E-08	1.19E-08	0.16	3.73E-08	5.84E-09	0.16	
CuO	5.68E-15	5.68E-15	1.00	5.63E-15	5.63E-15	1.00	5.18E-15	5.18E-15	1.00	2.87E-15	2.87E-15	1.00	
CuO <sub>2</sub> <sup>2–</sup>	9.16E-38	1.43E-38	0.16	9.08E-38	1.41E-38	0.16	8.34E-38	1.30E-38	0.16	4.59E-38	7.19E-39	0.16	
CuOH <sup>+</sup>	2.83E-09	1.35E-09	0.48	2.81E-09	1.34E-09	0.48	2.57E-09	1.23E-09	0.48	1.41E-09	6.80E-10	0.48	
Cu(OH) <sub>3</sub> -	5.99E-24	5.71E-24	0.95	5.94E-24	5.66E-24	0.95	5.45E-24	5.20E-24	0.95	3.01E-24	2.88E-24	0.96	
Cu(OH)4 <sup>2–</sup>	3.57E-36	8.10E-37	0.23	3.54E-36	8.03E-37	0.23	3.25E-36	7.38E-37	0.23	1.79E-36	4.09E-37	0.23	
Cu <sub>2</sub> OH <sub>3</sub> <sup>+</sup>	4.77E-09	1.13E-10	0.02	4.69E-09	1.11E-10	0.02	3.96E-09	9.42E-11	0.02	1.22E-09	2.89E-11	0.02	
$Cu_2(OH)_2^{2+}$	2.13E-12	4.86E-13	0.23	2.09E-12	4.78E-13	0.23	1.77E-12	4.04E-13	0.23	5.46E-13	1.24E-13	0.23	
Cu <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	5.17E-22	8.04E-23	0.16	5.03E-22	7.83E-23	0.16	3.91E-22	6.08E-23	0.16	6.61E-23	1.03E-23	0.16	
HCuO <sub>2</sub> <sup>-</sup>	4.93E-26	3.10E-26	0.63	4.89E-26	3.07E-26	0.63	4.49E-26	2.82E-26	0.63	2.48E-26	1.56E-26	0.63	
Cu(OH) <sub>2</sub>	3.18E-16	3.18E-16	1.00	3.15E-16	3.15E-16	1.00	2.90E-16	2.90E-16	1.00	1.61E-16	1.61E-16	1.00	

Table A.9 Copper species in 1 M chloride solution at pH 1.5 and 25 °C

[Cu <sup>2+</sup> ]/[Cu <sup>+</sup> ]		1			10			100			1000	
Aqueous	Conc Moles/L	Activity	Act Coeff									
$\mathbf{H}^{+}$	4.15E-03	3.16E-02	7.61	4.16E-03	3.16E-02	7.61	4.19E-03	3.16E-02	7.54	4.38E-03	3.16E-02	7.22
OH-	1.73E-13	3.24E-13	1.87	1.73E-13	3.24E-13	1.87	1.73E-13	3.24E-13	1.87	1.72E-13	3.24E-13	1.88
H <sub>2</sub> O	55.51	1	1.00	55.51	1	1.00	55.51	1	1.00	55.51	1	1.00
Na <sup>+</sup>	4.07E-01	2.81E-01	0.69	4.07E-01	2.81E-01	0.69	4.08E-01	2.82E-01	0.69	4.08E-01	2.83E-01	0.69
NaOH	5.31E-14	5.31E-14	1.00	5.31E-14	5.31E-14	1.00	5.32E-14	5.32E-14	1.00	5.35E-14	5.35E-14	1.00
Cl⁻	4.77E-01	3.30E-01	0.69	4.76E-01	3.29E-01	0.69	4.70E-01	3.25E-01	0.69	4.44E-01	3.08E-01	0.69
HCl	2.03E-03	2.03E-03	1.00	2.03E-03	2.03E-03	1.00	2.01E-03	2.01E-03	1.00	1.90E-03	1.90E-03	1.00
NaCl	1.54E-02	1.54E-02	1.00	1.54E-02	1.54E-02	1.00	1.52E-02	1.52E-02	1.00	1.45E-02	1.45E-02	1.00
Cu <sup>+</sup>	4.16E-10	2.84E-10	0.68	4.04E-09	2.76E-09	0.68	3.13E-08	2.14E-08	0.68	1.26E-07	8.66E-08	0.69
CuCl	2.00E-08	2.00E-08	1.00	1.94E-07	1.94E-07	1.00	1.49E-06	1.49E-06	1.00	5.69E-06	5.69E-06	1.00
CuCl <sub>2</sub> -	8.59E-06	6.13E-06	0.71	8.33E-05	5.94E-05	0.71	6.29E-04	4.49E-04	0.71	2.27E-03	1.63E-03	0.72
CuCl <sub>3</sub> <sup>2–</sup>	2.23E-05	5.06E-06	0.23	2.16E-04	4.90E-05	0.23	1.61E-03	3.66E-04	0.23	5.41E-03	1.25E-03	0.23
CuOH	9.09E-23	9.09E-23	1.00	8.84E-22	8.84E-22	1.00	6.84E-21	6.84E-21	1.00	2.77E-20	2.77E-20	1.00
Cu <sub>2</sub> Cl <sub>4</sub> <sup>2–</sup>	5.83E-08	1.16E-08	0.20	5.48E-06	1.09E-06	0.20	3.12E-04	6.24E-05	0.20	4.03E-03	8.18E-04	0.20
Cu <sup>2+</sup>	2.56E-02	5.58E-03	0.22	2.54E-02	5.53E-03	0.22	2.34E-02	5.09E-03	0.22	1.29E-02	2.85E-03	0.22
CuCl <sub>2</sub>	1.00E-04	1.00E-04	1.00	9.93E-05	9.93E-05	1.00	8.93E-05	8.93E-05	1.00	4.47E-05	4.47E-05	1.00
CuCl <sup>+</sup>	5.72E-03	4.46E-03	0.78	5.67E-03	4.41E-03	0.78	5.16E-03	4.02E-03	0.78	2.75E-03	2.13E-03	0.77
CuCl <sub>3</sub> <sup>-</sup>	1.25E-06	8.38E-07	0.67	1.24E-06	8.28E-07	0.67	1.10E-06	7.36E-07	0.67	5.19E-07	3.48E-07	0.67
CuCl <sub>4</sub> <sup>2–</sup>	6.84E-09	1.36E-09	0.20	6.74E-09	1.34E-09	0.20	5.90E-09	1.18E-09	0.20	2.60E-09	5.28E-10	0.20
CuO	7.33E-15	7.33E-15	1.00	7.26E-15	7.26E-15	1.00	6.69E-15	6.69E-15	1.00	3.75E-15	3.75E-15	1.00
CuO <sub>2</sub> <sup>2–</sup>	9.21E-38	1.84E-38	0.20	9.13E-38	1.82E-38	0.20	8.39E-38	1.68E-38	0.20	4.63E-38	9.40E-39	0.20
CuOH <sup>+</sup>	3.00E-09	1.74E-09	0.58	2.97E-09	1.72E-09	0.58	2.73E-09	1.59E-09	0.58	1.51E-09	8.88E-10	0.59
Cu(OH) <sub>3</sub> -	9.04E-24	7.36E-24	0.81	8.96E-24	7.29E-24	0.81	8.25E-24	6.72E-24	0.81	4.60E-24	3.76E-24	0.82
Cu(OH)4 <sup>2–</sup>	4.38E-36	1.04E-36	0.24	4.35E-36	1.04E-36	0.24	3.99E-36	9.54E-37	0.24	2.20E-36	5.34E-37	0.24
Cu <sub>2</sub> OH <sub>3</sub> <sup>+</sup>	5.64E-09	1.88E-10	0.03	5.54E-09	1.85E-10	0.03	4.69E-09	1.57E-10	0.03	1.44E-09	4.93E-11	0.03
$Cu_2(OH)_2^{2+}$	3.33E-12	8.08E-13	0.24	3.27E-12	7.94E-13	0.24	2.77E-12	6.74E-13	0.24	8.66E-13	2.11E-13	0.24
Cu <sub>3</sub> (OH) <sub>4</sub> <sup>2+</sup>	8.64E-22	1.72E-22	0.20	8.42E-22	1.68E-22	0.20	6.56E-22	1.31E-22	0.20	1.14E-22	2.31E-23	0.20
HCuO <sub>2</sub> <sup>-</sup>	5.97E-26	3.99E-26	0.67	5.92E-26	3.96E-26	0.67	5.45E-26	3.64E-26	0.67	3.04E-26	2.04E-26	0.67
Cu(OH) <sub>2</sub>	4.10E-16	4.10E-16	1.00	4.07E-16	4.07E-16	1.00	3.75E-16	3.75E-16	1.00	2.10E-16	2.10E-16	1.00

Table A.10 Copper species in 0.5 M chloride solution at pH 1.5 and 25 °C

## Appendix B

## **Type I leaching:**



Figure B.1 Polarization curve for Type I leaching (Dixon, 1999)

**Type II leaching:** 



Figure B.2 Polarization curve for Type II leaching (Dixon, 1999)

#### **Type III leaching:**



Figure B.3 Polarization curve for Type III leaching (Dixon, 1999)

#### Kinetic modeling procedure

The procedure to model the kinetics of the first stage of chalcocite leaching in ferric chloride media using the general model is presented here. This procedure could be then applied for the second stage in ferric chloride or cupric chloride media by adjusting the leaching parameters. Overall, the least squares method was used in an Excel spreadsheet to minimize the summation of the squared difference between the experimental copper extraction and the modeled copper extraction. Hence, one needs to obtain the modelled data. The integrated form of Eq. (4.1) is presented here as Eq. (B.1). To use this equation, initial values are required for activation energy  $(E_a)$ , rate constant (K<sub>Tref</sub>), phi value ( $\varphi$ ) and the reaction orders with respect to ferric concentration (*n*), ferrous concentration (*m*), chloride concentration (*p*), and particle size (*q*).

$$x = 1 - \left(1 - \frac{K_{Tref}t}{d^{q}} \exp\left(\frac{E_{a}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) (C_{Fe^{3+}})^{n} (C_{Fe^{2+}})^{m} (C_{Cl^{-}})^{p}\right)^{\frac{1}{1-\varphi}}$$
(B.1)

It was assumed that shrinking core models could model the experimental data. Therefore, the unknown initial values were obtained by applying the shrinking core models. As explained in Chapter 4, to study the effect of each leaching parameter including ferric concentration, ferrous concentration, chloride concentration, particle size and temperature, a set of leaching tests was conducted. The experimental data from each set of leaching experiments were used to calculate the reaction order with respect to that variable by applying the shrinking core models. In addition, the activation energy was calculated by modeling the experimental data from the leaching tests at varied temperature.

The reaction orders and the activation energy were used as the initial values for modeling the kinetics of chalcocite leaching by the general model, Eq. (B.1). The model data points were subtracted from the experimental data points and the summation of the squared differences was minimized using the Solver feature of Excel. In the minimization process, activation energy ( $E_a$ ), reaction rate ( $K_{Tref}$ ), and the reaction orders including *m*, *n*, *p*, and *q* were subjected to vary.