IODINE-ASSISTED HEAP LEACHING OF CHALCOPYRITE: LABORATORY AND MODELLING STUDIES

by

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**Iodine-assisted heap leaching of chalcopyrite: laboratory and modelling studies**

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Abstract

Copper mine operations face increasing challenges of processing low-grade chalcopyrite ores with elevated concentrations of impurities. Heap leaching is considered to be an effective and economically viable technology for treating these low-grade, complex copper sulfide ores. The addition of iodide in ferric sulfate solution is found to significantly enhance the dissolution of chalcopyrite at ambient temperatures. The aim of this research was to better understand the key factors that control the reaction rate and the mechanisms by which iodine accelerates the leaching kinetics. This research aim was achieved by conducting experimental and modelling studies of the iodine-assisted leaching of chalcopyrite concentrate and ore. Specifically, a series of leaching tests of increasing scale, from 50-mL bottle to 1-L reactor to 1-m and 6-m column tests, were carried out under partially- or fully-controlled leaching conditions; these leaching tests data were used to develop a kinetic model that correlates the copper extraction with the leaching conditions; the solid surface properties were examined by XRD, MLA, and XPS to uncover the leaching mechanisms; the calibrated kinetic model was finally used to assess the effect of key design and operating parameters on the performance of chalcopyrite dissolution in heap leaching.

The experimental results show that the redox potential is the primary factor controlling the chalcopyrite leaching by controlling the iodine speciation in solution. Either diiodine or triiodide is considered to be the active oxidant responsible for chalcopyrite dissolution depending on the solution potential. The solid surface examination shows that the elemental sulfur and iron precipitates formed during leaching did not hinder the dissolution of chalcopyrite and that pyrite was inert during leaching. The kinetic model developed could simulate the copper extraction as a function of solution potential, total iodide concentration, and temperature. The sensitivity tests
with the calibrated kinetic model show that the performance of the iodine-assisted leaching process can be improved by increasing irrigation rate, ferric concentration, iodide concentration, and temperature. The experimental and modelling results obtained in the present study can guide the design and implementation of the iodine-assisted heap leaching of chalcopyrite at an industrial scale.
Lay Summary

The addition of iodide in ferric sulfate solution is found to significantly enhance the dissolution of chalcopyrite at ambient temperatures. However, key factors that control the reaction rate and the mechanisms by which iodine accelerates the leaching kinetics were not well understood. The present study investigated the kinetics of chalcopyrite dissolution in ferric sulfate media in the presence of iodide. The mineralogical and morphological changes of chalcopyrite concentrate after leaching were also studied to understand the mechanism. The kinetic equation developed was used to simulate column leaching tests and evaluate the performance of copper extraction in response to variations in key design and operating parameters.
Preface

This dissertation is the original work by the author, R. Winarko. I was the investigator who was responsible for experimental design, data collection, analysis, and simulation. All experiments presented in Chapter 5 and Chapter 6 were carried out at the Hydrometallurgy Laboratory at UBC, Vancouver campus, while the solid characterization presented in Chapter 7 was performed at the laboratory of JX Nippon Mining and Metals in Hitachi, Japan. The column leaching data used for the simulations in Chapter 8 were provided by Mr. Miura from JX Nippon Mining and Metals Corporation. The column leaching experiments were carried out at the JX laboratory in Hitachi, Japan.

A version of Chapter 5 has been published in Hydrometallurgy [R. Winarko, D. B. Dreisinger, A. Miura, C. Tokoro, W. Liu, “Kinetic modelling of chalcopyrite leaching assisted by iodine in ferric sulfate media”, Hydrometallurgy 197, November 2020, Article 05481] and in the Conference of Metallurgists 2019 [R. Winarko, D. B. Dreisinger, W. Liu, “Enhanced leaching of chalcopyrite in ferric sulfate media by the presence of iodide/iodine”, Copper Conference, August 18-21, 2019, Vancouver, Canada]. I wrote the original drafts, performed the experiments, and collected and analyzed the experimental data. As the supervisors, Prof. Liu and Prof. Dreisinger were involved in the project administration and conceptualization. They also reviewed and edited the manuscripts. Mr. Miura and Tokoro Sensei provided resources and access to sample characterization.

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Kinetic study under fully controlled redox potential and pH”, Hydrometallurgy 208, February 2022, Article 105797] and in the Conference of Metallurgists 2021 [R. Winarko, D. B. Dreisinger, W. Liu, “Column leaching of chalcopyrite ore in ferric sulfate media in the presence of iodine under controlled solution potential and pH”, Copper Conference, August 17-19, 2021, Virtual event, Canada]. I wrote the original drafts, conducted the experiments, and collected and analyzed the data. Prof. Liu and Prof. Dreisinger reviewed and edited the manuscripts. Mr. Miura provided resources and access to the laboratory of JX Nippon Mining and Metals, Japan. Mr. Fukano helped with the sample characterization in the laboratory.

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<th>Meaning</th>
<th>Common Unit</th>
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<tr>
<td>$a$</td>
<td>Activity</td>
<td>–</td>
</tr>
<tr>
<td>$a_i^{w}$</td>
<td>The activity of analyte ion in the sample solution</td>
<td>–</td>
</tr>
<tr>
<td>$A$</td>
<td>Area</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration of interested element</td>
<td>kmol/kg</td>
</tr>
<tr>
<td>$d$</td>
<td>Mean particle diameter</td>
<td>mm</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusivity or diffusion coefficient</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;/s</td>
</tr>
<tr>
<td>$E$</td>
<td>Redox potential</td>
<td>mV vs SHE</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard potential</td>
<td>mV vs SHE</td>
</tr>
<tr>
<td>$E^{0'}$</td>
<td>Formal potential</td>
<td>mV vs SHE</td>
</tr>
<tr>
<td>$E_i^{0}$</td>
<td>The sum of the potential differences for a particular analyte ion</td>
<td>mV vs SHE</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>$Eh$</td>
<td>Redox potential</td>
<td>mV vs SHE</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
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</tr>
<tr>
<td>$g$</td>
<td>Acceleration of gravity</td>
<td>m/s&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>$h$</td>
<td>Head difference</td>
<td>m</td>
</tr>
<tr>
<td>$J$</td>
<td>Diffusion flux</td>
<td>mol/m&lt;sup&gt;2&lt;/sup&gt;/s</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant</td>
<td>–</td>
</tr>
<tr>
<td>$k_{app}$</td>
<td>The apparent rate constant</td>
<td>–</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Reaction rate constant at the reference temperature</td>
<td>–</td>
</tr>
<tr>
<td>$K$</td>
<td>Permeability</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt;</td>
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<tr>
<td>$K_{sp}$</td>
<td>Solubility product constant</td>
<td>–</td>
</tr>
<tr>
<td>$L$</td>
<td>Length</td>
<td>m</td>
</tr>
<tr>
<td>$m$</td>
<td>Total mass</td>
<td>kg</td>
</tr>
<tr>
<td>$n$</td>
<td>Mol of interested element</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
<td>kg/m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
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<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>Pa or kg/m/s$^2$</td>
</tr>
<tr>
<td>$Q$</td>
<td>Flow rate</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius</td>
<td>m</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>J/mol/K</td>
</tr>
<tr>
<td>$t$</td>
<td>Leaching time</td>
<td>day or hour or second</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Reference temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time scale</td>
<td>day or hour or second</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity</td>
<td>Pa · s or kg/m/s</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Topological exponent</td>
<td>–</td>
</tr>
<tr>
<td>$X_b$</td>
<td>Fraction of the total copper dissolved</td>
<td>–</td>
</tr>
<tr>
<td>$z_i$</td>
<td>The charge of the analyte ion</td>
<td>–</td>
</tr>
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**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAC/UBC</td>
<td>Anglo American – University of British Columbia</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic absorption spectrometry</td>
</tr>
<tr>
<td>AEC</td>
<td>Anion exchange chromatography</td>
</tr>
<tr>
<td>BRISA</td>
<td>Biolixiviación rápida Indirecta con Separación de Acciones: Fast Indirect Bioleaching with Actions Separation</td>
</tr>
<tr>
<td>emf</td>
<td>Electromotive force</td>
</tr>
<tr>
<td>ETC</td>
<td>Ethylene trithiocarbonate</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma-mass spectrometry</td>
</tr>
<tr>
<td>ISA</td>
<td>Ionic-strength adjusters</td>
</tr>
<tr>
<td>ISE</td>
<td>Ion-selective electrode</td>
</tr>
<tr>
<td>MLA</td>
<td>Mineral liberation analysis</td>
</tr>
<tr>
<td>ORP</td>
<td>Oxidation/reduction potential</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum group metals</td>
</tr>
<tr>
<td>PLS</td>
<td>Pregnant leach solution</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RH</td>
<td>Reverse phase</td>
</tr>
<tr>
<td>ROL</td>
<td>Rapid oxidative leach</td>
</tr>
<tr>
<td>RPC</td>
<td>Reverse phase chromatography</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>SCM</td>
<td>Shrinking core model</td>
</tr>
<tr>
<td>SDDC</td>
<td>Sodium-dimethyldithiocarbamate</td>
</tr>
<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electron</td>
</tr>
<tr>
<td>SMRt</td>
<td>Stirred media reactors</td>
</tr>
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<td>Term</td>
<td>Abbreviation</td>
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<tr>
<td>------</td>
<td>--------------</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid phase extraction</td>
</tr>
<tr>
<td>TA</td>
<td>Thioacetamide</td>
</tr>
<tr>
<td>TPOX</td>
<td>Total pressure oxidation</td>
</tr>
<tr>
<td>TSCA</td>
<td>Thiosemicarbazide</td>
</tr>
<tr>
<td>TU</td>
<td>Thiourea</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photo-emission spectrometry</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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My deepest appreciation to my parents, my brother, and my wife for always supporting and being patient during this arduous endeavor.
Dedication

For my father, my mother, and my beloved wife Nisa.
Chapter 1: Introduction

1.1 Research context and significance

Copper mine operations face increasing challenges of processing low-grade chalcopyrite ores with elevated concentrations of impurities, such as arsenic. Treatment of these materials by traditional ore beneficiation-pyrometallurgical processes can create a range of production and environmental problems. An additional challenge is the high consumption of water associated with concentrate production by froth flotation, especially in regions with scarce freshwater, such as northern Chile where many mining operations are located (Cochilco, 2017). A potential strategy to address these challenges is to directly process low-grade and complex copper sulfide ores on site instead of off-site smelting (Dreisinger, 2018). Hydrometallurgical methods may find niche applications for treating low-grade, complex primary copper concentrates and ores.

Heap leaching is considered to be an effective and economically viable technology for treating low-grade copper sulfide ores. Among all oxidants studied, ferric sulfate is the most commonly used lixiviant because of process simplicity, proven downstream processes, and low capital and operating costs (Watling, 2014, 2013). However, the dissolution of chalcopyrite in traditional ferric sulfate media at ambient temperature and pressure exhibits poor kinetics due to the so-called passivation (Hackl et al., 1995; O’Connor and Eksteen, 2020). The passivating layer has been reported to be metal-deficient sulfide (M_{1-x}S_{2}) (Buckley and Woods, 1984; Lu et al., 2000; Mikhlin et al., 2004), copper-rich, iron-deficient polysulfides (MS_n, n > 2) (Hackl et al., 1995), elemental sulfur (Dutrizac, 1989; Munoz et al., 1979), and iron precipitates (Antonijević and Bogdanović, 2004; Córdoba et al., 2008).
Various catalysts have been added in an attempt to accelerate chalcopyrite dissolution in ferric sulfate media, such as pyrite, silver, and carbon. Dixon et al. (2008) observed that the addition of pyrite could enhance chalcopyrite dissolution by providing alternative surfaces for ferric reduction. Nazari et al. (2011) reported that the amount of silver present in pyrite affected the effectiveness of pyrite as a catalyst, because silver was believed to react with sulfur on the surface of chalcopyrite, thus improving the conductivity of the product layer. Nakazawa (2018) showed that the addition of carbon black could enhance the kinetics of chalcopyrite dissolution at potentials less than 600 mV vs SHE via galvanic interactions.

JX Nippon Mining and Metals Corporation has developed a process named the iodine-assisted heap leaching of chalcopyrite. This process involves the addition of 50 – 200 mg/L iodide to significantly enhance the dissolution of chalcopyrite in ferric sulfate media at ambient temperature (Manabe, 2012). Some initial studies have focused on copper extraction in the process without considering the loss of iodine by evaporation (Granata et al., 2019; Manabe, 2012), resulting in potential underestimation of the rate of chalcopyrite dissolution. The key factors that control the reaction rate and the mechanisms by which iodine accelerates the leaching kinetics were not well understood. This knowledge is essential to optimize the performance of the JX iodine process in an industrial scale heap leach pad. This was the general motivation of the present research.

1.2 Research aims and general methodology

This research aims to comprehensively investigate the kinetics and mechanisms of copper extraction from the iodine-assisted heap leaching of chalcopyrite. Specifically, this research studied the effect of various leaching parameters on the rate of copper extraction from chalcopyrite in the presence of iodine (Chapter 5), developed kinetic equations that correlate copper extraction
with different process variables, including redox potential, iodide addition, temperature, and particle size (Chapter 6), elucidate the leaching mechanisms by examining the mineralogical and morphological transformation of chalcopyrite and pyrite under different leaching conditions (Chapter 7), and calibrated the kinetic model and evaluated the leaching performance in response to variations in the key design and operating parameters (Chapter 8).

To develop the kinetic equations, batch leaching tests of increasing scale and complexity were carried out, from 50-mL PTFE bottle tests, to 1-L fully-controlled reactor tests, to 1-m and 6-m column leaching tests. Iodine loss and material corrosion were prevented by using specially-designed fully-sealed reactors made of PTFE. To investigate the mineralogical and morphological transformation, solid surfaces were examined by X-ray diffraction (XRD), mineral liberation analysis (MLA), and X-ray photoelectron spectroscopy (XPS). Simulation of column and heap leaching were carried out using the HeapSim 2D software.

1.3 Thesis outline

This thesis is divided into nine chapters to show the current status of research and gaps in chalcopyrite leaching, the research objectives identified and research methods used, and the research findings on the kinetics and mechanisms of chalcopyrite leaching in ferric sulfate media in the presence of iodine.

Chapter 1 provides the general context of this research and the significance of studying chalcopyrite leaching in ferric sulfate media in the presence of iodine.

Chapter 2 provides a detailed literature review of chalcopyrite crystal structure, methods of copper extraction from chalcopyrite, sulfur chemistry, and hydrometallurgical processes for chalcopyrite treatment.
After literature review, the research gaps were identified and the research objectives were outlined in Chapter 3. Chapter 4 describes in detail the research methods applied to achieve the objectives outlined in Chapter 3.

Chapter 5 reports the experimental results on the effect of various leaching parameters on the rate of copper extraction from chalcopyrite in the presence of iodine and iodine speciation. The parameters studied including redox potential, total iodide added, temperature, and particle size. The leaching experiments were carried out in 50-mL PTFE bottles without controlling the redox potential.

Chapter 6 first reports the experimental results collected from the fully-controlled reactor and saturated column leaching tests to study the effect of different leaching parameters on the copper extraction in the iodine-assisted chalcopyrite leaching. These batch leaching data were then used to derive a kinetic equation that correlates the copper extraction as a function of redox potential, total iodide added, temperature, particle size.

Chapter 7 deals with the mineralogical and morphological characterizations of chalcopyrite concentrate and solid residues collected under different leaching conditions. The solid surfaces were characterized by XRD, MLA and XPS techniques.

Chapter 8 shows the calibration of the kinetic models using the 1-m and 6-m column leaching data and the application of the calibrated model to evaluate the performance of copper extraction in response to variations in key design and operating parameters.

Chapter 9 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 first reviews the research and process development of hydrometallurgical methods for treating chalcopyrite concentrate, including low-, medium-, and high-temperature processes. The nature of the passivating layers causing the slow leaching at low temperatures and the leaching kinetics and mechanisms are then reviewed. Given the decreasing ore grade and increasing levels of impurities, heap leaching of chalcopyrite whole ore is considered more economically and environmentally viable. The heap leach processes developed for processing chalcopyrite ore are summarized, with a focus on the iodine-assisted chalcopyrite leaching. The iodine speciation and analytical methods for measurement of iodine concentration were then reviewed. This Chapter finally reviews the application of the HeapSim 2D model to simulate heap leach performance.

2.2 Chalcopyrite crystal structure

Chalcopyrite is a covalent copper sulfide that is isostructural with sphalerite, but the c-parameter of the tetragonal unit cell of chalcopyrite is around twice the length of the unit cell of sphalerite (Li et al., 2013). The crystallized chalcopyrite does not contain metal-metal and sulfur-sulfur bonds. Instead, each sulfur atom is coordinated to four metal atoms, presenting only M-S-M tetrahedral linkages with two Cu and two Fe atoms occupying interstitial positions within the sulfur network (Hall and Stewart, 1973). The dimensions of the CuFeS₂ unit cell are a = b = 5.2890 Å and c = 10.4230 Å (Li et al., 2013). Figure 2.1 shows the Fe coordination is close to a perfect tetrahedron (109.47°), but Cu and S are coordinated in tetrahedra flattened in the z direction of the cell (108.68 – 111.06°). The Cu–S and Fe–S bond lengths are 2.30 Å and 2.26 Å, respectively (Hall and Stewart, 1973). The model of chalcopyrite unit cell is shown in Figure 2.1.
Figure 2.1 (a) Unit-cell model showing the crystal structure of chalcopyrite (large circle: sulfur, grey circle: copper, white circle: iron), (b) Interatomic bond lengths and angles of each atom in chalcopyrite (Hall and Stewart, 1973)

Chalcopyrite is a good conductor. Most natural chalcopyrite exists as n-type, which is characterized by the excess of metal in the compound. The p-type semiconductor, which is enriched by anions, has also been found in natural chalcopyrite from several locations and synthetic chalcopyrite (Shuey, 1975). The anodic dissolution of n-type minerals is slower than that of p-type minerals, because the anodic process in n-type semiconductors is limited by the diffusion of minority carriers to the surface (Crundwell, 1988).

Despite being different types of semiconductor, chalcopyrite dissolution is still very slow, compared with other copper minerals. The slow dissolution is more related to the covalency between the metal cations and S anions, which are the dominant bonds in the chalcopyrite structure (Shuey, 1975). The highest occupied orbitals (uppermost valence band) in chalcopyrite are Cu 3d – S 3p, while the lowest conduction band is Fe 3d (Figure 2.2). The band gap for chalcopyrite is approximately 0.53 - 0.6 eV (Crundwell, 1988; Tributsch and Bennett, 2007). To break the
covalent bonds, the electrons in the uppermost valence band need to be captured by a suitable redox couple, which is known as a hole formation process. The presence of a hole in the valence band means that one of the bonding electrons has been removed since bonding electron states belong to the valence band of the solid. As a result, the bond weakened. Holes can be supplied by the electrode interior as a result of an electrical current or injected into the valence band using an oxidizing agent (Crundwell, 1988). According to Parker et al. (1981), the rate of reduction of oxidants was in the order: \( \text{Br}_2, \text{CuCl}_2, \text{I}_3^- > \text{Fe(CN)}_6^{3-} > \text{FeCl}_3 > \text{Fe}_2(\text{SO}_4)_3, \text{Cl}_2 \).

![Figure 2.2 The energy level diagram of the chalcopyrite showing valence band contribution from the Cu 3d and S 3p orbitals and conduction band contribution from Fe 3d and the relative reduction potentials of various oxidant couples (Absolon, 2008; Crundwell, 1988).](image)

2.3 Overview of chalcopyrite processing technologies

Currently, around 83% of the global copper is produced by processing of copper ores, with the remaining produced by recycling (Pietrzyk and Tora, 2018). The copper ore processed is
dominated by chalcopyrite, which accounts for around 70% of global copper reserve (Singer, 2017).

![Pyrometallurgical process for copper sulfide ore](image)

**Figure 2.3 Pyrometallurgical process for copper sulfide ore (Schlesinger et al., 2011)**

The main route to extract copper from chalcopyrite is pyrometallurgy, consisting of concentration–smelting–electrorefining processes (Figure 2.3). Despite a proven technology, the pyrometallurgical method has several challenges associated with it. According to Cochilco (2017), the concentration process consumes large volumes of water. In 2016, around 82% of the seawater used in the mine plants was consumed by the concentration process. The percentage is predicted to increase because of increased concentrate production and decreasing ore grade. This is particularly challenging for mine operations located in regions with scarce freshwater, such as
northern Chile. Moreover, the presence of impurities such as arsenic and mercury in concentrates may result in emissions of toxic compounds during smelting. Another challenge is handling concentrates with toxic impurities during shipping of concentrates from mines to smelters (Dreisinger, 2018).

As an alternative to the pyrometallurgical route, various hydrometallurgical processes for processing chalcopyrite have been developed. Hydrometallurgical methods use different types of lixiviants in different leaching media, for example, sulfate, chloride, ammonia, or the combination of these lixiviants. However, dissolution of chalcopyrite may exhibit very slow kinetics under mild conditions due to surface passivation. To overcome the slow dissolution rate and incomplete leaching, various methods have been applied, including using oxidants stronger than ferric, adding catalysts, using microorganism to break sulfide matrix, increasing particle surface area by fine grinding, and increasing leaching temperature and pressure in an autoclave environment. These methods are reviewed here.

At temperatures $< 110 \, ^\circ C$, chalcopyrite leaches slowly and tends to form product layers composed of elemental sulfur or iron precipitates. Diffusion through the product layers tends to be the rate-limiting step in leaching. A copper-polysulfide passive film is also believed to form on chalcopyrite surface and hinder the leaching reaction (Hackl et al., 1995). In this case, the kinetics of copper leaching can be accelerated by using oxidants stronger than ferric, by addition of small amounts of catalysts, by using microorganism, or by increasing surface area and leaching temperature. Table 2.1 summarizes the studies of different oxidants stronger than ferric for chalcopyrite leaching at atmospheric pressure. Table 2.2 summarizes the studies of addition of different catalysts to enhance the rate of chalcopyrite dissolution.
Table 2.1 Overview of chalcopyrite leaching at atmospheric pressure using different oxidants

<table>
<thead>
<tr>
<th>Oxidants</th>
<th>Leaching media</th>
<th>Activation energy</th>
<th>Rate-limiting step</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent</td>
<td>mol/L</td>
<td>Media mol/L</td>
<td>$E_a$ (kJ/mol)</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>0.2</td>
<td>H$_2$SO$_4$ 0.5</td>
<td>49</td>
<td>30-80</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>0.1</td>
<td>H$_2$SO$_4$ 0.4</td>
<td>24</td>
<td>50-97</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>2</td>
<td>H$_2$SO$_4$ 2</td>
<td>60</td>
<td>25-50</td>
</tr>
<tr>
<td>Fe(SO$_4$)$_3$</td>
<td>0.21</td>
<td>H$_2$SO$_4$ 1</td>
<td>81.4</td>
<td>30-75</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>0.5-1.0</td>
<td>HCl 1</td>
<td>55.5</td>
<td>40-80</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>0.1</td>
<td>HCl 0.2</td>
<td>69</td>
<td>55-84</td>
</tr>
<tr>
<td>Fe(SO$_4$)$_3$</td>
<td>0.25</td>
<td>H$_2$SO$_4$ 1</td>
<td>83.7</td>
<td>60-90</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>0.79</td>
<td>Cl$^-$ 6.23</td>
<td>134.7</td>
<td>60-90</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0.005</td>
<td>NH$_3$ 0.25</td>
<td>50</td>
<td>16-35-35-60</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>0.6</td>
<td>H$_2$SO$_4$ 1.5</td>
<td>83</td>
<td>70-90</td>
</tr>
</tbody>
</table>

Table 2.2 Overview of the catalysts added in chalcopyrite leaching in ferric sulfate at atmospheric pressure

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Total iron (g/L)</th>
<th>Potential (mV vs SHE)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>13.3</td>
<td>624 – 684</td>
<td>Dixon et al., 2008</td>
</tr>
<tr>
<td>Ag + pyrite (100 mg Ag/1-kg pyrite)</td>
<td>14.0</td>
<td>619 – 649</td>
<td>Nazari et al., 2011</td>
</tr>
<tr>
<td>Black carbon</td>
<td>0 – 0.22</td>
<td>&lt; 600</td>
<td>Nakazawa, 2018</td>
</tr>
<tr>
<td>I$^-$ (0.003 mol/L)</td>
<td>12</td>
<td>-</td>
<td>Granata et al., 2019</td>
</tr>
<tr>
<td>I$^-$ (0.0012 mol/L)</td>
<td>10</td>
<td>669 – 769</td>
<td>This study</td>
</tr>
</tbody>
</table>

Another method to overcome the passivation on chalcopyrite surface is by using sulfur-oxidizing microorganisms in sulfate media. Ferric ions, which is the main oxidant in chalcopyrite leaching, can be regenerated by iron-oxidizing bacteria. All bioleaching processes for chalcopyrite are operated at temperature $> 40$ °C and fine solid particles to improve dissolution kinetics. The current bioleaching processes that have been developed are presented in Table 2.3. In addition, many atmospheric chemical leaching processes have also been developed for treating chalcopyrite (Table 2.4). In general, the processes are operated near the boiling temperature of water and require ultrafine grinding. Most of the sulfur is transformed to elemental sulfur as the leaching product.
### Table 2.3 An overview of the bioleaching processes developed for treating chalcopyrite

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature (°C)</th>
<th>Particle size (µm)</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mintek-BacTech</td>
<td>40 to 50 and 70 (high)</td>
<td>10 – 35</td>
<td>Fine grinding and high temperature bioleaching to overcome the slow leaching kinetic of chalcopyrite.</td>
<td>Gericke et al., 2009</td>
</tr>
<tr>
<td>BioCOP™</td>
<td>65 – 80</td>
<td>37</td>
<td>Temperature is higher than other bioleaching processes.</td>
<td>Batty and Rorke, 2006</td>
</tr>
<tr>
<td>BRISA</td>
<td>70</td>
<td>-</td>
<td>It comprises of two steps: chalcopyrite leaching in ferric sulfate solution and biooxidation of ferrous to ferric using mesophilic bacteria</td>
<td>Carranza et al., 1997a</td>
</tr>
<tr>
<td>GEOCOAT®</td>
<td>50</td>
<td>-</td>
<td>Concentrates are coated onto sized support barren rocks or low-grade ores.</td>
<td>Harvey et al., 2002</td>
</tr>
</tbody>
</table>

### Table 2.4 An overview of the atmospheric chemical leaching processes for processing chalcopyrite at temperatures < 100 °C

<table>
<thead>
<tr>
<th>Process</th>
<th>Media</th>
<th>Temperature (°C)</th>
<th>Particle size (µm)</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albion</td>
<td>Sulfate</td>
<td>85 – 90</td>
<td>10 – 15</td>
<td>Ultrafine grinding using the IsaMill technology, followed by atmospheric leaching at the boiling point of solution</td>
<td>Hourn et al., 1999</td>
</tr>
<tr>
<td>FLSmidth® Rapid Oxidative Leach (ROL)</td>
<td>Sulfate</td>
<td>80</td>
<td>-</td>
<td>Concentrates are leached in acidic ferric sulfate media in continuous stirred media reactors (SMRt) made of ceramic.</td>
<td>Mulligan, 2017</td>
</tr>
<tr>
<td>Galvanox™</td>
<td>Sulfate</td>
<td>80</td>
<td>75</td>
<td>Fine grinding is not required because of the absence of surface passivation. Pyrite acts as a catalytic surface for ferric reduction.</td>
<td>Dixon et al., 2008</td>
</tr>
<tr>
<td>HydroCopper™</td>
<td>Chloride/brine solution</td>
<td>85 – 95</td>
<td>-</td>
<td>Cupric ions are used as the oxidant to dissolve chalcopyrite in chloride media</td>
<td>Hietala and Varien, 2003</td>
</tr>
<tr>
<td>Intec Copper</td>
<td>Chloride</td>
<td>85</td>
<td>-</td>
<td>The process uses BrCl₂- (named “Halex™”) in chloride media to oxidize copper sulfides at a high potential of 900 mV vs Ag/AgCl</td>
<td>Moyes et al., 2002</td>
</tr>
<tr>
<td>Sumitomo</td>
<td>Chloride</td>
<td>110</td>
<td>-</td>
<td>Chlorine gas is used to oxidize chalcopyrite and generate cupric and ferric ions</td>
<td>Asano et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Imamura et al., 2006</td>
</tr>
<tr>
<td>Cuprex</td>
<td>Chloride</td>
<td>95</td>
<td>-</td>
<td>Ferric ion is the oxidant; all copper is dissolved as cupric ion and sulfide is converted to elemental sulfur</td>
<td>Dalton et al., 1991</td>
</tr>
<tr>
<td>Cymex</td>
<td>Chloride</td>
<td>98</td>
<td>-</td>
<td>It consists of four stages: oxidation using ferric and cupric chloride, reduction using fresh copper sulfides, electrolysis, and regeneration-purge</td>
<td>Kruesi, 1973</td>
</tr>
<tr>
<td>Arbiter</td>
<td>Ammonia</td>
<td>75 -80</td>
<td>-</td>
<td>Copper concentrate was leached with ammonia and oxygen at a low oxygen partial pressure.</td>
<td>Arbiter and Fletcher, 1994</td>
</tr>
</tbody>
</table>
At a medium temperature (~150 °C), the initial rate of chalcopyrite leaching is high. However, liquid elemental sulfur formed tends to block the chalcopyrite surface on partially leached particles, preventing full extraction. This can be overcome with the use of surfactants and medium-fine grinding of the concentrate. Sulfur is partially oxidized to sulfate; hence, the consumption of oxidant is higher than in the low temperature leaching processes. The hydrometallurgical processes developed for leaching chalcopyrite at medium temperatures are shown in Table 2.5.

At temperatures > 180 °C, chalcopyrite leaches quickly and completely with a high level of elemental sulfur oxidation to sulfate. At 220 °C, a leach time of less than 1 h is sufficient to achieve copper extractions higher than 98% (Dreisinger, 2005). Table 2.6 presents the high temperature leaching processes for treating chalcopyrite. The drawback of the high temperature processes is a high level of oxygen consumption due to the oxidation of sulfur to sulfate ions.

Table 2.5 Chemical leaching processes developed for treating chalcopyrite at medium operating temperatures

<table>
<thead>
<tr>
<th>Process</th>
<th>Media</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLEAR</td>
<td>Chloride</td>
<td>145</td>
<td>1</td>
<td>Chalcopyrite is oxidized at atmospheric pressure to cuprous chloride, followed by aggressive leaching to recover remaining copper.</td>
<td>Wilson and Fisher, 1981</td>
</tr>
<tr>
<td>Activox</td>
<td>Sulfate</td>
<td>90 – 110</td>
<td>10 – 12</td>
<td>The process incorporates ultrafine grinding and mild pressure and temperature conditions to overcome passivation.</td>
<td>Corrans and Angove, 1993</td>
</tr>
<tr>
<td>Anglo American-University of British Columbia (AAC/UBC)</td>
<td>Sulfate</td>
<td>150</td>
<td>10 – 12</td>
<td>Ultrafine grinding to overcome passivation and the addition of surfactants to disperse the molten elemental sulfur.</td>
<td>Dempsey and Dreisinger, 2003</td>
</tr>
<tr>
<td>Dynatec</td>
<td>Sulfate</td>
<td>150</td>
<td>10 – 12</td>
<td>Carbonaceous materials are added as additives</td>
<td>Collins and Kofluk, 1998</td>
</tr>
<tr>
<td>Noranda</td>
<td>Sulfate-chloride</td>
<td>135 – 145</td>
<td>18</td>
<td>chalcopyrite is leached in a mixture of HCl–CuCl₂–CuSO₄</td>
<td>Stanley et al., 1982</td>
</tr>
<tr>
<td>CESL</td>
<td>Sulfate-chloride</td>
<td>150</td>
<td>10 – 12</td>
<td>of surfactant is added to act as a sulfur dispersant.</td>
<td>Barr et al., 2005</td>
</tr>
</tbody>
</table>
Despite extensive efforts in research and process development, the hydrometallurgical technologies developed cannot achieve sustained commercial production due to low copper recoveries, difficulties in recovering platinum group metals (PGM), difficulties in recovering sulfur, and difficulties in stabilizing the leaching waste (Dreisinger, 2005). The current challenge of process development is to leach chalcopyrite quickly and completely with a high yield of elemental sulfur to minimize the consumption of oxidant.

### 2.4 Chalcopyrite passivation at ambient temperature

Passivation, as understood in corrosion, is caused by the formation of a layer composed of a new chemical species on the surface of the mineral. Different hypotheses exist to explain the nature of this layer in chalcopyrite leaching: elemental sulfur, iron precipitates, metal-deficient sulfide, and polysulfide.

- **Elemental sulfur layer**

  The Eh-pH diagram of the sulfur-water system indicates that increasing acid concentration and increasing sulfate concentration result in an increased area of stability of elemental sulfur (Figure 2.4). Dutrizac (1989) observed that elemental sulfur is the main reaction product from chalcopyrite leaching at 95 °C in ferric sulfate, with a small percentage of sulfate formation. The author reported

---

**Table 2.6 Chemical leaching processes developed for treating chalcopyrite at high operating temperatures**

<table>
<thead>
<tr>
<th>Process</th>
<th>Media</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure oxidation (TPOX)</td>
<td>Sulfate</td>
<td>220</td>
<td>30 – 40</td>
<td>It applies ultrafine grinding and surfactant addition. Sulfur is oxidized to sulfate</td>
<td>Dreisinger, 2006</td>
</tr>
<tr>
<td>PLATSOL™</td>
<td>Sulfate-chloride</td>
<td>220</td>
<td>30 – 40</td>
<td>It contains 5 – 10 g/L NaCl to dissolve PGM</td>
<td>Dreisinger, 2005</td>
</tr>
</tbody>
</table>
the formation of 94% elemental sulfur and less than 6% sulfate, regardless of the leaching time (0 – 70 h), the ferric concentration (0 – 2 M Fe(III)), and the chalcopyrite particle size. At temperatures lower than 200 °C, chalcopyrite dissolution in ferric solution produces elemental sulfur, which is found to cover chalcopyrite particles and act as a barrier to oxidant diffusion to chalcopyrite surfaces (Figure 2.5). This is believed to be responsible for surface passivation.

Figure 2.4 Eh-pH diagram of S-H2O system at 25 °C, solute activities of 1 M, and 1 atm pressure with the extended stability that is realized by a 300 kJ/mol barrier to the formation of sulfate (Peters, 1992)

Munoz et al. (1979) also observed sulfur coatings on chalcopyrite leached in ferric sulfate and proposed that the transport of electrons through the sulfur layer was rate-limiting. Wan et al. (1984) showed that when leaching was interrupted and S0 was removed, the initial reaction kinetics were restored. Dutrizac et al. (1969) reported that kinetics was influenced by a progressively thickening sulfur layer and the diffusion of ferric ions through this surface film
was rate-limiting, leading to parabolic leaching. The author also reported that acid had no effect beyond keeping iron in solution and those variations of ferric ions concentration only had an effect below 0.01 M. However, the formation of elemental sulfur layer is not universally accepted as the cause of slow chalcopyrite dissolution. Buttinelli et al. (1992) noted that chalcopyrite still leaches slowly even though $S^0$ is removed during leaching with an organic solvent.

![Figure 2.5](image)

**Figure 2.5** (a) The proportion of various sulfur species during sulfide oxidation at pH < 3 and in the temperature range from 0 – 175 °C (Mackiw et al., 1966); (b) Effect of temperature on the proportion of sulfur oxidized to $S^0$ vs $SO_4^{2-}$ at temperatures > 110 °C. (Hackl et al., 1995)

- **Iron precipitates**

Iron precipitates may coat chalcopyrite surfaces, thus reducing the dissolution rate (Córdoba et al., 2008). The formation of jarosite and other iron-hydroxy precipitates may retard chalcopyrite leaching by restricting the mass transfer of ions and by preventing Fe(III) access to the mineral surface. Ferric ions can be hydrolyzed according to Eqs. (2.1) – (2.4).

\[
\begin{align*}
\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} & = 2\text{Fe(OH)}_3 + 3\text{H}_2\text{SO}_4 \quad (2.1) \\
\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} & = 2\text{Fe(OH)}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \quad (2.2)
\end{align*}
\]
$\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} = 2\text{FeO(OH)} + 3\text{H}_2\text{SO}_4$ \hspace{1cm} (2.3)

$3 \text{Fe}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O} + 2A^+ = 2\text{AFe}_3(\text{SO}_4)_2(\text{OH})_6 + 5\text{H}_2\text{SO}_4 + 2\text{H}^+$ \hspace{1cm} (2.4)

where A represents K$^+$, Na$^+$, NH$_4^+$, H$_3$O$^+$, Ag$^+$ or (Pb$^{2+}$)$_{0.5}$

Ferric is mainly present in solution at pH values below 2. The precipitation of jarosite starts at around pH 2 in the presence of suitable monovalent cations. Jarosite formation cannot be avoided in ferric leaching in the temperature range of 20 to 100 °C. At pH values above 3, ferric completely precipitates to a range of insoluble iron precipitates, such as ferric hydroxide, goethite, and hematite. Hematite forms only at temperatures higher than 100 °C. It has been found that in high temperature and pressure processes, iron readily and rapidly precipitates as hematite or basic iron sulfate. However, formation of these species does not seem to impede chalcopyrite oxidation (Hackl et al., 1995). The precipitation of iron compounds reduces the concentration of ferric ions in solution, which could affect the ferric ion oxidative leaching (Klauber, 2008). Jarosite ($\text{HFe}_3(\text{SO}_4)_2(\text{OH})_6$) is sometimes proposed to inhibit chalcopyrite leaching, particularly in bioleaching applications that have high concentrations of ferric and sulfate ions. (Klauber, 2008) concluded that sulfur and iron precipitates are the most likely candidates causing the slow dissolution of chalcopyrite.

- **Metal-deficient sulfide**

Linge (1976) proposed that ferric leaching of chalcopyrite is too slow to be controlled by reactant/product diffusion through a porous sulfur layer and that the rate is controlled by a solid-state diffusion process. The passivating layer has been reported to be metal-deficient sulfide ($\text{M}_1\cdot\text{S}_2$) formed on chalcopyrite surfaces from a non-stoichiometric dissolution of iron and copper.
from CuFeS$_2$ structure (Buckley and Woods, 1984; Lu et al., 2000; Mikhlin et al., 2004). It was observed that iron was solubilized at twice the rate of copper and the term “metal-deficient chalcopyrite-like surface phase” was introduced (Linge, 1976).

- **Metal-deficient polysulfides**

Metal-deficient polysulfide refers to a bulk chalcopyrite but with different properties (Klauber, 2008; Parker et al., 1981). The metal-deficient sulfide and the polysulfide were distinctly different species (Hackl et al., 1995). Initially, iron is preferentially leached over copper and an intermediate disulfide phase is formed: Cu$_{1-x}$Fe$_{1-y}$S$_2$, where $y \gg x$ and $x + y = 1$. In the second stage, slower than the former one, the disulfide dissolves to form a copper polysulfide, Cu$_{1-x-z}$S$_2$, which is considered to be responsible for the passivation of chalcopyrite due to its slow dissolution (Córdoba et al., 2009). Hackl et al. (1995) identified polysulfide on chalcopyrite surface using X-ray photoelectron spectroscopy (XPS) and concluded that this polysulfide was the cause of passivation of chalcopyrite. However, Crundwell (2013) found that metal-deficient polysulfide did not hinder the dissolution reaction; Instead, the slow rate was caused by a low solution potential, which renders the leaching to occur in the “passive” region and produce polysulfides.

2.5 **Kinetics of chalcopyrite leaching**

2.5.1 **Kinetic models for sulfide mineral leaching**

Shrinking core model (SCM) is the commonly used kinetic model to determine the rate limiting step in mineral leaching. The model was firstly developed by Yagi and Kunii (1961, 1955). This model assumes that the particle is spherical in shape and the reaction occurs first at the outermost surface of the particle. The zone of reaction then moves towards the unreacted core of the solid, leaving behind completely converted material and inert solid. The unreacted core shrinks in size
over time during reaction. The steps for a reagent to react with the mineral include diffusion of the reactant through the film surrounding the particle to the surface of the solid, diffusion of the reactant through the ash layer to the surface of the unreacted core, and chemical reaction between the reactant and the solid at a reaction surface. The leaching rate is determined by the slowest step (Levenspiel, 1999).

Nicol (1993) and Dixon (1999) classified the leaching reactions into three types according to the polarization curves and the Butler-Volmer equation: type I, type II, and type III. Type I leaching occurs when the exchange current densities of both half cells are similar in magnitude, but the reversible potentials of the half cells are far apart. The rate-limiting step is the reduction of the oxidant on the mineral surface and the reaction order with respect to the ferric concentration is 0.5. In type II leaching, the exchange current density of the oxidant couple is much higher than that of the mineral dissolution and thus the mixed potential corresponds to the reversible potential of the oxidant. The dissolution reaction of type II is controlled by the rate of mineral dissolution and the dissolution rate is proportional to the square root of the concentration ratio of the oxidized and reduced forms of the oxidant. In type III leaching, reactions are fast and the reaction rate is limited by the mass transfer of oxidants to the mineral surfaces. The reversible potentials of the half-cell 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.
Figure 2.6 Polarization curve in electrochemical leaching mechanism: (a) Type I; (b) Type II; and (c) Type III (Dixon, 1999)

It is well known that chalcopyrite leaches extremely slowly in ferric sulfate media at ambient conditions (Dutrizac, 1989, 1981; Munoz et al., 1979). Some studies report a parabolic rate law and posit that the low rate of dissolution is caused by the slow diffusion of reactants or products through a passivating layer (Dutrizac, 1989; Dutrizac et al., 1969; Parker et al., 1981). Most studies found that the leaching rate was inversely related to the square of the initial particle size (Muñoz et al., 1979). These results support a diffusion-controlled mechanism of chalcopyrite dissolution.
In contrast, some researchers found that the leaching curve is linear over an extended leaching period (Jones and Peters, 1976). Another study reported initial parabolic kinetics followed by linear kinetics (Hirato et al., 1987), which was attributed to the initial formation of elemental sulfur layer and the absence of elemental layer in the latter stage of leaching. Parker et al. (1981) studied the electrochemical behavior of chalcopyrite leaching and showed that the oxidative dissolution of chalcopyrite was controlled by the formation of an unstable, metal-deficient polysulfide film on the surface of chalcopyrite. In spite of extensive research, controversies still exist over the nature of the passivating layer.

2.6 Heap leaching processes for chalcopyrite ore

Hydrometallurgical processes that have been discussed earlier in Section 2.3 are mainly focused on concentrate leaching. Given the challenges discussed above, including high water consumption in concentrate production and possible exposure to toxic elements such as arsenic and heavy metals, it is recommended that chalcopyrite ore be treated on mine sites (Dreisinger, 2018). As the copper ores are continuously exploited, the ore grade is reduced significantly and the levels of impurities increase. Heap leach technology is considered suitable to directly recover copper from low grade sulfide ores. Several heap leach processes have been developed for treating chalcopyrite, including hot heap, chloride leaching, Jetti process, and iodine leaching.

2.6.1 HotHeap™

HotHeap™ was developed by Geobiotics, which includes GEOCOAT® and GEOLEACH™. In the GEOCOAT® process, chalcopyrite is concentrated and coated onto sized support rock, while the GEOLEACH™ is applied in a whole ore system (Harvey and Bath, 2007). Both technologies use temperatures > 70 °C to optimize the biological performance (Pradhan et al., 2008). The main
idea of the GEOLEACH™ technology is that the oxidation of low-grade sulfide ores generates sufficient energy to achieve a desired temperature, but the increase in temperature could be hindered by poor heat management. High temperatures in the HotHeap™ technology can be achieved by carefully controlling aeration and irrigation rates.

2.6.2 Chloride heap leaching

Chloride heap leaching was developed by BHP Billiton SA Limited (Muller et al., 2011). It involves dissolution of primary copper sulfides in an acidic chloride-sulfate media in the presence of oxygen. The mineral surface potential is maintained between 550 and 600 mV vs SHE for an optimum chalcopyrite dissolution. The potential is controlled by manipulating the ratio of cupric and cuprous ions. The pH is preferably between 1 and 2 to prevent iron precipitation. The chloride concentration is controlled at a level of 5 – 100 g/L using HCl, chloride salt, sea water, or chloride containing process water. The proposed dissolution reactions occur through non-oxidative (Eq. (2.5)) and oxidative reactions (Eqs. (2.6) – (2.7)).

\[
\begin{align*}
    \text{CuFeS}_2 + 2\text{H}^+ &= \text{CuS} + \text{Fe}^{2+} + \text{H}_2\text{S}_{(aq)} \quad (2.5) \\
    \text{CuS} + 0.5\text{O}_2 + 2\text{H}^+ &= \text{Cu}^{2+} + \text{S}^0 + \text{H}_2\text{O} \quad (2.6) \\
    2\text{H}_2\text{S}_{(aq)} + 0.5\text{O}_2 &= 2\text{S}^0 + \text{H}_2\text{O} \quad (2.7)
\end{align*}
\]

2.6.3 Jetti process

Jetti process was developed by Prof. Dixon group in University of British Columbia. It is a leaching process of chalcopyrite in acidic ferric sulfate media using reagents that have a thiocarbonyl functional group as catalysts, including thiourea (TU), thioacetamide (TA), sodium - dimethyldithiocarbamate (SDDC), ethylene trithiocarbonate (ETC), and
thiosemicarbazide (TSCA) (Dixon et al., 2020). Among the reagents having thiocarbonyl functional group, thiourea has high water solubility and no complexation with targeted metal ions, ferric, and ferrous. Therefore, it is an effective catalyst to improve chalcopyrite dissolution rate. However, thiourea can react with ferric to form formamidine disulfide, which has no thiocarbonyl functional group. Formamidine disulfide can decompose to cyanamide and elemental sulfur (Grigorova and Wright, 1986). The process can be operated at temperature in the range of 0 to 80 °C and at atmospheric pressure.

2.6.4 JX iodine process

The JX iodine process was developed and patented by JX Nippon Mining and Metals Corporations. This process involves the addition of iodide into ferric sulfate media to accelerate the dissolution of primary copper sulfides, including chalcopyrite and enargite at ambient temperature. Ferric iron is regenerated in a separate heap or reactor (Figure 2.7).

It is proposed that iodide is oxidized by ferric to diiodine, which can act as a strong oxidant (Eq. (4.6)). Diiodine oxidizes chalcopyrite to release copper and iron and diiodine is reduced to iodide (Eq. (4.7)). Diiodine is continuously regenerated by ferric during leaching; hence, theoretically, the process does not require a continuous addition of iodine. As the chalcopyrite is oxidized, the concentration of ferric ions decreases during leaching. To maintain the concentration of ferric, ferrous ions in the pregnant leach solution are separately oxidized by iron-oxidizing bacteria (Kuwano et al., 2011).

\[
2I^- + 2Fe^{3+} = I_2 + 2Fe^{2+} \tag{2.8}
\]

\[
CuFeS_2 + 2I_2 = Cu^{2+} + Fe^{2+} + S + 4I^- \tag{2.9}
\]
Manabe (2012) reported that the addition of 200 mg/L iodide could significantly enhance the dissolution rate. Further increases in the iodide concentration to 300 mg/L did not significantly improve the dissolution. Furthermore, significant improvements were achieved when ferric was 0.8 times or higher than the mass of chalcopyrite. The loss of iodine by evaporation could lead to reduced leaching rates. The addition of sodium chloride up to 33 g/L NaCl could improve the leaching performance. Further addition of NaCl has an adverse effect on the copper extraction.

![Flow diagram of the iodine-assisted heap leaching of chalcopyrite](Kuwano et al., 2011)

Before the iron oxidation step, it is necessary to remove iodine from the leaching solution because iodine has high toxicity to the bacteria used in the bio-oxidation of ferrous to ferric. Iodine can be separated by using activated carbon. To recover iodine absorbed onto the activated carbon, the loaded activated carbon is eluted with sulfite ions. In this process, iodine adsorbed onto the activated carbon is reduced into iodide ions (I\(^{-}\)), which released into the solution (Eq. (2.10)) (Yiin and Margerum, 1990). The preferably weight ratio of sulfite to iodide during elution is 33 to 100.
The concentration of iodine less than 0.5 mg/L has no impact on the bacterial growth (Figure 2.8). Table 2.7 shows the corresponding iodine concentration in the solution after the addition of activated carbon (Kuwano et al., 2011).

\[
I_2 + H_2O + SO_3^{2-} = SO_4^{2-} + 2I^- + 2H^+ \tag{2.10}
\]

![Graph showing ferric concentration during biooxidation of ferrous after leaching solution containing 42 mg/L iodine is treated using activated carbon (Kuwano et al., 2011)](image)

Table 2.7 The final iodine concentration after the addition of activated carbon (Kuwano et al., 2011)

<table>
<thead>
<tr>
<th>Treated solution</th>
<th>Activated carbon (g/L)</th>
<th>Activated carbon per iodine (g/g)</th>
<th>Final iodine concentration after treatment (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>2.2</td>
<td>22</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>222</td>
<td>0.7</td>
</tr>
<tr>
<td>E</td>
<td>50</td>
<td>1111</td>
<td>0.5</td>
</tr>
</tbody>
</table>
2.7 Iodine chemistry and speciation

Iodine is a nonmetallic element of the halogen family, which makes up Group 17 of the periodic table. It has an atomic mass of 126.9044 and atomic number of 53. The resublimed crystalline iodine was first observed by the industrial chemist, B. Courtois, in 1811. The name, proposed by J. L. Gay Lussac in 1813, reflects this most characteristic property (Greek ιώδης, violet-coloured) (Greenstein, 2007). Iodine is recognized as an important element in the environment (Fuge and Johnson, 1986). Under normal environmental conditions, iodine can exist in the oxidation state –1 (iodide, I\(^-\)), 0 (diiodine, I\(_2\)), and +5 (iodate, IO\(_3^-\)). It can also possess oxidation state +1, +3, and +7 when forming compounds with other elements (Osterc et al., 2011). Under standard conditions, iodine in the form of diiodine is a lustrous, black solid with a glittering crystalline appearance. It melts at a relatively low temperature (113.7 °C) and turns dark brown although the liquid is often obscured by a dense violet vapor of gaseous iodine. The vapor pressure of iodine is 0.031 kPa at 25 °C and 9.17 kPa at 113.6 °C (Kaiho, 2014). It sublimes readily and boils at 185.2 °C (Greenwood and Earnshaw, 1997).

2.7.1 Solubility of iodine in water and salt solution

Unlike iodide ions, which is highly soluble in water, diiodine has a low solubility in water at 25 °C (0.34 g/kg-solvent), but it easily dissolved in most organic solvents (Table 2.8). The solubility of diiodine in water increases as temperature increases (Figure 2.9). Kracek (1931) reported that two liquid layers were formed in water-iodine solutions above 112.3° and that the mutual solubility increased with temperature. Below 112.3° the solutions are saturated with solid iodine. Solubility of diiodine as a function of temperature can be formulated as Eqs. (2.11) – (2.12) (Ramette and Sandford, 1965).
Table 2.8 Solubility of diiodine in various solvents at 25 °C (Kaiho, 2014)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Benzene</th>
<th>Butan-2-ol</th>
<th>Carbon disulfide</th>
<th>Carbon tetrachloride</th>
<th>Chloroform</th>
<th>Ether</th>
<th>Ethanol</th>
<th>Ethyl acetate</th>
<th>Hexane</th>
<th>Toluene</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (g/kg)</td>
<td>164</td>
<td>97</td>
<td>197</td>
<td>19.2</td>
<td>49.7</td>
<td>337.3</td>
<td>271.7</td>
<td>157</td>
<td>13.2</td>
<td>182.5</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Figure 2.9 Solubility of diiodine in water-iodine system up to 200 °C (Kracek, 1931)

\[ I_2(s) = I_2(aq) \quad K = f[I_2] \]  

\[ \log K \text{ (in } H_2O) = -2.18812 + 1.334 \times 10^{-2}(T - 25) + 2.52 \times 10^{-5}(T - 25)^2 \]  

where \( K \) is the equilibrium constant, \([I_2]\) is the diiodine molarity, \( f \) is the activity coefficient, and \( T \) is temperature in °C. Table 2.9 shows that the solubility of diiodine can also be increased by the addition of iodide ions to form triiodide anion (I\(_3^\text{-}\)) (Eq. (2.13)) (Kaiho, 2014; Palmer et al., 1984).
It also shows that the diiodine solubility increases with temperature regardless of the presence of iodide ions.

\[
\text{I}_2 (aq) + \text{I}^- (aq) = \text{I}_3^- (aq)
\]  

(2.13)

Table 2.9 Comparison of solubility of diiodine in solution in the absence of NaI and 10 g NaI/100 mL at different temperatures (Kaiho, 2014)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in the absence of NaI</td>
<td>0.293</td>
<td>0.399</td>
<td>0.549</td>
<td>0.769</td>
<td>1.06</td>
</tr>
<tr>
<td>Solubility in 10 g NaI/100 mL</td>
<td>9.6</td>
<td>10.3</td>
<td>10.9</td>
<td>11.7</td>
<td>13.6</td>
</tr>
</tbody>
</table>

2.7.2 Eh-pH diagram of I-H_2O system

The Eh-pH diagram of I-H_2O system at 25 °C is shown in Figure 2.10 constructed using the HSC database (Table 2.10) (Yang, 1997). Iodine can exist in the form of iodide (I^-), triiodide (I_3^-), diiodine (I_2), iodate acid (HIO_3), iodate (IO_3^-), and periodate (IO_4^-), depending on the potential and pH ranges. Iodide is the dominant species when an oxidant is not present. At a higher solution potential associated with the presence of an oxidant, iodide is oxidized to triiodide, diiodine, iodate, or periodate.

Table 2.10 Potential of half-cell reactions for iodide species at 25 °C (Yang, 1997)

<table>
<thead>
<tr>
<th>Half cell reaction</th>
<th>Potential (V vs SHE) at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3I^- = I_3^- + 2e^-</td>
<td>0.536 + 0.0295 log ([I_3^-]/[I^-]^3)</td>
</tr>
<tr>
<td>2I^- = I_2 + 2e^-</td>
<td>0.621 + 0.0295 log ([I_2]/[I^-]^2)</td>
</tr>
<tr>
<td>I^- + 3H_2O = HIO_3 + 5H^+ + 6e^-</td>
<td>1.077 – 0.0493 pH + 0.0098 log ([HIO_3]/[I^-])</td>
</tr>
<tr>
<td>I^- + 3H_2O = IO_3^- + 6H^+ + 6e^-</td>
<td>1.085 – 0.0591 pH + 0.0098 log ([IO_3^-]/[I^-])</td>
</tr>
<tr>
<td>2I_3^- = 3I_2 + 2e^-</td>
<td>0.789 + 0.025 log ([I_2]^3/[I_3^-]^2)</td>
</tr>
<tr>
<td>I_3^- + 9H_2O = 3HIO_3 + 15H^+ + 16e^-</td>
<td>1.145 – 0.0554 pH + 0.0037 log ([HIO_3]^3/[I^-])</td>
</tr>
<tr>
<td>I_3^- + 9H_2O = 3IO_3^- + 18H^+ + 16e^-</td>
<td>1.154 – 0.0665 pH + 0.0037 log ([IO_3^-]^3/[I^-])</td>
</tr>
<tr>
<td>I_2 + 6H_2O = 2HIO_3 + 10H^+ + 10e^-</td>
<td>1.169 – 0.0591 pH + 0.0059 log ([HIO_3]^2/[I_2])</td>
</tr>
<tr>
<td>I_2 + 6H_2O = 2IO_3^- + 12H^+ + 10e^-</td>
<td>1.178 – 0.0709 pH + 0.0059 log ([IO_3^-]^2/[I_2])</td>
</tr>
</tbody>
</table>
2.7.3 I-Fe-H$_2$O system

In the presence of ferric ions, iodide can be oxidized to diiodine or triiodide via Eqs. (2.14) – (2.15) (Fudge and Sykes, 1952; Nikolaychuk and Kuvaaeva, 2016). The reaction rate is temperature dependent. The equilibrium is achieved within 3 – 4 h at the room temperature, 1.5 – 2 h at 35 – 45 °C, and 40 – 70 min at 45 – 50 °C (Nikolaychuk and Kuvaaeva, 2016).

\[
2\text{Fe}^{3+} + 2\text{I}^- = 2\text{Fe}^{2+} + \text{I}_2 \quad (2.14)
\]

\[
2\text{Fe}^{3+} + 3\text{I}^- = 2\text{Fe}^{2+} + \text{I}_3^- \quad (2.15)
\]

Kistiakowsky (1927) reported that the iodide oxidation reaction by ferric ions to produce ferrous ions and iodine is reversible and photosensitive (Eq. (2.16)).
**dark**

\[
2\text{Fe}^{3+} + 2\Gamma \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_2
\]

**light**

\[
2\text{Fe}^{3+} + 2\Gamma \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_2
\]

### 2.7.4 I-S-H\text{H}_2\text{O} system

In the presence of persulfate ions, iodide can be oxidized in acidic and neutral solutions via Eqs. (2.17) – (2.18) (Moews and Petrucci, 1964; Yang, 1997). The oxidation reaction is second order and the rate is dependent upon iodide and persulfate concentrations.

\[
\text{S}_2\text{O}_8^{2-} + 3\Gamma = 2\text{SO}_4^{2-} + \text{I}_3^{-} \tag{2.17}
\]

\[
\text{S}_2\text{O}_8^{2-} + 3\Gamma + 2\text{H}^+ = 2\text{HSO}_4^{-} + \text{I}_3^{-} \tag{2.18}
\]

In the presence of hydrogen sulfite (\(\text{HSO}_3^{-}\)) or thiosulfate (\(\text{S}_2\text{O}_3^{2-}\)), diiodine and triiodide can be rapidly reduced to iodide ions via Eqs. (2.19) – (2.20).

\[
\text{I}_2 + \text{HSO}_3^{-} + \text{H}_2\text{O} = 2\Gamma + \text{SO}_4^{2-} + 3\text{H}^+ \tag{2.19}
\]

\[
\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} + = 2\Gamma + \text{S}_4\text{O}_6^{2-} \tag{2.20}
\]

Carter (1928) studied the equilibrium triiodide concentration in pure water and sodium sulfate solution. It is found that the value of \([\Gamma]/[\text{I}_3^{-}]\) ratio is about 1.05 for the sulfate-free solutions and about 3.5 for the sulfate solutions containing 1.698 M sodium sulfate. It indicates that the extent of polyiodide formation is greatly depressed in the presence of sulfate ions.

### 2.7.5 I-Cu-H\text{H}_2\text{O} system

Iodide ions can react with copper ions to form copper (I) iodide (CuI) precipitate, as shown in Figure 2.11. The \(K_{sp}\) of CuI in water is around \(1.1 \times 10^{-12}\) (Haq et al., 1980). The half-cell reactions involving CuI and the corresponding potentials as a function of concentrations at 25 °C are presented as Eq. (2.21) and (2.22) (Wu et al., 1993). To avoid the formation of CuI precipitate, it
is necessary to maintain solution potential sufficiently high and control the concentration of dissolved copper and total iodide in the solution.

$$\text{Cu} + \Gamma = \text{CuI} + e^- \quad \text{E (V vs SHE)} = -0.1852 + 0.059 \log ([\Gamma]) \quad (2.21)$$

$$\text{CuI} = \text{Cu}^{2+} + \Gamma + e^- \quad \text{E (V vs SHE)} = 0.86 + 0.059 \log ([\text{Cu}^{2+}][\Gamma]) \quad (2.22)$$

![Figure 2.11 Eh-pH diagram of Cu-I-H$_2$O system (V vs SHE) at 25 °C for 10$^{-6}$ M Cu$^{2+}$ and 10$^{-2}$ M I$^-$. Redrawn from Wu et al., 1993)](image)

2.7.6 Iodine adsorption on platinum, pyrite and minerals

Hubbard et al. (1966) observed that iodide ions and diiodine were rapidly adsorbed on a platinum surface. The adsorption process for iodide ion is irreversible. To remove the adsorbed iodide, potential needs to be adjusted to the iodate region (E > 1.1V vs. SCE) in 1 M H$_2$SO$_4$ (Johnson, 1972). Diodine can adsorb and desorb from the platinum surface in the presence of iodide ion. Without iodide ion, the desorption of diiodine can be achieved by adjusting the potential to the iodate region, similar to the case of iodide desorption. The attachment of iodide onto the platinum
surface results in a lower potential measurement due to iodide ions concentrating around the platinum surface, leading to inaccurate measurements of the bulk potential.

It is reported that iodide ions are also adsorbed on sulfide minerals and oxides. Balsley et al. (1996) found that iodide ions are strongly adsorbed on cinnabar (HgS) and chalcocite (Cu\textsubscript{2}S) by exchanging hydroxyls attached to Hg and Cu sites. Aimoz et al. (2011) reported a low level of iodide adsorption on pyrite in water. The authors suggested that iodide sorption was linked to the presence of oxidized clusters on the pyrite surface, which were presumably formed by the reaction with limited amounts of dissolved oxygen. In term of clays and other silicates, the adsorption of iodide ions is insignificant because their surfaces are negatively charged at neutral to alkaline pH prevailing in such environments (Aimoz et al., 2011; Nagra, 2002). Iodide can also be adsorbed on oxides, such as cuprite (Cu\textsubscript{2}O), and zeolite that contains silver, lead or thallium (Faghihian et al., 2002; Lefèvre et al., 2000). Iodide adsorption on cuprite surface occurs through the formation of CuI precipitates on cuprite surface at lower pH and substitution of hydroxyl groups on cuprite surface in alkaline pH (Lefèvre et al., 2000). Moreover, Dai et al. (2009) investigated the adsorption and desorption of iodide and iodate ions by various type of soils and found that soils rich in organic matters and with a high cation exchange capacity had high affinities for iodide, but low iodate adsorption.

2.7.7 Analytical techniques for determination of iodine concentration

Techniques for measurement of the total iodine concentration can be classified into direct and indirect methods. The direct method measures all forms of iodine present in a liquid sample. Indirect measurement involves treating a sample to convert all iodine forms to a specific iodine species, which can be measured using an analytical instrument (Moreda-Piñeiro et al., 2011).
Atomic absorption spectrometry (AAS) is a common instrument to determine the concentration of a metallic element, but typically unsuitable for measuring the concentration of non-metallic elements, such as iodine (Bermejo-Barrera et al., 1999). This is mainly because resonance lines for iodine, among other halides, are within the vacuum UV region, in which air is an important interference. Therefore, all iodine forms are converted to iodide with the use of a metal and the measurement of the fraction of the metal reacted indirectly measures the total iodide concentration (Bermejo-Barrera et al., 2001).

Other spectrometric techniques for determination of iodine concentrations include inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). ICP-OES requires generation of molecular iodine by oxidizing iodine forms with nitrite in hydrochloric acid followed by direct vapor introduction (Anderson and Markowski, 2000). ICP-MS can directly be applied to measure total iodine in aqueous solutions, such as water, seawater, and drinking water with the highest sensitivity (Moreda-Piñeiro et al., 2011). Moreda-Piñeiro et al. (2011) summarized that ICP-MS is the most widely used analytical technique for iodine determination in solid samples, for instance, rock, soil, and coal. However, sample preparations such as wet digestion, pyrohydrolysis, and ashing methods can lead to inaccurate measurements of iodine due to iodine losses (Fecher et al., 1998).

High performance liquid chromatography (HPLC) operated in reverse phase (RP) mode and with UV or electrochemical detection can also be used to assess total iodine. However, these techniques require the conversion of all iodine forms to iodide (Andersson and Forsman, 1997; Rebary et al., 2010).
To measure iodine speciation, samples need to be pre-treated to isolate iodine species. The pre-treatments depend on the type of the sample. The pre-treatments include direct analysis, redox speciation, solid phase extraction (SPE), liquid-liquid and solid-liquid extractions, enzymatic hydrolysis, and distillation (Moreda-Piñeiro et al., 2011). The most common technique to measure iodine species is high performance liquid chromatography (HPLC), mainly based on anion exchange properties of the iodine forms. In addition to anion exchange chromatography (AEC), separations by reverse phase chromatography (RPC) and size exclusion chromatography (SEC) have been used to determine iodine species (Moreda-Piñeiro et al., 2011). Because of the volatile nature of some iodine species, gas chromatography (GC), mainly with MS detection, has also been used for iodine determination/speciation (McConnell and Fenical, 1977; Moreda-Piñeiro et al., 2011).

2.7.8 **Ion-selective electrode**

Ion-selective electrodes (ISEs) are used in a wide variety of applications for determining the concentrations of various ions in aqueous solutions (Oh et al., 2015). ISEs are based on ion-selective membranes, i.e., regions of space that separate two phases in such a way that material transport between the outer, contacting phases is in some way modified or inhibited compared to transport that would occur when the phases are in direct contact (Figure 2.12). Membranes can be made of glass, a crystalline solid, or a liquid. They are usually thick enough that they possess an inside region and two outer, boundary-defining surfaces that separate the membrane from the exterior phases.
Figure 2.12 Schematic of an ion-selective electrode (Freiser, 1978)

The potential difference across the membrane is measured with two reference electrodes positioned in the respective aqueous phases (Amemiya, 2007). Potentials arising at interfaces in membrane systems can be affected by the difference in single-ion chemical potentials, abrupt concentration changes, and accumulation of adsorbed ions and aligned dipoles (Freiser, 1978). Under equilibrium conditions, the measured potential (or emf of the cell), $E$, can be expressed as Eq. (2.23).

$$E = E_i^0 + \frac{RT}{z_iF} \ln a_i^w$$  \hspace{1cm} (2.23)

Where $E$ is the measured potential, $E_i^0$ is the sum of the potential differences at all interfaces other than the membrane/sample solution interface, $z_i$ is the charge of the analyte ion, $a_i^w$ is the activity of analyte ions in the sample solution. The value of $E_i^0$ is unique and a constant term for particular analyte ions (Amemiya, 2007).

Three types of ion selective electrodes are available, i.e., solid state electrode, liquid membrane electrode, and gas sensor electrode. Solid state and liquid membrane electrodes are available as both single half-cells or as combination electrodes with reference electrode included. A solid state electrode incorporates a solid sensing surface made of compressed silver halides, or solid
crystalline material. A solid state electrode produces a voltage due to ion exchange occurring between the sample and the inorganic membrane. An equilibrium mechanism occurs due to the very limited solubility. The ISE for determining iodide concentration is categorized as a solid state electrode with silver iodide as the solid sensing surface (Instruments, 2022). A liquid membrane electrode has a sensing surface made of a homogeneous polymer matrix containing organic ion-exchangers selective for the ion of interest. A gas sensor electrode is a combination electrode that detects dissolved gases, such as ammonia and carbon dioxide. The sensing element is separated from the sample (Instruments, 2022).

The use of ISE is limited by interference from other ions. No ISE is completely ion-specific. ISEs are sensitive to other ions having similar physical properties, the extent of which depends on the degree of similarity. For these reasons, ionic-strength adjusters (ISA) are added into sample solutions to enhance sensitivity of detection of the target ions (Adams and Kramer, 1999).

2.8 Heap leach modelling

Heap leach modelling is an essential tool to understand the effect of key design parameters on the extraction rate and determine the optimum key design parameters in a heap leach process. A mathematical model of heap leaching accounts for the heap hydrology, mineral dissolution reactions, gangue reactions, mass transport of lixiviants and gaseous species, and heat transport (van Staden and Petersen, 2021). These processes are intimately linked. Heap hydrology is a key factor that determines the percolation of leaching solution and the distribution of moisture within a heap. Miller (2003) concluded that a significant proportion of the moisture in a bed of rock is immobile, whereas mobile solution flow occurs via relatively sparsely distributed channels on the outside of the immobile zones.
Mineral dissolution reactions can affect the overall heap leaching kinetics. However, an instantaneous chemical dissolution reaction with respect to the time scale of heap leaching is not expected to govern the overall heap leaching kinetics because of the mineral depletion as soon as the heap leaching is started. The gangue minerals can hinder the dissolution rate of valuable minerals due to the acid consumption, causing precipitation of solute or passivate the mineral surfaces (van Staden and Petersen, 2021).

The rate of transport of solutes, including reagents and dissolved elements can be described by Fick’s first law of diffusion (Eq. (2.24)). The flux ($J$) of a diffusing species through a conductive medium is proportional to the free diffusivity ($D$) and the concentration gradient ($\partial C$) along the spatial dimension ($\partial Q$), from the position of a higher concentration to a lower concentration (van Staden and Petersen, 2021).

$$J = -D \frac{\partial C}{\partial r}$$

(2.24)

The water volume and gas mass flux can be described by Darcy’s law (Eq. (2.25)).

$$\frac{Q}{A} = \frac{K \Delta P}{\mu L}$$

(2.25)

where $Q$ is flow rate (cm$^3$/s), $A$ is area of column (cm$^2$), $K$ is permeability (cm$^2$), $\Delta P$ is pressure difference ($\rho gh$), $\rho$ is density of water (kg/cm$^3$), $g$ is acceleration due to gravity (cm/s$^2$), $h$ is head difference between solution inlet and outlet (cm), $\mu$ is viscosity of water (kg/(cm s)), and $L$ is the length of the column occupied by the agglomerates (cm) (Dhawan et al., 2013).

Heap leach models, specifically, the HeapSim 2D model used in the present study, require various input parameters. The HeapSim 2D model, a Microsoft Excel package, was originally developed
in the UBC hydrometallurgy group by Professor Dixon and his coworkers. The model simulates copper heap leaching by incorporating five fundamental processes that can occur in a heap leach process: (1) the transport of leaching solution that provides lixiviants to ore surfaces and carries reaction products away from ore surfaces; (2) gas and gas species transport that provides oxygen and carbon dioxide for microbial activities; (3) chemical leaching reaction kinetics; (4) microbial activities that convert ferrous to ferric and elemental sulfur to sulfate; and (5) heat transport that controls heap temperature. The model contains a large number of input variables (independent variables), which are user-defined design variables and have clear physical meaning. Examples are heap height, irrigation rate, and ore characteristics. The input variables can be directly manipulated by mine operations to optimize the heap leach design. The model output variables (dependent variables) are PLS composition (concentrations of copper, total iron, acid, pH and Eh) and heap temperature. A user interacts with the model through a graphical user interface. Figure 2.13 shows a snapshot of the user interface.

In the application of the model, the most challenging task is to obtain reliable values for the model parameters contained in the equations that define the relationships between the model input and output. The input parameters can be classified into three categories, i.e., design parameters, empirical parameters, and fundamental parameters (Petersen and Dixon, 2007). Design parameters are user-defined operating parameters with clear physical meaning. The values can be directly manipulated by mine operations to achieve the desired outcome. Examples of design parameters are irrigation rate, dripping spacing, heap height, and initial moisture. Unlike design parameters, the values of empirical parameters are obtained from either the laboratory or estimated based on the operational experience. Some empirical parameters may not possess clear physical meaning.
For instance, the value of $m$ factor in the VGM model to define the relative hydraulic permeability is adjusted in the calibration process. Fundamental parameters represent the intrinsic properties of materials and processes. The values of fundamental parameters are not expected to change significantly from one operation to another, e.g., molecular mass (Liu and Hashemzadeh, 2017).

![Figure 2.13 Snapshot of HeapSim 2D model user interface](image)

Figure 2.13 Snapshot of HeapSim 2D model user interface

The HeapSim model has been applied to assess and simulate solution flow, heap temperature profile, and microbial activities in bioleaching within columns and heaps (Bouffard and Dixon, 2009a; Liu and Granata, 2018; Liu and Hashemzadeh, 2017). It has also been used to simulate the performance of biooxidation of pyrite, bioleaching of zinc from sphalerite, and bioleaching of chalcocite (Bouffard, 2008; Bouffard and Dixon, 2009a, 2009b; Petersen and Dixon, 2007, 2003).
Chapter 3: Research gaps and objectives

3.1 Research gaps

The following research gaps were identified from the literature review regarding copper leaching from chalcopyrite in ferric sulfate media.

The factors affecting chalcopyrite leaching in ferric sulfate media in the presence of iodine were not well understood.

Chalcopyrite leaching in ferric sulfate media has been extensively studied (Córdoba et al., 2009; Dutrizac, 1989; Nazari and Asselin, 2009). The dissolution at ambient conditions exhibits slow kinetics due to the so-called passivation. The addition of iodine to ferric sulfate media has been found to enhance the dissolution at ambient conditions (Granata et al., 2019; Manabe, 2012; Miura et al., 2016). However, it is not well understood what factors could affect the behavior of chalcopyrite leaching in ferric sulfate media in the presence of iodine. The volatility and corrosive behavior of iodine make it particularly challenging to study the process.

The kinetics of the iodine-assisted chalcopyrite leaching in ferric sulfate media was not studied.

There was no kinetic equation to correlate copper extraction with key factors that determine the performance of the iodine-assisted chalcopyrite leaching. Kinetic equations are essential for subsequent scale up of the process from laboratory to pilot to full-scale heap leach pads. Development of a kinetic equation requires careful interpretation of batch leaching data collected
under fully-controlled leaching conditions, such as redox potential, pH, temperature, and lixiviant concentration.

**It is not well understood whether chalcopyrite surface would passivate in the iodine-assisted chalcopyrite leaching process.**

The reason for the slow dissolution of chalcopyrite in ferric sulfate media is proposed to be the formation of a passivation layer, which could be elemental sulfur, iron precipitates, metal-deficient sulfides, and polysulfides (Klauber, 2008; O’Connor and Eksteen, 2020). It was unclear whether passivation would still exist in the presence of iodine.

**It is essential to scale up the iodine-assisted chalcopyrite leaching process from laboratory to pilot to commercial-scale heap leach.**

To scale up the process to industrial-scale heap leaching, it is essential to understand the fundamental processes that control the performance of the iodine-assisted chalcopyrite leaching in a heap leach environment. These fundamental processes include hydrodynamics, reactions kinetics and heat transport, which can be controlled by manipulating various design variables, such as ore crush size, irrigation method and solution composition. This task can be effectively achieved by mathematical modelling assisted by carefully-designed laboratory column testing that provides reliable values for the model parameters.

### 3.2 Research objectives

To address the research gaps outlined above, the main objective of the present study was to quantify the leaching kinetics of increasing scale and understand the mechanisms by which chalcopyrite is leached in the presence of iodine in ferric sulfate media. This knowledge is
necessary to optimize the performance of the iodine-assisted chalcopyrite leaching in an industrial-scale heap leach pad.

**Objective I:** To investigate the effect of various leaching parameters on the rate of copper extraction from chalcopyrite in the presence of iodine and iodine speciation (results reported in Chapter 5).

**Objective II:** To develop kinetic equations for the iodine-assisted chalcopyrite dissolution in ferric sulfate media via collecting and interpreting fully-controlled batch reactor leaching data (results reported in Chapter 6).

**Objective III:** To examine the mineralogical and morphological transformation of chalcopyrite and pyrite under different leaching conditions by various surface characterization techniques (results reported in Chapter 7).

**Objective IV:** To calibrate the kinetic model using the data collected from 1-m and 6-m column leaching tests and to evaluate the performance of copper extraction in response to variations in key design and operating parameters (results reported in Chapter 8).
Chapter 4: Research methods

4.1 Introduction

This Chapter describes the research methods applied to achieve the research objectives. Objective I aimed to investigate the effect of various leaching parameters on the kinetics of chalcopyrite dissolution in the presence of iodine. The detailed research method for Objective I was described in Section 4.2. Objective II aimed to refine the kinetic equation of chalcopyrite leaching in ferric sulfate in the presence of iodine. The research method for objective II was explained in Section 4.3. Section 4.4 describes the research method for Objective III, which was to examine solid surface properties of the leach residues by various surface characterization techniques. The research method for Objective IV was described in Section 4.5. Objective IV aimed to calibrate the kinetic equation of chalcopyrite leaching in ferric sulfate media using 1-m and 6-m column leaching data.

4.2 Research methods for Objective I

Objective I: To investigate the effect of various leaching parameters on the rate of copper extraction from chalcopyrite in the presence of iodine and iodine speciation

4.2.1 Experimental design

The main objective of the leaching experiments was to investigate the effect of various leaching parameters on the kinetics of copper extraction from chalcopyrite in the presence of iodine. The overall experimental design is presented in Table 4.1. The range of each leaching parameter was chosen in reference to the study carried out by Manabe (2012). The initial solution potential used was in the range of 660 to 771 mV vs SHE (standard hydrogen electrode), a range relevant to heap
leaching. A desired value was obtained by adjusting the ratio of total Fe(III) to total Fe(II) in a solution. The total iron concentration was maintained at 10 g/L, higher than the typical range of 2 – 5 g/L in heap leaching. This was chosen to prevent solution potential from decreasing to less than 621 mV vs SHE, where the formation of CuI precipitate becomes possible. The iodide concentration was varied from 0 to 200 mg/L, beyond which no significant increase in copper extraction was observed in the previous shaking flask tests carried out by Manabe (2012). Chalcopyrite concentrate was used in the leaching tests with particle size in three fractions in the range of 38 to 90 µm. Polytetrafluoroethylene (PTFE) bottles of 50 mL equipped with a screw thread cap were used to prevent iodine loss by evaporation and corrosion of experimental apparatus by iodine. A total of seven PTFE bottles containing solutions of identical composition were used to obtain one leaching curve, each representing one data point in the curve.

4.2.2 Materials

The chalcopyrite concentrate sample was provided by JX Nippon Mining and Metals Corporation. Prior to leaching, the concentrate was wet sieved to obtain three size fractions: − 90 + 75 µm, − 75 + 53 µm, and − 53 + 38 µm. Each size fraction was washed in acetone to remove organic flotation reagents on the mineral surfaces, followed by sulfuric acid washing (1 mol/L) to remove acid soluble copper minerals. The solid sample collected through filtration was washed by dilute sulfuric acid and deionized water and then dried in an oven at 50 °C. This washed concentrate sample was characterized by X-ray Diffraction and head grade analysis (Section 4.2.3).
Table 4.1 Experimental design to investigate the effect of solution potential, iodide concentration, particle size and temperature on iodine-assisted chalcopyrite leaching in ferric sulfate media

<table>
<thead>
<tr>
<th>Leaching parameters</th>
<th>Initial potential (mV vs SHE)</th>
<th>[Fe(III)] (g/L)</th>
<th>[Fe(II)] (g/L)</th>
<th>Initial [I⁻] (mg/L)</th>
<th>Particle size (µm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution potential</td>
<td>769</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>725</td>
<td>9</td>
<td>1</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
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<tr>
<td></td>
<td>704</td>
<td>8</td>
<td>2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>5</td>
<td>5</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td>Iodide concentration</td>
<td>768</td>
<td>9.8</td>
<td>0.2</td>
<td>200</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>769</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>9.8</td>
<td>0.2</td>
<td>100</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>768</td>
<td>9.8</td>
<td>0.2</td>
<td>50</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>769</td>
<td>9.8</td>
<td>0.2</td>
<td>0</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>666</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td>Particle size</td>
<td>769</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 53 + 38</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>766</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>765</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 90 + 75</td>
<td>25</td>
</tr>
<tr>
<td>Temperature</td>
<td>769</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>766</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>767</td>
<td>9.8</td>
<td>0.2</td>
<td>150</td>
<td>– 75 + 53</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>665</td>
<td>5</td>
<td>5</td>
<td>150</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>667</td>
<td>5</td>
<td>5</td>
<td>150</td>
<td>– 75 + 53</td>
<td>35</td>
</tr>
<tr>
<td>Iodine species</td>
<td>889</td>
<td>0</td>
<td>0</td>
<td>100 (as diiodine)</td>
<td>– 75 + 53</td>
<td>25</td>
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<tr>
<td></td>
<td>494</td>
<td>0</td>
<td>0</td>
<td>170</td>
<td>– 75 + 53</td>
<td>25</td>
</tr>
</tbody>
</table>

All chemical reagents used were of analytical grade. Ferric sulfate Fe₂(SO₄)₃ was purchased from Acros Organics, and ferrous sulfate FeSO₄ and potassium iodide KI were purchased from Sigma Aldrich. Stock solutions of 20 g/L Fe(III) as ferric sulfate, 10 g/L Fe(II) as ferrous sulfate, and 12.5 g/L I⁻ as potassium iodide were separately prepared. Ferric and ferrous sulfate were dissolved in acidified deionized water (pH 1.7) to prevent iron hydrolysis. Potassium iodide was directly dissolved in deionized water. Saturated potassium chloride from LabChem was used for refilling pH electrodes and 4 M potassium chloride saturated with silver chloride from Fisher Scientific was used for refilling the ORP electrodes.
4.2.3 Characterization of the chalcopyrite concentrate sample

The mineralogy of the as-received chalcopyrite concentrate sample used was characterized by X-ray Diffraction. The diffractogram was analyzed using the International Centre for Diffraction Database PDF-4 with the Search-Match software by Bruker. The particle size of the concentrate sample was reduced to the optimum range for quantitative X-ray analysis (< 10 µm) by grinding under ethanol in a vibratory McCrone Micronizing Mill for 10 min. Step-scan X-ray powder-diffraction data were collected over a range 3-80 °2θ with CoKα radiation on 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. 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 powder-diffraction data of the sample were refined with Rietveld program Topas 4.2 (Bruker AXS). In addition, the copper head grade of the washed concentrate was determined in each size fraction. This was done by acid digestion of the sample in aqua regia using a microwave digestion system (Ethos UP-EASY), followed by analysis of copper concentration using an ICP-OES (Agilent 5100).

4.2.4 Measurement of the formal potential of the Fe(III)/Fe(II) couple in sulfate media

Ferric forms complexes with sulfate to a larger extent than ferrous in aqueous solutions, thus lowering the reduction-oxidation (redox) potential of the Fe³⁺/Fe²⁺ couple. The Nernst equation expressed as Eq. (4.1) relates the redox potential of the Fe³⁺/Fe²⁺ couple to the standard reduction potential (E⁰) and the activities of Fe³⁺ and Fe²⁺ at 25 °C. To account for the effect of iron-sulfate complexation, Eq. (4.1) was rearranged to Eq. (4.2), which correlates the redox potential of the Fe³⁺/Fe²⁺ couple to the formal potential (E⁰') and the total molar concentration of Fe(III) and Fe(II).
Here, Fe$^{3+}$ and Fe$^{2+}$ represent free ferric and free ferrous ions and Fe(III) and Fe(II) represent the total molar concentration of ferric and ferrous. The formal potential applies under a set of specific solution conditions, such as pH, ionic strength, and solution composition.

$$E_{Fe^{3+}/Fe^{2+}} = E^0 + 0.059 \log \left( \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \right)$$ (4.1)

$$E_{Fe^{3+}/Fe^{2+}} = E^{0f} + 0.059 \log \left( \frac{[Fe(III)]}{[Fe(II)]} \right)$$ (4.2)

A series of tests was carried out to determine the formal potential at a fixed total iron concentration of 10 g/L, pH 1.5, and 25 °C. Six concentration ratios of Fe(III) to Fe(II) in the range of 0.25 to 100 were studied. For each ratio, a 50 mL solution was prepared in a volumetric flask at the desired ratio by mixing different volumes of ferric and ferrous sulfate stock solutions. The solution pH was adjusted to 1.5 by adding drops of concentrated H$_2$SO$_4$. The redox potential of the solution was measured using an ORP electrode with Ag/AgCl reference (saturated 4 mol/L KCl) at 25 °C.

4.2.5 Leaching test procedure

A leaching solution was prepared at a desired concentration ratio of Fe(III) to Fe(II) and a fixed total iron concentration of 10 g/L by mixing certain volumes of their respective stock solutions. The pH of the leaching solution was adjusted to 1.5 by adding sulfuric acid. For each leaching condition tested, seven PTFE bottles were used to obtain seven data points on a leaching curve. A mass of 0.1 g of chalcopyrite concentrate sample was added into each bottle, followed by the transfer of 50 mL of the leaching solution. The pulp density was 2 g/L. A desired volume of KI stock solution was injected into each bottle. For the tests at a higher temperature, the bottles containing the leaching solutions were first placed in a water bath set at the desired temperature.
for 1 h, followed by addition of the concentrate and the iodide solution. The bottles were then tightly closed and shaken on a rotary shaker (Corning LSE Benchtop shaking Incubator) set at the desired temperature and 250 rpm. One bottle was removed from the shaker every 24 h for sampling.

A liquid sample of 2 mL was taken from a bottle through a 0.2 μm syringe filter (Fisherbrand™ Basix™) for determination of copper, iron, and sulfur concentrations by an ICP-OES (Agilent 5110). The pH and potential of the remaining solution were measured, followed by the analysis of the total iodide concentration. All measurements were temperature-dependent and therefore were performed at 25 °C. For those tests at elevated temperatures, the bottles were immersed in cold water for 1 h to lower the temperature of the leaching solution to 25 °C before measurements. All solution potentials were measured using an ORP electrode with Ag/AgCl reference (saturated 4 mol/L KCl) and reported against the standard hydrogen electrode (+ 199 mV vs SHE at 25 °C). Before measurement of the total iodide concentration, around 1 g of zinc powder was added into a bottle to reduce diiodine/triiodide to the form of iodide, together with ferric, ferrous, cupric and protons to their corresponding reduced forms. The solution was then filtered and collected in a glass vial. To maintain the ionic strength constant during measurement, 2 mL ionic strength adjuster (HI4000-0) was added into 20 mL of the solution. The ionic strength adjuster is a buffer solution to increase the ionic strength of the solution to a relatively high level. The total iodide concentration was measured in the form of iodide ions by an ion selective electrode (Hanna Instruments HI 4111).

The percentage of copper extraction was calculated based on the solution analysis and copper head grade in the washed concentrate. The formula is shown in Eq. (4.3).
Cu extraction = \left( \frac{[Cu]_{solution} \times V_{solution}}{[Cu]_{solid} \times m_{sample}} \right) \times 100\%  \quad (4.3)

Where \([Cu]_{solution}\) is the concentration of copper in the solution in mg/L, \(V_{solution}\) is the solution volume in L, \([Cu]_{solid}\) is the copper head grade in the concentrate in %, and \(m_{sample}\) is the mass of the concentrate added in mg.

**4.2.6 Kinetic analysis**

The shrinking core chemical reaction-controlled model was selected as a preliminary model to describe the leaching kinetics of chalcopyrite in the presence of iodine. The general format of this model is expressed as Eq. (4.4) (Szekely et al., 1976):

\[
1 - (1 - X_b)^{1/3} = k_{app}t
\]

Where \(X_b\) is the fraction of the total copper dissolved, \(t\) is the leaching time (in days), and \(k_{app}\) is the apparent rate constant. Plotting the left-hand side of Eq. (4.4) against the leaching time \(t\) gives a linear regression through the origin with \(k_{app}\) being the slope. The apparent rate constant includes two fundamental terms: temperature and reactant concentrations, and therefore its value depends on the actual leaching conditions. The temperature term is based on the Arrhenius equation and the reactant concentration term depends on the reaction mechanism. The function is shown in Eq. (4.5):

\[
k_{app} = k_0 \exp \left( - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right) \left( \frac{[Fe(III)]}{[Fe(II)]} \right)^a [I_{total}]^b
\]

Where \(k_0\) is the reaction rate constant at the reference temperature \(T_0\) in Kelvin, \(E_a\) is the activation energy in J/mol, \(R\) is the gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)), \(T\) is the leaching temperature in Kelvin, \([Fe(III)]\), \([Fe(II)]\), and \([I^-]\) are the total concentration in mol/L of ferric, ferrous, and iodide, and \(a\) and \(b\) are coefficients.
and $b$ are the reaction orders with respect to ferric/ferrous ratio and the total iodide concentration. The effect of redox potential on the copper extraction was represented by the Fe(III)/Fe(II) concentration ratio term. The redox potential is related to the logarithm of ferric to ferrous concentration ratio by Eq. (4.2).

4.3 Research methods for Objective II

Objective II: To develop kinetic equations for the iodine-assisted chalcopyrite dissolution in ferric sulfate media via collecting and interpreting fully-controlled batch reactor leaching data.

4.3.1 Experimental design

Because the solution potential was not controlled in the bottle tests (Objective I), the kinetic equation developed may have underestimated the extraction. To refine the kinetic equation, reactor and saturated column leaching tests were carried out to determine the leaching kinetic parameters under constant potential conditions. This objective was achieved by carrying out a series of fully-controlled leaching tests at different solution potential, total iodide concentration, temperature, and size fraction. The effect of solution potential, total iodide concentration, and temperature was investigated using a chalcopyrite concentrate sample by reactor tests, while the effect of size fraction was studied using a primary copper sulfide ore by saturated column tests. The range of each parameter was chosen based on the study carried out by Manabe (2012). The solution potential was varied by adjusting the concentration ratio of the total ferric to the total ferrous while maintaining the total iron concentration at 5 g/L, a typical iron concentration encountered in heap leaching. The solution potential was maintained constant during leaching by adding potassium permanganate solution. To investigate the possibility of potassium permanganate directly oxidizing the minerals present in the concentrate sample, two tests without iodide addition were
firstly carried out as control. The overall experimental design is presented in Table 4.2 and Table 4.3.

The total iodide concentration was in the range of 50 to 200 mg/L and maintained constant during leaching by using a fully-sealed glass reactor with a PTFE lid. The temperatures investigated were chosen in reference to the typical temperature range in heap leaching and maintained constant during leaching by circulating constant-temperature water through the jacketed reactor. Furthermore, a test was performed twice at the highest temperature of 45 °C but the lowest potential of 669 mV vs SHE to verify that the solution potential was the primary factor determining the performance of the iodine-assisted chalcopyrite leaching.

Table 4.2 Experimental design for iodine-assisted chalcopyrite concentrate (− 53 + 38 μm) reactor leaching tests in ferric sulfate media

<table>
<thead>
<tr>
<th>Leaching tests</th>
<th>Solution potential</th>
<th>[Fe(III)] (g/L)</th>
<th>[Fe(II)] (g/L)</th>
<th>[Fe(II)] (g/L)</th>
<th>[Fe(II)] (mg/L)</th>
<th>[I_total] (mg/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control tests</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>0</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>669</td>
<td>2.500</td>
<td>2.500</td>
<td>1</td>
<td>0</td>
<td>25</td>
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<tr>
<td>Tests in triplicate</td>
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<tr>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
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<tr>
<td>744</td>
<td>4.750</td>
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<td>150</td>
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<tr>
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<td>9</td>
<td>150</td>
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<td>689</td>
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<td>Total iodide</td>
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</tr>
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</tr>
<tr>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tests in duplicate</td>
<td>669</td>
<td>2.500</td>
<td>2.500</td>
<td>1</td>
<td>150</td>
<td>45</td>
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</tr>
</tbody>
</table>
Table 4.3 Experimental design for iodine-assisted chalcopyrite ore saturated column leaching tests in ferric sulfate media to investigate the effect of particle size

<table>
<thead>
<tr>
<th>Leaching tests</th>
<th>Size fraction</th>
<th>Solution potential (mV vs SHE)</th>
<th>[Fe(III)] (g/L)</th>
<th>[Fe(II)] (g/L)</th>
<th>[Fe(III)] (mg/L)</th>
<th>[I\text{total}] (mg/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–4.75 +3.35</td>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>–1.70 +1.00</td>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>–0.71 +0.43</td>
<td>769</td>
<td>4.900</td>
<td>0.100</td>
<td>49</td>
<td>150</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Materials

The chalcopyrite concentrate and the primary copper sulfide ore samples were provided by JX Nippon Mining and Metals Corporation. The preparation of chalcopyrite concentrate has been described in Section 4.2.2. The reactor leaching tests were carried out with the size fraction of –3 + 38 μm. The primary copper sulfide ore was wet sieved to obtain size fractions of –4.75 + 3.35, –1.70 + 1.00, and –0.71 + 0.43 mm. Each size fraction of the ore was washed by sulfuric acid (1 mol/L) to remove acid soluble copper minerals. The solid sample collected through filtration was washed by dilute sulfuric acid and deionized water and then dried in an oven at 50 °C. Each washed fraction was divided into several subsamples of 200 g using the coning and quartering method.

4.3.3 Reactor leaching test procedure

To prepare a leaching solution of a desired potential, the concentration ratio of the total ferric to the total ferrous was varied to obtain a particular solution potential according to Eq. (4.2). Ferric was continuously consumed in the course of leaching by the oxidation of iodide to iodine (Eq. (4.6)), which is considered to be the actual oxidant for chalcopyrite dissolution (Eq. (4.7)). To maintain a constant solution potential during leaching, potassium permanganate solution was added to regenerate ferric. Ferrous oxidation to ferric by permanganate consumes protons, as
shown in Eq. (4.8). Therefore, if needed, 1 mol/L sulfuric acid solution was added to maintain a constant pH of 1.5 during leaching.

\[ 2I^- + 2Fe^{3+} = I_2 + 2Fe^{2+} \]  
(4.6)

\[ CuFeS_2 + 2I_2 = Cu^{2+} + Fe^{2+} + S + 4I^- \]  
(4.7)

\[ 5Fe^{2+} + 8H^+ + MnO_4^- = 5Fe^{3+} + Mn^{2+} + 4H_2O \]  
(4.8)

The leaching tests for chalcopyrite concentrate were carried out in a jacketed-glass reactor with a working volume of 1 L, covered by a PTFE lid with five ports for pH and ORP probes, a sampling tube, a stirrer shaft, and tubes for pH and ORP adjustment reagents. The schematic diagram of the experimental setup is presented in Figure 4.1. All experiments were conducted at 2 g/L of solid content by adding 2 g of the solid sample into 1 L of the leaching solution. The relatively low solid content (2 g/L) was chosen for the following reasons: to mimic the concentration of copper in solution for the column leaching tests; to prevent a significant change in the solution volume due to the addition of potassium permanganate and sulfuric acid solutions to maintain the potential and pH. The solution was agitated by an overhead stirrer, which prevented grinding of the solid particles during leaching, with a PTFE blade stirring at 400 rpm. The pH and ORP probes were connected to the controller and submerged in the leaching solution for pH and ORP monitoring every 30 s. The potential was displayed against standard hydrogen electrode (SHE). Two metering pumps were also connected to the controller for pH and ORP adjustment. If the measured pH or ORP values deviated from its setpoint, the controller sent a signal to the pumps to add potassium permanganate for ORP adjustment and sulfuric acid solution for pH adjustment. The iodide loss by evaporation was prevented by using the fully sealed reactor. The decrease in the total iodide concentration due to dilution by the addition of potassium permanganate and sulfuric acid solutions
was kept at less than 8%. The temperature of the reactor was controlled by circulating water from a water bath set at a desired temperature.

The percentage of copper extraction in fully controlled batch reactor test was calculated based on the solution and residue analyses. The formula is shown in Eq. (4.9).

\[
\text{Cu extraction} = \frac{[\text{Cu}]_{\text{solution}} \times V_{\text{remaining solution}}}{m_{\text{Cu total in solution}} + m_{\text{Cu in residue}}} \times 100\% \tag{4.9}
\]

Where \([\text{Cu}]_{\text{solution}}\) is the concentration of copper in the solution in mg/L, \(V_{\text{remaining solution}}\) is the solution volume remained during sampling in L, \(m_{\text{Cu total in solution}}\) is the total copper mass in the solution at the end of leaching in mg, and \(m_{\text{Cu in residue}}\) is the copper mass remained in the residue at the end of leaching in mg.

During leaching 3 mL of liquid samples were taken periodically for determination of the concentrations of copper, iron, and sulfur by an inductively coupled plasma optical emission spectrometry (ICP-OES). The total iodide concentration in solution was measured using an ion selective electrode (ISE). The leaching residues were collected and dried at 50 °C. Mineralogical and chemical analysis of the residues were carried out using the mineral liberation analysis (MLA) and ICP-OES. Details on the procedures for surface characterization are given in Section 4.4.
4.3.4 Saturated column leaching test procedure

Saturated column leaching tests were performed with the chalcopyrite ore sample of different size fractions under controlled solution potentials at 25 °C. The experimental setup consisted of two glass reactors equipped with overhead stirrers and one column (Figure 4.2). A total of 500 g of washed ore was added into 2.7 L of leaching solution. The solution potential was maintained at a fixed value in the first reactor (on the left), the solution from which was transferred into the second reactor (in the middle) for pH control. To accurately adjust the potential, 0.5 g/L pyrite was added into the first reactor. The pyrite particles served as the surfaces for the oxidation of iodide to occur. Then the solution was further circulated into the saturated column from the bottom and flowed through the packed column for the leaching reaction to occur. The solution left the column from
the top and circulated back to the first reactor for another round of potential and pH adjustment. The solution was circulated constantly at 1.45 mL/s using peristaltic pump to avoid significant potential gradient in the saturated column. During leaching 3 mL of liquid samples were taken periodically for determination of the concentrations of copper, iron, and sulfur by an inductively coupled plasma optical emission spectrometry (ICP-OES).

**Figure 4.2** The schematic diagram of the saturated column leaching setup: 1. pH and ORP controller (left reactor for ORP control and right reactor for pH control); 2. overhead stirrer with PTFE stirring paddle; 3. ORP probe; 4. pH probe; 5. oxidant (KMnO₄) for ORP control; 6. H₂SO₄ for pH control; 7. metering pumps; 8. peristaltic pumps; 9. Glass leaching column; 10. ore; 11. Sampling tube, equipped with syringe and syringe filter

### 4.3.5 Kinetic analysis and modelling

Because chalcopyrite leaching at atmospheric pressure produces a solid product layer, mainly elemental sulfur, the shrinking core model (SCM) are commonly used to describe the kinetics of leaching reactions. 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 SCM,
which has been successfully applied to study leaching rates (Bouffard and Dixon, 2007; Hashemzadeh et al., 2019a, 2019b). This model, shown in Eq. (4.10) in a differential form, is referred to as the “general model” in this study. The application of this model is explained in detail in Section 6.4.

\[
\frac{dx}{dt} = \frac{(1 - x)^\phi}{\tau}
\]  

(4.10)

4.4 Research methods for Objective III

Objective III: To examine the mineralogical and morphological transformation of chalcopyrite and pyrite under different leaching conditions by various surface characterization techniques.

4.4.1 Sample preparation

Representative solid residues collected from the chalcopyrite concentrate leaching tests were characterized to investigate modifications of the solid surfaces after leaching. The surface characterization techniques used included X-ray powder diffraction (XRD), Mineral Liberation Analyzer (MLA), and X-ray photoelectron spectroscopy (XPS). The washed chalcopyrite concentrate sample prior to leaching was also analyzed for comparison. Table 4.4 shows the leaching test conditions under which the solid residues were collected for surface characterization.

<table>
<thead>
<tr>
<th>Leaching tests</th>
<th>Solution potential (mV vs SHE)</th>
<th>[Fe(III)] (g/L)</th>
<th>[Fe(II)] (g/L)</th>
<th>[Fe(III)]/[Fe(II)]</th>
<th>[I\text{total}] (mg/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the absence of iodide</td>
<td>769</td>
<td>4.9</td>
<td>0.1</td>
<td>49</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>669</td>
<td>2.5</td>
<td>2.5</td>
<td>1</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>In the presence of iodide</td>
<td>769</td>
<td>4.9</td>
<td>0.1</td>
<td>49</td>
<td>150</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>669</td>
<td>2.5</td>
<td>2.5</td>
<td>1</td>
<td>150</td>
<td>25</td>
</tr>
<tr>
<td>Temperature and high potential</td>
<td>769</td>
<td>4.9</td>
<td>0.1</td>
<td>49</td>
<td>150</td>
<td>25</td>
</tr>
<tr>
<td>Temperature and low potential</td>
<td>669</td>
<td>2.5</td>
<td>2.5</td>
<td>1</td>
<td>150</td>
<td>40</td>
</tr>
</tbody>
</table>
4.4.2 XRD analysis

The XRD data were obtained using using a Rigaku SmartLab X-ray diffractometer fitted with a Co long-fine-focus tube operated at 40 kV and 40 mA, and a curved graphite post-diffraction monochromator. The beam path was defined using 1° divergence, 0.3 mm receiving and 1° scatter slits. Data were collected over the range 5 < 2h < 80θ in steps of 0.02θ 2h. The crystalline phases in each sample were determined using Rietveld-based analysis.

4.4.3 MLA analysis

The Mineral Liberation Analyzer (MLA) is an automated mineral analysis system used to identify the type of minerals in solid materials and measure mineral characteristics, such as mineral abundance, grain size and liberation. The MLA analysis (MLA 650F) was used to examine the cross sections of the solid particles in the residues. Around 0.2 g of a residue was mixed with 0.4 g graphite (Fisher grade 38) and 0.6 mL of EpoFix hardener as the binder. The mixture was cured for 24 h. The hardened mixture was then cut in half and mounted in a resin, the surface of which was polished to reveal the cross-sectional area of the particles. Data collected included the backscatter emission images and the X-ray mapping. The MLA analysis was carried out in the laboratory of the sponsor company in Hitachi, Japan.

4.4.4 XPS analysis

PHI 5000 Versa Probe II XPS manufactured by Albac Phi Co., Ltd was used for the XPS analysis of the washed chalcopyrite concentrate and the leaching residues. Prior to the analysis, the samples were not kept in an inert atmosphere and the samples were exposed to the atmosphere during preparation. Around 0.2 g of a representative sample was placed on a sample holder and carefully pressed into a pellet. The X-ray photoelectron spectra were generated using the Monochromatic
Al Kα as the excitation source. The normal sensitivity and high sensitivity measurements were performed under 90 degrees incident angle, 45 degrees extraction angle, and with neutralization gun. The first sensitivity measurement was collected under the condition of 25.1 W output and 100 µm X-ray beam diameter. The latter measurement was done under the condition of 100 W output, 100 µm X-ray beam diameter, and 1400 µm sweep distance. To determine the iron and sulfur species present in the leach residues, high-purity jarosite, elemental sulfur, pyrite, chalcopyrite, hematite (Fe₂O₃), and iron oxide (FeO) were also analyzed by XPS.

4.5 Research methods for Objective IV

Objective IV: To calibrate the kinetic model using the data collected from 1-m and 6-m column leaching tests and to evaluate the performance of copper extraction in response to variations in key design and operating parameters

The main objective of the column leaching experiments was to calibrate the kinetic model using the data collected from the column tests. Three sets of tests of increasing scale were carried out in Japan and Chile, namely, the Hitachi 1-m column tests, the Chile 1-m column tests, and the Chile 6-m column tests. The calibrated model was then used to evaluate the performance of the copper extraction in response to variations in the key design and operating parameters.

4.5.1 The Hitachi 1-m column tests

• Experimental design

The Hitachi 1-m column tests were carried out in polypropylene columns of 10 cm in diameter and 1 m in height. The inner surface was coated with a PTFE film to prevent iodine loss by adsorption onto the plastic materials. The column contained 12 kg primary copper sulfide ore. The
column leach tests were performed at two total iodide concentrations, i.e., 100 and 200 mg/L. A control test, i.e., a conventional ferric sulfate leaching in the absence of iodine, was also performed. All column leach tests were conducted at the atmospheric pressure and the room temperature (~25 °C). Table 4.5 shows the conditions for the three Hitachi 1-m column tests. A schematic of the column setup is shown in Figure 4.3.

Table 4.5: Experimental design for the Hitachi 1-m column tests at the atmospheric pressure and the room temperature (~25 °C)

<table>
<thead>
<tr>
<th>Leaching tests</th>
<th>[Fe(III)]</th>
<th>[I\text{total}]</th>
<th>Solution flow rate, L/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control test</td>
<td>5 g/L</td>
<td>0 mg/L</td>
<td>0</td>
</tr>
<tr>
<td>Total iodide</td>
<td>5 g/L</td>
<td>100 mg/L</td>
<td>0.5</td>
</tr>
<tr>
<td>concentration</td>
<td>5 g/L</td>
<td>200 mg/L</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 4.3: The schematic of the 1-m column leaching tests carried out in Hitachi, Japan

- **Materials preparation**

A crude copper ore was initially crushed to 100% passing 12.7 mm in diameter and sieved to > 11.2 mm, – 11.2 + 4.75 mm, and < 4.75 mm. The three size fractions were combined into a new sample, which contained 46% > 11.2 mm, 25% – 11.2 + 4.75 mm, and 29% < 4.75 mm. The copper content of the new sample was analyzed using the sequential leaching method to obtain the
acid-soluble copper, the secondary copper sulfides or cyanide-soluble copper, and the primary copper sulfide minerals. Before being leached, the new sample was ground. The first leaching was carried out in a sulfuric acid solution to obtain the acid-soluble copper content. Then, the residue was washed and leached in a cyanide solution to measure copper as secondary copper sulfides. The residue from the cyanide leaching was digested in nitric acid and perchloric acid solutions at a high temperature until the mixture was dried. Then, the residue was leached in hydrochloric acid to obtain copper content as primary copper sulfide minerals. The chemical analysis was performed using inductively coupled plasma-optical emission spectrometry (ICP-OES). The percentage distribution of copper minerals is shown in Table 4.6.

Table 4.6 The distribution of copper as acid soluble copper, secondary copper sulfide, and primary copper sulfide minerals

<table>
<thead>
<tr>
<th></th>
<th>Total Cu</th>
<th>Acid soluble Cu</th>
<th>Secondary Cu sulfides</th>
<th>Primary Cu sulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade (%)</td>
<td>0.616</td>
<td>0.026</td>
<td>0.026</td>
<td>0.564</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>100</td>
<td>4.22</td>
<td>4.22</td>
<td>91.56</td>
</tr>
</tbody>
</table>

- **Column leaching test procedure**

The column leach tests were run in three sequential stages: acid leaching, ferric leaching, and iodine leaching. The solution flowrate for each stage was set at 1 L/day.

a. Acid leaching stage: the columns were initially irrigated with acidified water adjusted with sulfuric acid (pH 1.2) for 8 days. The ratio of the total volume of leaching solution versus the mass of the ore was 0.7 m$^3$/tonne ore for this stage.

b. Ferric leaching stage: the columns were then irrigated with a ferric sulfate solution at 5 g/L Fe(III) for 14 days. The ratio of the total volume of leaching solution versus the mass of the ore was 1.9 m$^3$/tonne ore for this stage.
c. Iodine leaching stage: All columns were continued to be irrigated with a ferric sulfate solution, but two of the three columns (except the control test) were also irrigated with an iodide solution. For the two columns with the iodide addition, ferric sulfate and iodide were supplied to the columns via two separate feed solutions to prevent iodine loss via volatilization during solution preparation. The flow rate of the two feed solutions was fixed at 0.5 L/day, which gave a total solution flow rate of 1 L/day. The ferric sulfate concentration in the feed solution was set at 10 g/L Fe(III) in order to achieve 5 g/L Fe(III) in the final mixed solution. Similarly, the iodide concentration in the feed solution was twice that of the final mixed solution. The tests were completed when the ratio of the total volume of the leaching solution versus the mass of the ore reached 10 m³/tonne ore (125 days).

Solution samples were collected from the pregnant leach solution (PLS) container and the irrigation volume was recorded weekly. The concentrations of the total Cu and the total Fe in the sampling solution were analyzed by ICP-OES. The solution pH and ORP and the total iodide concentration were measured weekly. At the end of the column leach tests, the residues were digested and analyzed for the copper and iron contents by ICP-OES.

4.5.2 The Chile 1-m column tests

The Chile 1-m column tests were carried out with around 25 kg of primary copper sulfide ore in each column at a solution flowrate of 1.9 L/day: one test without iodide addition as control and the other test at 100 mg/L total iodide. The particle size of the ore was P₈₀ 20 mm. The total copper content in this ore was 0.57% – 0.60%. The acid soluble and secondary copper sulfides were 0.02% and 0.01% – 0.02%, respectively. The primary copper sulfide was 0.53 – 0.57%. The control test
was a conventional ferric sulfate leaching test, which was performed to assess the leaching performance in the absence of iodine. The column test with iodide addition was initiated by circulating only ferric sulfate solution for 21 days to remove secondary copper sulfides. Then ferric sulfate and iodide solutions were supplied separately to the column. The total iron and iodide concentrations were set at 5.6 g/L and 1.1 g/L. The flowrate of ferric sulfate was adjusted at about 1.7 L/day and iodide solution was at 0.2 L/day. Both column leach tests were conducted at the atmospheric pressure and the room temperature (~25 °C).

4.5.3 The Chile 6-m column tests

The Chile 6-m column tests were carried out in 15-cm diameter columns with 220 kg primary copper sulfide ore placed in each column. The total copper content in this ore was 0.57% – 0.64%. The acid soluble, secondary, and primary copper sulfides were 0.01% – 0.03%, 0.02% – 0.03%, and 0.51 – 0.61%, respectively. The total ferric and total iodide concentration in the 6-m columns was set at 6 g/L and 100 mg/L, respectively. All column leach tests were conducted at the atmospheric pressure and the room temperature (~25 °C). The total flowrate was set at 4 L/day. In the case of the tests with the iodide addition, the columns were irrigated with ferric sulfate solution only for 40 days. Then the iodide solution was introduced separately at 0.43 L/day. The concentration and flowrate of ferric in the feed solution was adjusted to account for the additional volume of the iodide solution. The control tests, i.e., conventional ferric sulfate leaching, were performed to assess the leaching performance in the absence of iodine. Both the iodine leaching and the control tests were carried out in triplicate.
4.5.4 Model calibration

The kinetic model developed from the reactor leaching tests (Objective II) was incorporated into the HeapSim 2D model, which was calibrated using the 1-m and 6-m columns tests (Objective IV). The ultimate goal is to use this calibrated model to predict copper extraction in the iodine-assisted chalcopyrite leaching process in a heap leach environment.

Table 4.7 The variation of design parameters in column leaching tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Irrigation rate (L/m²/h)</th>
<th>[Fe³⁺] (g/L)</th>
<th>[I_{total}] (mg/L)</th>
<th>Temperature (°C)</th>
<th>Column height (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irrigation rate</td>
<td>2.65</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>7.95</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>10.60</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>Ferric concentration</td>
<td>5.30</td>
<td>2.5</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>10.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>15.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>50</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>100</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>Iodide concentration</td>
<td>5.30</td>
<td>5.0</td>
<td>150</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>250</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>15</td>
<td>1.0</td>
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<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
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<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>35</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>30</td>
<td>1.0</td>
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<td>200</td>
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<tr>
<td>Column height</td>
<td>5.30</td>
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<td>200</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>1.0</td>
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<td></td>
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<td>2.0</td>
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<tr>
<td></td>
<td>5.30</td>
<td>5.0</td>
<td>200</td>
<td>25</td>
<td>4.0</td>
</tr>
</tbody>
</table>

4.5.5 Simulation under various design parameters

The calibrated model was used to simulate column leaching performance under different design parameters, i.e., irrigation rate, solute concentration (including ferric and iodide concentration),
temperature, and column height. The data obtained from the simulations included the percentage of copper extraction and solution potential. The conditions under which the simulations were performed are shown in Table 4.7.
Chapter 5: Iodine-assisted chalcopyrite leaching in ferric sulfate media: bottle leaching tests and iodine speciation

5.1 Introduction

This Chapter reports experimental and modelling results on the effect of different parameters on the performance of the iodine-assisted chalcopyrite leaching in ferric sulfate media and iodine speciation. All leaching experiments were carried out in 50-mL PTFE bottles under uncontrolled pH and ORP. The leaching parameters studied include ferric to ferrous concentration ratio, total iodide concentration, particle size, and temperature. The extents of copper extraction were then correlated with the stability region of different iodine species. Finally, iodine speciation was investigated as a function of ferric to ferrous concentration ratio and the total iodide concentration added into the leaching solution.

5.2 Characterization of the chalcopyrite concentrate sample

The mineralogy of the chalcopyrite concentrate sample was characterized by quantitative X-ray analysis and is shown in Figure 5.1 and Table 5.1. The sample contained around 60% chalcopyrite and 29% pyrite. The copper head grades of the three size fractions studied were analyzed by ICP-OES and are shown in Table 5.2. No significant difference was observed in the copper grade in different size fractions. The average copper grade of the sample was around 24%.
Figure 5.1 X-ray diffraction pattern of the as-received chalcopyrite concentrate sample

Table 5.1 Quantitative X-ray analysis of the as-received chalcopyrite concentrate sample

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Percentage, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>59.7</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>28.6</td>
</tr>
<tr>
<td>Orpiment</td>
<td>As₂S₃</td>
<td>0.3</td>
</tr>
<tr>
<td>Beaverite (Zn-bearing)</td>
<td>Pb(Fe³⁺Zn)(SO₄)₂(OH)₆</td>
<td>0.2</td>
</tr>
<tr>
<td>Chalcyanthite</td>
<td>CuSO₄.5H₂O</td>
<td>2.6</td>
</tr>
<tr>
<td>Clinochlore</td>
<td>(Mg, Fe²⁺)₅Al(AlSi₃O₁₀)(OH)₈</td>
<td>0.7</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄.2H₂O</td>
<td>0.8</td>
</tr>
<tr>
<td>Illite-Muscovite 2M1</td>
<td>~K₀.₆₅Al₂₀Al₀.₆₅Si₁₃₅O₁₀(OH)₂-KAl₂AlSi₃O₁₀(OH)₂</td>
<td>0.7</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>KAlSi₃O₈</td>
<td>0.8</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS₂</td>
<td>0.4</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>NaAlSi₃O₈ – CaAl₂Si₂O₈</td>
<td>2.7</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>2.1</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>0.4</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 5.2 Head grades in the chalcopyrite concentrate sample in each particle size fraction

<table>
<thead>
<tr>
<th>Size fraction</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 90 + 75 μm</td>
<td>24.43</td>
</tr>
<tr>
<td>- 75 + 53 μm</td>
<td>23.66</td>
</tr>
<tr>
<td>- 53 + 38 μm</td>
<td>24.29</td>
</tr>
</tbody>
</table>
5.3 Measurement of the formal potential of the Fe(III)/Fe(II) couple in sulfate media

The relationship between solution potential in sulfate media and the ratio of ferric to ferrous was investigated. In aqueous sulfuric acid solutions, iron can exist as free ions (Fe$^{3+}$, Fe$^{2+}$) or complex compounds. Ferric sulfate complexes can be in the form of FeSO$_4^+$, Fe(SO$_4$)$_2^-$, and FeHSO$_4^{2+}$ (Casas et al., 2005; Dry and Bryson, 1988). Ferrous sulfate complexes can exist as FeSO$_4^0$, FeHSO$_4^+$ (Dry and Bryson, 1988). The concentration of these species is strongly dependent on solution composition and temperature. The complexation between ferric and sulfate ions could shift the standard reduction potential of Fe$^{3+}$/Fe$^{2+}$ couple because it reduces the amount of free ions in the solution. Figure 5.2 shows that the slope (59.52 mV) was similar to the theoretical value calculated from the Nernst equation at 25 °C and that the formal potential ($E^\prime_0$) measured was 669 mV vs SHE. It suggests that the tendency of ferric ions to form complexes in sulfuric acid solution is higher than ferrous ions. The same result was also obtained by Hiroyoshi et al. (2000).

![Figure 5.2 Solution potential measured in the solution containing 5 g/L total iron and different ferric to ferrous ratio](image)

Figure 5.2 Solution potential measured in the solution containing 5 g/L total iron and different ferric to ferrous ratio

The iodide addition was found to interfere the measurement of the solution potential. Figure 5.3 shows that the potential dropped significantly when ferric to ferrous ratio was set at above 1. The
low potential measured was related to the attachment of iodide ions onto the platinum sensor at the ORP electrode (Johnson, 1972). The potential increased to the actual value when the concentrate sample was added. Sulfide minerals have been reported to be capable of adsorbing iodine species. Figure 5.6 compares the potential and the total dissolved iodide in the absence and the presence of the copper concentrate. The potential was set at 769 mV and immediately fell to around 690 mV after the addition of 150 mg/L iodide. After the concentrate was added, the potential value was recovered and the total dissolved iodide was reduced (Figure 5.6b). This was attributed to the adsorption of iodide ions onto mineral surfaces. The total iodide concentration increased again after 30 min, indicating the desorption of the iodine species from the mineral surfaces. The decrease in the total iodide concentration for the first 5 min of mixing in Figure 5.4b was attributed to the loss of iodine by evaporation and adsorption onto the rubber stopper. It also suggests that the rate of iodide oxidation could be improved by the presence of sulfide minerals, mainly chalcopyrite and pyrite. In contrast, the total iodide concentration in the absence of the concentrate sample remained stable at around 89 mg/L within 5 h of mixing.

![Figure 5.3 Solution potential measured as a function of the ratio of ferric to ferrous with and without iodide addition in sulfate media at 25 °C](image)

Figure 5.3 Solution potential measured as a function of the ratio of ferric to ferrous with and without iodide addition in sulfate media at 25 °C
5.4 The role of iodine in chalcopyrite dissolution

5.4.1 Control tests without addition of iodine

Conventional chalcopyrite leaching in ferric sulfate media was first carried out as the control tests without the addition of iodine. It is well known that chalcopyrite leaching in ferric sulfate media exhibits slow kinetics and is strongly influenced by the redox potential. Therefore, two potentials were chosen for the control tests: 769 mV vs SHE representing a high solution potential and 669 mV vs SHE representing a low solution potential. Figure 5.5 shows the copper extraction at both potentials and the changes in the solution potential during leaching in the absence of iodide at 25 °C. Consistent with the general consensus on the slow kinetics at ambient temperature, a minimal copper extraction of 5% was achieved in a 7-day leaching period at both potentials in the absence of iodide. The copper extraction was not affected by the solution potential at this temperature. There were minimal changes in the solution potential during leaching. These results also confirmed that the sample used did not contain any acid-soluble copper or secondary copper sulfide minerals.
5.4.2 Tests with iodine addition but without ferric

To investigate the role of iodine in chalcopyrite leaching, two tests were conducted in acidified water without the addition of ferric and ferrous ions: one with 170 mg/L iodide (I\(^{-}\)) and the other with 50 mg/L diiodine (I\(_2\)). Figure 5.6a shows that a negligible amount of copper (1.8%) was extracted in the presence of 170 mg/L iodide over a 7-day leaching period. This indicated that copper could not be leached from chalcopyrite by iodide. In the presence of 50 mg/L of diiodine (I\(_2\)), copper was rapidly extracted (5.5%) until diiodine was depleted on the first day, after which the copper extraction plateaued due to insufficient amounts of diiodine as the actual oxidant to sustain the reaction. Figure 5.6b shows that the initial potential of the iodide-containing solution was as low as 500 mV due to the reducing nature of iodide. In contrast, the initial potential of the diiodine-containing solution was as high as 890 mV due to the oxidizing nature of diiodine. It dropped sharply to 617 mV within 1 day of leaching because of the reduction of diiodine to iodide.
by chalcopyrite oxidation. The solution potential in both tests remained low, which was consistent with the low copper extractions obtained.

Figure 5.6 Two tests conducted for chalcopyrite concentrate leaching in sulfuric acid without the addition of ferric and ferrous ions: one with 170 mg/L iodide and the other with 50 mg/L diiodine, pH 1.5 and 25 °C: (a) cumulative copper extraction; (b) solution potential measured during leaching

5.5 Response of copper extraction to different leaching parameters

5.5.1 Reproducibility tests

To determine the reproducibility of the leaching test method, one leaching test was performed in triplicate under the following conditions: initial solution potential of 769 mV vs SHE, total iodide concentration 150 mg/L, size fraction – 75 + 53 μm, solid density 2 g/L, and 25 °C. Figure 5.7a shows the cumulative copper extractions of the three repeated tests and their average at a specific sampling time. The corresponding solution potential measured and their averages are also shown in Figure 5.7a. Figure 5.7b shows the concentrations of the total iron, the total sulfur, and the total iodide measured in the course of leaching. The standard deviation at a specific sampling time was calculated and multiplied by 1.96 to provide a 95% confidence interval. The average confidence interval for the cumulative copper extraction was calculated to be 2.3% from the seven specific
sampling times in the test performed in triplicate. Differences in the copper extraction higher than 2.3% from the average value were considered statistically significant.

Meanwhile, measurements of the solution potential during leaching were reproducible. The solution potential decreased due to the consumption of ferric ions by chalcopyrite oxidation. A constant iodide concentration during leaching indicated that the leaching apparatus was reliable in preventing iodine loss. The concentrations of the total iron and sulfur in solution were relatively constant in all tests. Changes in their concentrations were too small to be detected, because the total iron as ferric and ferrous and the total sulfur as sulfate initially added to the leaching system were considerably high. It was concluded that the leaching test method used in the present study was reproducible.

Figure 5.7 Chalcopyrite concentrate leaching in ferric sulfate media in triplicate under the following conditions: initial solution potential 769 mV vs SHE, total iodide concentration 150 mg/L, size fraction –75 + 53 µm, pH 1.5, and 25 °C. (a) copper extraction and solution potential over time; (b) total iron, total sulfur, and total iodide concentrations over time.

5.5.2 Effect of solution potential on chalcopyrite dissolution

Figure 5.8a shows the copper extraction over time under four different initial solution potentials at a constant iodide concentration of 150 mg/L and 25 °C. The copper dissolution rate increased
with the initial solution potential. The copper extraction ceased at 17% after 3 days of leaching at an initial potential of 669 mV. In contrast, the extraction reached 57% after 7 days of leaching at 725 and 769 mV. Figure 5.8b shows the decrease in the solution potential in the course of leaching, resulting from the consumption of ferric ions and generation of ferrous ions by chalcopyrite oxidation. The change in the solution potential could be directly correlated with the amount of copper dissolved, indicating that pyrite remained unreacted during leaching. The initial more significant drop in the solution potential at 769 mV was caused by the high concentration ratio of ferric to ferrous (a ratio of 49) used, i.e., a small amount of ferric reduced to ferrous significantly lowered this ratio. These results indicate that solution potential is a key factor determining the behavior of chalcopyrite leaching in the presence of iodine.

![Graph showing copper extraction and solution potential](image)

**Figure 5.8** Chalcopyrite concentrate leaching in ferric sulfate media: total iron concentration 10 g/L, total iodide concentration 150 mg/L, size fraction – 75 + 53 µm, pH 1.5, and 25 °C: (a) cumulative copper extraction at four initial solution potentials; (b) solution potential measured during leaching

### 5.5.3 Effect of total iodide concentration on chalcopyrite dissolution

Figure 5.9a shows the chalcopyrite dissolution rate at different total iodide concentrations at 25 °C and an initial solution potential of 769 mV. An increase in the total iodide concentration had a positive effect on the chalcopyrite leaching kinetics. About 75% of copper was extracted in 7 days
with 200 mg/L of iodide and the leaching reaction had not plateaued. An increase in the iodide concentration was associated with a more significant drop in the solution potential (Figure 5.9b), because more ferric ions were consumed for copper extraction. The changes in the solution potential were directly correlated with the copper extraction, confirming that ferric ions were only consumed by chalcopyrite oxidation. In other words, pyrite, which accounted for 28.6% of the concentrate sample used, did not leach in the presence of iodine.

![Figure 5.9 Chalcopyrite concentrate leaching in ferric sulfate media: total iron concentration 10 g/L, initial solution potential 769 mV, size fraction – 75 + 53 µm, pH 1.5, and 25 °C. (a) cumulative copper extraction at different iodide concentrations; (b) solution potential measured during leaching](image)

### 5.5.4 Effect of particle size on chalcopyrite dissolution

Figure 5.10a shows the effect of particle size on the dissolution of chalcopyrite at an initial solution potential of 769 mV, 150 mg/L of iodide, and 25 °C. Similar leaching curves were obtained with different particle size fractions, suggesting that the particle size had no significant effect on the copper extraction kinetics. Jones (1974) reported that the rate of chalcopyrite leaching in sulfate media was independent of particle size when the mean particle size was less than 149 µm. Therefore, the relatively narrow size fractions used in this study were considered to be the reason
for the insensitivity of the copper extraction kinetics to the particle size change. Correspondingly, the trends in the solution potential were similar for all particle sizes studied.

![Graphs showing copper extraction and solution potential over time](image)

**Figure 5.10** Chalcopyrite concentrate leaching in ferric sulfate media: total iron concentration 10 g/L, initial solution potential 769 mV, total iodide concentration 150 mg/L, pH 1.5, and 25 °C: (a) cumulative copper extraction under three size fractions; (b) solution potential measured during leaching

### 5.5.5 Effect of temperature on chalcopyrite dissolution

The effect of temperature on the chalcopyrite leaching kinetics was investigated at two different initial solution potentials: 769 mV (Figure 5.11a) and 669 mV (Figure 5.11c), in the temperature range of 25 to 45 °C. By raising the temperature to 45 °C, a complete dissolution was achieved within 6 days at 769 mV, whereas only about 25% of copper was dissolved at 669 mV. These results support that solution potential is the primary factor determining the copper leaching kinetics in the iodine-assisted process. In other words, redox potential must be sufficiently high for the temperature effect to manifest. The changes in the solution potential for these tests were shown in Figure 5.11b and Figure 5.11d. Again, the drop in the solution potential was directly correlated with the amount of copper extracted. Total iodide concentration during leaching under all
conditions was remained stable, suggesting that iodine loss was prevented in bottle tests (Appendix A).

Figure 5.11 Chalcopyrite concentrate leaching in ferric sulfate media at different temperatures under the following conditions: total iron concentration 10 g/L, total iodide concentration 150 mg/L, and pH 1.5: (a) cumulative copper extraction at initial potential 769 mV; (b) solution potential changes during leaching at initial potential 769 mV; (c) cumulative copper extraction at initial potential 669 mV; (d) solution potential change during leaching at initial potential 669 mV

5.6 Kinetic analysis of iodine-assisted chalcopyrite leaching

5.6.1 Iodine speciation

Figure 5.12 shows the Eh-pH diagram of the I-Cu-Fe-S-H₂O system at 25 °C and different total iodide concentrations. Figure 5.13 depicts the Eh-pH diagram of the I-Cu-Fe-S-H₂O system at
different temperatures. The diagrams depict that iodine speciation depends on the redox potential at a fixed total iodide concentration. Figure 5.12 shows that the regions of iodide, triiodide, and diiodine slightly shift to lower potential ranges as the total iodide concentration was increased. However, the difference between the maximum and the minimum potential in which triiodide is the predominant species does not change due to the low total iodide concentrations used. In the case of a large difference in the total iodide concentration, for instance, from 0.005 m to 0.05 m (data shown in Appendix C), the region of triiodide stability changes significantly because diiodine tends react with iodide to form triiodide at a high total iodide concentration (Kaiho, 2014). In addition, the region of CuI precipitate increases as copper and iodide concentration increase (see Appendix C).

The corresponding potential and pH from all leaching data points were plotted in the Eh-pH diagrams shown in Figure 5.12 and Figure 5.13, depending on the leaching conditions. These data points could be grouped into three clusters according to the extent of copper extraction: negligible (without ferric and ferrous addition), low extraction, and high extraction. In the absence of ferric ions, the solution potential is in the range of 567 to 617 mV, which is slightly above the range of CuI precipitation (556 mV). In the potential range of 556 to 699 mV, the predominant species is iodide. In this range, the leaching reaction exhibited slow kinetics and low copper extraction (less than 24.6%) even after the temperature was increased to 45 °C. When the solution potential is higher than 692 mV (for solution containing 0.20 g/L I), 699 mV (for solution containing 0.15 g/L I), 710 mV (for solution containing 0.10 g/L I), and 728 mV (for solution containing 0.05 g/L I), the predominant species are triiodide (I₃⁻) or diiodine (I₂). Fast leaching kinetics and high copper extraction were obtained when the solution potential was above these values. It can be concluded
from these results that triiodide and diiodine are the actual oxidants in chalcopyrite dissolution and that the ratio of ferric to ferrous is crucial for maintaining the solution potential in the range where triiodide or diiodine are the stable species. The iodine speciation is also affected by the total concentration of iodide added into the leaching system.

Figure 5.12 Eh-pH diagram for the I-Cu-Fe-S-H$_2$O system at 25 °C and copper molality 0.787 m, total iron molality 0.179 m, total sulfur molality 0.313 m, and different total iodide molality: (a) 0.00158 m (~0.20 g/L), (b) 0.00118 m (~0.15 g/L), (c) 0.00079 m (~0.10 g/L), and (d) 0.00039 m (~0.05 g/L) (constructed using HSC 7.1). The pH and solution potential measured from all leaching tests were plotted.
Figure 5.13 Eh-pH diagram for the I-Cu-Fe-S-H\(_2\)O system with total iodide molality 0.00118 m, copper molality 0.00787 m, total iron molality 0.179 m, and total sulfur molality 0.313 m at different temperature: (a) 35 °C and (b) 45 °C (constructed using HSC 7.1). The pH and solution potential measured from all leaching tests were plotted.

Thermodynamic calculations were carried out to determine the concentrations of each iodine species, i.e., free iodide [I\(^-\)], triiodide [I\(_3^-\)], and diiodine [I\(_2\)], as a function of solution potential at the four total iodide concentrations tested. The equations of iodine speciation are shown as Eq. 5.1 and 5.2. The corresponding Nernst equations are expressed as Eq. (5.3) and (5.4). \(E\) is the redox potential and is equal to the solution potential (a function of Fe(III)/Fe(II) ratio) at equilibrium. \(E_{1}^{0}\) and \(E_{2}^{0}\) are the standard reduction potential for the respective redox couple. The mass balance of iodine is expressed as Eq. (5.5), with \(I_{\text{total}}\) being the total concentration of iodide added into the leaching system. Eq. (5.3), (5.4) and (5.5) are combined to derive Eq. (5.6), which shows that the free iodide concentration at equilibrium can be calculated if the solution potential \((E)\) and the total iodide concentration \((I_{\text{total}})\) are known. The concentrations of triiodide and diiodine species can also be calculated by this set of equations.

\[
I_{3}^- + 2e^- \rightarrow 3I^- \quad E_{1}^{0} = 0.699 \, V
\]  

\(\text{(5.1)}\)
\[ 3I_2 + 2e^- \rightarrow 2I_3^- \quad E_2^0 = 0.734 \, V \]  
\[ E = E_1^0 + \frac{RT}{2F} \ln \left( \frac{[I_3^-]}{[I^-]^3} \right) \]  
\[ E = E_2^0 + \frac{RT}{2F} \ln \left( \frac{[I_2]^3}{[I_3^-]^2} \right) \]  
\[ [I_{\text{total}}] = [I^-] + 3[I_3^-] + 2[I_2] \]  
\[ 3[I^-]^3 \exp \left( \frac{2F(E - E_1^0)}{RT} \right) + 2[I^-]^2 \exp \left( \frac{4F(E - E_1^0)}{3RT} \right) \exp \left( \frac{2F(E - E_2^0)}{3RT} \right) + [I^-] - [I_{\text{total}}] = 0 \]  

Figure 5.14 The percentage of the total iodide added present as free iodide (I\(^-\)), triiodide (I\(_3^-\)), and diiodine (I\(_2\)) as a function of Fe(III)/Fe(II) ratio at different total iodide concentrations in solution containing 5 g/L total iron, 0.5 g/L total copper, 25 °C
Figure 5.14 shows the percentage of iodide ($I^-$), triiodide ($I_3^-$), and diiodine ($I_2$) as a function of Fe(III)/Fe(II) at the four total iodide concentrations investigated. Iodine speciation depends on the solution potential and the total iodide concentration added. In the lower potential range, i.e., $1 < \text{Fe(III)/Fe(II)} < 10$, the predominant species is triiodide, the percentage of which is higher than that of diiodine except at 50 mg/L $I_{\text{total}}$ where iodide is the predominant species. At higher Fe(III)/Fe(II) ratios, diiodine is the predominant species in all cases, accounting for around 62 – 72% of the total iodide added.

5.6.2 Kinetic analysis of iodine-assisted chalcopyrite leaching

Assuming the formation of elemental sulfur on chalcopyrite surfaces and given the sensitivity of the dissolution rate to temperature, the shrinking core chemical reaction-controlled model was selected to describe the leaching kinetics of chalcopyrite in the presence of iodine. In other words, the kinetics was thought to be controlled by the chemical reaction on chalcopyrite surfaces rather than diffusion through the product layer. The general form of this model is expressed as Eq. (5.7) (Szekely et al., 1976):

$$1 - (1 - X_b)^{1/3} = k_{\text{app}}t$$  \hspace{1cm} (5.7)

Where $X_b$ is the fraction of the total copper dissolved, $t$ is the leaching time (in days), and $k_{\text{app}}$ is the apparent rate constant. Plotting the left-hand side of Eq. (5.7) against the leaching time $t$ gives a linear regression through the origin with $k_{\text{app}}$ being the slope. The apparent rate constant includes two fundamental terms: temperature and reactant concentrations; therefore, its value depends on the actual leaching conditions. The temperature term is based on the Arrhenius equation and the reactant concentration term depends on the reaction mechanism. The function is shown in Eq. (5.8):
\[ k_{app} = k_0 \exp \left( -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \left( \frac{[\text{Fe(III)]}}{[\text{Fe(II)]}} \right)^a [I_{\text{total}}]^b \right) \] (5.8)

Where \( k_0 \) is the reaction rate constant at the reference temperature \( T_0 \) in Kelvin, \( E_a \) is the activation energy in J/mol, \( R \) is the gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)), \( T \) is the leaching temperature in Kelvin, [Fe(III)], [Fe(II)], and [I] are the total concentration in mol/L of ferric, ferrous, and iodide, and \( a \) and \( b \) are the reaction orders with respect to ferric/ferrous ratio and the total iodide concentration. The effect of redox potential on the copper extraction was represented by the Fe(III)/Fe(II) concentration ratio term. The redox potential is related to the logarithm of ferric to ferrous concentration ratio by Eq. (4.2).

The leaching data shown in Figure 5.8, Figure 5.9, and Figure 5.11 were rearranged according to Eq. (5.7) and replotted in Figure 5.15 to derive the apparent rate constant, \( k_{app} \), under different leaching conditions. The slope of the linear regression of \( 1 - (1-X_b)^{1/3} \) against the leaching time represents the apparent rate constant under a specific leaching condition. Figure 5.15a shows the apparent rate constant at different initial solution potentials. Figure 5.15b shows the linear regression of the natural logarithm of \( k_{app} \) against the natural logarithm of the Fe(III) to Fe(II) concentration ratio, the slope of which represents the reaction order (0.38) with respect to the concentration ratio of Fe(III) to Fe(II). Figure 5.15c shows the apparent rate constant at different total iodide concentrations. The linear regression of the natural logarithm of \( k_{app} \) against the natural logarithm of the total iodide concentration (Figure 5.15d) shows that the reaction order with respect to the total iodide concentration was 0.91. These reaction orders are only estimates, because the model assumption is that the solution potential is constant during leaching, which is obviously not the case. To improve the accuracy of the reaction order, a constant solution potential should be
maintained during leaching. This can be achieved by continuously supplying oxidants to regenerate ferric, such as hydrogen peroxide (Nikoloski and O’Malley, 2018), oxygen (Third et al., 2002), and potassium permanganate (Sandström et al., 2005), to the leaching system. This is studied in Chapter 6.

Figure 5.15e shows the apparent rate constants at different temperatures. The Arrhenius plot drawn in Figure 5.15f shows that the activation energy was 47 kJ/mol, supporting that the oxidation of chalcopyrite was controlled by chemical reaction. Granata et al. (2019) found an activation energy of 33.8 kJ/mol for chalcopyrite dissolution in acidic ferric sulfate in the presence of iodine, but the authors did not discuss whether iodine loss was prevented during testing. The value obtained in the present study was less than those reported for the conventional chalcopyrite leaching in ferric sulfate media, which ranges from 77 to 131 kJ/mol in the temperature range of 35 to 90 °C (Al-Harahsheh et al., 2005; Córdoba et al., 2008; Dutrizac, 1981; Hirato et al., 1987; Munoz et al., 1979). The comparison shows that the presence of a small amount of iodine could significantly reduce the activation energy, thereby enabling faster chalcopyrite dissolution at lower temperatures.

After all leaching parameters were determined, the reaction rate constant, $k_0$, at the reference temperature, $T_0$, was calculated according to Eq. (5.8). The reference temperature was chosen to be 25 °C, because all leaching tests, except the temperature variation, were carried out at 25 °C. The optimal value of $k_0$ was found to be 4.458. This value was obtained using the least squares method, i.e., minimizing the sum of the squares of the errors between experimental and predicted copper extraction values. Accordingly, the preliminary kinetic equation was derived as Eq. (5.9) to describe chalcopyrite leaching in acidic ferric sulfate media in the presence of iodine.
Figure 5.15 Kinetic analysis by the shrinking core chemical reaction-controlled model of chalcopyrite concentrate leaching in ferric sulfate media at pH 1.5, total iron concentration 10 g/L, and –75+53 µm: (a) and (b) at different initial solution potentials, 150 mg/L total iodide and 25 °C; (c) and (d) at different total iodide concentration, initial potential 769 mV and 25 °C; (e) and (f) at different temperatures, initial potential 769 mV and 150 mg/L total iodide concentration.
$$1 - (1 - X_b)^{\frac{1}{3}} = 4.458 \exp \left( -\frac{46,960}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) \left( \frac{[\text{Fe(III)}]}{[\text{Fe(II)}]} \right)^{0.38} \left[ I^- \right]^{0.91} t \text{ (day)}$$ (5.9)

Figure 5.16 The comparison between the experimental (scatter plot) and the predicted copper extractions (solid lines) under different leaching conditions: (a) different initial solution potential, (b) different total iodide concentration, and (c) different temperature.

The comparisons of the copper extractions between the experimental data and the values predicted by Eq. (5.9) are shown in Figure 5.16. The kinetic equation (Eq. (5.9)) could describe the copper extractions from chalcopyrite at different iodide concentrations and temperature. However, for tests at different potentials, the equation could not describe copper extractions at 725 mV and 769 mV. At 725 mV, the predicted copper extractions were lower than the experimental values, presumably due to the model not considering the change in the iodine concentration in response to the potential change. At 769 mV, the experimental data showed that leaching became slower due...
to the significant drop of potential, which affected the iodine speciation. At 669 mV, leaching
plateaued and behaved similarly as conventional ferric sulfate leaching, because iodide was the
dominant species of iodine at this potential. In this case, the leaching reaction was hindered by the
solid product and hence, the leaching kinetics was controlled by diffusion. These results
demonstrated that variations of the solution potential during leaching led to inaccurate predictions
of the copper extraction. Given the limitations of this kinetic model, further leaching tests were
carried out under fully controlled redox potentials to refine the model (Chapter 6).

5.7 Conclusions
The kinetics of iodine-assisted chalcopyrite leaching in ferric sulfate media were studied. A series
of leaching tests were carried out to investigate the response of copper extraction from chalcopyrite
to variations in the redox potential, total iodide concentration, particle size, and temperature. To
prevent iodine loss during leaching and sampling, a total of seven PTFE bottles with high chemical
resistance were used to obtain one leaching curve, each representing one data point in the curve.
The experimental results show that the copper extraction increased with increasing redox potential,
increasing total iodide concentration, and increasing temperature. The particle size had no effect
on the kinetics of copper extraction. Redox potential was the primary factor controlling the
chalcopyrite leaching performance by controlling the iodine speciation in solution. Higher copper
extractions were associated with higher potential values where diiodine or triiodide was the
predominant species. When the redox potential falls in the region of iodide stability, a minimal
percentage of copper was extracted. Redox potential must be sufficiently high for the effect of
temperature to manifest.
The preliminary kinetic modelling was done using the shrinking core model for chemical reaction-controlled leaching. The results show that the reaction order was 0.38 with respect to the ferric to ferrous concentration ratio and 0.91 with respect to the total iodide concentration. The activation energy obtained (47 kJ/mol) was significantly lower than those reported for the conventional chalcocpyrite leaching in ferric sulfate media, supporting that the presence of iodine species lowers the activation energy and thus alters the leaching mechanism.
Chapter 6: Iodine-assisted chalcopyrite leaching in ferric sulfate media: batch reactor studies and saturated column leaching under controlled potential

6.1 Introduction

The experimental results of the bottle tests reported in Chapter 5 show that solution potential is a crucial factor controlling the performance of iodine-assisted chalcopyrite leaching in ferric sulfate media at ambient temperature. However, the solution potential was not controlled in the bottle tests and kept decreasing in the course of leaching. Therefore, the kinetic equation developed may have underestimated the copper extraction. This main objective of this Chapter is to refine the kinetic equation using the experimental data obtained from the reactor and saturated column tests carried out at constant potentials. Two tests without iodide addition were first carried out as the control tests to investigate the possibility of potassium permanganate, which was used for potential control, directly oxidizing the minerals present in the concentrate sample. A series of chalcopyrite concentrate leaching tests was then carried out in a stirred jacketed-glass reactor to investigate the effect of solution potential, total iodide concentration, and temperature on chalcopyrite dissolution rate. Finally, the effect of particle size was studied using a primary copper sulfide ore in a saturated column.

6.2 Effects of leaching parameters on chalcopyrite concentrate leaching in reactor tests

6.2.1 Control tests

The conventional chalcopyrite leaching in ferric sulfate media was carried out at 25 °C in the absence of iodide as control. The tests were performed at two solution potentials (versus SHE): 669 mV representing the lowest potential and 769 mV representing the highest values tested in the
current study. As expected, chalcopyrite dissolved to a minimal extent in the absence of iodide (Figure 6.1a). The extent of chalcopyrite dissolution was the same at both potentials, with only around 11% of the copper extracted for 14 days of leaching. Accordingly, the concentration of the dissolved iron remained almost constant during leaching due to the negligible contribution from chalcopyrite dissolution. The concentration of dissolved sulfur remained constant at 669 mV, but increased by around 0.2 g/L at 769 mV due to the addition of sulfuric acid for pH control.

Figure 6.1b shows that the solution potential and pH could be maintained at near constant values during leaching. The same levels of copper extraction at the two potentials suggested that the same amounts of ferric ions were reduced to ferrous ions in both cases. Given that the ratio of ferric to ferrous at 769 mV (49:1) was considerably higher than that at 669 mV (1:1), for the same amount of ferric consumed, the drop in the ferric to ferrous ratio and thus the potential was much more pronounced at 769 mV. That was to say that a higher amount of permanganate was required to maintain a constant potential at 769 mV, theoretically, 0.996 mol at 769 mV as opposed to 0.900 mol KMnO₄ per mole of copper extracted. However, the ORP controller and the probe were more sensitive to larger magnitudes of potential drop. Therefore, the actual permanganate added tended to be higher than the theoretical value when the potential drop was large and lower than the theoretical value when the potential drop was small.

Table 6.1 shows the final permanganate consumption monitored at the end of leaching. A final copper extraction of 10% corresponded to a potential drop of 30 mV at 769 mV compared with a potential drop of 4 mV at 669 mV. Therefore, the actual consumption at 769 mV was 1.257 mol KMnO₄ per mole of copper extracted, which was higher than the theoretical value. This also caused the total dissolved sulfur to increase due to the addition of sulfuric acid for ferrous
oxidation by permanganate. A negligible amount of permanganate was consumed at 669 mV due to the very small potential drop. Despite different levels of permanganate addition at the two potentials, there was no significant difference in the copper extraction between the two tests. This result implied that the permanganate added was rapidly consumed by ferrous oxidation to ferric ions, as reported by Kametani and Aoki (1985), and did not participate as a direct oxidant in mineral dissolution.

Figure 6.1 (a) Cumulative copper extraction and the total iron and sulfur concentrations in the leachates at 669 and 769 mV and 25 °C without iodide addition over a 14-day leaching period; (b) the corresponding measurements of pH and solution potential during leaching

Table 6.1 The comparison of calculated and actual consumption of potassium permanganate

<table>
<thead>
<tr>
<th>Leaching conditions</th>
<th>Calculated KMnO₄ (mol/mol-copper)</th>
<th>Actual KMnO₄ (mol/mol-copper)</th>
</tr>
</thead>
<tbody>
<tr>
<td>769 mV; 25 °C</td>
<td>0.996</td>
<td>1.257</td>
</tr>
<tr>
<td>669 mV; 25 °C</td>
<td>0.990</td>
<td>0.000</td>
</tr>
</tbody>
</table>

6.2.2 Reproducibility of the reactor test method

Figure 6.2a shows the cumulative copper extraction of the three repeated tests and their averages at specific sampling times. The standard deviation at a specific sampling time was calculated and multiplied by 1.96 to provide a 95% confidence interval. The average confidence interval for the
cumulative copper extraction was calculated to be ±2.4%. The test method was deemed reproducible. Differences in the copper extraction higher than 2.4% were considered statistically significant. The corresponding total iron and sulfur concentrations in the leachates from the three tests were also shown in Figure 6.2a. The total iron concentration increased by around 0.4 g/L resulting from the chalcopyrite dissolution. The increase by around 1 g/L in the total dissolved sulfur concentration was caused by the addition of sulfuric acid to maintain a constant pH, because the oxidation of ferrous to ferric by permanganate consumes acid.

Figure 6.2 (a) Cumulative copper extraction; (b) solution potential during leaching; (c) solution pH during leaching in the iodine-assisted chalcopyrite leaching process from three repeated tests over a 14-day leaching period at 769 mV, 150 mg/L I_{total}, and 25 °C
Figure 6.2c shows that the solution pH was also well maintained at 1.5 in the course of leaching by using sulfuric acid. However, the initial pH was lower than the setpoint (pH 1.5). Therefore, acid was not added for the first two days of leaching, after which pH increased to 1.5 due to proton consumption and was maintained at this value thereafter. The pH trend also indicated that the oxidation of pyrite and the iron hydrolysis, both of which generate protons, were negligible at 25 °C. The measurement of the total iodide concentration at the beginning and end of a leaching test showed that the total iodide concentration did not change during leaching, meaning that the experimental apparatus was effective in preventing iodine loss via evaporation.

6.2.3 Effect of potential, iodide concentration, and temperature on copper extraction

Figure 6.3 shows the effect of the solution potential on the leaching rate of chalcopyrite at 25 °C and 150 mg/L iodide. Similar to what was observed in the bottle tests reported in Chapter 5, the dissolution rate was sensitive to changes in the solution potential and increased with increasing solution potential. At the lowest potential tested (669 mV), leaching proceeded during the first 3 days, followed by a very slow increment with a slope similar to the case without iodide addition. Increases in the solution potential beyond 669 mV accelerated the leaching rate and the leaching curves did not plateau. At the highest potential tested (769 mV), a complete dissolution was achieved within 10 days. Significantly slower kinetics was found when solution potential was lower than 719 mV (Figure 6.3b and Figure 6.3c). The dX/dt was calculated using Eq. (6.1).

\[
\frac{dX}{dt} = \frac{X_i - X_{i-1}}{t_i - t_{i-1}} \tag{6.1}
\]

Where \(X_i\) is the copper extraction in percentage at sampling time \(t_i\), and \(X_{i-1}\) is the copper extraction in percentage at sampling time \(t_{i-1}\).
Figure 6.3 (a) Cumulative copper extraction; (b) the rate of dissolution (dX/dt) at potential of 719 – 769 mV; (c) the rate of dissolution (dX/dt) at potential of 669 – 714 mV in the iodine-assisted chalcopyrite leaching process over a 14-day leaching period at different solution potentials, 150 mg/L I_{total}, and 25 °C

Figure 6.4 shows the effect of the iodide addition on chalcopyrite dissolution kinetics at 25 °C and a solution potential of 769 mV for 14 days. The leaching curve without iodide addition was also plotted in the graph for comparison. The result shows that the addition of iodide in ferric sulfate media could significantly enhance the dissolution rate. At the end of the leaching period, the conventional ferric sulfate leaching could only achieve around 11% copper extraction. By contrast, the presence of only 50 mg/L of iodide can increase the copper extraction to 58%. Further increase in the iodide concentration had a positive effect on the leaching rate and a complete dissolution could be achieved within 14 days of leaching.
Figure 6.4 (a) Cumulative copper extraction; (b) the rate of dissolution (dX/dt) in the iodine-assisted chalcopyrite leaching process over a 14-day leaching period at different total iodide concentrations, 769 mV, and 25 °C.

Figure 6.5 shows that increasing temperature significantly accelerated the leaching kinetics at 769 mV and 150 mg/L total iodide and a complete dissolution was achieved in 5 days at 40 °C. One test was carried out in duplicate at 45 °C but at 669 mV, the lowest potential tested. Even though the temperature was the highest, the rate of dissolution was the slowest. These results confirmed that solution potential must be kept sufficiently high for the effect of temperature to manifest. Because potential could be controlled at constant values during leaching in these reactor tests, the dissolution rates were greater in the reactor tests than those reported in the bottle tests at the same temperature and the same total iodide concentration.
6.2.4 Mass balance of leaching residue and permanganate consumption

The mass of each leaching residue was calculated under the assumption that only chalcopyrite was dissolved during leaching, releasing copper and iron to the solution and generating elemental sulfur in the solid form. Table 6.2 shows the mass calculated and actual value measured experimentally and their relative difference, which describes the absolute difference between the two as a fraction of the calculated mass. In general, the mass calculated agreed with the actual value measured experimentally, except for those tests at 40 °C and 45 °C. For those tests the calculated values were
significantly lower, suggesting that iron precipitation occurred. This agrees with the drop in the solution pH during leaching at 40 °C and 45 °C, as shown in Figure 6.6c.

The volumes of permanganate consumed during leaching were monitored to determine the actual consumptions of potassium permanganate, which were then compared with the calculated values. The actual concentration of KMnO₄ solution used was 0.259 mol/L measured by titration with Na₂C₂O₄. This concentration was lower than intended (0.3 mol/L) because of its decomposition by sunlight during solution preparation. Therefore, the tubes, the container of KMnO₄ solution and the reactors were covered with aluminum foil to prevent photodecomposition of KMnO₄ during leaching.

Table 6.2 The comparison of calculated and actual mass of leaching residues

<table>
<thead>
<tr>
<th>Leaching condition</th>
<th>Initial mass (g)</th>
<th>Mass of Cu dissolved (mg)</th>
<th>Mass of CuFeS₂ oxidized (g)</th>
<th>Calculated mass of residue (g)</th>
<th>Actual mass of residue (g)</th>
<th>Relative difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>669 mV; 150 mg/L; 25 °C</td>
<td>2.0016</td>
<td>108.516</td>
<td>0.204</td>
<td>1.797</td>
<td>1.803</td>
<td>0.309</td>
</tr>
<tr>
<td>689 mV; 150 mg/L; 25 °C</td>
<td>2.1019</td>
<td>181.564</td>
<td>0.342</td>
<td>1.660</td>
<td>1.753</td>
<td>5.581</td>
</tr>
<tr>
<td>694 mV; 150 mg/L; 25 °C</td>
<td>2.1008</td>
<td>357.909</td>
<td>0.674</td>
<td>1.327</td>
<td>1.436</td>
<td>8.197</td>
</tr>
<tr>
<td>704 mV; 150 mg/L; 25 °C</td>
<td>2.0014</td>
<td>288.060</td>
<td>0.542</td>
<td>1.459</td>
<td>1.428</td>
<td>-2.117</td>
</tr>
<tr>
<td>714 mV; 150 mg/L; 25 °C</td>
<td>2.002</td>
<td>335.151</td>
<td>0.631</td>
<td>1.371</td>
<td>1.401</td>
<td>2.148</td>
</tr>
<tr>
<td>719 mV; 150 mg/L; 25 °C</td>
<td>2.1004</td>
<td>381.212</td>
<td>0.718</td>
<td>1.383</td>
<td>1.373</td>
<td>-0.683</td>
</tr>
<tr>
<td>725 mV; 150 mg/L; 25 °C</td>
<td>2.0017</td>
<td>459.057</td>
<td>0.864</td>
<td>1.137</td>
<td>1.163</td>
<td>2.338</td>
</tr>
<tr>
<td>744 mV; 150 mg/L; 25 °C</td>
<td>2.0011</td>
<td>475.422</td>
<td>0.895</td>
<td>1.106</td>
<td>1.192</td>
<td>7.738</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C</td>
<td>2.0024</td>
<td>501.180</td>
<td>0.943</td>
<td>1.055</td>
<td>1.092</td>
<td>3.229</td>
</tr>
<tr>
<td>769 mV; 50 mg/L; 25 °C</td>
<td>2.0024</td>
<td>275.390</td>
<td>0.518</td>
<td>1.484</td>
<td>1.415</td>
<td>-4.645</td>
</tr>
<tr>
<td>769 mV; 100 mg/L; 25 °C</td>
<td>2.0019</td>
<td>475.392</td>
<td>0.895</td>
<td>1.107</td>
<td>0.921</td>
<td>-16.817</td>
</tr>
<tr>
<td>769 mV; 200 mg/L; 25 °C</td>
<td>2.0021</td>
<td>513.603</td>
<td>0.967</td>
<td>1.035</td>
<td>0.949</td>
<td>-8.331</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 30 °C</td>
<td>2.2011</td>
<td>522.913</td>
<td>0.984</td>
<td>1.217</td>
<td>1.209</td>
<td>-0.660</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 35 °C</td>
<td>2.2001</td>
<td>514.231</td>
<td>0.968</td>
<td>1.232</td>
<td>1.156</td>
<td>-6.182</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 40 °C</td>
<td>2.2000</td>
<td>513.985</td>
<td>0.967</td>
<td>1.233</td>
<td>2.048</td>
<td>66.154</td>
</tr>
<tr>
<td>669 mV; 150 mg/L; 45 °C (Rep 1)</td>
<td>2.1994</td>
<td>215.790</td>
<td>0.406</td>
<td>1.793</td>
<td>2.380</td>
<td>32.744</td>
</tr>
<tr>
<td>669 mV; 150 mg/L; 45 °C (Rep 2)</td>
<td>2.0007</td>
<td>204.627</td>
<td>0.385</td>
<td>1.622</td>
<td>1.963</td>
<td>21.042</td>
</tr>
<tr>
<td>769 mV; 25 °C</td>
<td>2.0002</td>
<td>56.920</td>
<td>0.107</td>
<td>1.893</td>
<td>1.874</td>
<td>-1.033</td>
</tr>
<tr>
<td>669 mV; 25 °C</td>
<td>2.0003</td>
<td>49.350</td>
<td>0.093</td>
<td>1.907</td>
<td>1.912</td>
<td>0.235</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C (Rep 1)</td>
<td>2.1009</td>
<td>490.338</td>
<td>0.923</td>
<td>1.178</td>
<td>1.196</td>
<td>1.558</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C (Rep 2)</td>
<td>2.1013</td>
<td>475.487</td>
<td>0.895</td>
<td>1.206</td>
<td>1.202</td>
<td>-0.373</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C (Rep 3)</td>
<td>2.1003</td>
<td>482.931</td>
<td>0.909</td>
<td>1.191</td>
<td>1.131</td>
<td>-5.027</td>
</tr>
</tbody>
</table>
The calculations were done under the assumption that permanganate was only consumed by ferrous oxidation to ferric ions and that ferric ions were only consumed by chalcopyrite oxidation. If this assumption were valid, the consumption of permanganate should be directly proportional to copper extraction. The comparison in Table 6.3 shows that the $\text{KMnO}_4$ consumption calculated mostly agreed with the actual values, indicating that the assumption was valid. But when the ferric to ferrous ratio was close to 1 (669 mV), the consumption of $\text{KMnO}_4$ was much less than estimated. It is because potential is a logarithmic function of ferric to ferrous ratio. At a ratio close to 1, the change in the ferric to ferrous ratio does not change the potential significantly enough to trigger
the pump to inject KMnO₄ solution. The large relative difference obtained at 769 mV, 150 mg/L and 35 °C was caused by malfunction of an overhead stirrer.

### Table 6.3 The comparison of calculated and actual consumption of potassium permanganate

<table>
<thead>
<tr>
<th>Leaching test</th>
<th>Calculated KMnO₄ (mol/mol Cu)</th>
<th>Actual KMnO₄ (mol/mol Cu)</th>
<th>Relative Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>669 mV; 150 mg/L; 25 °C</td>
<td>0.900</td>
<td>0.061</td>
<td>-93.26</td>
</tr>
<tr>
<td>689 mV; 150 mg/L; 25 °C</td>
<td>0.937</td>
<td>0.824</td>
<td>-12.04</td>
</tr>
<tr>
<td>694 mV; 150 mg/L; 25 °C</td>
<td>0.945</td>
<td>0.997</td>
<td>5.50</td>
</tr>
<tr>
<td>704 mV; 150 mg/L; 25 °C</td>
<td>0.960</td>
<td>0.993</td>
<td>3.48</td>
</tr>
<tr>
<td>714 mV; 150 mg/L; 25 °C</td>
<td>0.971</td>
<td>0.962</td>
<td>-0.95</td>
</tr>
<tr>
<td>719 mV; 150 mg/L; 25 °C</td>
<td>0.975</td>
<td>0.953</td>
<td>-2.21</td>
</tr>
<tr>
<td>725 mV; 150 mg/L; 25 °C</td>
<td>0.980</td>
<td>0.964</td>
<td>-1.66</td>
</tr>
<tr>
<td>744 mV; 150 mg/L; 25 °C</td>
<td>0.990</td>
<td>1.045</td>
<td>5.33</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C</td>
<td>0.996</td>
<td>0.994</td>
<td>-0.17</td>
</tr>
<tr>
<td>769 mV; 50 mg/L; 25 °C</td>
<td>0.996</td>
<td>1.045</td>
<td>4.93</td>
</tr>
<tr>
<td>769 mV; 100 mg/L; 25 °C</td>
<td>0.996</td>
<td>1.027</td>
<td>3.16</td>
</tr>
<tr>
<td>769 mV; 200 mg/L; 25 °C</td>
<td>0.996</td>
<td>1.025</td>
<td>2.88</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 30 °C</td>
<td>0.996</td>
<td>1.028</td>
<td>3.26</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 35 °C</td>
<td>0.996</td>
<td>1.134</td>
<td>13.83</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 40 °C</td>
<td>0.996</td>
<td>1.078</td>
<td>8.27</td>
</tr>
<tr>
<td>699 mV; 150 mg/L; 45 °C (rep 1)</td>
<td>0.900</td>
<td>0.000</td>
<td>-100.00</td>
</tr>
<tr>
<td>699 mV; 150 mg/L; 45 °C (rep 2)</td>
<td>0.900</td>
<td>0.000</td>
<td>-100.00</td>
</tr>
<tr>
<td>669 mV; 25 °C</td>
<td>0.900</td>
<td>0.000</td>
<td>-100.00</td>
</tr>
<tr>
<td>769 mV; 25 °C</td>
<td>0.996</td>
<td>1.257</td>
<td>26.19</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C (Rep 1)</td>
<td>0.996</td>
<td>0.959</td>
<td>-3.69</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C (Rep 2)</td>
<td>0.996</td>
<td>1.017</td>
<td>2.10</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C (Rep 3)</td>
<td>0.996</td>
<td>0.991</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

### 6.3 Effect of particle size on copper extraction from ore in saturated column tests

#### 6.3.1 Reproducibility of the saturated column test method

As reported in Chapter 5, particle size was found to have no effect on the copper extraction from the concentrate sample in the size range of 38 to 90 µm. The reason was thought to be the narrow size fraction used and the full liberation of chalcopyrite particles in the concentrate sample. For leaching of an actual ore, the particle size is expected to affect the degree of liberation and the diffusion length of a lixiviant through the particle. Saturated column tests were carried out to
determine the effect of particle size on the copper extraction from an ore sample. The use of saturated columns ensures that mass transport of the lixiviant does not become rate-limiting.

To determine the reproducibility of the saturated column test method, one leaching test was performed in duplicate using the washed primary copper sulfide ore under the following conditions: initial solution potential of 769 mV vs SHE, total iodide of 150 mg/L, size fraction of –1.7 + 1.0 mm, and 25 °C. The results in Figure 6.7 show that the saturated column test method was reproducible. The copper extraction reached around 30% on average within 7 days of leaching. The iron concentration slightly increased by 0.08 g/L due to the dissolution of chalcopyrite. The sulfur concentration increases by 1.1 g/L as a result of sulfuric acid addition for pH control.

![Figure 6.7 Cumulative copper extraction and concentrations of iron and sulfur in the iodine-assisted chalcopyrite ore leaching in saturated columns over a 7-day leaching period at 769 mV, 150 mg/L I\text{total}, and 25 °C](image)

**6.3.2 Saturated column test result**

Figure 6.8a shows the effect of particle size on the copper extraction from the chalcopyrite ore at solution potential of 769 mV vs SHE, total iodide of 150 mg/L, and 25 °C for a leaching period of 14 days. The copper extraction increased with decreasing particle size. At the end of leaching, the
The smallest size fraction (−0.71 + 0.425 mm) had the highest copper extraction (43.9%); the lowest copper extraction was obtained with the largest size fraction (−4.75 + 3.35 mm); the extraction with the medium size fraction (−1.70 + 1.00 mm) was in between. This result could be related to the degree of liberation, where the smallest size fraction has the highest degree of liberation. Interestingly, the initial dissolution rates were sensitive to the particle size, but after two days of leaching, the dissolution rates decreased and became similar for the three different size fractions studied (Figure 6.8b). The decrease in the dissolution rate was attributed to the depletion of fully liberated chalcopyrite minerals after two days of leaching.

Figure 6.8 (a) Cumulative copper extraction; (b) the rate of dissolution (dX/dt); (c) total iron concentration; (d) total sulfur concentrations in the iodine-assisted chalcopyrite leaching process over a 14-day leaching period, 769 mV, 150 mg/L \( I_{\text{total}} \), and 25 °C
Figure 6.9 The trend of solution potentials (vs SHE) in the three reactors used (a, c, e); and the trend of solution pH in the two reactors used (b, d, f) in the iodine-assisted saturated column leaching test over a 14-day leaching period at different size fractions, 769 mV, 150 mg/L I\textsubscript{total}, and 25 °C.
Figure 6.8c and d show the total dissolved iron and sulfur concentrations in the solution. The iron and sulfur concentrations increased during leaching because iron was released from chalcopyrite dissolution and sulfur was added as sulfuric acid to maintain constant solution pH. However, after 10 days of leaching, the total iron and sulfur concentrations from the test with \(-0.71 + 0.425\) mm started to decrease. Meanwhile, pH for this test also started to drop (Figure 6.9f). These decreases were attributed to iron hydrolysis, which was confirmed by subsequent solid surface characterization (Chapter 7).

### 6.3.3 Mass balance of leaching residue and permanganate consumption

Two different types of solid samples were obtained from the saturated column tests. The first type was pyrite added in the first reactor for the purpose of accurately monitoring the solution potential. The measurements of the initial and final mass and the chemical analysis of pyrite are presented in Table 6.4. The measurements of the initial and final mass show that there was no significant loss in mass, indicating that pyrite remained unreactive during leaching. The analysis of iron and sulfur content in pyrite and the corresponding Fe:S molar ratio shows that there was no change in pyrite composition.

**Table 6.4 The analysis of pyrite added in the first reactor in saturated column testing to maintain solution potential**

<table>
<thead>
<tr>
<th>Tests</th>
<th>Initial mass (g)</th>
<th>Final Mass (g)</th>
<th>Fe (%)</th>
<th>S (%)</th>
<th>Fe:S (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-4.75 + 3.35) mm</td>
<td>1.351</td>
<td>1.342</td>
<td>0.480</td>
<td>0.576</td>
<td>0.478</td>
</tr>
<tr>
<td>(-1.70 + 1.00) mm (rep 1)</td>
<td>1.35</td>
<td>1.347</td>
<td>0.483</td>
<td>0.554</td>
<td>0.499</td>
</tr>
<tr>
<td>(-1.70 + 1.00) mm (rep 2)</td>
<td>1.350</td>
<td>1.343</td>
<td>0.476</td>
<td>0.546</td>
<td>0.499</td>
</tr>
<tr>
<td>(-0.71 + 0.43) mm</td>
<td>1.353</td>
<td>1.339</td>
<td>0.449</td>
<td>0.519</td>
<td>0.496</td>
</tr>
</tbody>
</table>

Table 6.5 shows the analysis of the ore before and after the saturated column leaching tests. The extraction of copper was the highest at the smallest particle size tested, with a maximum of 38.13%
of copper extracted over a 14-day leaching period. However, the iron and sulfur content in the leaching residues did not decrease; on the contrary, they increased in some cases to beyond what was contained in the original ore sample, particularly in the case of the smallest particle size (−0.71 + 1.00 mm). The iron content was attributed to the precipitation of iron, partially in the form of jarosite, which contributed to the increases in iron and sulfur contents in the leaching residue. In addition, elemental sulfur was generated as a leaching product and remained in the leaching residue. Correspondingly, the concentrations of total iron and total sulfur in solution decreased and the solution pH also decreased, supporting the formation of jarosite during leaching.

Table 6.5 The analysis of the mass of the leaching residues before and after saturated column leaching

<table>
<thead>
<tr>
<th>Tests</th>
<th>Mass</th>
<th>Cu</th>
<th>% Cu remained</th>
<th>Fe</th>
<th>% Fe remained</th>
<th>S</th>
<th>% S remained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g)</td>
<td>(g)</td>
<td>(%)</td>
<td>(g)</td>
<td>(%)</td>
<td>(g)</td>
<td>(%)</td>
</tr>
<tr>
<td>−4.75 + 3.35 mm</td>
<td>Initial 522.3</td>
<td>2.67</td>
<td>76.70</td>
<td>20.20</td>
<td>99.66</td>
<td>8.48</td>
<td>102.77</td>
</tr>
<tr>
<td></td>
<td>Final  513.3</td>
<td>2.05</td>
<td>20.13</td>
<td>20.13</td>
<td>101.20</td>
<td>7.71</td>
<td>102.77</td>
</tr>
<tr>
<td>−1.70 + 1.00 mm</td>
<td>Initial 500.5</td>
<td>2.24</td>
<td>64.76</td>
<td>18.38</td>
<td>97.68</td>
<td>11.65</td>
<td>111.56</td>
</tr>
<tr>
<td>(Rep 1)</td>
<td>Final  497.5</td>
<td>1.45</td>
<td>17.95</td>
<td>17.95</td>
<td>100.65</td>
<td>11.56</td>
<td>111.56</td>
</tr>
<tr>
<td>−1.70 + 1.00 mm</td>
<td>Initial 500.8</td>
<td>2.24</td>
<td>61.87</td>
<td>18.39</td>
<td>98.06</td>
<td>11.66</td>
<td>101.55</td>
</tr>
<tr>
<td>(Rep 2)</td>
<td>Final  490.6</td>
<td>1.39</td>
<td>18.03</td>
<td>18.03</td>
<td>100.35</td>
<td>11.84</td>
<td>101.55</td>
</tr>
<tr>
<td>−0.71 + 0.43 mm</td>
<td>Initial 543.4</td>
<td>2.53</td>
<td>57.47</td>
<td>20.23</td>
<td>106.72</td>
<td>13.25</td>
<td>105.47</td>
</tr>
<tr>
<td></td>
<td>Final  539.0</td>
<td>1.46</td>
<td>21.59</td>
<td>21.59</td>
<td>101.49</td>
<td>13.98</td>
<td>105.47</td>
</tr>
</tbody>
</table>

6.4 Modelling the kinetics of iodine-assisted chalcopyrite leaching in stirred reactors

Figure 6.10 shows the kinetic analysis of the iodine-assisted chalcopyrite reactor leaching tests using the shrinking core chemical reaction-controlled model. The slopes of the regression lines represent the apparent rate constants at different solution potential (Figure 6.10a), total iodide concentration (Figure 6.10c), and temperature (Figure 6.10e). The logarithm of the apparent rate constants was plotted against the logarithm of the total ferric to total ferrous ratio (Figure 6.10b),
the logarithm of the total iodide concentration (Figure 6.10d), and the inverse temperature (Figure 6.10f) to obtain the reaction orders and the activation energy.

Linear relationships could be obtained in the case of the total iodide concentration and temperature. The reaction order with respect to the total iodide concentration was found to be 1.1723, and the activation energy was 45.7 kJ/mol. Interestingly, three distinctive regions were observed on the regression line in the case of the total ferric to total ferrous ratio. The Fe(III) to Fe(II) concentration ratio determines the solution potential, which, in turn, influences the iodine speciation. Therefore, the kinetic model was further modified to incorporate an iodine speciation term.

As described in Section 5.5, iodine can exist as free iodide (I⁻), triiodide (I₃⁻), and diiodine (I₂) depending on the solution potential. In the presence of the ferric/ferrous couple and at increasing solution potential, iodide ions are oxidized to triiodide (Eq. (6.2)) and then diiodine (Eq. (6.3)). Triiodide is formed by combining equimolar amounts of diiodine and iodide (Eq. (6.4)). Because diiodine was considered to be the actual oxidant responsible for chalcopyrite dissolution, in the potential region where triiodide is stable, only the diiodine incorporated inside the triiodide was considered to participate in chalcopyrite leaching. In other words, only 2/3 of the total iodide added is available for chalcopyrite dissolution (Eq. (6.5)). In the potential region where diiodine is the predominant species, 100% of the total iodide added is available for chalcopyrite oxidation (Eq. (6.6)).
Figure 6.10 Kinetic analysis of iodine-assisted chalcopyrite concentrate dissolution by the shrinking core chemical reaction-controlled model: (a) and (b) at different solution potential, i.e., different [Fe(III)]/[Fe(II)], 150 mg/L I\text{total}, and 25 °C; (c) and (d) at different total iodide concentration, 769 mV, and 25 °C; (e) and (f) at different temperature, 769 mV, and 150 mg/L I\text{total}
\[ 2\Gamma + 4/3\text{Fe}^{3+} = 2/3\text{I}_3^- + 4/3\text{Fe}^{2+} \] (6.2)
\[ 2\Gamma + 2\text{Fe}^{3+} = \text{I}_2 + 2\text{Fe}^{2+} \] (6.3)
\[ \text{I}_2 + \Gamma = \text{I}_3^- \] (6.4)
\[ \text{CuFeS}_2 + 2\text{I}_3^- = \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}_0 + 6\Gamma \] (6.5)
\[ \text{CuFeS}_2 + 2\text{I}_2 = \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}_0 + 4\Gamma \] (6.6)

The concentration of diiodine available for chalcopyrite oxidation could be expressed by Eq. (6.7), which was incorporated into the kinetic model to reflect the effect of solution potential on iodine speciation.

\[ [\text{I}_2] = \alpha [\text{I}_{\text{total}}] + \frac{2}{3} \beta (1 - \alpha) [\text{I}_{\text{total}}] \] (6.7)

Where \([\text{I}_2]\) is the concentration of diiodine available for chalcopyrite oxidation, \([\text{I}_{\text{total}}]\) is the total iodide concentration added, and \(\alpha\) and \(\beta\) are conversion factors ranging from 0 to 1. The dependence of iodine speciation on solution potential is summarized in Table 6.6. The potentials of 689 mV and 719 mV were assumed to be the values at which iodide and triiodide coexist and triiodide and diiodine coexist. At potentials lower than 689 mV, 100% of the total iodide added would exist as iodide (\(\Gamma\)) and therefore no diiodine is available for chalcopyrite oxidation. In the potential range of 689 to 719 mV, 100% of the total iodide added would exist as triiodide, 2/3 of which is available for chalcopyrite oxidation. At higher than 719 mV, 100% of the total iodide added would exist as diiodine, all of which is available for chalcopyrite oxidation.

\[ 1 - (1 - X)^{\frac{1}{3}} = k_{\text{app}} t \] (6.8)
\[ 1 - (1 - X)^{(1 - \varphi)} = k_{\text{app}} t \] (6.9)
\[ k_{\text{app}} = k_0 \exp \left( \frac{E_a}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right) \left( \frac{[\text{Fe(III)}]}{[\text{Fe(II)}]} \right)^a \left[ I_{\text{total}} \right]^b \]  

(6.10)

The \( k_{\text{app}} \) in Eq. (6.9) was refined by substituting the total iodide concentration term for the iodine speciation term, Eq. (6.7).

Table 6.6 The dependence of iodine speciation on potential, with \( \alpha \) and \( \beta \) being the conversion factors

<table>
<thead>
<tr>
<th>Solution potential</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORP &lt; 689 mV</td>
<td>0</td>
<td>0</td>
<td>100% as iodide ions</td>
</tr>
<tr>
<td>ORP = 689 mV</td>
<td>0</td>
<td>0.5</td>
<td>50% as triiodide; 50% as iodide</td>
</tr>
<tr>
<td>689 mV &lt; ORP &lt; 719 mV</td>
<td>0</td>
<td>1</td>
<td>100% as triiodide</td>
</tr>
<tr>
<td>ORP = 719 mV</td>
<td>0.5</td>
<td>0.5</td>
<td>50% as diiodide; 50% as triiodide</td>
</tr>
<tr>
<td>ORP &gt; 719 mV</td>
<td>1</td>
<td>0</td>
<td>100% as diiodine</td>
</tr>
</tbody>
</table>

The kinetic parameters in the general model (Eq. (6.10)) were determined by the non-linear least squares method, i.e., minimizing the sum of the squares of the difference between an observed extraction value and the fitted value predicted by the general model. By iteration, the least squares method finds the optimal set of parameters, including reaction orders, activation energy \( (E_a) \), and the topological exponent \( \varphi \) value, by minimizing the sum. The parameter values previously obtained using the shrinking core model were used as the initial values for iteration. The initial and the final values for the kinetic parameters are summarized in Table 6.7. The final kinetic model obtained from these reactor tests is expressed as Eq. (6.11). Figure 6.11 shows that the model can satisfactorily describe the copper extraction from chalcopyrite as a function of ferric to ferrous concentration ratio, total iodide concentration, and temperature in the iodine-assisted chalcopyrite leaching.
\[ X = 1 - \left( 1 - 49.712 \exp \left( \frac{43.096}{R} \left( \frac{1}{298.15} - \frac{1}{T} \right) \right) \right)^{0.322} \left( \alpha \left[ I_{\text{total}} \right] + \frac{2}{3} \beta \left( 1 - \alpha \right) \left[ I_{\text{total}} \right] \right)^{1.167} \cdot t(\text{day})^{3.236} \] (6.11)

Table 6.7 Kinetic parameters for stirred reactor leaching of chalcopyrite concentrate in the presence of iodine at 25 °C

<table>
<thead>
<tr>
<th>Mineral leaching kinetic parameters</th>
<th>Symbol</th>
<th>Unit</th>
<th>Initial value</th>
<th>Final value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant at reference temperature</td>
<td>( k_0 )</td>
<td>1/day</td>
<td>160.8997</td>
<td>160.881</td>
</tr>
<tr>
<td>Reaction order of ([\text{Fe(III)}]/[\text{Fe(II)}]) in M</td>
<td>( a )</td>
<td>-</td>
<td>0.264</td>
<td>0.322</td>
</tr>
<tr>
<td>Reaction order of ([I_2]) in mM</td>
<td>( b )</td>
<td>-</td>
<td>1.172</td>
<td>1.167</td>
</tr>
<tr>
<td>Particle size effect in mm</td>
<td>( c )</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Activation energy</td>
<td>( E_a )</td>
<td>J/mol</td>
<td>45,710</td>
<td>43,096</td>
</tr>
<tr>
<td>Topological exponent</td>
<td>( \varphi )</td>
<td>-</td>
<td>0.667</td>
<td>0.691</td>
</tr>
</tbody>
</table>

Figure 6.11 The comparison between the experimental (scatter plot) and the predicted copper extraction (solid lines) under different leaching conditions

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6.5 Kinetic modelling of iodine-assisted chalcopyrite ore leaching in saturated columns

The kinetic parameters for the saturated column tests were initialized with values obtained from the reactor tests (Table 6.7). During model fitting, the intrinsic parameters obtained from the stirred reactor tests remained the same, i.e., the activation energy and the reaction orders with respect to the ferric to ferrous ratio and the total iodide concentration. The optimum values for the exponent of the particle size term, the rate constant at the reference temperature ($k_0$), and the topological exponent ($\varphi$) were determined by the non-linear least squares method.

The kinetic parameters derived from the saturated column tests are presented in Table 6.8. The final kinetic equation derived from the saturated column tests is shown as Eq. (6.12). The topological exponent is larger than 1. Mathematically, this means that the leaching reaction would require infinite time to reach completion, which may be attributed to incomplete liberation of the chalcopyrite particles from the ore. Correspondingly, the rate constant of the saturated column leaching of ore was lower than that of the stirred reactor leaching of concentrate. The exponent of the particle size term was found to be 0.740, meaning that the leaching rate has an inverse relationship to the particle size. Figure 6.12 shows that the final kinetic equation can well describe the copper extraction from the chalcopyrite-bearing ore in the saturated column tests.

<table>
<thead>
<tr>
<th>Mineral leaching kinetic parameters</th>
<th>Symbol</th>
<th>Unit</th>
<th>Initial value</th>
<th>Final value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant at reference temperature</td>
<td>$k_0$</td>
<td>1/day</td>
<td>160.881</td>
<td>127.174</td>
</tr>
<tr>
<td>Reaction order of $[\text{Fe(III)}/[\text{Fe(II)}]$ in M</td>
<td>$a$</td>
<td>-</td>
<td>0.322</td>
<td>0.322</td>
</tr>
<tr>
<td>Reaction order of $[\text{I}_2]$ in mM</td>
<td>$b$</td>
<td>-</td>
<td>1.167</td>
<td>1.167</td>
</tr>
<tr>
<td>Particle size effect in mm</td>
<td>$c$</td>
<td>-</td>
<td>1</td>
<td>0.740</td>
</tr>
<tr>
<td>Activation energy</td>
<td>$E_a$</td>
<td>J/mol</td>
<td>43,096</td>
<td>43,096</td>
</tr>
<tr>
<td>Topological exponent</td>
<td>$\varphi$</td>
<td>-</td>
<td>0.691</td>
<td>6.143</td>
</tr>
<tr>
<td>$k_0 \frac{1}{d^c}$</td>
<td></td>
<td>(D = 0.0455 mm)</td>
<td>160.88</td>
<td>101.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D = 1.35 mm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ X = 1 - \left( 1 + \frac{654.056}{\alpha^{0.371}} \exp \left( \frac{43.096}{R} \left( \frac{1}{298.15} - \frac{1}{T} \right) \right) \right)^{0.322} \left( \alpha[I_{\text{total}}] + \frac{2}{3} \beta(1-\alpha)[I_{\text{total}}] \right)^{1.167} \cdot t(\text{day})^{-0.194} \] (6.12)

**Figure 6.12** The comparison between the experimental (scatter plot) and the predicted copper extraction (solid lines) under different size fraction

It is worth noting that the iodine speciation term in the kinetic equation (Eq. (6.12)) is non-continuous, representing the predominance of different iodine species in different potential region. Beyond the thermodynamic calculations reported in Chapter 5, the present study did not unravel the complexity of the iodine chemistry in the leaching system. Therefore, it is very likely that this iodine speciation term does not represent the actual complexity of the iodine chemistry in the leaching system. Nevertheless, the kinetic equation was capable of correlating the three key design parameters as the model input and the copper extraction as the model output. This kinetic equation was incorporated into the heap leach model (Chapter 8). Given the three design parameters as input, the heap leach model (HeapSim 2D software) calculates the solution potential at various locations of a heap and automatically determines the corresponding concentrations of different iodine species in reference to Table 6.6 coded inside the software.
6.6 Conclusions

This main objective of this Chapter is to refine the kinetic equation using the experimental data obtained from the reactor and saturated column tests carried out at constant potentials. The control tests without iodide addition showed that potassium permanganate used for control of solution potential did not directly oxidize chalcopyrite. A series of concentrate leaching tests was carried out in specially-designed sealed reactors that allowed all leaching parameters to be fully controlled. The experimental results showed that the rate of copper extraction was accelerated by increasing solution potential in the range of 669 to 769 mV vs SHE, increasing total iodide concentration in the range of 50 to 200 mg/L, and increasing temperature between 25 and 40 °C. Solution potential must be sufficiently high for the effect of temperature to manifest, because iodine speciation is controlled by solution potential. Diiodine was considered to be the active oxidant responsible for chalcopyrite dissolution, which can exist as the predominant species or incorporated inside triiodide depending on the solution potential.

A kinetic model incorporating iodine speciation was derived to correlate the rate of copper extraction with solution potential, iodine speciation, and temperature. The reaction order with respect to the ferric to ferrous concentration ratio, which determines the solution potential, was 0.322. The reaction order with respect to the concentration of diiodine was 1.167. The activation energy was 43.1 kJ/mol. The experimental results from the saturated column tests with chalcopyrite ore allow the effect of particle size to be included in the model. The rate of chalcopyrite leaching was found to correlate inversely with the particle size, with an exponent of 0.740 in the particle size term. The kinetic analysis supports that the leaching process is controlled by surface chemical reaction.
Chapter 7: Surface characterization of selected reactor leaching residues by XRD, MLA and XPS

7.1 Introduction

Leaching residues collected from a total of six reactor tests were examined in order to investigate: (1) whether pyrite was reactive during leaching; (2) whether elemental sulfur was formed as the reaction product; and (3) whether the formation of elemental sulfur and iron precipitates could cause surface passivation. These questions were answered by analyzing selected leaching residues using Qualitative X-ray analysis (XRD), Mineral Liberation Analyzer (MLA), and X-Ray Photoelectron Spectroscopy (XPS).

7.2 Copper extraction, permanganate consumption, and leaching residue mass

To investigate the mechanism of the iodine-assisted chalcopyrite leaching, representative leaching residues were collected from a total of six reactor tests, which have been reported in Chapter 6. The six tests represent the following distinct leaching conditions: without and with iodide addition, two different potentials (669 and 769 mV vs SHE), and three different temperatures (25, 40 and 45 °C). A summary of the cumulative copper extractions under these conditions is given in Figure 7.1 (details reported in Section 6.2). Chalcopyrite did not leach to any significant extent in the absence of iodine at 25 ºC regardless of the solution potential applied. In contrast, the addition of 150 mg/L iodide significantly improved chalcopyrite dissolution at 769 mV but not 669 mV at 25 ºC. At the same iodine concentration, increasing temperature to 45 ºC only slightly increased the copper extraction at 669 mV. The fastest kinetics was achieved by increasing temperature to
40 °C and maintaining the potential at 769 mV. These experimental results demonstrated the importance of maintaining solution potential to achieve a higher copper extraction.

![Graph](image)

**Figure 7.1** Cumulative copper extraction in the iodine-assisted chalcopyrite leaching process at 669 and 769 mV in the presence and absence of iodide and at different temperatures

The consumption of permanganate for potential control and the mass of the leaching residues were measured to understand whether pyrite was reactive and what form of sulfur was generated from leaching. The amount of permanganate consumed in these tests were measured and compared with the calculated values. The calculations were done under the assumptions that permanganate was only consumed by ferrous oxidation to ferric ions and that ferric ions were only consumed by chalcopyrite oxidation to elemental sulfur. Under these assumptions, the theoretical KMnO₄ consumption is 0.900 mol KMnO₄ per mol Cu extracted at 669 mV and 0.996 mol KMnO₄ per mol Cu dissolved at 769 mV.

Table 7.1 shows the comparison between the calculated KMnO₄ consumption and the actual values measured experimentally. The actual consumption of KMnO₄ at 669 mV was negligible because potential only slightly dropped in the course of leaching and the drop was not sufficient to trigger
the pump to inject KMnO₄ solution. In contrast, the actual consumption of KMnO₄ at 769 mV in the presence of iodine was similar to the calculated values, confirming the validity of the assumption. This supports that pyrite was inert in the iodine-assisted chalcopyrite leaching process and that the sulfur oxidation product was elemental sulfur.

Table 7.1 The comparison of calculated and experimental consumption of potassium permanganate

<table>
<thead>
<tr>
<th>Leaching test conditions</th>
<th>KMnO₄ consumption, mol per mol Cu dissolved</th>
<th>Mass of leaching residues, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Experimental</td>
</tr>
<tr>
<td>669 mV; 0 mg/L; 25 °C</td>
<td>0.900</td>
<td>0.000</td>
</tr>
<tr>
<td>769 mV; 0 mg/L; 25 °C</td>
<td>0.996</td>
<td>1.257</td>
</tr>
<tr>
<td>669 mV; 150 mg/L; 25 °C</td>
<td>0.900</td>
<td>0.061</td>
</tr>
<tr>
<td>769 mV; 150 mg/L; 25 °C</td>
<td>0.996</td>
<td>0.994</td>
</tr>
<tr>
<td>669 mV; 150 mg/L; 45 °C</td>
<td>0.900</td>
<td>0.000</td>
</tr>
<tr>
<td>769 mV; 100 mg/L; 40 °C</td>
<td>0.996</td>
<td>1.078</td>
</tr>
</tbody>
</table>

Table 7.1 also shows the calculated mass of the leaching residues and the actual values measured experimentally. The mass of each leaching residue was calculated under the assumption that pyrite was inert and that only chalcopyrite was dissolved during leaching, releasing copper and iron to the solution and generating elemental sulfur in the solid form. The actual mass of the residues from all tests at 25 °C was consistent with the calculated values, supporting that pyrite was unreactive and elemental sulfur was generated in the iodine-assisted chalcopyrite leaching process. However, at higher temperatures (40 °C and 45 °C), the actual mass was higher than the calculated values because of iron precipitation. This observation is supported by the decrease in pH in the tests at higher temperatures, indicating that a significant amount of iron was hydrolyzed (Figure 7.2).
The measurements of pH in the iodine-assisted chalcopyrite leaching process at 669 and 769 mV in the presence and absence of iodide and at different temperatures

**7.3 Mineralogical analysis by XRD**

Qualitative X-ray analysis was applied to characterize the mineralogy of the washed concentrate and the leaching residues. Figure 7.3 shows the mineralogical comparison between the chalcopyrite concentrate before and after leaching at different conditions. In the absence of iodine, the mineralogy of the leaching residue at 669 mV and 769 mV was similar to that of the washed concentrate, as indicated by the intensity of each phase. This result is consistent with the general consensus that chalcopyrite does not leach to any significant extent in conventional ferric sulfate media at ambient temperature. When iodide was added, the chalcopyrite peaks of high intensities were still observed in the residues at 669 mV, but were absent at 769 mV due to a complete dissolution of chalcopyrite at 769 mV. This result confirms that solution potential must be sufficiently high for the iodine-assisted chalcopyrite leaching to occur. If potential is not raised to a sufficiently high level, the effect of increasing temperature does not manifest, as evidenced by the existence of chalcopyrite peaks at 45 °C and 669 mV. When temperature was raised to 40 °C and at the highest potential tested (769 mV), chalcopyrite peaks disappeared and elemental sulfur was observed in the residue.
Pyrite, on the other hand, was present in all leaching residues, suggesting that pyrite was unreactive during leaching. The jarosite peak started to appear in the presence of iodine at 769 mV and 25 °C because of the considerable addition of potassium permanganate to maintain the solution potential. This explains the result that the mass of the leaching residues at 769 mV and 25 °C was slightly higher than the calculated value. In contrast, the intensity of the jarosite peak significantly increased as the temperature was raised, indicating that jarosite precipitation occurred to a greater extent at higher temperatures. This result agrees with the increase in the residue mass (Table 7.1) and the decrease in pH (Figure 7.2) due to release of acid by jarosite precipitation at high temperatures.

![Figure 7.3 Qualitative XRD analysis of the washed concentrate and the leaching residues at various leaching conditions (c: chalcopyrite; p: pyrite; s: elemental sulfur; j: jarosite; f: ferric hydrate)](image)

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7.4 Cross-sectional analysis of the leaching residues by MLA

The Mineral Liberation Analyzer (MLA) was used to investigate the mineralogical and morphological changes of the chalcopyrite concentrate during leaching. According to the XRD analysis shown in Figure 7.3, the chalcopyrite concentrate did not leach at 669 mV and 25 ºC, whether iodide was added or not; therefore, these leaching residues were excluded from the MLA analysis. In contrast, the leaching residues collected at 769 mV showed very different mineralogy and hence, these leaching residues were characterized by MLA. The leaching residue at 669 mV, 150 mg/L total iodide, and 45 ºC was also analyzed because of the partial leaching and jarosite precipitation.

Figure 7.4 and Figure 7.5 show the mineralogical composition of the leaching residues analyzed and the corresponding backscatter images and mapping. Figure 7.4A shows that the concentrate sample was thoroughly cleaned prior to leaching and was composed of chalcopyrite shown in blue and pyrite shown in yellow. The surfaces of the pyrite particles seemed to be smooth, whereas the chalcopyrite particles had microcracks (Figure 7.5A). Similar to what was observed from the XRD results in Figure 7.3, after being leached in the absence of iodide at 769 mV and 25 ºC, the mineralogy (Figure 7.4A) and morphology (Figure 7.5B) of the chalcopyrite and pyrite remained the same as prior to leaching. This result agrees with the low cumulative copper extraction achieved (10%) after 14 days of leaching under this condition.
A: washed chalcopyrite concentrate prior to leaching

B: 769 mV, without iodide, 25 °C, 14 days

C: 769 mV, 150 mg/L I, 25 °C, 14 days

D: 669 mV, 150 mg/L I, 45 °C, 7 days

E: 769 mV, 150 mg/L I, 40 °C, 7 days

**Figure 7.4 The mineralogical composition of chalcopyrite concentrate and different leaching residues using cross-sectional MLA analysis**

Chalcopyrite

Pyrite

A: washed chalcopyrite concentrate prior to leaching
B: leaching residue at 769 mV, without iodide, 25 °C, 14 days

C: leaching residue at 669 mV, 150 mg/L I, 45 °C, 7 days

D: leaching residue at 769 mV, 150 mg/L I, 40 °C, 7 days

Figure 7.5 The MLA-mapping images of cross-sectional observation of chalcopyrite concentrate and different leaching residues
After leaching with the addition of iodide at 769 mV and 25 °C, the surfaces of the chalcopyrite particles were covered by elemental sulfur (red), suggesting that chalcopyrite dissolution in the iodine-assisted leaching process generated elemental sulfur (Figure 7.4C). When the temperature was raised to 40 °C, jarosite (orange) was found on the surface of chalcopyrite and pyrite (Figure 7.4E); the mapping (Figure 7.5D) shows that the surfaces of chalcopyrite and pyrite were rich in potassium and oxygen associated with jarosite formation; chalcopyrite particles became smaller and were enveloped in elemental sulfur. Given that complete dissolution was achieved under both test conditions, it could be concluded that the presence of jarosite and elemental sulfur did not passivate the chalcopyrite surface. Furthermore, pyrite particles were inert and did not leach under both test conditions. Jarosite formation was also observed in the presence of iodine at 669 mV and 45 °C, even though the rate of copper extraction under this condition was lower than at 769 mV (Figure 7.4D and Figure 7.5C).

### 7.5 Surface analysis by XPS

X-Ray Photoelectron Spectroscopy (XPS) analysis was performed to examine the transformation of the mineral surfaces and possible compounds formed on the mineral surfaces during leaching. The term ‘surface’ was defined as the outer layer of a mineral particle with a typical depth of 1 – 10 nm, which is the depth resolution of XPS (Hackl et al., 1995). XPS provides information on the chemical state important for determining the surface compounds. The samples used for the XPS analysis included the washed chalcopyrite concentrate and all selected leaching residues. In addition, high-purity elemental sulfur, chalcopyrite, jarosite, pyrite, hematite, and wustite were analyzed for comparison. The Cu, Fe, S, I, Mn and O spectra were examined.
7.5.1 Cu spectra

Figure 7.6 shows the high-resolution spectra of Cu 2p and Cu LMM from XPS analysis. The binding energies obtained in the current study were compared with those reported in the literature in Table 7.2. The washed concentrate had Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks at 932.2 eV and 952.1 eV, respectively. These peaks were very close to those of the pure chalcopyrite examined, which has Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks at binding energies of 932.3 eV and 952.5 eV, respectively. These binding energies were indicative of the presence of monovalent copper (Cu$^+$) originating from chalcopyrite, because the electronic structure of chalcopyrite is considered to be Cu$^+$Fe$^{3+}$(S$^{2-}$)$_2$ (Hackl et al., 1995). The presence of divalent copper (Cu$^{2+}$) can be characterized by the existence of a Cu 2p$_{3/2}$ peak at binding energies of 939 – 944 eV (Wang et al., 2016). The peak of Cu$^{2+}$ was not observed on the surface of the washed concentrate, even though the sample was exposed to air during preparation. The Cu LMM spectra in Figure 7.6b allowed for further differentiation of Cu bonds between Cu–Cu and Cu$^+$ bonds in the chalcopyrite sample. The pure chalcopyrite and the washed concentrate had a peak located at 568.6 eV, which is close to the value of 568.5 eV measured for the Cu$^+$ bond in CuS (Krylova and Andrulevičius, 2009).

The two leaching residues in the absence of iodide had the same peak locations in Cu 2p and Cu LMM spectra as the washed concentrate. However, the intensities were lower, despite only 10% of copper being extracted in these two tests. This indicates that once leaching was initiated, chalcopyrite surface started to be modified. Even though the copper extractions were not high at 669 mV in the presence of iodine, the residues collected showed no peaks in the Cu 2p and Cu LMM spectra, indicating that the chalcopyrite surfaces were covered by non-copper compounds. Detectable peaks in Cu 2p and Cu LMM spectra were also absent in the residues collected at
769 mV in the presence of iodine. These results agree with the MLA analysis in Figure 7.4 and Figure 7.5 that layers of elemental sulfur and jarosite were formed on chalcopyrite surfaces.

Figure 7.6 The XPS spectra of Cu peaks of pure minerals, washed chalcopyrite concentrate and leaching residues

Table 7.2 The comparison of binding energies of Cu 2p$_{3/2}$, Cu 2p$_{1/2}$, and Cu LMM

<table>
<thead>
<tr>
<th>Cu 2p$_{3/2}$ (eV)</th>
<th>Cu 2p$_{1/2}$ (eV)</th>
<th>Cu LMM (eV)</th>
<th>References</th>
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<td>932.2</td>
<td>952.3</td>
<td>568.6</td>
<td>Current study</td>
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<tr>
<td>932.4</td>
<td>952.1</td>
<td>-</td>
<td>Nakai et al., 1978</td>
</tr>
<tr>
<td>932.0</td>
<td>953.1</td>
<td>-</td>
<td>Rath et al., 2001</td>
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<td>932.1</td>
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<td>Nie et al., 2020</td>
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<td>932.4</td>
<td>952.3</td>
<td>568.9</td>
<td>Ghahremaninezhad et al., 2013</td>
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<td>932.1</td>
<td>952 – 953</td>
<td>568.8</td>
<td>Wang et al., 2016</td>
</tr>
</tbody>
</table>
7.5.2 Fe spectra

Figure 7.7 shows the Fe 2p and Fe LMM spectra of the pure minerals, the washed concentrate, and the leaching residues. The pure chalcopyrite had the Fe 2p3/2 peak at 711.7 eV and the Fe 2p1/2 peak at 725.3 eV. Pyrite had multiple peaks in the Fe 2p spectra, namely, at 707.3 eV, 711.9 eV, 720.1 eV, and 726.1 eV. The washed concentrate showed peaks similar to those of pure chalcopyrite and pyrite, because the sample consisted of mainly chalcopyrite and pyrite as shown by the XRD result in Figure 7.1. Ghahremaninezhad et al. (2013) and Wu et al. (2015) reported that the peaks in the binding energy range of 710 to 712 eV are related to the Fe(III)–O, –OH, or –OOH, whereas the peak of Fe–S in chalcopyrite is found near 708 eV. This binding energy is the same as that of the Fe 2p peak found in hematite (Fe₂O₃) and iron oxide (FeO) (Figure 7.7). The higher Fe2p₃/₂ peak in chalcopyrite in our test was due to the exposure of chalcopyrite to air. Buckley and Woods (1984) reported that the increase in the exposure time shifted the Fe 2p peak from 708 eV to 711 eV. The two residues in the absence of iodine showed Fe peaks in the Fe 2p spectra similar to the washed chalcopyrite. However, similar Fe peaks were not found in the residues in the presence of iodine. Instead, these residues showed a peak at 712 eV, which could be assigned to jarosite (Wu et al., 2015), confirming that the mineral surfaces were coated by jarosite.
Figure 7.7 The XPS spectra of Fe peaks of pure minerals, washed chalcopyrite concentrate and leaching residues

7.5.3 S spectra

The S 2p and S 2s spectra are presented in Figure 7.8. The washed concentrate had the same S peaks as in chalcopyrite and pyrite. The S peaks in the leaching residues without iodide addition were similar to those of the washed concentrate. By contrast, the S peaks of the leaching residues in the presence of iodide at 25 °C had the same binding energies as those of elemental sulfur and pyrite-sulfide. In addition, another peak at around 169 eV was detected at 769 mV, which was correlated to sulfate (SO$_4^{2-}$) peak in jarosite. A similar peak at 169 eV was also observed in the two residues at higher temperatures, but the elemental sulfur peaks disappeared. These results indicated that at 25 °C and 150 mg/L iodide, pyrite and elemental sulfur were the dominant
chemical species on the mineral surfaces and that jarosite formation only occurred at 769 mV. At higher temperatures, only jarosite was observed on the mineral surfaces.

Figure 7.8 The XPS spectra of S peaks of pure minerals, washed chalcopyrite concentrate and leaching residues

7.5.4 Spectra of K, O, Mn and I

The K 2p and O 1s spectra are shown in Figure 7.9a and Figure 7.9b. The washed concentrate and the pure chalcopyrite had a peak in the O1 spectra but not in the K 2p spectra. This observation suggests that the washed concentrate and the pure chalcopyrite did not contain potassium jarosite. The observed peak in the O 1s spectra was related to other forms of iron oxide, which could be formed from the exposure of the samples to air. The leach residue from the test at 769 mV, 150 mg/L I and 25 °C had peaks in K 2p spectrum, which was assigned to potassium jarosite. The jarosite peaks were also found in the residues at a higher temperature, either at the low potential
(669 mV) or the high potential (769 mV). All residues with potassium jarosite peaks also had a SO$_4^{2-}$ peak at 169 eV. The higher intensities of the K and O peaks at higher temperatures indicated that the jarosite layer became denser at higher temperatures, but the jarosite formation did not passivate the chalcopyrite surfaces.

![Figure 7.9 The XPS spectra of K and O peaks of pure minerals, washed chalcopyrite concentrate and leaching residues](image)

The Mn and I spectra were also analyzed to verify whether manganese and iodide precipitated during leaching. The Mn spectra in Figure 7.10a show that the concentrate had Mn peaks at 649.2 eV and 641.2 eV. After the concentrate was leached in the absence of iodide, the intensities of those peaks were reduced, which was thought to be associated with the copper dissolution. Those peaks disappeared when the concentrate was leached in the presence of 150 mg/L iodide. These results show that the addition of potassium permanganate for controlling solution potential
during leaching did not lead to formation of Mn precipitate. Figure 7.10b shows two main I 3d peaks at binding energies of 630.3 eV and 618.9 eV in the washed concentrate. These peaks indicate that the washed concentrate contained a small amount of iodide compounds and these peaks were not related to the precipitation of iodide forms due to the iodine-assisted leaching test. The peaks were also found in the leach residues from the tests without iodide and with iodide at 669 mV, and 25 °C, where copper extraction was found to be low. The I 3d peaks disappeared when the concentrate was leached in the presence of iodide at higher potential and higher temperatures.

Figure 7.10 The XPS spectra of Mn and I peaks of pure minerals, washed chalcopyrite concentrate and leaching residues
7.6 Conclusions

To investigate changes in mineralogy and morphology, the leaching residues from six selected reactor tests under different leaching conditions were examined by XRD, MLA, and XPS. The experimental results allowed better understanding of the reactivity of pyrite, the form of sulfur product generated by leaching, and chalcopyrite surface passivation during leaching. The XRD analyses of the bulk residues showed that as leaching progressed in the presence of iodine, chalcopyrite was transformed and iron precipitation occurred, but pyrite was unaffected. The MLA analyses suggested that in the presence of iodine the chalcopyrite phase was transformed to elemental sulfur and that pyrite was stable in the course of leaching; jarosite was found on the surfaces of chalcopyrite and pyrite at higher temperatures. The XPS analyses further confirmed that the surfaces of chalcopyrite particles were covered by jarosite and elemental sulfur. CuI precipitate was not observed in the leaching residues, suggesting that copper did not precipitation as CuI during leaching. Based on the surface characterization results, the following conclusions can be made on the iodide-assisted chalcopyrite leaching: (1) pyrite is inert during leaching; (2) elemental sulfur is the sulfur product generated from chalcopyrite leaching; (2) the formation of elemental sulfur and jarosite does not passivate chalcopyrite surface and therefore does not hinder its leaching.
Chapter 8: Modelling the kinetics of chalcopyrite column leaching in ferric sulfate media in the presence of iodine

8.1 Introduction

This main objective of this Chapter is to calibrate the HeapSim 2D model to simulate the iodine-assisted chalcopyrite column leaching process. This was done by incorporating into the HeapSim 2D model the kinetic equation developed for chalcopyrite reactor leaching in ferric sulfate media in the presence of iodine reported in Chapter 6. In the calibration process, the extrinsic leaching parameters, including the reaction rate constant and the topological exponent, were adjusted using the experimental data of the 1-m and 6-m column leaching tests. The calibrated HeapSim 2D model was used to assess the response of copper extraction to variations in key design and operating parameters, including irrigation rate, ferric concentration, total iodide concentration, and temperature.

8.2 Experimental results of the column leaching tests

8.2.1 The 1-m column leaching tests carried out in Hitachi

The 1-m and 6-m column leaching tests reported in this Chapter were carried out by the sponsor company personnel. The characterization of the ore sample used, including analyses of the particle size, mineralogy, and chemical composition, was performed by the sponsor company. The sponsor company provided the raw experimental data to the UBC research team for data analysis and modelling. Each column contained 12 kg chalcopyrite-bearing ore of three different size fractions: 45% mass in the size range of – 26.5 + 11.2 mm, 27% in the size range of – 11.2 + 4.75 mm, and 27% in the size range of < 4.75 mm. The main copper mineral was chalcopyrite, accounting for
1.74% of the total mass of the ore. Small percentages of bornite and tennantite were also present, but only in the size fraction of < 4.75 mm. Pyrite accounted for 7% of the total mass of the ore sample and was found in all size fractions at different concentrations: 5.8% in the size fraction of – 26.5 + 11.2 mm, 6.4% in the size fraction of – 11.2 + 4.75 mm, and 9.5% in the size fraction of < 4.75 mm. The main gangue minerals were quartz (27.9%), albite (9.9%), orthoclase (22.7%), muscovite (25.5%). The 1-m column leaching tests were carried out at the room temperature (~25 °C) with the total iodide concentration varied from 0 to 200 mg/L.

Figure 8.1a shows the copper extraction over time at three different total iodide concentrations for the 1-m column tests. For all three tests, the conventional ferric sulfate leaching was carried out for the initial 21 days to remove acid soluble copper minerals and secondary copper sulfides. From day 21 onwards, copper dissolved very slowly in the absence of iodine, with a dissolution rate of < 0.05% copper per day. On the other hand, the addition of iodide significantly accelerated the kinetics of the copper dissolution. The copper extraction reached 54.7% in the presence of 200 mg/L total iodide on day 125, whereas the conventional ferric sulfate leaching achieved only 6.5% copper extraction during the same leaching period. Figure 8.1b shows that the copper dissolution rate was higher at 200 mg/L iodine than at 100 mg/L iodine, but started to decrease on day 41 at both iodine concentrations.
Figure 8.1 Experimental results of 1-m column leaching tests without and with the addition of 100 and 200 mg/L of iodide at room temperature (~25 °C) carried out in Hitachi, Japan: (a) Cumulative copper extraction; (b) the leaching rate (dX/dt); (c) solution potential; (d) Fe(III)/Fe(II) ratio; (e) total iron concentration; and (f) total iodide concentration during leaching.
Figure 8.1c and Figure 8.1d show the solution potential of the leachates generated from the three column tests and the corresponding ferric to ferrous ratio in the course of leaching. The solution potential measured of the conventional ferric sulfate leaching test was the highest among the three tests, because the least amount of ferric was consumed by chalcopyrite oxidation. The potentials were similar in the presence of 100 mg/L and 200 mg/L total iodide. This was attributed to the existence of a potential window, within which the oxidized iodine species are predominant and act as the oxidants for chalcopyrite dissolution. The existence of a potential window was observed in both the bottle (Chapter 5) and reactor leaching tests (Chapter 6). Once the solution potential decreased to below the lower limit of the potential window, ferric became the main oxidant and the conventional ferric leaching kicked in. Figure 8.1e shows that the total iron concentrations in the presence of iodine were higher than in the absence of iodine, because 1 L of 20 g/L ferrous solution was added to the leachates generated from the two tests with the iodide addition. This was done to ensure all oxidized forms of the iodine species were reduced to iodide, thus minimizing the iodine loss as diiodine by evaporation. Figure 8.1f shows that the total iodide concentration remained relatively constant, indicating that the iodine loss was negligible during leaching.

### 8.2.2 The 1-m column leaching tests carried out in Chile

Two 1-m column leaching tests were carried out at the room temperature (~25 °C) in Chile, one without the addition of iodide and the other with the addition of 100 mg/L total iodide. The total iron concentration in the feed solution was 5.6 g/L. The ore sample contained 0.6% total copper, with 93% copper in the form of insoluble copper sulfides. The total ore mass in each column was 25 kg.
The tests were initialized with ferric leaching until day 25. The copper extractions achieved in both tests during this period were similarly low. However, the copper extraction was significantly enhanced after the addition of 100 mg/L iodide (Figure 8.2a). In the presence of iodine, the rate of copper dissolution was high and the leaching reaction did not cease after 144 days (Figure 8.2b), indicating that chalcopyrite particles were not yet fully leached. Note that the copper dissolution rates in this test were lower than those obtained from the 1-m column leaching tests carried out in Hitachi (Section 8.2.1). For example, 28% copper extraction was achieved in this test as opposed to 42% copper extraction in the Hitachi 1-m column tests for a leaching period of 100 days. This was attributed to the lower ratio of iodine to the mass of ore used in the column test carried out in Chile.

Figure 8.2c shows that the solution potentials with the addition of 100 mg/L iodide were lower than those without iodide addition because the former had higher levels of ferric consumption and ferrous generation from chalcopyrite oxidation. Correspondingly, the ferric/ferrous ratios were lower and the total iron concentrations were higher in the former (Figure 8.2d and e). Figure 8.2f shows that the iodide concentration fluctuated around 100 mg/L, which might be related to the adsorption and desorption of iodine species on silicate minerals in the gangue.
Figure 8.2 Experimental results of 1-m column leaching tests without and with the addition of 100 mg/L of iodide at room temperature (~25 °C) carried out in Chile: (a) Cumulative copper extraction; (b) the leaching rate (dX/dt); (c) solution potential; (d) Fe(III)/Fe(II) ratio; (e) total iron concentration; and (f) total iodide concentration during leaching.
8.2.3 The 6-m column leaching tests carried out in Chile

To investigate the effect of the height of the packed ore bed on the leaching performance, two sets of 6-m column leaching tests were performed: one without iodide addition (in triplicate) and the other with the addition of 100 mg/L of iodide (in triplicate). Around 216 kg of copper ore was added into each column. The experimental results are shown in Figure 8.3. Figure 8.3a and b show that the copper extraction and the rate of copper dissolution with the addition of 100 mg/L iodide were significantly higher than in the absence of iodide addition. The leaching curve in the presence of iodine did not plateau after 300 days of leaching. The 6-m column tests used the same solution flowrate and ferric concentration as the 1-m column tests carried out in Chile, meaning that the total amounts of oxidant provided to the columns per unit time was the same. However, the mass of the ore samples in the 6-m columns was higher than that in the 1-m columns, meaning that the iodine to chalcopyrite ratio was lower in the 6-m column tests. This led to a longer leaching time for the 6-m column tests to achieve the same level of copper extraction.

Unlike the 1-m column tests, the solution potential and the corresponding ferric to ferrous ratio in the 6-m column tests had a small difference between the absence and the presence of iodine (Figure 8.3c and d). It indicates that the taller column allowed ferric to oxidize other minerals for a longer period of time. Moreover, the test in the absence of iodine had a lower total iron concentration in the PLS (3 – 4 g/L) than the test in the presence of iodine (at least 5 g/L), resulting in a more significant drop in the potential due to the conversion of ferric to ferrous (Figure 8.3e). The concentration of the total iodide present in the leachates was lower than the initial concentration as a result of the adsorption of iodine species on silicate gangue minerals and iodine loss via evaporation.
Figure 8.3 Experimental results of 6-m column leaching tests without and with the addition of 100 mg/L of iodide at room temperature (~25 °C) carried out in Chile: (a) Cumulative copper extraction; (b) the leaching rate (dX/dt); (c) solution potential; (d) Fe(III)/Fe(II) ratio; (e) total iron concentration; and (f) total iodide concentration.

8.3 Modelling the kinetics of iodine-assisted chalcopyrite column leaching

The HeapSim 2D model was applied to simulate the kinetics of copper extraction in the 1-m and 6-m column tests. The kinetic equation obtained in Chapter 6 (Eq. (6.12)) was incorporated into the HeapSim 2D model. The fraction unreacted (1-X) was first converted to the concentration of...
unreacted chalcopyrite (Eq. (8.1)) in the ore and then the kinetic equation in Chapter 6 (Eq. (6.9)) was modified and derived to Eq. (8.2). The other values for heap, solution, and solute parameters used in the simulation are presented in Appendix G.

\[
[1 - X]^{(1-\psi)} = \left[\frac{n_{cpy,0} - n_{cpy,dissolved}}{n_{cpy,0}}\right]^{(1-\psi)} = \left[\frac{n_{cpy}}{n_{cpy,0}}\right]^{(1-\psi)} = \left[\frac{n_{cpy}/m_{ore,0}}{n_{cpy,0}/m_{ore,0}}\right]^{(1-\psi)} = \left[\frac{C_{cpy}}{C_{cpy,0}}\right]^{(1-\psi)} \tag{8.1}
\]

\[
r = \frac{dC_{cpy}}{dt} = \rho_b \frac{k_0}{C_{cpy,0}} \left(\frac{1}{\varphi - 1}\right) \exp\left[\frac{E_A}{R\left(\frac{1}{T_0} - \frac{1}{T}\right)}\right] \left[\frac{[Fe(III)]}{[Fe(II)]}\right]^a \left[\alpha[l_{initial}] + \beta(1 - \alpha) \frac{2}{3} [l_{initial}]\right]^b C_{cpy}^{\psi} \tag{8.2}
\]

**Table 8.1 Description of parameters in Eq. (8.1)**

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<tr>
<th>Symbols</th>
<th>Description</th>
<th>Units</th>
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<td>(C_{cpy,0})</td>
<td>Concentration of chalcopyrite in ore at (t = 0)</td>
<td>kmol/kg</td>
</tr>
<tr>
<td>(C_{cpy})</td>
<td>Concentration of chalcopyrite in ore at time (t)</td>
<td>kmol/kg</td>
</tr>
<tr>
<td>(n_{cpy})</td>
<td>Mol of chalcopyrite remained at time (t)</td>
<td>kmol</td>
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<tr>
<td>(n_{cpy,0})</td>
<td>Mol of chalcopyrite in ore at (t = 0)</td>
<td>kmol</td>
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<td>(n_{cpy,dissolved})</td>
<td>Mol of chalcopyrite dissolved at time (t)</td>
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<tr>
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<tr>
<td>(1-X)</td>
<td>Fraction of unreacted chalcopyrite at time (t)</td>
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The goal of the model calibration is to fit the model to the experimental data by adjusting certain model parameters. In the model calibration, the intrinsic parameters, including the activation energy and the reaction orders were maintained the same as derived from the reactor tests. Because the size fraction and the characteristics of the ore used in the column tests were different from those in the reactor tests, the topological exponent and the rate constant that could represent these differences were adjusted in the model calibration. The model calibration was first carried out using the experimental data of the 1-m column leaching tests carried out in Hitachi. The calibrated parameter values are presented in Table 8.2. The model with these calibrated parameters could satisfactorily simulate the copper extraction and the solution potential during leaching (Figure 8.4).
Table 8.2 The refined values of each leaching kinetic parameters for Hitachi 1-m column leaching

<table>
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<th>Parameters</th>
<th>Description</th>
<th>Value</th>
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<td>Topological exponent, corresponding to degree of liberation</td>
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<tr>
<td>$C_{\text{cpy,0}}$</td>
<td>Initial concentration of chalcopyrite in the ore (0.564% Cu as chalcopyrite)</td>
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<td>$k_{\text{cpy}}$</td>
<td>The rate constant at reference temperature (25 °C)</td>
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Figure 8.4 The calibration of the kinetic parameters in the 1-m column leaching tests carried out in Hitachi: (a) copper extraction; (b) solution potential trend

By using the same topological exponent, the model was further calibrated using the experimental data of the 1-m column leaching test carried out in Chile. The results show that it was necessary to reduce the rate constant from 34.56/day (Hitachi 1-m column) to 10.37/day (Chile 1-m column) to satisfactorily describe the leaching kinetics of the Chile 1-m column test. This slower kinetics was caused by the lower ratio of iodine to chalcopyrite for the Chile 1-m column tests. The simulation results of the copper extraction and the solution potential for the Chile 1-m column tests are shown in Figure 8.5.
Figure 8.5 The calibration of the kinetic parameters in the 1-m column leaching tests carried out in Chile: (a) copper extraction; (b) solution potential

The calibrated model was used to describe the experimental data of a larger scale test, i.e., the 6-m column tests. To satisfactorily describe the leaching kinetics of the 6-m column tests, the rate constant must be further reduced to 8.51/day to account for the significant iodide loss and much lower iodine to chalcopyrite ratio in the 6-m column tests. After adjusting the rate constant, the model could well simulate the kinetics of the 6-m column leaching, as shown in Figure 8.6.

Figure 8.6 The application of the calibrated model to describe the kinetics of the 6-m column leaching tests: (a) copper extraction; (b) solution potential trend
8.4 Sensitivity tests

Sensitivity tests were performed to investigate the response of the leaching performance to variations in key design and operating parameters. The key parameters investigated were irrigation rate, ferric concentration, total iodide concentration, temperature, and column height. The values of these parameters in all tests performed are presented in Table 8.3.

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<td>5.30</td>
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<tr>
<td>Iodide concentration</td>
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<td>5.30</td>
</tr>
</tbody>
</table>

Figure 8.7 shows the leaching performance in response to changes in the irrigation rate. The results indicate the existence of an optimal irrigation rate, beyond which the leaching performance can no longer be improved. A similar conclusion can be drawn on the ferric concentration that the copper
Extraction increased with the ferric concentration up to a certain value, as shown in Figure 8.8. This corresponds to the potential window within which the oxidized forms of the iodine species are predominant and act as the oxidants for chalcopyrite dissolution. To further improve the leaching performance, a higher concentration of iodide is required to be added, along with sufficient ferric concentration or irrigation rate to maintain the potential value in the suitable range (Figure 8.9). However, the actual choice of these design and operating parameters must take into consideration the geotechnical stability of the heap and the possible occurrence of iron precipitation at higher ferric concentrations. Raising temperature leads to an increase in the copper extraction, as shown in Figure 8.10. The increase in the column height lowers the rate of copper extraction because of the decreasing amounts of the oxidant available per unit mass of ore (Figure 8.11).

A significant drop of the solution potential to 650 mV vs SHE was observed for almost all leaching tests under conditions (Figure 8.7 – Figure 8.11) where the ratio of ferric concentration to the mass of ore was low. Under these conditions, the column was segregated into two regions, the iodine leaching region and the conventional ferric leaching region. The former appeared when the solution potential was relatively high (above 650 mV vs SHE), while the latter occurred when the potential was lower than 650 mV vs SHE. The iodine leaching region gradually expanded as leaching proceeded. As the dissolution rate became slower, the potential of the pregnant leach solution (PLS) gradually increased. According to the simulation, solution potential can be used as an indicator to monitor the amount of oxidant available and the leaching performance.
Figure 8.7 The effect of irrigation rate in (L/m²/h) on the leaching performance in 1-m column: (a) copper extraction and (b) solution potential trend

Figure 8.8 The effect of ferric concentration on the leaching performance in 1-m column: (a) copper extraction and (b) solution potential trend

Figure 8.9 The effect of total iodide concentration on the leaching performance in 1-m column: (a) copper extraction and (b) solution potential trend
8.5 Conclusions

The kinetic equation derived from the reactor leaching tests (reported in Section 6.4) was incorporated into the HeapSim 2D model to simulate the 1-m and 6-m column leaching tests. In the model calibration process, the reaction orders and the activation energy were considered intrinsic to the leaching reaction and were not adjusted, whereas the reaction rate constant and the topological exponent were adjusted to fit the model to the column leaching test data. The reaction rate constant was smaller and the topological exponent was larger for the column leaching tests.
because the column tests used ore samples of larger particle sizes with partially-liberated chalcopyrite particles.

The kinetic modelling of the column tests shows that the performance of the iodide-assisted chalcopyrite leaching is dependent on the solution potential. The potential measured in the PLS from all column tests was around 650 mV vs SHE, regardless of the amount of chalcopyrite, irrigation rate, and iodide concentration. This indicates that the amount of ferric is insufficient to maintain the potential in the entire column within the range where diiodine or triiodide are predominant. Instead, the predominant iodine species becomes iodide as the solution percolates towards the end of the column; thus, the leaching process becomes conventional ferric sulfate leaching. However, all copper extraction curves show that the leaching did not plateau, meaning that the leaching would proceed as long as a fresh ferric solution is supplied continuously.

The simulations indicate that there is an optimal value of irrigation rate and ferric concentration, beyond which further increases do not lead to significant improvements in the copper extraction. To further improve the leaching performance, a higher concentration of iodide is required to be added, along with sufficient ferric concentration or irrigation rate to maintain the potential value in the suitable range. In general, the copper extraction increases with increasing temperature. The actual choices of these design and operating parameters must take into consideration the geotechnical stability of the heap and the possible occurrence of iron precipitation at higher ferric concentrations.
Chapter 9: Conclusions and recommendations

There are a range of challenges associated with pyrometallurgical processing of low-grade, complex primary sulfides. Hydrometallurgical methods may find niche applications for treating these low-grade, complex concentrates and ores. The addition of iodine has been found to significantly accelerate the kinetics of chalcopyrite leaching in ferric sulfate media at ambient temperatures. To better understand this process, this research comprehensively investigated the factors affecting the rate of chalcopyrite leaching in the presence of iodine (Objective I), the kinetics of the iodine-assisted chalcopyrite leaching in ferric sulfate media (Objective II), the mineralogical and morphological transformation of chalcopyrite and pyrite under different leaching conditions (Objective III), and the scale-up of the process and the performance of copper extraction in response to variations in key design and operating parameters (Objective IV). The key conclusions of the present study and recommendations for further study are presented here.

9.1 Conclusions

In general, the copper extraction in the iodine-assisted chalcopyrite leaching increases with increasing solution potential, the total iodide concentration, and temperature, and decreases with increasing particle size. Redox potential is found to be the primary factor controlling the chalcopyrite leaching by controlling the iodine speciation in solution. Solution potential must be sufficiently high for the effect of temperature to manifest. The particle size has a negligible effect on the concentrate leaching, but noticeably affects the leaching of chalcopyrite-bearing ore. Either diiodine or triiodide is considered to be the active oxidant responsible for chalcopyrite dissolution depending on the solution potential.
The surface characterization by XRD, MLA and XPS allows for understanding of the form of sulfur generated, the reactivity of pyrite, and chalcopyrite surface passivation. The results show that chalcopyrite is transformed into elemental sulfur; pyrite is inert during leaching, which is supported by the measurements of residue mass; iron precipitates are formed on the mineral surfaces at higher temperatures. Even though chalcopyrite surface is fully covered by elemental sulfur or jarosite, the formation of these layers does not hinder the dissolution of chalcopyrite.

The kinetic analyses support that the leaching process is controlled by surface chemical reaction without surface passivation. A kinetic equation is developed that correlates the rate of copper dissolution with the ferric to ferrous concentration ratio, total iodide concentration, and temperature. The kinetic model developed is capable of simulating reactor leaching of chalcopyrite concentrate. Incorporation of this kinetic model into a heap leach model enables simulation of the performance of copper extraction from chalcopyrite ore in column leaching, which is essential for subsequent scale-up of this process to an industrial scale heap leach pad.

### 9.2 Contributions to knowledge

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

- The effect of various leaching conditions, i.e., solution potential, iodide concentration, temperature, size fraction, and iodine species, was investigated. The range of the conditions are based on the conditions observed in the actual heap leaching, which is generally operated at ambient temperatures. The solution potential was set in the range of the values observed in the feed solution and pregnant leach solution in heap leach operations. The size fraction used is based on the typical size fraction in heap leaching. The iodide concentration is based on the
design range for the iodine-assisted process developed by JX Nippon Mining and Metals Corporation.

- The kinetics of chalcopyrite leaching in ferric sulfate media in the presence of iodine was developed under fully-controlled conditions, i.e., solution potential, pH, and temperature. Most studies on chalcopyrite leaching in ferric sulfate media were carried out at elevated temperatures and pressures and the kinetic equation was developed under uncontrolled conditions. This may lead to an underestimation of the actual kinetics. In addition, monitoring of solution potential trend shows that potassium permanganate is a suitable oxidant to control solution potential. The reaction between permanganate and ferrous ions are very fast.

- The mineralogical and morphological of chalcopyrite and leaching residues were investigated using XRD, MLA and XPS. These analyses show that chalcopyrite is transformed to elemental sulfur, pyrite is unreactive in the course of leaching, and iron precipitates as potassium jarosite.

- The kinetic model developed can be applied to simulate the iodine-assisted column leaching. The simulation shows that an optimum value exists for ferric concentration, iodide concentration, and temperature. The modelling results suggest that the potential within the columns needs to be maintained sufficiently (> 650 mV vs SHE) high to obtain a faster kinetics.

9.3 The practical implications

The main purpose of the present study was to evaluate and optimize the iodine-assisted heap leaching of chalcopyrite. Mine operations face challenges of dealing with low grade and complex copper sulfide ores. To solve the production and environmental problems caused by transporting and processing “dirty” concentrates, direct leaching of the ores can be an alternative (Dreisinger,
The addition of iodide into ferric sulfate media improves the kinetics of chalcopyrite dissolution at the ambient conditions (Manabe, 2012; Miura et al., 2016). The experimental and modelling results obtained in the present study can provide guidelines in the design and implementation of the iodine-assisted heap leaching of chalcopyrite at an industrial scale.

One important finding in the present study is the kinetic model developed for chalcopyrite leaching in ferric sulfate media in the presence of iodine. This model can be used to simulate the leaching process and assist the optimization of the process. For example, solution potential was found to be the main factor affecting the iodine-assisted process performance. Therefore, to improve the leaching performance, the solution potential must be maintained sufficiently high by either using higher ferric concentrations or increasing the solution irrigation rate. The findings that elemental sulfur is the leaching product and pyrite is inert during leaching imply that the oxidant requirement is lower than the case where sulfate is the leaching product and pyrite is dissolved. The findings in this research strengthen the understanding of the key factors that determine the copper extraction from chalcopyrite and would help pinpoint options to optimize the leaching performance.

9.4 Recommendations

The behavior of secondary and other primary copper sulfides in the presence of iodine was not studied, even though these minerals are commonly found associated with chalcopyrite. These minerals may also react with iodine, thus lowering the solution potential. This would negatively affect the performance of chalcopyrite leaching.
In this study, pyrite was found to be unreactive during leaching in the presence of iodine, but it is unclear whether pyrite can enhance the leaching performance via galvanic interactions with chalcopyrite.

The effect of chloride ions was not investigated in the present study, because the presence of chloride could damage the ion selective electrode used for measurement of the total iodide concentration. Manabe (2012) found that the addition of sodium chloride could enhance the leaching performance of the iodine-assisted process. Furthermore, chloride is the major ions in seawater and the presence of chloride in ferric sulfate media has been reported to be beneficial to chalcopyrite dissolution (Ruiz et al., 2011; Watling, 2013). It is essential to understanding the effect of chloride on chalcopyrite dissolution in this process.

The adsorption and desorption of iodine species on silicate minerals and clays were not investigated. Silicates and clays are the main components in the ore and these minerals have been reported to be capable of adsorbing iodine species (Atkinson and Nickerson, 1988; Toyohara et al., 2002; Yoshida et al., 1992). It is essential to study this in order to reveal the behavior of iodine species within a heap.
Bibliography


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Nakazawa, H., 2018. Effect of carbon black on chalcopyrite leaching in sulfuric acid media at 50 °C. Hydrometallurgy 177, 100–108. https://doi.org/10.1016/j.hydromet.2018.03.001


Appendices

Appendix A  Total iodide concentration measured during bottle leaching tests

(a) 170 mg/L total iodide as iodide
     - 100 mg/L total iodide as diiodine

(b) 769 mV  725 mV
     - 704 mV  669 mV

(c) 200 mg/L  150 mg/L
     - 100 mg/L  50 mg/L

(d) 38-53 μm
    - 53-75 μm
    - 75-90 μm
Figure A.1 Total iodide concentration over time from chalcopyrite concentrate leaching in ferric sulfate media under standard leaching condition (5 g/L total of iron concentration, 769 mV vs SHE of initial potential, – 75 + 53 µm, 150 mg/L of total iodide concentration, 25 °C, pH 1.5, 2 g/L of solid content), except parameter under investigation: (a) in the absence of iron concentration, (b) different solution potential, (c) different total iodide concentration, (d) different size fraction, (e) different temperature at 769 mV, and (f) different temperature at 669 mV
Appendix B  Solution for cubic equation by Cardano’s method

General cubic equation can be written as Eq. (1).

\[ ax^3 + bx^2 + cx + d = 0 \]  \hspace{1cm} (1)

The solution of cubic equation in Eq. (1) is written as Eq. (2). It was first published by Cardano in 1545 (Schechter, 2022).

\[ x = \sqrt[3]{\left(\frac{-b^3}{27a^3} + \frac{bc}{6a^2} - \frac{d}{2a}\right)} + \sqrt[3]{\left(\frac{-b^3}{27a^3} + \frac{bc}{6a^2} - \frac{d}{2a}\right)^2 + \left(\frac{c}{3a} - \frac{b^2}{9a^2}\right)^3} \]

\[ + \sqrt[3]{\left(\frac{-b^3}{27a^3} + \frac{bc}{6a^2} - \frac{d}{2a}\right) - \sqrt[3]{\left(\frac{-b^3}{27a^3} + \frac{bc}{6a^2} - \frac{d}{2a}\right)^2 + \left(\frac{c}{3a} - \frac{b^2}{9a^2}\right)^3} - \frac{b}{3a} \]  \hspace{1cm} (2)

The formula in Eq. (2) can be simplified to Eq. (3)

\[ x = \sqrt[3]{q + \sqrt{q^2 + (r - p)^3}} + \sqrt[3]{q - \sqrt{q^2 + (r - p)^3}} + p \]  \hspace{1cm} (3)

where,

\[ p = \frac{-b}{3a} \]

\[ q = p^3 + \frac{bc - 3ad}{6a^2} \]

\[ r = \frac{c}{3a} \]
Appendix C  Measurements of solution potential in ferric/ferrous sulfate media at 25 °C

Table C.1 Solution compositions used to investigate the effect of iodide addition on solution potential

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Fe(III) (g/L)</th>
<th>Fe(II) (g/L)</th>
<th>Iodide (g/L)</th>
<th>Fe(III)/Fe(II)</th>
<th>Measured potential (mV vs SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without iodide</td>
<td>4.950</td>
<td>0.050</td>
<td>0</td>
<td>98.96</td>
<td>791.4</td>
</tr>
<tr>
<td></td>
<td>4.900</td>
<td>0.100</td>
<td>0</td>
<td>49.00</td>
<td>768</td>
</tr>
<tr>
<td></td>
<td>4.750</td>
<td>0.250</td>
<td>0</td>
<td>19.00</td>
<td>744.1</td>
</tr>
<tr>
<td></td>
<td>4.500</td>
<td>0.500</td>
<td>0</td>
<td>9.00</td>
<td>730.2</td>
</tr>
<tr>
<td></td>
<td>2.500</td>
<td>2.501</td>
<td>0</td>
<td>1.00</td>
<td>672.6</td>
</tr>
<tr>
<td></td>
<td>2.500</td>
<td>2.501</td>
<td>0</td>
<td>1.00</td>
<td>666.5</td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>4.002</td>
<td>0</td>
<td>0.25</td>
<td>636.3</td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>4.000</td>
<td>0</td>
<td>0.25</td>
<td>632.5</td>
</tr>
<tr>
<td>With iodide</td>
<td>4.931</td>
<td>0.069</td>
<td>150</td>
<td>71.85</td>
<td>681</td>
</tr>
<tr>
<td></td>
<td>4.931</td>
<td>0.118</td>
<td>150</td>
<td>41.77</td>
<td>679.8</td>
</tr>
<tr>
<td></td>
<td>4.925</td>
<td>0.567</td>
<td>150</td>
<td>8.68</td>
<td>676.8</td>
</tr>
<tr>
<td></td>
<td>4.914</td>
<td>1.068</td>
<td>150</td>
<td>4.60</td>
<td>674</td>
</tr>
<tr>
<td></td>
<td>4.617</td>
<td>13.653</td>
<td>150</td>
<td>0.34</td>
<td>652.2</td>
</tr>
</tbody>
</table>

Figure C.1 Images of solutions containing different ratios of ferric to ferrous in the absence of iodide

\[
\begin{align*}
\frac{\text{Fe(III)}}{\text{Fe(II)}} &= 0.25 \\
\frac{\text{Fe(III)}}{\text{Fe(II)}} &= 1.00 \\
\frac{\text{Fe(III)}}{\text{Fe(II)}} &= 9.00 \\
\frac{\text{Fe(III)}}{\text{Fe(II)}} &= 19.00 \\
\frac{\text{Fe(III)}}{\text{Fe(II)}} &= 49.00 \\
\frac{\text{Fe(III)}}{\text{Fe(II)}} &= 98.96
\end{align*}
\]
## Appendix D  Eh-pH diagrams and their databases

Table D.1 Databases obtained from HSC 7.1 software for enthalphy (H), entropy (S), and specific heat capacity (Cp) for constructing the pH-pH diagram of the I-H$_2$O system

<table>
<thead>
<tr>
<th>Species</th>
<th>H</th>
<th>S</th>
<th>Cp = a + b $\times 10^3$ T + c $\times 10^5$ T$^2$ + d $\times 10^6$ T$^3$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIO$_3$</td>
<td>-211.292</td>
<td>166.942</td>
<td>-3612.6  15215.53  643.912  -17649.4</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0</td>
<td>0</td>
<td>-212705  929.584  55.930  -820.237</td>
<td>298.15 – 398.00</td>
</tr>
<tr>
<td>I$^-$</td>
<td>-58</td>
<td>103</td>
<td>20914.78  -8670.7  -3671.37  100680.4</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>I$_3$</td>
<td>-51.463</td>
<td>239.325</td>
<td>3615.127  -14603.3  -613.328  16691.59</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>IO$_3^+$</td>
<td>-221.334</td>
<td>118.407</td>
<td>25508.51  -105488  -4470  122669.1</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>IO$_5^-$</td>
<td>-219.7</td>
<td>118.407</td>
<td>25508.51  -105488  -4470  122669.1</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>S$^-$.</td>
<td>0</td>
<td>32.07</td>
<td>7.835  79.793  -0.207  -97.893</td>
<td>100.00 – 368.30</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-38.6</td>
<td>126</td>
<td>-71397.721  317297.563  10921.873  -397187.839</td>
<td>273.15 – 298.15</td>
</tr>
<tr>
<td>HSO$_3^-$</td>
<td>-886.9</td>
<td>131.7</td>
<td>10331.012  -4242.4285  -1791.349  48997.357</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>S$^2$</td>
<td>33.095</td>
<td>-14.602</td>
<td>-2299.798  6089.98  723.472  -5252.899</td>
<td>298.15 – 573.00</td>
</tr>
<tr>
<td>SO$_2^-$</td>
<td>-909.602</td>
<td>18.828</td>
<td>71609.552  -296484.778  -12565.429  344882.969</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>Cu$^0$</td>
<td>0.000</td>
<td>33.150</td>
<td>21.988  15.303  -0.736  -14.437</td>
<td>100.00 – 400.00</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>-67.781</td>
<td>96.100</td>
<td>258.571  -788.164  -40.299  847.700</td>
<td>298.15 – 643.00</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-16.071</td>
<td>153.000</td>
<td>70.100  19.900  0.000  0.000</td>
<td>298.15 – 1000.00</td>
</tr>
<tr>
<td>CuO$^-$</td>
<td>-168.615</td>
<td>92.550</td>
<td>64.550  17.581  -6.393  -0.001</td>
<td>298.15 – 1517.00</td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>-450.400</td>
<td>108.400</td>
<td>95.802  11.478  -18.869  0.027</td>
<td>298.15 – 1000.00</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>64.900</td>
<td>-98.000</td>
<td>19652.914  -81020.651  -3428.102  93946.449</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>Cu$^{3+}$</td>
<td>71.680</td>
<td>40.585</td>
<td>2118.213  -8458.134  -355.578  96857.775</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>CuO$_2$$^-$</td>
<td>-311.290</td>
<td>-96.650</td>
<td>58807.444  -243364.076  -10305.088  282613.379</td>
<td>273.15 – 333.15</td>
</tr>
<tr>
<td>Fe$^{0}$</td>
<td>0.000</td>
<td>27.280</td>
<td>19.867  21.972  -0.994  -3.193</td>
<td>100.00 – 298.15</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.000</td>
<td>0.000</td>
<td>31.873  16.108  -0.207  -97.893</td>
<td>298.15 – 1517.00</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>-92.257</td>
<td>-105.855</td>
<td>20392.986  -84181.099  -3562.709  97657.927</td>
<td>273.15 – 333.15</td>
</tr>
</tbody>
</table>
Figure D.1 Eh-pH diagram for I – H₂O system at 25 °C at different total iodide concentrations: (a) 0.0005 m; (b) 0.001 m; (c) 0.005 m
Figure D.2 Eh-pH diagram for I – H₂O system (I = 0.001 m) at different temperatures: (a) 30 °C; (b) 35 °C; (c) 40 °C; (d) 45 °C
Figure D.3 Eh-pH diagrams for I – S – H₂O system (I = 0.001 m) at 25 °C at different total sulfur concentrations: (a) 0.01 m; (b) 0.05 m; (c) 0.1 m; (d) 0.5 m
Figure D.4 Eh-pH diagram for I – S – Fe – H₂O system (I = 0.001 m, S = 0.1 m) at 25 °C at different total iron concentrations: (a) 0.01 m; (b) 0.05 m; (c) 0.1 m; (d) 0.5 m
Figure D.5 Eh-pH diagram for the I – S – Fe – Cu – H₂O system (I = 0.001 m, S = 0.1 m, Fe = 0.1 m) at 25 °C at different total copper concentrations: (a) 0.001 m; (b) 0.005 m; (c) 0.01 m; (d) 0.05 m
Appendix E  Preparation of stock solution

- The stock solution of 20 g/L Fe(III) as ferric sulfate

The ferric sulfate used for the experiments was prepared according to the following steps:

1. Adjust the pH of 2 L deionized water to 1.80 by slowly adding concentrated sulfuric acid (95.0 – 98.0% ACS reagent),
2. transfer 1.5 L acidified deionized water to 2L beaker,
3. weight 181 g Fe₂(SO₄)₃·5H₂O (97% purity from Acros Organics),
4. slowly add the Fe₂(SO₄)₃·5H₂O solid into 1.5 L acidified deionized water and stir the solution to dissolve all Fe₂(SO₄)₃·5H₂O solid,
5. transfer the ferric solution from 2L beaker to 2L volumetric flask,
6. top up the solution in 2L volumetric flask until the mark using acidified deionized water pH 1.8,
7. stir the solution using magnetic stirrer to homogenize the ferric solution,
8. filter through Whatman filter paper grade 1 into a clean container,
9. label the container.

- The stock solution of 10 g/L iodide as potassium iodide

The iodide solution used for the experiments was prepared according to the following steps:

1. Carefully weigh 8.21 g KI (Sigma Aldrich),
2. dissolve in 200 mL deionized water in a beaker,
3. transfer all solution to 500 mL volumetric flask
4. rinse the beaker using deionized water and pour the solution to the volumetric flask to collect all KI solution,
5. top up the solution in 500 mL volumetric flask until the mark using deionized water,
6. transfer the ferric solution from 2L beaker to 2L volumetric flask,
7. top up the solution in 2L volumetric flask until the mark using acidified distilled water pH 1.8,
8. stir the solution using magnetic stirrer to homogenize the ferric solution,
9. transfer the solution to a clean container,
10. label the container.

• The stock solution of 0.3 M potassium permanganate

The permanganate solution used for the experiments was prepared according to the following steps:

1. Weigh 47.41 g KMnO₄ (Sigma Aldrich),
2. dissolve in 1 L deionized water in a beaker,
3. cover the beaker and boil the solution for 20 min to ensure the dissolution of all KMnO₄,
4. cool the solution,
5. filter through 0.22 µm syringe filter into a clean amber glass bottle,
6. cover the glass bottle with aluminum foil to avoid decomposition by sunlight.
The actual concentration of permanganate was determined by titration using sodium oxalate. The titration procedure was as follows:

1. Prepare 1 L of 1.0 M sulfuric acid by adding slowly 55 mL of concentrated sulfuric acid to 700 mL deionized water in 1L volumetric flask then top up the solution until the mark using deionized water,
2. dry approximately 1.5 g of primary – standard sodium oxalate, Na$_2$C$_2$O$_4$, at 110 °C for 1 h,
3. cool the Na$_2$C$_2$O$_4$ in a desiccator, 
4. weigh the Na$_2$C$_2$O$_4$ and then dissolve it in 50 mL of 1.0 M sulfuric acid,
5. put potassium permanganate solution in an amber burette,
6. slowly add potassium permanganate solution to sodium oxalate solution until the solution becomes a faint purple due to a slightly excess of permanganate (Eq. (4)),
7. measure the volume of permanganate added to calculate the actual concentration of permanganate.

\[
2\text{MnO}_4^{-}(aq) + 5\text{C}_2\text{O}_4^{2-}(aq) + 16\text{H}^+(aq) = 2\text{Mn}^{2+}(aq) + 10\text{CO}_2(g) + 8\text{H}_2\text{O(l)}
\]  
(Eq. (4))

dark purple                                          colorless
Appendix F  Kinetic modelling considering iodine as a function of potential

The kinetic modelling is also performed by considering the continuous change in iodine species (Section 5.6.1). Diiodine concentration ([I₂]) can be calculated based on the mass balance equation (Eq. (5.5)) and (Eq. (5.6)). The values of the kinetic equations derived using this method is presented in Table F.1 and the kinetic equation is written as Eq. (5). The \( k_0 \) increases from 160.881/day to 300.310/day due to the change in iodine term.

Table F.1 Kinetic parameters for stirred reactor leaching of chalcopyrite concentrate in the presence of iodine at 25 °C

<table>
<thead>
<tr>
<th>Mineral leaching kinetic parameters</th>
<th>Symbol</th>
<th>Unit</th>
<th>(Iodine is determined using Eq. (6.6))</th>
<th>(Iodine is determined using Eq. (5.5) and Eq. (5.6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant at reference temperature</td>
<td>( k_0 )</td>
<td>1/day</td>
<td>160.881</td>
<td>400.310</td>
</tr>
<tr>
<td>Reaction order of [Fe(III)]/[Fe(II)] in M</td>
<td>( a )</td>
<td>-</td>
<td>0.322</td>
<td>0.322</td>
</tr>
<tr>
<td>Reaction order of [I₂] in mM</td>
<td>( b )</td>
<td>-</td>
<td>1.167</td>
<td>1.167</td>
</tr>
<tr>
<td>Particle size effect in mm</td>
<td>( c )</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Activation energy</td>
<td>( E_a )</td>
<td>J/mol</td>
<td>43,096</td>
<td>43,096</td>
</tr>
<tr>
<td>Topological exponent</td>
<td>( \varphi )</td>
<td>-</td>
<td>0.691</td>
<td>0.691</td>
</tr>
</tbody>
</table>

\[
X = 1 - \left( 1 - 123.539 \exp \left( \frac{43,096}{R} \left( \frac{1}{298.15} - \frac{1}{T} \right) \right) \left( \frac{[\text{Fe(III)}]}{[\text{Fe(II)}]} \right)^{0.322} [I₂]^{1.167} . t(\text{day}) \right)^{3.236}
\]  

(5)

Table F.1 shows the comparison between the experimental data and the simulation using Eq. (5), assuming the iodine concentration continuously changes as a function of potential. The model can simulate leaching tests under different iodide concentration and temperature. However, it is failed simulation Cu extraction when the potential is lower than 719 mV, in which the triiodide starts to be the predominant species.
Figure F.1 The comparison between the experimental (scatter plot) and the predicted copper extraction (solid lines) under different leaching conditions comparison between leaching data and model simulation using Eq. (5)
Appendix G  Values of parameters used in HeapSim 2D program

Table G.1 Column parameters in HeapSim 2D program

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column radius (R)</td>
<td>Depend on the test</td>
<td>m</td>
</tr>
<tr>
<td>Height (h)</td>
<td>Depend on the test</td>
<td>m</td>
</tr>
<tr>
<td>Bed packed density (ρₖₜ)</td>
<td>Depend on the test</td>
<td>m</td>
</tr>
<tr>
<td>Elevation above sea level</td>
<td>100</td>
<td>m</td>
</tr>
<tr>
<td>P₀</td>
<td>100,129</td>
<td>Pa</td>
</tr>
<tr>
<td>Initial temperature (T₀)</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td>Water inlet temperature (Tₜ,ₜₜ)</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td>Irrigation rate</td>
<td>Depend on the test</td>
<td>L/m²/h</td>
</tr>
<tr>
<td>Aeration rate</td>
<td>0</td>
<td>m³/m²/h</td>
</tr>
</tbody>
</table>

Table G.2 Water transport in HeapSim 2D program

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic permeability (κₜ)</td>
<td>0.000000000005</td>
<td>m²</td>
</tr>
<tr>
<td>Empirical constant, 0 &lt; m &lt; 1</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Empirical constant, taken as (1–m)⁻¹</td>
<td>7.143</td>
<td></td>
</tr>
<tr>
<td>Capillary head scaling factor (hₑ)</td>
<td>0.052</td>
<td>m</td>
</tr>
<tr>
<td>Residual (or fully drained) volumetric water content (θᵣ)</td>
<td>0.12</td>
<td>m³ water/m³</td>
</tr>
<tr>
<td>Saturated volumetric water content (θₛ)</td>
<td>0.37</td>
<td>m³ water/m³</td>
</tr>
<tr>
<td>Initial volumetric water content (θ₀)</td>
<td>0.1</td>
<td>m³ water/m³</td>
</tr>
</tbody>
</table>

Table G.3 Solute transport in HeapSim 2D program

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular diffusivity of solute A in water (Dₐₜₜ)</td>
<td>0.00000000186</td>
<td>m²/s</td>
</tr>
<tr>
<td>Aqueous molecular diffusivity coefficient (function of θ) (εₐₜₜ,θ)</td>
<td>2, 3</td>
<td></td>
</tr>
<tr>
<td>Aqueous longitudinal dispersivity coefficient (function of θ) (αₐₜₜ,θ)</td>
<td>43,240, 0.06929</td>
<td>m/m³/s</td>
</tr>
<tr>
<td>Resultant water volume flux (Vₚ)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ratio aqueous transverse and aqueous longitudinal dispersivity coefficient (function of θ) (αₚₜₜ,αₐₜₜ,θ)</td>
<td>10</td>
<td>%</td>
</tr>
</tbody>
</table>