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Advanced Mineralogy and Hydrometallurgy Solutions for Cu-Au Sulfide Concentrate Processing

Bachelor Thesis

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I hereby affirm in lieu of oath that I independently prepared the submitted bachelor thesis.

Advanced Mineralogy and Hydrometallurgy Solutions for Cu-Au Sulfide Concentrate Processing

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TERMINOLOGY

Abbreviation	Definition
APS	Ammonium persulfate, $(NH_4)_2S_2O_8$
AAS	Atomic Absorption Spectrometry
ICP-OES	Inductively Coupled Plasma–Optical Emission Spectrometry
MLA	Mineral Liberation Analyser (automated SEM-based mineralogy)
OT	Oyu Tolgoi (Cu–Au porphyry deposit, Mongolia)
PLS / PLC	Pregnant leach solution / pregnant leach concentrate
QEMSCAN	Quantitative Evaluation of Minerals by Scanning electron microscopy
SEM-EDS	Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy
SX–EW	Solvent Extraction – Electrowinning
XRD / XRPD	X-ray Diffraction / X-ray Powder Diffraction
XRF	X-ray Fluorescence Spectrometry

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ABSTRACT

This thesis investigates the hydrometallurgical processing of chalcopyrite-bearing copper sulfide concentrate from the Oyu Tolgoi deposit in Mongolia. Although this concentrate is suitable for conventional smelting, hydrometallurgical treatment remains challenging because chalcopyrite dissolves slowly under simple acidic conditions and tends to form passivating surface layers during leaching.

The study aimed to evaluate the effects of acid type, oxidizing agents, and temperature on copper extraction, and to assess whether dissolved copper could subsequently be recovered from solution by electrowinning. Laboratory-scale leaching experiments were carried out using three acids, sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl), at different temperatures and under different oxidizing conditions, including acid-only leaching, ammonium persulfate (APS), and a combined APS + iodine system.

The results demonstrated that temperature exerted a strong influence on copper dissolution, with extraction rates increasing consistently as temperature rose. Among the acid-only systems, nitric acid yielded the highest copper extraction, while sulfuric acid and hydrochloric acid showed significantly lower performance in the absence of additional oxidants.The introduction of ammonium persulfate (APS) enhanced copper dissolution across most systems, with the effect becoming more pronounced at elevated temperatures. The combined APS + iodine system achieved the highest overall copper extractions, indicating a synergistic interaction between the oxidant and the catalytic iodine additive.

Optimal performance was obtained at 70 °C using the $(NH_4)_2S_2O_8$ + I_2 system. These conditions were subsequently validated through a scale-up leaching experiment, which confirmed the reproducibility and practical viability of the results.The resulting pregnant leach solution was then used in an electrowinning experiment, in which copper was successfully deposited as metallic copper on the cathode, demonstrating the feasibility of integrating leaching with downstream copper recovery.

Overall, the findings show that atmospheric hydrometallurgical processing of Oyu Tolgoi copper sulfide concentrate is technically feasible when suitable acid media, oxidizing conditions, and operating temperatures are applied.The study provides a laboratory-scale basis for further development of a leach-electrowin route for copper recovery and contributes to the broader goal of expanding domestic copper processing options in Mongolia.

CHAPTER 1. INTRODUCTION

1.1. Background

Copper is one of the most important industrial metals in the modern world. It is widely used in electrical systems, construction, transportation, and renewable energy technologies due to its excellent electrical conductivity, corrosion resistance, and mechanical properties. With the global transition toward clean energy systems, such as electric vehicles, solar panels, and wind turbines, the demand for copper is expected to increase significantly in the coming decades.

Most of the world's copper is produced from sulfide ores, where chalcopyrite ($CuFeS_2$) is the dominant copper-bearing mineral [2]. These sulfide concentrates are typically processed by pyrometallurgical methods, including smelting and refining [8-10]. While these methods are well established and efficient for large-scale production, they require high energy consumption, complex infrastructure, and strict environmental control systems [10].

In countries like Mongolia, copper concentrates are often exported for processing abroad due to the limited availability of local smelting facilities. This reduces the opportunity for domestic value addition and increases dependence on external processing. Therefore, alternative processing methods that can be applied locally are of increasing interest. Hydrometallurgy offers a potential alternative route for copper extraction. This method involves dissolving metals into solution using chemical reagents, followed by recovery through processes such as electrowinning [3]. Compared to pyrometallurgy, hydrometallurgical processes can operate at lower temperatures and may be more suitable for smaller-scale or remote operations. However, the hydrometallurgical treatment of chalcopyrite-rich concentrates remains challenging. Copper dissolution is often slow under simple acidic conditions due to the formation of passivation layers on the mineral surface [11]. Therefore, the use of different acid systems, oxidizing agents, and temperature control becomes important to improve leaching efficiency.

1.2. Problem Statement

The copper concentrate produced from the Oyu Tolgoi deposit in Mongolia is dominated by chalcopyrite and associated sulfide minerals and is currently well suited to conventional smelting routes. However, hydrometallurgical processing of this concentrate remains underdeveloped because chalcopyrite is notoriously difficult to dissolve efficiently under atmospheric leaching conditions. Simple acid leaching typically

yields low copper extractions, and different acid systems can produce markedly different levels of copper recovery and iron dissolution, which directly affect process selectivity and downstream purification requirements.

The use of oxidizing agents has the potential to enhance chalcopyrite leaching, but their effectiveness depends strongly on operating parameters such as acid medium, temperature, and oxidant combination. In addition, any viable hydrometallurgical flowsheet must not only leach copper efficiently but also recover it from solution in a form suitable for sale, such as cathode copper produced by electrowinning. Consequently, there is a clear need for a systematic experimental study of how leaching conditions influence copper extraction from OT sulfide concentrate and how dissolved copper can be recovered. In particular, the present work seeks to clarify:

- Determine how the choice of acid (H_2SO_4, HNO_3, HCl) affects copper dissolution and iron co-dissolution
- Evaluate the extent to which selected oxidizing agents and catalytic systems improve leaching efficiency and selectivity
- Assess the influence of temperature on the kinetics of chalcopyrite leaching
- Demonstrate that copper recovered in solution can be converted to metallic copper by electrowinning

1.3. Objective of the study

The overall objective of this study is to evaluate the feasibility of hydrometallurgical processing of copper sulfide concentrate through acidic leaching and subsequent copper recovery from the pregnant leach solution. To achieve this aim, the following specific objectives were defined:

- To investigate the effect of different acid media (H_2SO_4, HNO_3, HCl) on copper extraction from chalcopyrite-bearing concentrate.
- To evaluate the influence of oxidizing agents, including ammonium persulfate and persulfate–iodine systems, on leaching performance.
- To study the effect of temperature on copper dissolution and leaching kinetics over the range 20–70 °C.
- To compare copper and iron dissolution behaviour under different combinations of acid type, oxidant, and temperature in order to assess leach selectivity.
- To assess the practicality of recovering copper from the leach solution by electrowinning and to demonstrate the overall leach–electrowinning concept at laboratory scale.

1.4. Scope and Limitations

This study focuses on laboratory-scale leaching experiments using copper sulfide concentrate obtained from the Oyu Tolgoi deposit. The experiments were carried out using three types of acids and different oxidizing conditions at controlled temperatures. Only basic mineralogical identification of the sample was performed using X-ray diffraction (XRD). Advanced mineralogical analysis techniques were not included in this work. The study also includes a preliminary electrowinning test to confirm the recovery of copper from the leach solution. However, detailed process optimization, economic evaluation, and large-scale industrial design are beyond the scope of this thesis.

1.5. Structure of the Thesis

This thesis is organized into five chapters. Chapter 1 presents the background, problem statement, objectives, and scope of the study. Chapter 2 reviews the relevant literature on copper processing, challenges in sulfide leaching, and hydrometallurgical methods. Chapter 3 describes the materials, experimental design, leaching procedures, and analytical methods used in this study. Chapter 4 presents and discusses the experimental results, including the effects of acid type, oxidizing agents, and temperature on copper extraction, as well as the electrowinning results. Chapter 5 summarizes the main findings and provides recommendations for future work.

CHAPTER 2. LITERATURE REVIEW

2.1. Importance of Copper in Modern Industry

Copper (*Cu*) is a chemical element with atomic number 29. It is a soft, malleable, and ductile metal with excellent electrical and thermal conductivity. Because of these properties, copper is widely used in power transmission, electronics, construction, transportation, renewable energy systems, smart grids, data centers, artificial intelligence infrastructure, and defense-related technologies.

Copper demand is also expected to grow because low-carbon energy technologies require large quantities of copper. Electric vehicles, wind turbines, solar systems, and power transmission infrastructure all depend on copper because of its excellent electrical conductivity, durability, and reliability. Although alternative materials such as aluminum may substitute copper in some applications, copper remains difficult to replace in many high-performance electrical and energy systems [3,4].

Due to its essential role in the global green and digital transition, copper is increasingly recognized as a strategic raw material. Recent studies indicate that global copper demand is expected to increase substantially by 2040, while new technologies and improved processing methods will be required to meet future demand [1,2]. This highlights the importance of developing more efficient and sustainable copper production pathways.

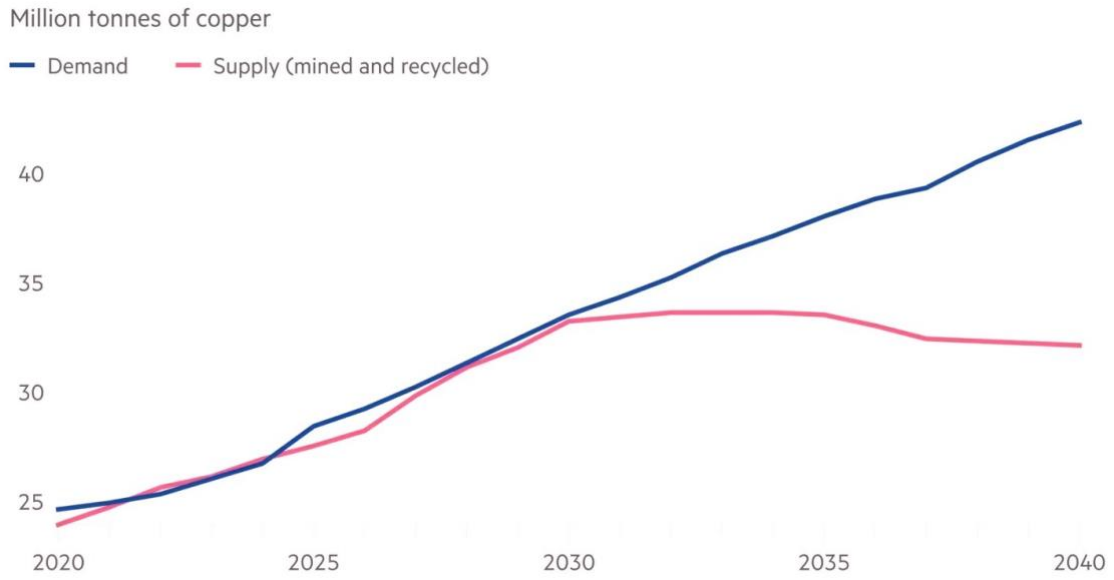


Figure 2.1 Global copper demand and supply outlook to 2040

This issue is highly relevant to Mongolia because Oyu Tolgoi is one of the largest copper–gold deposits in the world. The concentrate produced from Oyu Tolgoi contains approximately 25–30% copper, together with gold and other associated minerals, but it is currently exported for smelting outside Mongolia [5–7]. As a result, a significant portion of value-added processing takes place abroad rather than domestically.

2.2. Copper Sulfide Minerals and Their Characteristics

2.2.1. Geological occurrence and mineral associations

In porphyry Cu–Au deposits such as Oyu Tolgoi, chalcopyrite ($CuFeS_2$) commonly occurs as the principal copper-bearing sulfide within a complex assemblage rather than as a single isolated mineral phase. It is typically associated with bornite (Cu_5FeS_4), pyrite (FeS_2), and minor secondary copper sulfides such as chalcocite (Cu_2S) and covellite (CuS). These sulfide minerals are generally embedded within a quartz–feldspar gangue matrix, which controls mineral liberation during grinding and strongly influences the accessibility of copper-bearing phases during leaching.

Gold distribution in porphyry Cu–Au systems is often heterogeneous. Gold may occur as very fine native particles, as inclusions along sulfide grain boundaries, or in close association with Cu–Fe sulfide minerals. This deportment is important because gold enclosed within sulfide grains is not directly accessible to leach solutions unless the host mineral is physically liberated or partially dissolved. Consequently, the mineralogical relationship between copper sulfides, pyrite, gangue minerals, and gold-bearing phases has a direct impact on both copper extraction and potential gold recovery.

2.2.2. Mineralogical controls on leaching and passivation

For hydrometallurgical processing, these mineral associations are particularly critical. Chalcopyrite grains locked with pyrite or silicate gangue expose less reactive surface area to the leaching solution and therefore dissolve more slowly, while fine intergrowths can reduce leaching efficiency and increase reagent consumption. Detailed mineralogical characterisation is therefore required to understand why some concentrate fractions dissolve more readily than others and to interpret leaching performance in terms of underlying textures and associations.

Techniques such as SEM–EDS, QEMSCAN, and MLA are widely used to identify mineral phases, quantify liberation characteristics, determine grain-size distributions, and map sulfide–gangue associations. These methods provide information that cannot be obtained from bulk chemical analysis alone and are essential for linking mineralogy to leaching behaviour; for example, Togtokhbaatar et al. [19] showed that halide-assisted

leaching responses in Cu–Au concentrates could only be fully explained when mineral textures and sulfide assemblages were considered alongside solution chemistry.

Furthermore, surface passivation is one of the principal barriers to effective chalcopyrite leaching. Secondary products formed during oxidation—such as copper-deficient sulfide phases, covellite-like layers, elemental sulfur, and iron-bearing precipitates—can accumulate on the mineral surface, block contact between the leaching solution and fresh chalcopyrite, and hinder electron transfer at the mineral–solution interface. As leaching progresses, these passivating layers make conventional oxidants less effective and decrease the rate of copper extraction even when acid and oxidants remain in solution. Stronger oxidative conditions, appropriate acid media, elevated temperatures, and catalytic additives are therefore often required to mitigate passivation and promote sustained copper dissolution, which motivates the use of reagents such as ammonium persulfate and iodine in advanced leaching systems. [8–13].

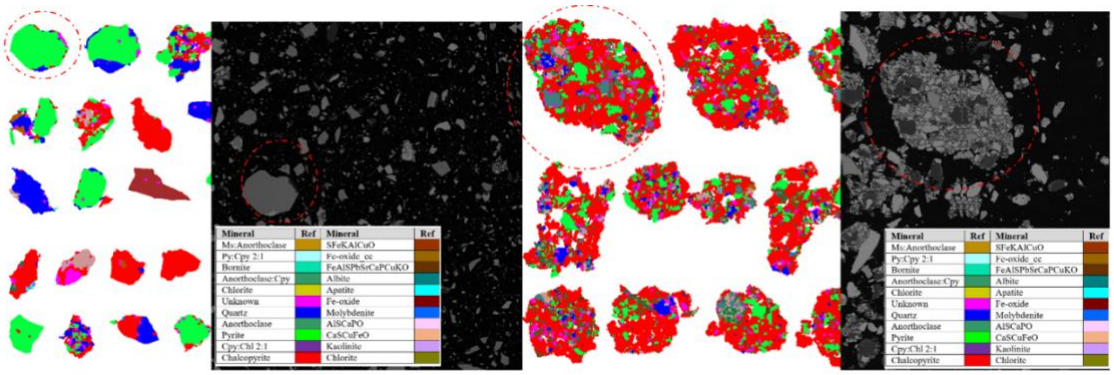


Figure 2.2 Leaching of copper and gold concentrate in the presence of halides *Togtokhbaatar, P., Frisch, G., & Bertau, M.*

The MLA mineral maps show that chalcopyrite and bornite occur predominantly as complex intergrowths with pyrite and quartz–feldspar gangue rather than as simple, liberated grains. Many particles contain multiple sulfide and silicate phases within a single composite grain (highlighted by the red circles), indicating that substantial portions of the copper-bearing minerals are locked with gangue. This texture reduces the effective reactive surface area available to the leach solution, contributes to slower dissolution in locked particles, and helps explain why some size fractions show lower copper extraction even under aggressive leaching conditions.

2.2.3. Challenges in chalcopyrite leaching

Under atmospheric conditions, chalcopyrite ($CuFeS_2$) is considered one of the most difficult primary copper minerals to leach due to its refractory nature. In acidic media, its dissolution is intrinsically slow and often yields low copper extraction unless high temperatures, strong oxidants, or pressure-leaching are employed. A major difficulty is the formation of passivating surface layers—such as covellite-like films, elemental sulfur, and iron-rich precipitates—that progressively coat the mineral surface, restrict contact between solution and fresh chalcopyrite, and impede electron transfer.

Processing of chalcopyrite-bearing concentrates is further complicated by complex mineralogical associations with pyrite, bornite, secondary copper sulfides, and silicate gangue, which can limit liberation and reduce the effective reactive surface area exposed to leaching solutions. Under strongly oxidizing conditions, pyrite and other gangue-associated metals may dissolve alongside chalcopyrite, generating high iron levels and other impurities in solution that increase reagent consumption and complicate downstream copper recovery operations such as solvent extraction and electrowinning. These combined factors—slow intrinsic kinetics, surface passivation, complex texture, and impurity dissolution—make the design of efficient and economically viable hydrometallurgical routes for chalcopyrite concentrates particularly challenging.

2.3. Metallurgical Processing Methods

2.3.1. Pyrometallurgical processing

Conventional processing of chalcopyrite concentrates is mainly based on pyrometallurgy. The typical route includes comminution, flotation, smelting, converting, fire refining, and electrorefining to produce high-purity cathode copper. This route is widely used because it can treat large volumes of concentrate and usually achieves high copper recovery, often above 95% [17–19]. Modern flash smelting also allows sulfur in the concentrate to be captured and converted into sulfuric acid, reducing direct sulfur dioxide emissions.

Despite these advantages, pyrometallurgical processing has several limitations. Smelters require high capital investment, large-scale infrastructure, reliable energy supply, and strict environmental control systems. They also generate large amounts of slag, which must be managed or treated further to recover remaining copper values. For remote mining regions, the lack of nearby smelting capacity can create dependence on foreign smelters and expose producers to treatment and refining charges. In the case of

Mongolia, this issue is important because exporting copper concentrate for smelting limits the amount of value-added processing carried out domestically [17,18,20].

2.3.2. Hydrometallurgical processing

Hydrometallurgy provides an alternative approach in which metals are dissolved into solution and then recovered by methods such as solvent extraction, electrowinning, or precipitation. Compared with pyrometallurgy, hydrometallurgical routes can operate at lower temperatures and may be more flexible for smaller or remote operations. They can also reduce direct sulfur dioxide emissions because sulfide concentrates are not treated by high-temperature smelting [21,22].

However, the hydrometallurgical treatment of chalcopyrite concentrates remains difficult. Chalcopyrite dissolves slowly under simple atmospheric acid leaching conditions and may form passivating surface layers that limit further copper extraction. Therefore, strong oxidants, suitable acid media, elevated temperature, or catalytic additives are often required to improve leaching performance.

As copper demand increases and environmental requirements become stricter, hydrometallurgical processing is receiving more attention as a possible complementary route to conventional smelting. For OT Cu–Au sulfide concentrate, this approach is especially relevant because it may support future domestic processing options with lower-temperature operation and potential integration with electrowinning.Central to the viability of this hydrometallurgical framework is the selection of an appropriate leaching technique, which functions as the critical unit operation responsible for effectively mobilizing copper and precious metals from the sulfide mineral matrix.

2.4. Oxidative Leaching Techniques

A range of oxidants and oxidative strategies has been investigated to overcome chalcopyrite passivation and improve copper extraction under hydrometallurgical conditions. The principal systems are reviewed below, with key reaction equations, advantages, and limitations for each.

2.4.1. Ferric sulfate leaching

Ferric sulfate [$Fe_2(SO_4)_3$] is the most widely studied oxidant in acidic chalcopyrite leaching systems. The primary dissolution reaction is:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S_0 \qquad (Eq.\ 2.1)$$

The Fe^{3+} ion oxidises chalcopyrite, releasing Cu^{2+} and Fe^{2+} into solution while liberating elemental sulfur. However, the progressive reduction of Fe^{3+} to Fe^{2+} slows the reaction, requiring continuous regeneration of the ferric oxidant through aeration, oxygen sparging, or microbial oxidation [17]. Maintaining an appropriate solution redox potential (approximately 450–600 mV vs. SHE) minimises passivation, and controlling pH around 1.5–2.5 reduces jarosite and iron precipitation [16].

2.4.2. Ferric chloride leaching

Ferric chloride ($FeCl_3$) has been investigated as an alternative to ferric sulfate due to its higher oxidation potential in chloride media and its ability to minimise passivation through chloride complexation. The principal reaction is:

$$CuFeS_2 + 3FeCl_3 \rightarrow CuCl_2 + 4FeCl_2 + 2S_0 \qquad (Eq.\ 2.2)$$

Chloride ions improve leaching efficiency by forming soluble copper chloro-complexes ($CuCl^+$, $CuCl_2$), keeping dissolved copper in solution and shifting the thermodynamic equilibrium towards further mineral dissolution. Chloride also enhances sulfur solubility and minimises the extent of passivating S_0 layer formation [17]. This study employs HCl as one of the three lixiviants precisely to exploit these chloride-media advantages.

2.4.3. Ammonium persulfate leaching

Ammonium persulfate [$(NH_4)_2S_2O_8$, APS] is a strong chemical oxidant that generates sulfate radical anions ($SO_4\bullet^-$) upon thermal activation in acidic solution. These radicals possess an oxidation potential substantially exceeding that of conventional ferric or cupric oxidants (E_0 ≈2.6 V vs. SHE for $SO_4\bullet^-$), enabling mechanistically distinct attack on chalcopyrite surfaces. The primary oxidation reaction can be expressed as:

$$CuFeS_2 + (NH_4)_2S_2O_8 \rightarrow Cu^{2+} + 3Fe^{3+} + SO_4^{2-} + 2S_0 \qquad (Eq.\ 2.3)$$

APS offers higher dissolution rates than traditional Fe^{3+}–based leaching and can be used under mild conditions, making it an attractive option for small- to medium-scale laboratory and commercial operations [17]. Thermal activation is strongly temperature-dependent: below approximately 40°C, radical generation is slow; above 50°C, decomposition accelerates markedly, producing $SO_4\bullet^-$ radicals that directly attack both chalcopyrite surfaces and the elemental sulfur passivation layer. This temperature dependence is clearly reflected in the OCLA Phase 2 results, where persulfate alone provides limited benefit at 25°C but significant gains at 50–°70°C (Section 4.4).

2.4.4. Acidic leaching

Acidic leaching is widely used for copper–gold primary sulfide concentrates because of its ability to dissolve metal sulfides in the presence of strong acids and oxidising agents. Sulfuric acid (H_2SO_4) is the most commonly employed lixiviant, typically combined with oxidants such as $Fe_2(SO_4)_3$, $FeCl_3$, or $(NH_4)_2S_2O_8$ to enhance dissolution kinetics. The main chalcopyrite dissolution reaction under ferric-oxidised acidic conditions is:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S_0 \qquad (Eq.\ 2.4)$$

Bornite (Cu_5FeS_4), which frequently co-occurs with chalcopyrite in OT-type concentrates, is considerably more reactive and contributes to early rapid copper dissolution before the more refractory chalcopyrite becomes the rate-controlling phase. Gold, often present as fine particles within the sulfide matrix, is not readily dissolved in simple acidic solutions; it requires subsequent cyanidation or direct chloride-complex leaching for recovery [17].

In the absence of added oxidants, copper dissolution from chalcopyrite proceeds mainly through proton attack and oxidation by dissolved oxygen. In sulfate or chloride media the overall reaction can be expressed as:

$$CuFeS_2 + 4H^+ + O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \qquad (Eq.\ 2.5)$$

For sulfuric acid systems this may be written explicitly as:

$$CuFeS_2 + 2H_2SO_4 + O_2 \rightarrow CuSO_4 + FeSO_4 + 2S^0 + 2H_2O \qquad (Eq.\ 2.6)$$

In hydrochloric acid, copper forms soluble chloro-complexes that stabilise Cu in solution and can shift equilibrium towards further dissolution:

$$CuFeS_2 + 4HCl + O_2 \rightarrow CuCl_2 + FeCl_2 + 2S^0 + 2H_2O \qquad (Eq.\ 2.7)$$

$$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+ \qquad (Eq.\ 2.8)$$

Nitric acid is distinctive because it acts as both acid and oxidant, which often leads to higher copper extractions than in sulfate or chloride systems at comparable conditions. A simplified overall reaction is:

$$3CuFeS_2 + 8HNO_3 \rightarrow 3Cu^{2+} + 3Fe^{2+} + 6S^0 + 8NO\uparrow + 4H_2O \qquad (Eq.\ 2.9)$$

While these purely acidic systems provide useful baseline behaviour, the slow kinetics and surface passivation of chalcopyrite have motivated the use of stronger oxidants and catalytic additives.

A widely studied oxidant in acidic media is ammonium persulfate ($(NH_4)_2S_2O_8$). In solution, persulfate dissociates completely:

$$(NH_4)_2S_2O_8 \rightarrow 2NH_4^+ + S_2O_8^{2-} \quad \text{(Eq. 2.10)}$$

At elevated temperature (typically 50–70 °C) and low pH, the $S_2O_8^{2-}$ ion undergoes homolytic cleavage to generate highly oxidising sulfate radicals:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} \quad \text{(Eq. 2.11)}$$

These radicals can further react with water to form secondary hydroxyl radicals:

$$SO_4^{\bullet -} + H_2O \rightarrow HSO_4^- + OH^{\bullet}. \quad \text{(Eq. 2.12)}$$

Both $SO_4^{\bullet -}$ and OH• are powerful oxidants capable of attacking chalcopyrite surfaces and disrupting passivating sulfur layers, leading to significantly enhanced leaching kinetics compared with ferric-only systems. A net persulfate oxidation of chalcopyrite can be written as:

$$CuFeS_2 + 2S_2O_8^{2-} \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 4SO_4^{2-}. \quad \text{(Eq. 2.13)}$$

Further improvements in chalcopyrite leaching have been reported when persulfate is combined with halogen-based catalysts, particularly iodine. In acidic chloride or sulfate media, iodine establishes the equilibrium:

$$I_2 + I^- \rightleftharpoons I_3^- \quad \text{(Eq. 2.14)}$$

In the presence of dissolved iron, a catalytic redox cycle operates in which persulfate continuously regenerates ferric ions, ferric ions regenerate active iodine species, and iodine directly oxidises chalcopyrite. The sequence can be summarised as:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \quad \text{(Eq. 2.15)}$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \quad \text{(Eq. 2.16)}$$

$$CuFeS_2 + 2I_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 4I^- + 2H_2O \quad \text{(Eq. 2.17)}$$

Combining these steps yields an overall reaction similar in stoichiometry to persulfate-only leaching:

$$CuFeS_2 + S_2O_8^{2-} + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2SO_4^{2-} + 2H_2O \quad \text{(Eq. 2.18)}$$

However, the presence of iodine improves electron-transfer pathways and accelerates the breakdown of passivating surface films, resulting in higher copper extraction and faster kinetics, particularly for refractory Cu–Au sulfide concentrates.

At elevated ferric concentrations and insufficient acidity, side reactions such as jarosite precipitation can consume iron and release acidity:

$$3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow Fe_3(SO_4)_2(OH)_6\downarrow + 6H^+ \quad \text{(Eq. 2.19)}$$

Similarly, iodine can be over-oxidised to iodate under unfavourable conditions:

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 10H^+ + 8e^- \quad \text{(Eq. 2.20)}$$

For this reason, successful application of persulfate–iodine systems generally requires careful control of acid concentration, redox potential, and temperature to maximise chalcopyrite oxidation while suppressing parasitic precipitation and iodine loss.

Table 2.1 Advantage vs disadvantage of Oxidative leaching

	Advantage	Disadvantage
Ferric Sulfate Leaching	Readily available and inexpensive oxidant Can be continuously regenerated by aeration or bioleaching Effective for initial copper dissolution from chalcopyrite	Slow leaching kinetics at low temperature Requires sustained Fe^{3+} regeneration Passivation layers (S_0, jarosite) still form over time
Ferric chloride Leaching	Higher oxidation potential than ferric sulfate in chloride media Copper chloro-complexation reduces passivation More effective than ferric sulfate in some chalcopyrite systems	Corrosive: requires specialised materials of construction High chloride concentrations raise environmental concerns Downstream SX–EW compatibility requires additional steps
Ammonium Persulfate Leaching	Very strong oxidising agent; sulfate radicals attack passivation layers directly Faster dissolution rates than Fe^{3+}–based systems at elevated temperature Compatible with H_2SO_4 media and SX–EW downstream circuits	More expensive than ferric-based oxidants Persulfate solutions can be unstable under some conditions Limited effectiveness at room temperature without activation

Acidic Leaching	Effective for dissolving metal sulfides from concentrates Well-established, industrially proven process Highly optimisable through choice of acid and oxidant combination [17]	Limited effectiveness for gold recovery without additional steps Sulfide passivation reduces efficiency without strong oxidants High acid consumption, especially with carbonate-bearing gangue [17]

2.5. Alternative Leaching Methods

Beyond conventional ferric and acid leaching, a range of alternative and advanced leaching methods have been developed to address the passivation limitations of chalcopyrite processing, particularly for refractory copper–gold sulfide ores and concentrates. The principal alternatives — chloride-based leaching, bioleaching, pressure oxidation, and commercial hybrid processes (Activox, Albion, CESL) — are reviewed below. The iodine–persulfate catalytic system investigated in this thesis work (Sections 2.4.5 and 2.4.6) represents the most recent development in this field and directly addresses the limitations common to all of the methods described here.

2.5.1. Chloride-based leaching

Chloride systems employing reagents such as $CuCl_2$, $FeCl_3$, and HCl provide enhanced leaching kinetics compared to sulfate-only systems, primarily because chloride ions form soluble copper chloro-complexes that stabilise dissolved copper and because Cl^-–bearing media support faster Fe^{3+}/Fe^{2+} redox kinetics. The addition of oxidising agents such as hypochlorite (ClO^-) or chlorine gas (Cl_2) can further improve metal extraction rates [17]. The chlorination process for copper extraction from chalcopyrite follows a sequence of chlorination, oxidation, leaching, and electrowinning, as illustrated in the flowsheet in Figure 2-2 (from the source literature).

Table 2.2 Advantage vs Disadvantage of Chloride-Based leaching

Advantages	**Limitations**
• Faster leaching kinetics due to copper chloro-complexation • More effective for gold dissolution than sulfate-based systems	• Requires handling of highly corrosive chloride solutions • Potential environmental impact from chloride waste disposal

• Reduces passivation compared to pure sulfate media [17]	• High reagent costs; compatibility with SX requires process adaptation [17]

2.5.2. Bioleaching

Bioleaching uses acidophilic microorganisms — principally Acidithiobacillus ferrooxidans and Leptospirillum ferriphilum — to oxidise sulfide minerals and regenerate ferric ions. These bacteria derive energy from the oxidation of Fe^{2+} to Fe^{3+}, which then serves as the chemical oxidant in chalcopyrite dissolution [17]. The process can operate at moderate temperatures (30–50°C) under atmospheric pressure, dissolving copper as soluble Cu^{2+} and exposing gold for subsequent cyanidation.

Table 2.3 Advantage vs Disadvantage of Bioleaching

Advantages	Limitations
• Environmentally friendly compared to chemical oxidant systems • Lower operational cost than pressure oxidation • Effective for low-grade refractory ores [17]	• Very slow leaching kinetics (days to months) • Requires carefully controlled conditions for bacterial activity • Sensitive to temperature, pH, and toxic metal fluctuations [17]

2.5.3. Pressure oxidation (POX)

Pressure oxidation is a high-temperature (200–230°C), high-pressure (10–35 bar) hydrometallurgical process that oxidises sulfide ores in an autoclave with oxygen and acid, enhancing metal recovery. The general reaction for chalcopyrite under POX conditions is:

$$CuFeS_2 + 2.5O_2 + H_2SO_4 \rightarrow CuSO_4 + 0.5Fe_2O_3 + 2S_0 + H_2O \quad \text{(Eq. 2.21)}$$

The elevated temperature and oxygen pressure completely break down passivation layers, achieving high copper and gold extraction from refractory concentrates [17]. POX is the benchmark against which atmospheric-pressure alternatives are evaluated.

Table 2.4 Advantage vs Disadvantage of Pressure oxidation

Advantages	Limitations
• Highly efficient for refractory ores; breaks all passivation layers • High copper and gold recoveries (>95%)	• Very high capital cost (autoclaves, pressure vessels) • Requires specialised autoclave technology and maintenance

• Suitable for large-scale operations with established infrastructure [17]	• Energy-intensive; high temperature and oxygen consumption [17]

2.5.4. Commercial hybrid processes: Activox, Albion, and CESL

Several commercial processes have been developed to balance the high recoveries of POX against the lower capital and operating costs of atmospheric leaching:

The Activox Process operates at moderate pressures and temperatures (100–120°C) using ultra-fine grinding to break down refractory sulfides in an oxygenated acidic environment. Fine grinding dramatically increases reactive surface area and disrupts passivation layers, improving metal extraction while reducing the temperature and pressure requirements relative to conventional POX [18].

The Albion Process combines ultra-fine grinding with atmospheric-pressure oxidative leaching. Fine particle size increases mineral reactivity when exposed to oxygen and ferric ions, making it particularly effective for refractory gold and copper concentrates without requiring pressure vessels [18].

The CESL Process employs a combination of chloride-based and moderate-pressure oxidation leaching. Copper is extracted in an acidic chloride medium that prevents passivation and enhances metal recovery. A purification step removes impurities before final electrowinning, enabling effective copper and gold recovery at lower temperatures than conventional POX [17].

Table 2.5 Advantage vs Disadvantage of Commercial Hybrid Processes

Process	Main concept	Advantages	Limitations
Activox	Moderate-pressure oxidative leaching with ultra-fine grinding	Operates at lower temperature and pressure than POX; efficient metal liberation from sulfide matrices	Requires ultra-fine grinding (high energy consumption); high capital cost for fine-grinding circuits
Albion	Ultra-fine grinding plus atmospheric oxidative leaching	No high-pressure autoclave required; effective for refractory sulfide ores at lower cost than POX	Needs additional fine-grinding equipment; possible passivation if grinding is insufficient
CESL	Chloride-based leaching with moderate-pressure	Efficient Cu and Au recovery at lower temperature than POX;	More complex flowsheet with chloride management; higher

	oxidation and purification [18]	reduced sulfur emissions vs smelting [17]	reagent and capital cost than simple atmospheric leaching [17]

2.5.5. Iodine–Iodide catalytic leaching

Iodine-based leaching has attracted growing research attention as an atmospheric-pressure alternative capable of overcoming chalcopyrite passivation without high temperature or pressure. The mechanism involves the I_2/I^- redox couple acting as a catalytic electron-transfer mediator at the chalcopyrite surface, providing a higher and more sustained mixed potential than Fe^{3+} alone. The three key reactions of the catalytic cycle are [19]:

$$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+} \quad \text{(Eq. 2.22)}$$

$$CuFeS_2 + I_2 + 2Fe^{3+} \rightarrow Cu^{2+} + 3Fe^{2+} + 2S_0 + 2I^- \quad \text{(Eq.2.23)}$$

$$2I^- \rightarrow I_2 + 2e^- \quad \text{(Eq. 2.24)}$$

Because iodide is continuously regenerated in step (Eq. 2.7) and re-oxidised to I_2 in step (Eq. 2.6), iodine functions as a true catalyst rather than a stoichiometric reagent. Castillo et al. (2023) demonstrated that iodide at concentrations as low as 100 ppm in sulfuric acid media at 45°C accelerates chalcopyrite leaching dramatically, with an apparent activation energy of approximately 43 kJ mol^{-1} — consistent with a surface-reaction-controlled rather than diffusion-controlled mechanism, distinguishing iodine-catalysed leaching from conventional ferric systems where diffusion through passivation layers is rate-limiting [32,33]. Heap-leach column tests with 100 mg/L iodide increased copper extraction from 8.5% (no iodide) to 37.1% over 144 days at ambient temperature, and residue mineralogy confirmed that elemental sulfur and jarosite did not accumulate as passivation barriers in the presence of iodine [19].

2.5.6. Persulfate–iodine synergistic system

Persulfate oxidants and iodine mediators can be combined to create a synergistic oxidant–catalyst system for chalcopyrite and other copper sulfides, building on the individual mechanisms described in Sections 2.3.3 and 2.4.5. In such systems, ammonium persulfate (or related persulfates) serves three functions: (i) it oxidises Fe^{2+} to Fe^{3+}, sustaining the Fe^{3+} pool needed to regenerate I_2 from I^- via Eq. 2.6; (ii) it generates $SO_4^{\cdot -}$ radicals at temperatures ≥50°C, which can directly attack chalcopyrite surfaces and elemental sulfur; and (iii) it maintains solution redox potential at levels that prevent Fe^{2+} accumulation and reductive precipitation. Iodine then catalyses the

surface-phase electron transfer step (Eq. 2.7), providing the high interfacial potential needed to overcome the p–n semiconductor junction barrier at the chalcopyrite surface and thereby suppressing passivation [19].

This mechanistic complementarity — persulfate sustaining the solution-phase oxidant cycle, iodine driving the surface-phase dissolution reaction — is expected to produce a synergistic enhancement that exceeds the performance of either reagent acting alone. Literature on iodine-assisted chalcopyrite systems and radical persulfate oxidation supports this concept, indicating that combinations of strong solution-phase oxidants with the I_2/I^- redox mediator can sustain high redox potentials while minimising formation of impermeable sulfur layers.

2.6. Electrowinning of Copper

Electrowinning (EW) is the final stage of many hydrometallurgical copper recovery circuits, cathodically depositing Cu^{2+} from pregnant leach solution (PLS) or solvent extraction (SX) electrolyte as metallic copper. The fundamental electrode reactions are: [19]:

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu^0$ ($E^0 = +0.34$ V vs. SHE) (Eq. 2.25)

Anode: $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ ($E^0 = +1.23$ V vs. SHE) (Eq. 2.26)

Practical operating cell voltages are typically 1.8–2.2 V, accounting for overpotentials, solution resistance, and mass-transfer losses. Titanium (Ti) cathodes are preferred for their inertness and ease of copper deposit stripping; lead (Pb) or lead-alloy anodes are standard in sulfuric acid electrolytes due to their resistance to anodic corrosion. Current efficiency in well-controlled industrial circuits is typically 85–95%, and theoretical specific energy consumption is approximately 1.7–2.0 kWh per kg of copper deposited [21,22].

CHAPTER 3. METHODOLOGY

3.1. Overview of Experimental Work

This study was carried out through a series of laboratory-scale leaching experiments to evaluate copper extraction from sulfide concentrate under different conditions. The main variables investigated were acid type, temperature, and the use of oxidizing agents. The experimental work consisted of three main stages. First, leaching experiments were performed using different acids at controlled temperatures. Second, the effect of oxidizing agents was studied to improve copper dissolution. Finally, a larger-scale leaching test was conducted to produce sufficient solution for copper recovery by electrowinning. The overall goal was to compare the effectiveness of different leaching conditions and to assess the possibility of recovering copper from the solution.

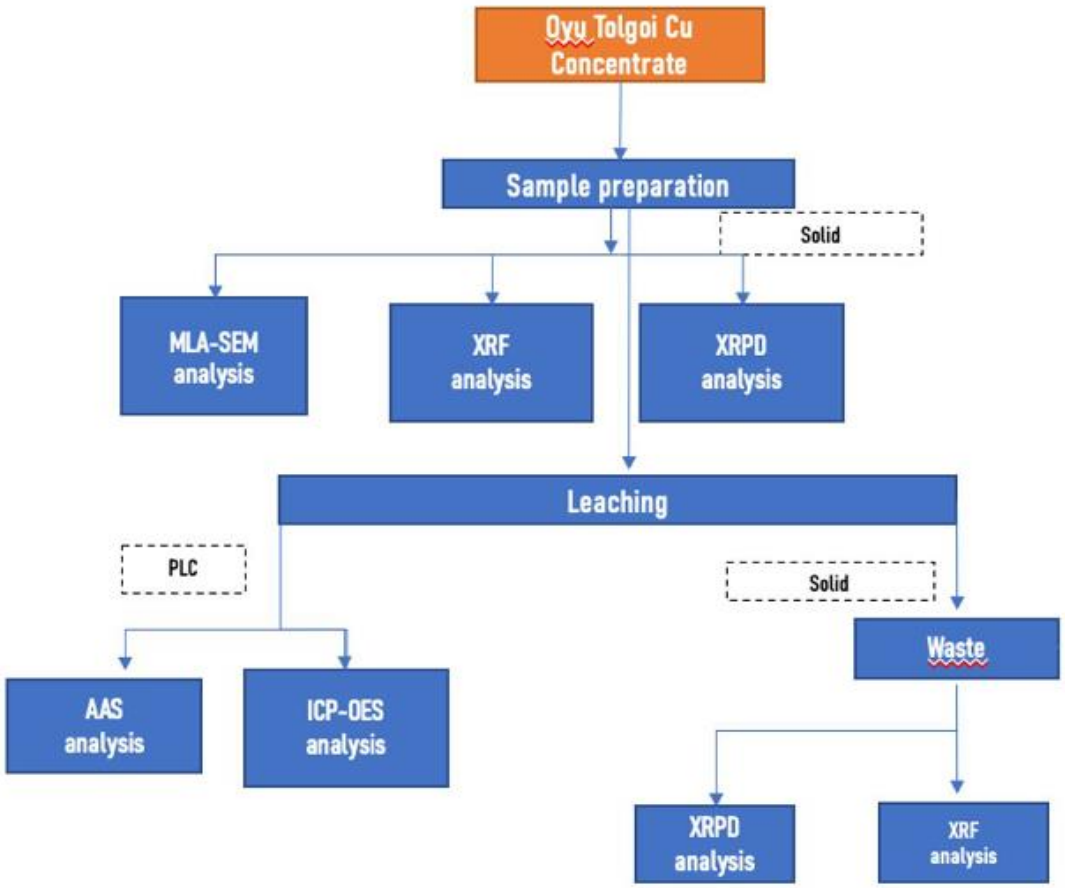


Figure 3.1 Schematic overview of the experimental methodology of the study

3.2. Materials

3.2.1. Copper concentrate sample

The copper concentrate investigated in this study was sourced from the Oyu Tolgoi porphyry copper–gold deposit located in the South Gobi region of Mongolia, one of the largest known copper deposits globally. The industrial concentrate is produced by conventional flotation and typically contains 25–30 wt.% Cu as sulfide minerals together with minor gold and other trace elements. The dominant copper-bearing phase is chalcopyrite ($CuFeS_2$), with accessory bornite and chalcocite reported in the deposit, while pyrite and other iron sulfides form the major gangue sulfides.

Upon receipt, the bulk concentrate was dried at ambient laboratory conditions, homogenized by gentle rolling and coning–quartering, and stored in sealed polyethylene containers to minimize oxidation and moisture uptake. For each leaching test in the main experimental matrix, a fixed mass of 1.00 g (±0.01 g) of concentrate was weighed.

3.2.2. Chemical reagents

The leaching media consisted of three mineral acids: sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl). Stock solutions were prepared from analytical-grade concentrated acids by dilution with deionized (DI) water to a working concentration of 1.0 M. All glassware and volumetric flasks were rinsed with DI water prior to solution preparation to prevent contamination.

Ammonium persulfate, $(NH_4)_2S_2O_8$ (APS), was employed as the primary oxidizing agent to promote the oxidative dissolution of copper sulfide minerals. APS provides persulfate ions, which generate sulfate radicals in acidic media and facilitate the conversion of Cu^{+}/Cu^{+1} species to the more stable Cu^{2+} state in solution. In selected tests, molecular iodine (I_2) was introduced as a catalyst to enhance leach kinetics, based on its ability to participate in redox cycles and potentially re-oxidize reduced sulfur species.

All reagents were of analytical grade and were used as received without further purification. Leach solutions were freshly prepared on the day of each experiment using DI water with a resistivity greater than 18 MΩ·cm. Volumes were measured using class A volumetric cylinders or flasks to maintain accurate and reproducible concentrations.

3.3. Experimental Design

3.3.1. Leaching conditions

The overall experimental design was developed to systematically examine the effect of key operating variables on copper dissolution from the Oyu Tolgoi concentrate under controlled hydrometallurgical conditions. The leaching conditions were selected to represent realistic acidic environments, a practical laboratory temperature range, and different levels of oxidizing strength, while keeping the solid–liquid ratio constant across all tests. The main factors investigated were:

Reagent: Three mineral acids were selected based on their reactivity, industrial relevance, and ability to support oxidative dissolution:

- Sulfuric acid (H_2SO_4)- Commonly used in industrial hydrometallurgy, supports ferric ion formation and sulfate complexation.
- Nitric acid (HNO_3)- A strong oxidizing acid capable of directly attacking sulfide matrices and dissolving both copper and iron species.
- Hydrochloric acid (HCl)- enhances chloride complexation of metal ions and is often used in oxidative leaching systems.

Temperature control: Reaction temperatures were maintained 25 °C (ambient), 50 °C, and 70 °C depending on experimental matrix. These temperatures were selected to observe the thermal effect on dissolution kinetics and passivation phenomena.

Oxidizing conditions: The oxidative environment was varied to evaluate its influence on sulfide mineral dissolution:

- No oxidant (acid leach only), representing purely acid attack without external oxidizing agents.
- Ammonium persulfate ($(NH_4)_2S_2O_8$), providing persulfate ions as a strong oxidant to promote conversion of copper sulfides to soluble Cu^{2+} species.
- Ammonium persulfate plus iodine ($(NH_4)_2S_2O_8$ + I_2), where iodine acts as a catalyst or co-oxidant to further enhance leaching kinetics through redox cycling.

These conditions create a progressive increase in oxidizing strength, from acid alone to APS and then APS combined with I_2

Stirring speed: All experiments were carried out at a constant stirring speed of 400 rpm using a magnetic stirrer. This agitation rate was selected to keep the solid particles in suspension, improve mass transfer between the solid and liquid phases, and ensure good mixing, while avoiding excessive splashing or vortex formation.

Sampling time: Leaching time was treated as a kinetic variable common to all experiments. Slurry samples were collected at: 2hour, 4 hour, 6hour and 24 hours. These

intervals allowed the evolution of copper dissolution to be monitored from the early stages of leaching through to near-equilibrium conditions, enabling assessment of both initial kinetics and overall extraction after 24 h.

Solid to Liquid ratio: The tests were conducted using a solid concentration of 10 g/L, which provides a practical and manageable concentration for both reaction kinetics and analytical resolution.

Those conditions ensured the reproducibility of results and allowed for clear comparison of leaching performance across different reagent combinations and conditions.

3.3.2. Experimental matrix

A matrix of 27 experiments was constructed by combining the three acids, three temperatures, and three oxidizing conditions, including selected replicates to check reproducibility. This matrix enabled direct comparison of copper extraction under different chemical and thermal regimes, as well as assessment of the influence of the oxidizing environment.

Table 3.1 Experimental matrix for copper concentrate leaching (1.00 g concentrate, 100 mL of 1 M acid).

Experiment No.	Acid (1 M)	T (°C)	Oxidant / I_2
1	H_2SO_4	70	–
2	HNO_3	70	–
3	HCl	70	–
4	H_2SO_4	50	–
5	HNO_3	50	–
6	HCl	50	–
7	H_2SO_4	25	–
8	HNO_3	25	–
9	HCl	25	–
10	H_2SO_4	70	$(NH_4)_2S_2O_8$
11	HNO_3	70	$(NH_4)_2S_2O_8$
12	HCl	70	$(NH_4)_2S_2O_8$
13	H_2SO_4	50	$(NH_4)_2S_2O_8$
14	HNO_3	50	$(NH_4)_2S_2O_8$
15	HCl	50	$(NH_4)_2S_2O_8$

16	H_2SO_4	25	$(NH_4)_2S_2O_8$
17	HNO_3	25	$(NH_4)_2S_2O_8$
18	HCl	25	$(NH_4)_2S_2O_8$
19	H_2SO_4	25	$(NH_4)_2S_2O_8 + I_2$
20	HNO_3	25	$(NH_4)_2S_2O_8 + I_2$
21	HCl	25	$(NH_4)_2S_2O_8 + I_2$
22	H_2SO_4	50	$(NH_4)_2S_2O_8 + I_2$
23	HNO_3	50	$(NH_4)_2S_2O_8 + I_2$
24	HCl	50	$(NH_4)_2S_2O_8 + I_2$
25	H_2SO_4	20	$(NH_4)_2S_2O_8 + I_2$
26	HNO_3	20	$(NH_4)_2S_2O_8 + I_2$
27	HCl	20	$(NH_4)_2S_2O_8 + I_2$

3.4. Leaching Procedure

3.4.1. Reactor setup and temperature control

Leaching experiments were carried out in 250–500 mL borosilicate glass reagent bottle placed on digital hot-plate magnetic stirrers. A PT100 (or K-type) thermocouple probe connected to the hot plate was immersed in the solution to monitor and control the temperature. A thermocouple probe was inserted into a separate borosilicate glass bottle containing water, positioned adjacent to the vessel containing the diluted acid, in order to monitor and control the temperature.

For tests at 25 °C, the hot-plate heating function was set to a minimal level to maintain near-ambient temperature, with occasional monitoring. For tests at 50 °C and 70 °C, the hot plate was adjusted until the solution temperature stabilized within ±1 °C of the set point. Temperature was recorded at the start of the experiment and at each sampling interval to verify that thermal conditions remained approximately constant throughout the 24 h period.

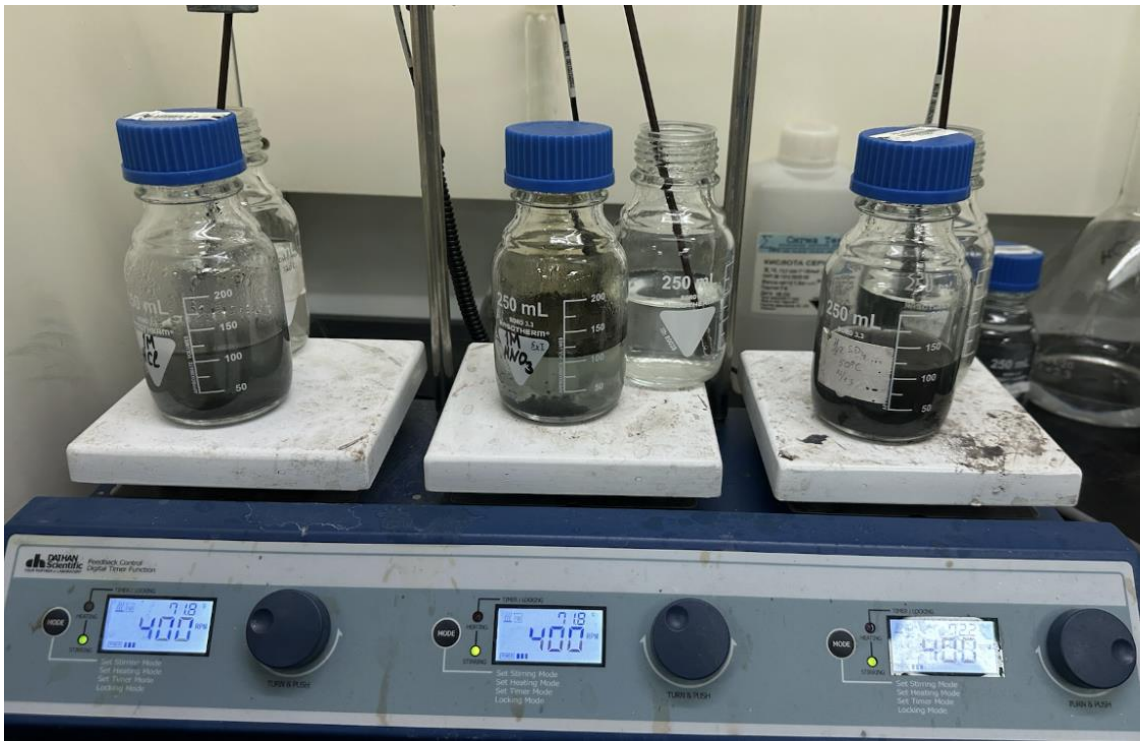


Figure 3.2 The setup of the Leaching experiment #10-12

3.4.2. Leaching process

After the solution reached and stabilized at the target temperature (25, 50, or 70 °C), a pre-weighed 1.00 g portion of copper concentrate was then added slowly to the beaker to minimize dusting and to wet the particles uniformly, resulting in a solid-to-liquid ratio of 10 g/L. Depending on the oxidizing condition defined in the experimental matrix, either no oxidant was used, a predetermined mass of 1 g ammonium persulfate was added directly to the slurry and allowed to dissolve, or ammonium persulfate was added first followed by 0.25 g iodine (as solid or standardized solution), ensuring complete mixing in all cases.

The start of leaching (t = 0) was defined as the time at which all solid reagents had been introduced and fully wetted by the solution. The slurry was then maintained at the target temperature with continuous stirring for a total of 24 h; temperature was monitored periodically, and the heating rate was adjusted as necessary to keep variations within approximately ±1 °C. At predetermined times of 2, 4, 6, and 24 h, small aliquots of slurry were withdrawn using a pipette while stirring to obtain representative samples, immediately subjected to solid–liquid separation by filtration and the clarified solutions were labelled and stored for dissolved copper analysis, while the corresponding solids were retained for potential mineralogical characterization. After the final 24 h sample was collected, the remaining slurry was filtered, and the residue was washed with deionized water, dried, and stored for further analytical work.

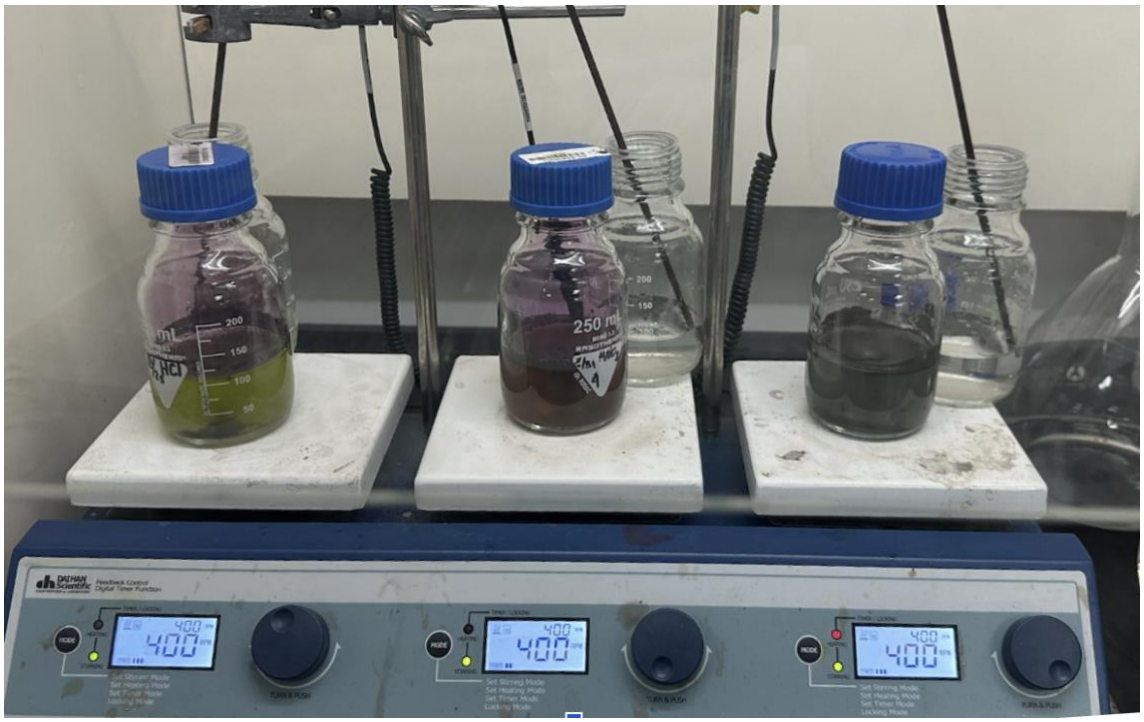


Figure 3.3 Leaching procedure of experiment # 25-27.

3.4.3. Sampling procedure

To follow the leaching kinetics, liquid samples were collected at predetermined times of 2, 4, 6, and 24 h. At each interval, a small volume of slurry which typically 2mL was withdrawn using a plastic pipette while maintaining stirring to obtain a representative sample.

The collected slurry was immediately filtered using fine quantitative filter paper to separate the liquid phase (pregnant leach solution) from the solid residue. The filtrate was transferred to acid-washed polyethylene vials and, where necessary, acidified with a few drops of concentrated acid to prevent precipitation prior to analysis. The solid fraction retained on the filter was washed with a small volume of DI water to remove adhering solution and then dried at low temperature for subsequent solid-phase analysis.

The total volume removed during intermediate sampling was kept below approximately 10% of the initial volume. If required, the volume loss was corrected when calculating metal concentrations and extraction efficiencies.

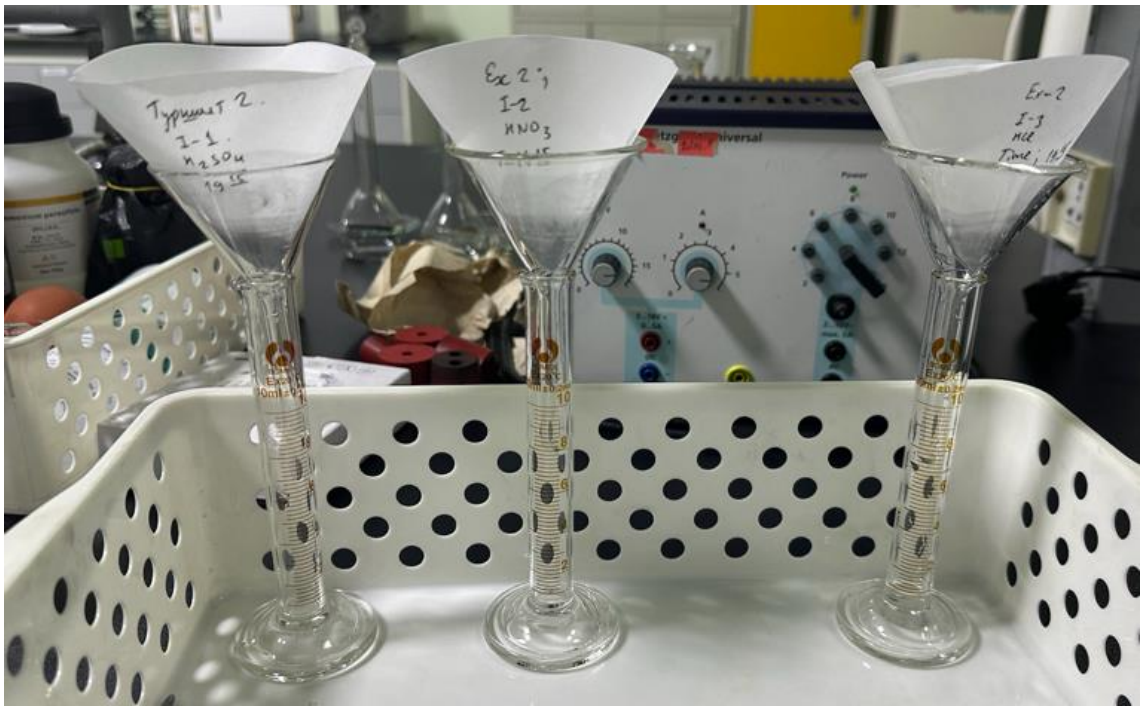


Figure 3.4 *Sampling setup with funnels and graduated cylinders used for leach solution collection.*



Figure 3.5 *Glassware and pipettes after solution sampling during leaching experiments.*

3.5. Analytical Methods

3.5.1. Solution analysis (AAS)

The concentration of dissolved copper in the leach liquors was determined by Atomic Absorption Spectrometry (AAS). Prior to analysis, the filtered leach solutions were diluted with acidified deionized water to bring the copper concentration within the linear calibration range of the instrument and to maintain consistent matrix conditions. Calibration standards were prepared from certified copper stock solutions covering the expected concentration range, and calibration blanks and quality-control standards were analyzed periodically to verify instrumental stability, drift, and accuracy.

For each sample, the AAS measurement provided the copper concentration in the solution phase, expressed in mg/L. This concentration was multiplied by the measured solution volume to obtain the total mass of copper present in solution at each sampling time. Copper extraction at time t*t* was then calculated as the ratio between the mass of copper in solution and the initial mass of copper in the solid feed, expressed as a percentage, according to:

$$Cu\ recovery\ (\%) = \frac{C_t \times V_t}{m_{ore} \times \frac{\%\ Cu}{100}} \times 100 \qquad \text{(Eq. 3.1)}$$

Where:

- C_t = copper concentration in solution at time t (mg/L)
- V_t = volume of the leach solution at time t (L)
- M_{ore}= ore mass

Using these expressions, time-dependent extraction curves were constructed for each leaching condition, allowing direct comparison of leaching performance between the different acids, temperatures, and oxidizing environments.



Figure 3.6. ***WFX-220 Series*** *Atomic Absorption Spectrometry (AAS)*

3.5.2. XRF analysis

X-ray fluorescence (XRF) spectroscopy was used to determine the elemental composition of the leach residues and, where needed, the original concentrate. Samples were dried, ground to a fine powder, and pressed into pellets or fused into glass beads according to the laboratory's standard operating procedures. The XRF data provided bulk copper contents in wt.% and enabled material balance calculations by comparing residual copper in the solids with copper dissolved in solution.



Figure 3.7 ***A Skyray Explorer 5000*** *handheld X-ray fluorescence (XRF) spectrometer*

3.5.3. XRD analysis

X-ray diffraction (XRD) was employed to characterize the mineralogical phases present in the feed and selected leach residues. Approximately 1–2 g of each sample was finely ground and mounted in standard powder holders. Diffractograms were collected over a suitable 2θ range with an appropriate step size and counting time to resolve the key sulfide and gangue phases. Qualitative phase identification was performed using reference patterns from standard databases, while semi-quantitative interpretation was used to infer the extent of phase transformation and the formation or disappearance of specific minerals during leaching.

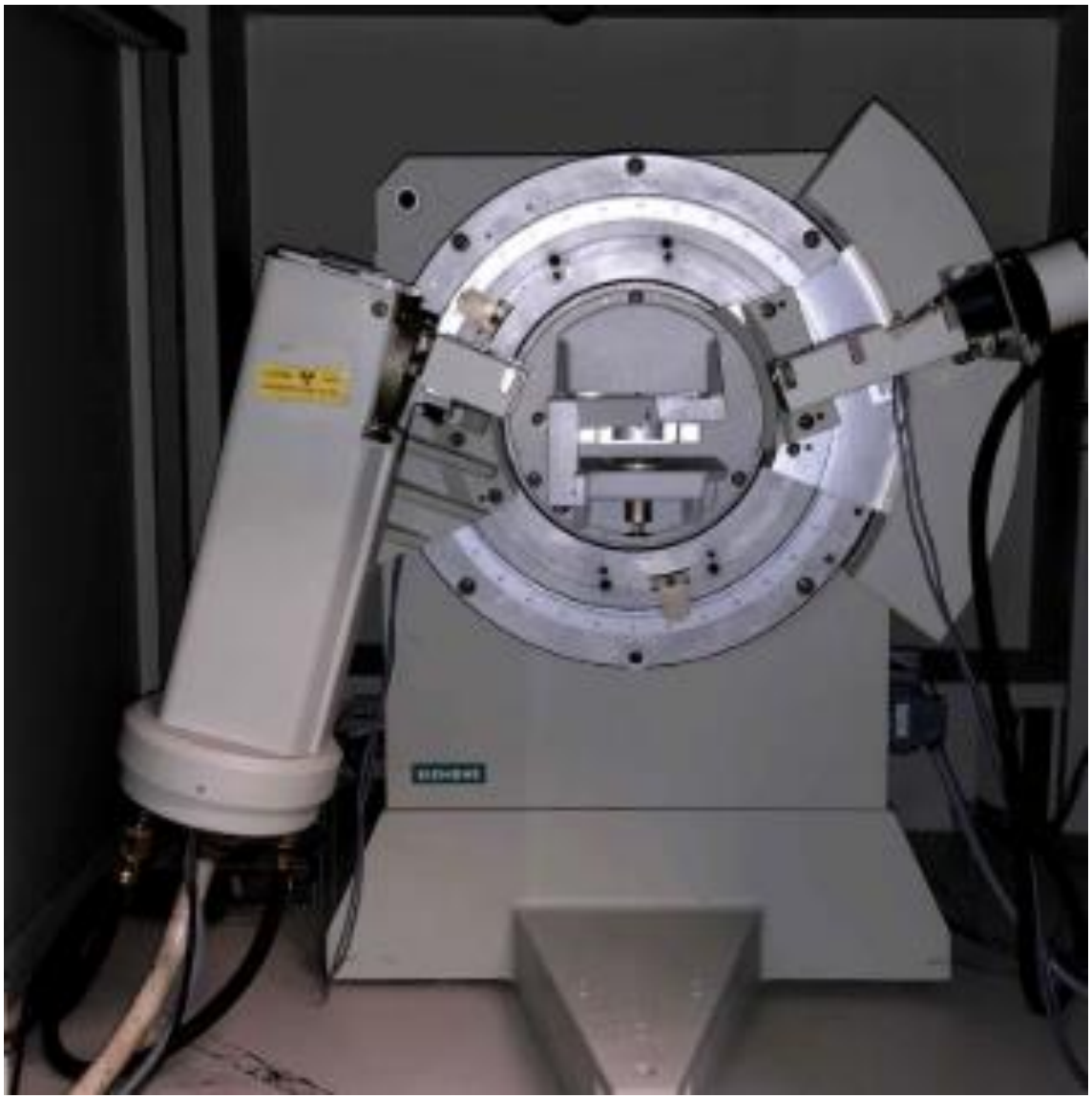


Figure 3.8 ***Siemens D5000*** *X-ray diffractometer (XRD).*

A larger-scale leaching experiment was carried out to confirm the trends observed in the laboratory-scale tests and to generate sufficient material for downstream processing. Scale-up leaching was performed in 1000 mL borosilicate glass vessels,

including reagent bottles and three-neck round-bottom flasks, under otherwise similar operating conditions to the bench-scale experiments. Separate scale-up series were conducted for each of the three acids media (sulfuric, nitric, and hydrochloric acid) to verify that the optimized leaching behaviour could be reproduced at increased volume.

For the final scale-up test, the leaching conditions identified as optimal from the 27 small-scale experiments were reproduced on a tenfold larger scale. The selected acid was used at a concentration of 1 M and a volume of 1000 mL, to which 10 g of copper concentrate was added, maintaining the same solid-to-liquid ratio as in the 100 mL tests. In addition, 10 g of ammonium persulfate ($(NH_4)_2S_2O_8$) and 2.5 g of iodine were introduced as oxidant and catalyst, respectively, and the slurry was leached at 70 °C for 24 h under continuous stirring.

This scale-up experiment had two principal objectives: (i) to demonstrate that the leaching performance observed at 100 mL scale—both in terms of copper extraction and solution chemistry—could be replicated at a volume of 1000 mL, and (ii) to produce a sufficient quantity of pregnant leach solution for subsequent copper electrowinning tests, along with enough solid residue to permit detailed mineralogical and chemical characterization. By increasing the volume and mass by a factor of ten while keeping the key operating parameters constant, the experiment provided a bridge between bench-scale leaching and integrated leach–electrowinning evaluation.

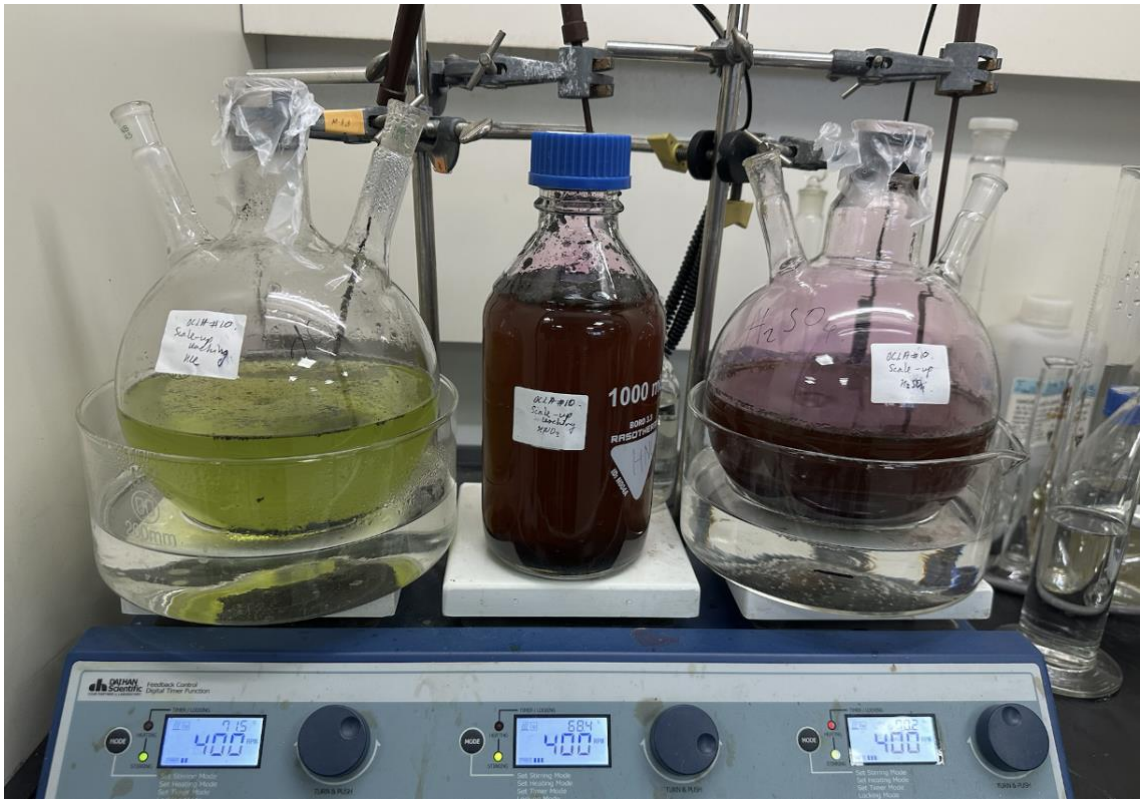


Figure 3.9 Scale-Up Validation of Optimized Copper Leaching Conditions



Figure 3.10 (a) OT Cu Con (10g) (b) Ammonium persulfate(10g)) (c) Iodine (2.5g)

3.6. Electrowinning Procedure

Electrowinning tests were performed using the sulfuric-acid pregnant leach solution (PLS) obtained from the scale-up leaching experiment. The PLS was transferred to an electrochemical cell equipped with a flat titanium plate cathode and a flat lead plate anode, arranged parallel to each other at a fixed spacing. A DC power supply was used to apply a constant voltage of 2 V, resulting in a current of approximately 1.8 A for the duration of the test. During electrolysis, the solution was kept under gentle stirring to maintain homogeneity, and the temperature was held near ambient laboratory conditions. At the end of the electrowinning period, the electrodes were removed, rinsed with deionized water, dried, and weighed to determine the mass of copper deposited on the cathode and any mass change of the anode.

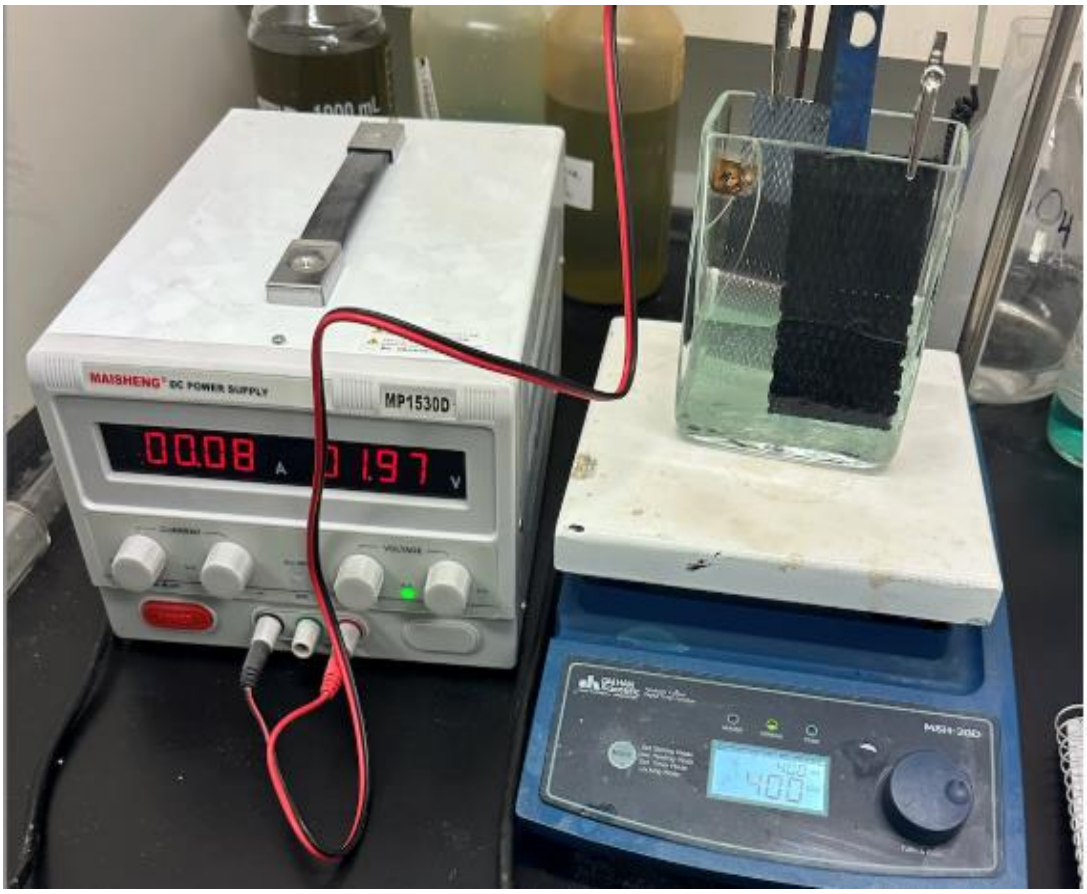


Figure 3.11 Electrowinning Setup

CHAPTER 4. RESULTS AND DISCUSSION

4.1. Sample Characterization

4.1.1. Chemical characteristic

The bulk chemical composition of the copper sulfide concentrate was determined using a handheld XRF analyzer. The results indicate that the concentrate is relatively rich in both copper and iron, consistent with a chalcopyrite-dominated mineralogy. According to the XRF measurements, the copper content is 18.41 ± 1.76 wt.% and the iron content is 21.18 ± 1.11 wt.%. Minor and trace elements such as Al, Si, S, Ca, and Zn are also present, together with a balance fraction representing undetected or unquantified components. Because the measurements were obtained using a handheld instrument, small systematic and random errors are possible, and the results should be regarded as semi-quantitative rather than fully certified values.

Table 4.1 XRF chemical composition of the sample

Element	Content (wt.%)	±4σ (wt.%)
Al	2.89	1.36
Bal	38.26	4.16
Si	3	0.28
S	14.61	0.76
Cl	0.062	0.017
K	0.166	0.069
Ca	0.402	0.061
Fe	21.18	1.11
Cu	18.41	1.76
Zn	0.395	0.055

4.1.2. Mineralogical characteristics

The copper concentrate used in this study was analyzed by X-ray diffraction (XRD) in order to identify its principal mineral phases and to verify the mineralogical context for the leaching experiments. The diffraction pattern shows that chalcopyrite ($CuFeS_2$) is the dominant copper-bearing mineral in the sample, consistent with the chemical composition obtained from XRF. Pyrite (FeS_2) is also present as a major iron sulfide phase, while quartz (SiO_2) is identified as the main silicate gangue mineral. Minor additional peaks may be attributable to other sulfide or silicate phases, but they are of much lower intensity than those of chalcopyrite, pyrite, and quartz.

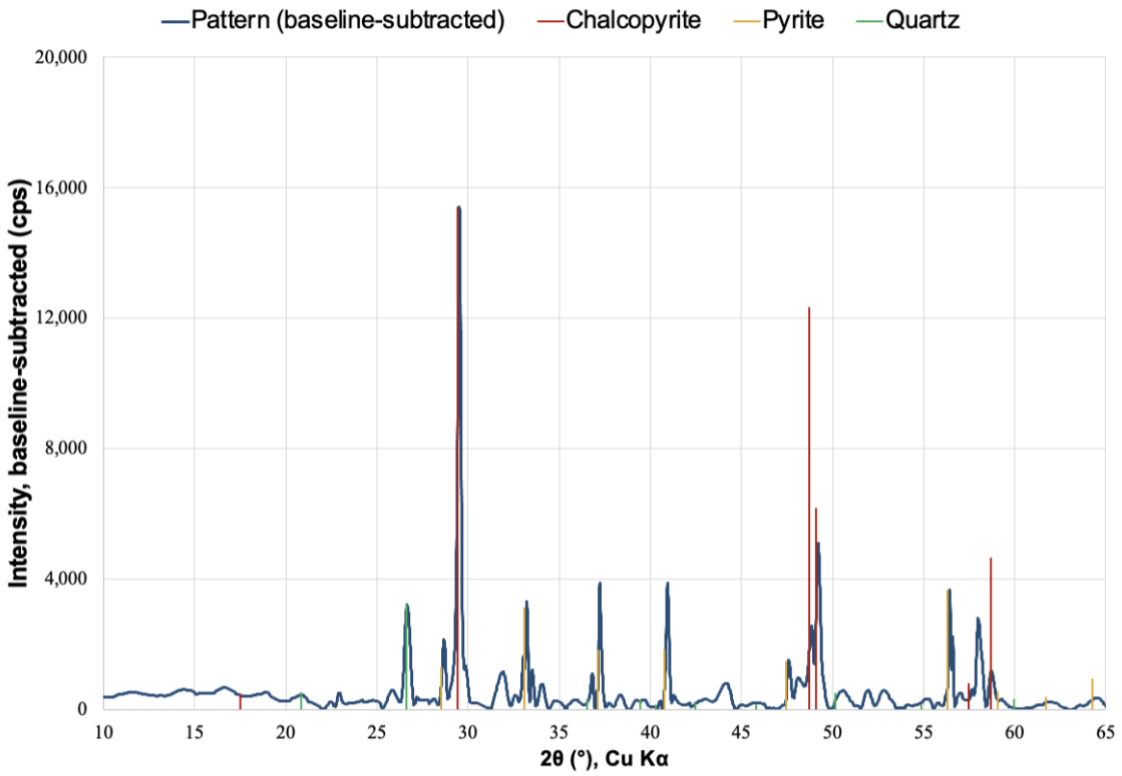


Figure 4.1 XRD pattern of the sample showing the presence of chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and quartz (SiO_2).

These XRD results confirm that the mineral assemblage of the sample is typical of Cu-Au sulfide concentrates. The predominance of chalcopyrite is particularly significant, because this mineral is generally regarded as relatively refractory and dissolves only slowly under simple acidic leaching conditions.

4.2. Effect of Acid Type on Copper Extraction

The influence of acid type on copper extraction was evaluated by comparing sulfuric, nitric, and hydrochloric acids under otherwise identical leaching conditions. For each acid system, tests were carried out at several temperatures and oxidizing environments, and copper extraction after 24 h was used as the main response variable. The results show that nitric acid consistently provided the highest copper extraction among the three acids across most conditions. Even in the absence of added oxidants, nitric acid achieved substantially higher copper dissolution than sulfuric and hydrochloric acids, particularly at elevated temperatures. This behaviour is attributed to the dual role of nitric acid, which acts both as a proton source and as an oxidizing agent capable of directly oxidizing sulfide minerals and promoting the formation of soluble Cu^{2+}.

By contrast, sulfuric acid generally produced the lowest copper extraction under acid-only conditions, especially at lower temperatures, confirming that simple sulfate media are relatively ineffective for chalcopyrite leaching without an additional oxidant. Hydrochloric acid showed intermediate performance: copper extraction increased with temperature and oxidant addition, but typically remained below that achieved in nitric acid systems. Overall, these observations demonstrate that the choice of acid has a critical influence on leaching efficiency, with oxidizing acids such as HNO_3 offering a significant advantage over purely non-oxidizing media when treating refractory chalcopyrite concentrates.

Table 4.2 Result that is copper recovery of leaching experiments after 24 hour

Exp	Acid (1 M)	T (°C)	Oxidant / I_2	Cu recovery %
1	H_2SO_4	70	–	48.52
2	HNO_3	70	–	95.15
3	HCl	70	–	87.20
4	H_2SO_4	50	–	4.57
5	HNO_3	50	–	80.55
6	HCl	50	–	43.02
7	H_2SO_4	25	–	1.56
8	HNO_3	25	–	2.18
9	HCl	25	–	1.83
10	H_2SO_4	70	$(NH_4)_2S_2O_8$	58.70
11	HNO_3	70	$(NH_4)_2S_2O_8$	104.03
12	HCl	70	$(NH_4)_2S_2O_8$	97.31
13	H_2SO_4	50	$(NH_4)_2S_2O_8$	40.26
14	HNO_3	50	$(NH_4)_2S_2O_8$	88.21
15	HCl	50	$(NH_4)_2S_2O_8$	48.18
16	H_2SO_4	25	$(NH_4)_2S_2O_8$	23.41
17	HNO_3	25	$(NH_4)_2S_2O_8$	18.82
18	HCl	25	$(NH_4)_2S_2O_8$	27.83
19	H_2SO_4	25	$(NH_4)_2S_2O_8 + I_2$	51.54
20	HNO_3	25	$(NH_4)_2S_2O_8 + I_2$	58.08
21	HCl	25	$(NH_4)_2S_2O_8 + I_2$	66.05
22	H_2SO_4	50	$(NH_4)_2S_2O_8 + I_2$	92.31
23	HNO_3	50	$(NH_4)_2S_2O_8 + I_2$	106.19
24	HCl	50	$(NH_4)_2S_2O_8 + I_2$	95.83

25	H_2SO_4	70	$(NH_4)_2S_2O_8 + I_2$	101.39
26	HNO_3	70	$(NH_4)_2S_2O_8 + I_2$	111.63
27	HCl	70	$(NH_4)_2S_2O_8 + I_2$	100.23
28	H_2SO_4	70	$(NH_4)_2S_2O_8 + I_2$	78.77
29	HNO_3	70	$(NH_4)_2S_2O_8 + I_2$	79.33
30	HCl	70	$(NH_4)_2S_2O_8 + I_2$	84.76

In some leaching conditions, the calculated copper extraction after 24 h slightly exceeds 100% (for example, up to about 111% in selected persulfate–iodine tests). These values do not indicate that more copper was leached than initially present in the concentrate; rather, they arise from experimental uncertainty in the determination of solution volume and metal concentration.

During long-duration tests at elevated temperature, partial evaporation of the acidic leach solution caused the final solution volume to be lower than the nominal value used in the extraction calculations. Because copper extraction was calculated from the measured concentration (mg/L) multiplied by an assumed solution volume, any uncorrected loss of liquid leads to an overestimation of the total dissolved copper and hence to apparent extractions above 100%. Additional minor contributions may come from weighing errors, sampling losses, and instrumental uncertainty in AAS measurements.

When the calculations are repeated using the actual post-leach solution volumes, the corresponding copper extractions decrease to physically reasonable values below 100%, while the relative trends between acids, oxidants, and temperatures remain unchanged. Therefore, the >100% values should be interpreted as an artefact of volume loss and analytical uncertainty, not as true recoveries greater than the copper content of the feed.

4.3. Effect of Temperature

Temperature had a strong and systematic impact on copper extraction in all leaching systems studied. In general, increasing the temperature from 20–25 °C to 70 °C led to a marked enhancement in copper dissolution, regardless of the acid type or oxidizing condition. This trend is clearly illustrated in Figure 4.2, which compares copper recovery in sulfuric-acid media at 25, 50, and 70 °C for different oxidant conditions. At higher temperatures, reaction kinetics are accelerated and diffusion limitations are reduced, so the leaching process becomes faster and more efficient. This effect was

particularly pronounced in sulfuric and hydrochloric acid systems, where copper extraction at low temperature was limited but improved substantially at 70 °C.

The results are consistent with the well-known refractory nature of chalcopyrite, which typically shows slow dissolution at ambient temperature and requires either elevated temperature or strongly oxidizing conditions to achieve high copper extraction. In nitric acid, the combined effects of higher temperature and intrinsic oxidizing power of the acid gave the highest extractions observed in this study. Overall, the data confirm that chalcopyrite leaching is strongly temperature-dependent and that higher temperatures are essential for efficient copper recovery, especially in non-oxidizing or weakly oxidizing acid systems.

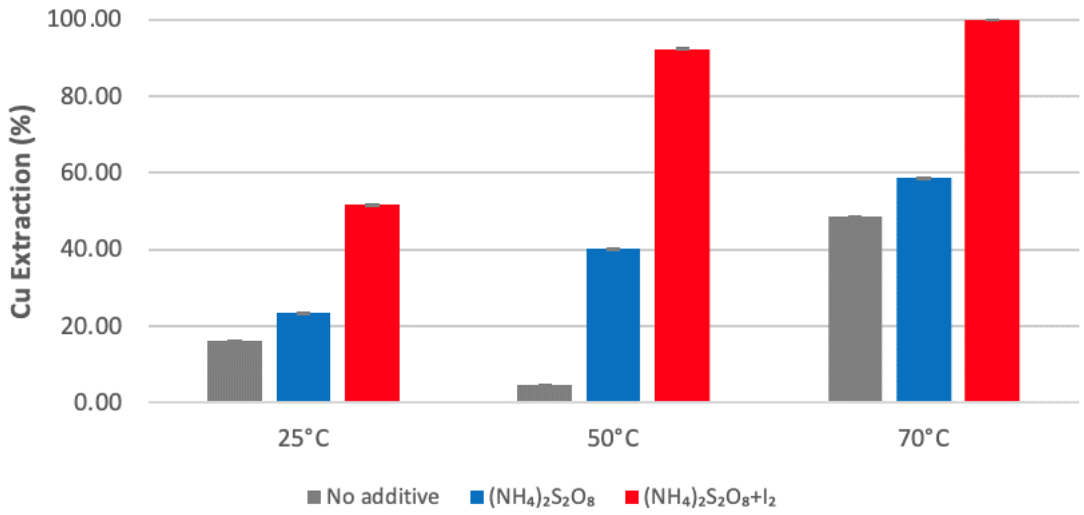


Figure 4.2 Graphic of Temperature comparison of Cu recovery at Sulfuric acid media leaching

4.4. Effect of Oxidizing Agents

4.4.1. Ammonium Persulfate

The addition of ammonium persulfate ($(NH_4)_2S_2O_8$, APS) significantly enhanced copper extraction in most leaching conditions compared with acid-only systems. For a given acid and temperature, the presence of APS generally increased the 24 h copper extraction, indicating that the persulfate ion provides a stronger oxidizing environment for sulfide dissolution. This improvement was most evident at higher temperatures, where persulfate decomposition and radical generation are more favourable, and particularly in sulfuric acid, where the baseline copper extraction without an oxidant was relatively low.

4.4.2. Combined oxidant system (APS + I_2)

The highest copper extractions were obtained when ammonium persulfate and iodine were used together as a combined oxidant system. Across the experimental matrix, APS + I_2 leaches consistently out-performed both acid-only and APS-only tests, indicating a synergistic effect between persulfate and iodine. This trend is clearly illustrated in Figure 4.3, where the hydrochloric-acid leaching curves show much faster and higher copper recovery for the APS + I_2 system than for APS alone or the acid-only baseline. The presence of iodine likely facilitates redox cycling and enhances the overall oxidizing strength of the solution, leading to faster and more extensive breakdown of chalcopyrite and associated sulfide minerals.

In some experiments with APS + I_2, the calculated copper extraction slightly exceeded 100%. These values do not represent true recoveries above 100% but are attributed to experimental uncertainties such as analytical error, minor inaccuracies in feed grade, small variations in sample mass, and slight evaporation of the leach solution during heating, which effectively increases the measured metal concentration. Nevertheless, even accounting for these uncertainties, the data clearly demonstrate that the combined APS + I_2 system is the most effective oxidizing environment tested in this study for promoting copper leaching from the OT chalcopyrite concentrate.

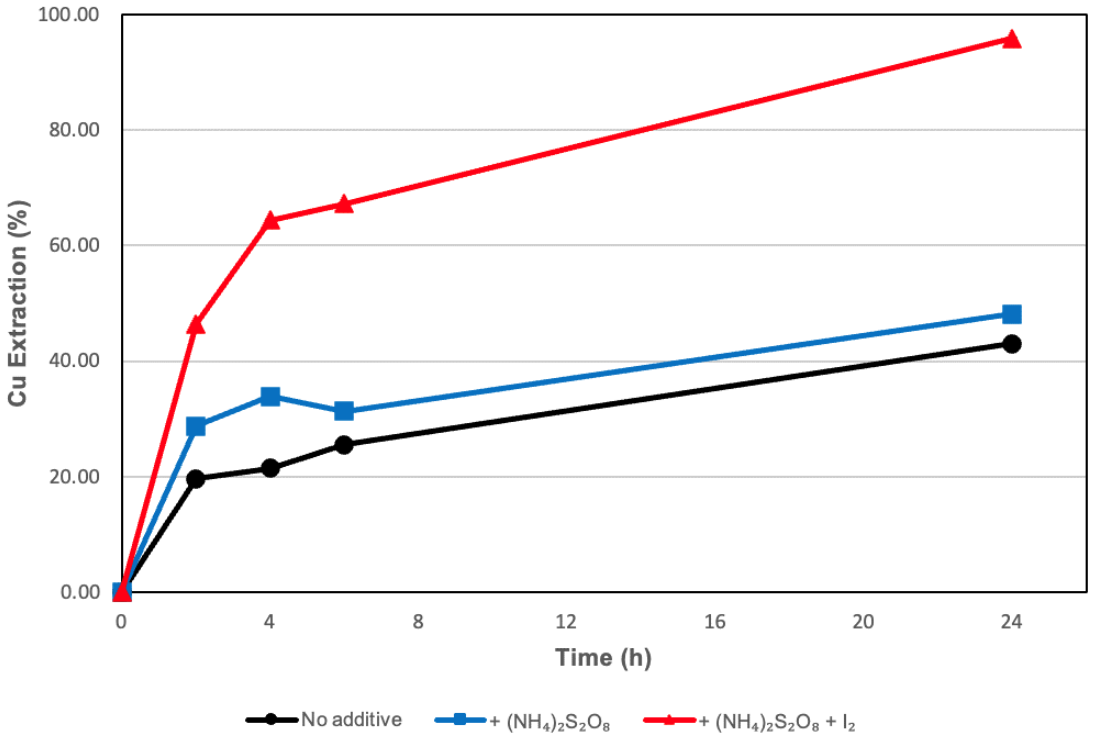


Figure 4.3 Graphic of Copper recovery of hydrochloric acid media

4.5. Copper Extraction Kinetics

The time-dependent leaching kinetic curves show that the majority of copper dissolution occurred within the first 6 h of contact between the concentrate and the leach solution. During this initial stage, the extraction curves rise steeply, indicating relatively fast reaction rates attributed to the abundance of fresh, reactive mineral surfaces. Beyond approximately 6 h, the rate of copper extraction decreased and only incremental gains were observed up to 24 h, suggesting that the system approached a quasi-steady state. This behaviour implies that the leaching process is initially controlled by surface chemical reactions and is later influenced by factors such as diffusion through product layers, depletion of easily leachable sites, or passivation by elemental sulfur and other reaction products on the chalcopyrite surface.

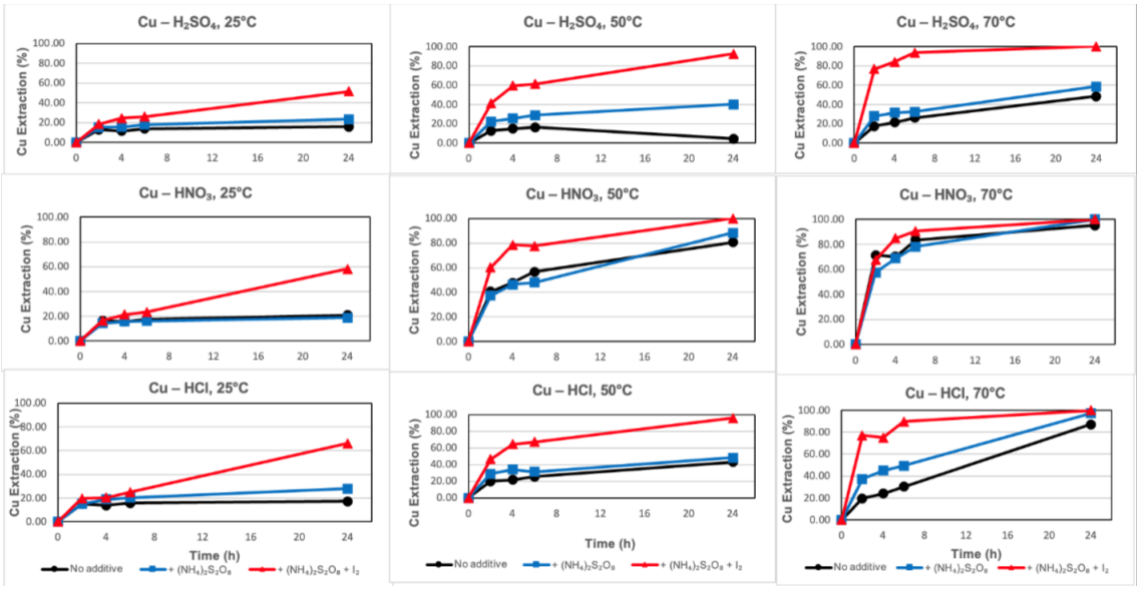


Figure 4.4 Copper extraction as a function of time (kinetic curves)

4.6. Iron Dissolution and Selectivity

In parallel with copper dissolution, iron was also leached from the concentrate under most conditions. Shown in Figure 4.5, nitric acid produced the highest dissolved iron concentrations, reflecting its strong oxidizing character and relatively low selectivity, as it attacks both copper- and iron-bearing sulfide minerals. While this contributes to greater overall sulfide breakdown, it also increases the iron content of the pregnant leach solution, which can complicate downstream purification and electrowinning due to impurity loading and the need for additional iron-control steps. In contrast, sulfuric and hydrochloric acid systems generally exhibited lower iron dissolution under comparable conditions, particularly when combined with oxidizing agents such as ammonium persulfate or APS + I_2. These systems therefore offer better selectivity for copper relative

to iron, highlighting the importance of choosing leaching conditions that balance copper recovery against unwanted iron dissolution.

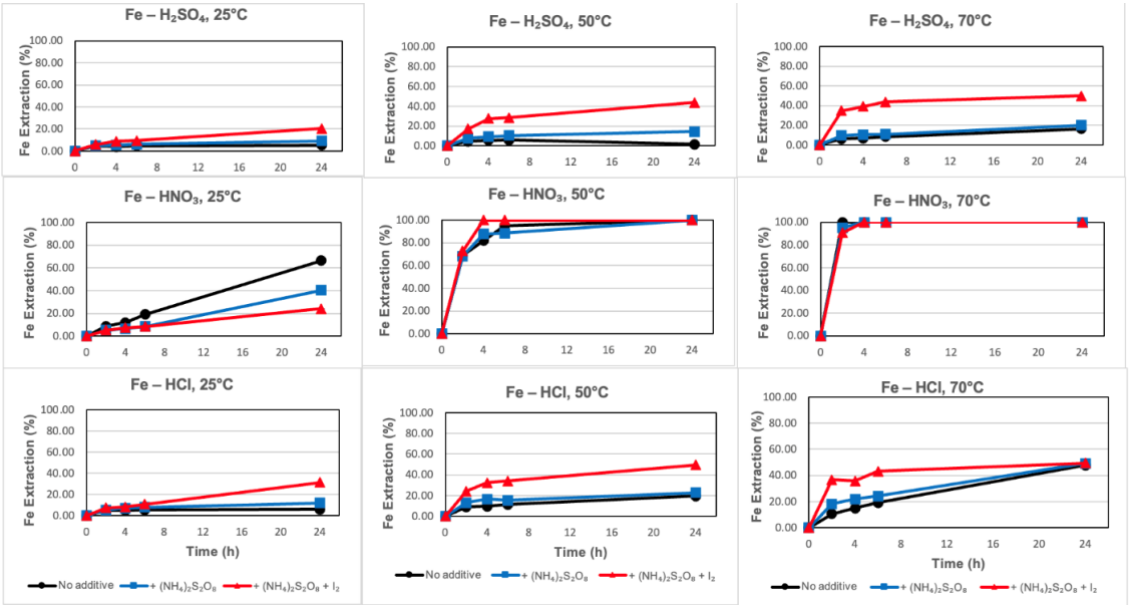


Figure 4.5 Iron dissolution under different leaching conditions

4.7. Comparison of Leaching Conditions

Taken together, the results indicate that copper extraction is governed by the combined effects of acid type, temperature, and oxidizing environment. Nitric acid typically yields the highest copper extraction, especially at elevated temperatures and in the presence of oxidants, but this comes at the cost of increased iron dissolution and reduced selectivity. Sulfuric and hydrochloric acids provide lower extractions under simple acid-only conditions; however, when supplemented with ammonium persulfate or APS + I_2, both systems achieve substantially improved copper recoveries while maintaining more moderate iron dissolution. From a practical standpoint, the most favourable leaching conditions are therefore those that deliver high copper extraction with acceptable selectivity, manageable impurity levels in solution, and operational conditions (temperature, reagent consumption) that are realistic for industrial application.

4.8. Discussion of Leaching Mechanism

The observed leaching behaviour is consistent with the established chemistry of chalcopyrite and related copper sulfide minerals and is particularly well illustrated by the persulfate–iodine tests conducted at 70 °C in the three acid media (experiments 26–27 in H_2SO_4, HCl, and HNO_3). Under acidic conditions, effective copper dissolution requires both proton attack on the mineral lattice and oxidation of sulfide to higher-valence sulfur species, ultimately forming soluble Cu^{2+}. In simple sulfate or chloride media, where

oxidizing power is limited, this reaction proceeds slowly and is prone to passivation by elemental sulfur or jarosite-like layers, especially at lower temperatures.

The combination of ammonium persulfate and iodine markedly raises the solution redox potential and supplies powerful oxidising species (sulfate radicals and active iodine), which continuously oxidise Cu–Fe sulfides and help remove or perforate passivating surface films. At 70 °C, where diffusion is faster and reaction barriers are lower, this leads to the very high copper extractions observed for the persulfate–iodine systems, with all three acids giving recoveries close to or slightly above 100% after 24 h. The visual differences in the pregnant leach solutions from experiments 25–27, shown in Figure 4.6, reflect these contrasting chemistries: intensely coloured, Cu-rich solutions are obtained when strong oxidants are combined with an appropriate acid medium at elevated temperature.

Nitric acid benefits from an additional mechanism because it acts simultaneously as a proton donor and as a direct oxidant of sulfide, so the HNO_3–persulfate–iodine system achieves the highest extractions among the three acids under otherwise comparable conditions. In contrast, sulfuric and hydrochloric acids rely more heavily on the external oxidants; without persulfate and iodine, their leaching performance remains modest even at 70 °C. Overall, these results confirm that chalcopyrite dissolution in OT concentrate is controlled by a balance between acid strength, oxidizing potential, and temperature, and that integrating a strong oxidant pair ($S_2O_8^{2-}/I_2$) with elevated temperature is an effective strategy for overcoming passivation and achieving near-complete copper extraction from refractory Cu–Au sulfide concentrates.

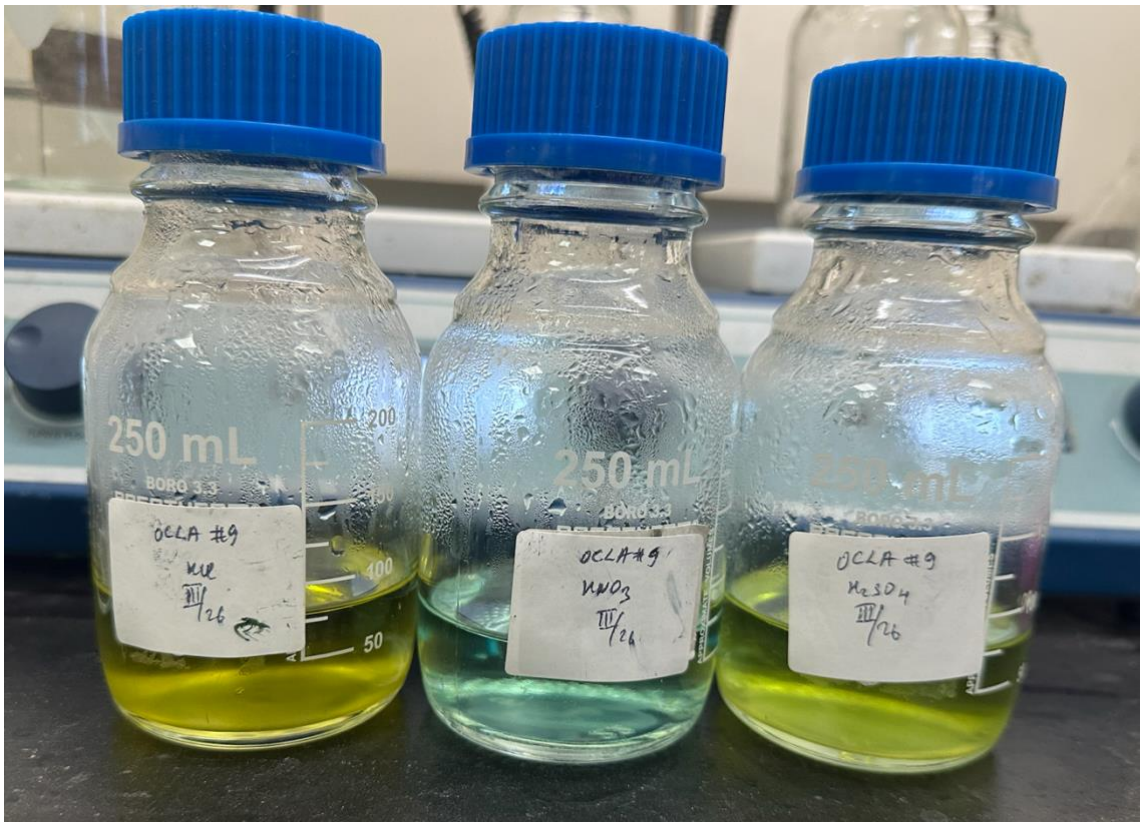


Figure 4.6 Pregnant Leaching solution (PLS) of experiments #25-27

4.9. Scale-Up Experiment Results

The scale-up leaching experiment confirmed that the trends observed in the laboratory-scale tests are reproducible at a larger volume. Copper was successfully dissolved under the selected conditions, and sufficient pregnant leach solution (PLS) was generated for downstream processing. This demonstrates the feasibility of applying the optimized leaching conditions beyond small-scale experiments and provides a practical link between bench-scale tests and potential pilot-scale operation.

4.9.1 Pregnant leach solution (PLS) results

In the scale-up series (Experiments 28–30), leaching was carried out in 1 M H_2SO_4, HCl and HNO_3 at 70 °C with $(NH_4)_2S_2O_8$ + I_2 as the oxidant system. The resulting PLS solutions showed clear differences in copper concentration and appearance between the three acids. Nitric acid produced the highest Cu extraction within 24 h, followed by hydrochloric acid, while sulfuric acid gave slightly lower but still significant extractions under the same conditions. Compared with the corresponding laboratory-scale leaching tests (Experiments 25–27), Cu extractions in the scale-up runs are slightly lower. This small decrease is attributed to less efficient mixing, longer

diffusion paths and a reduced surface-area-to-volume ratio in the larger reactor, but the overall extraction trends and acid ranking remain unchanged.

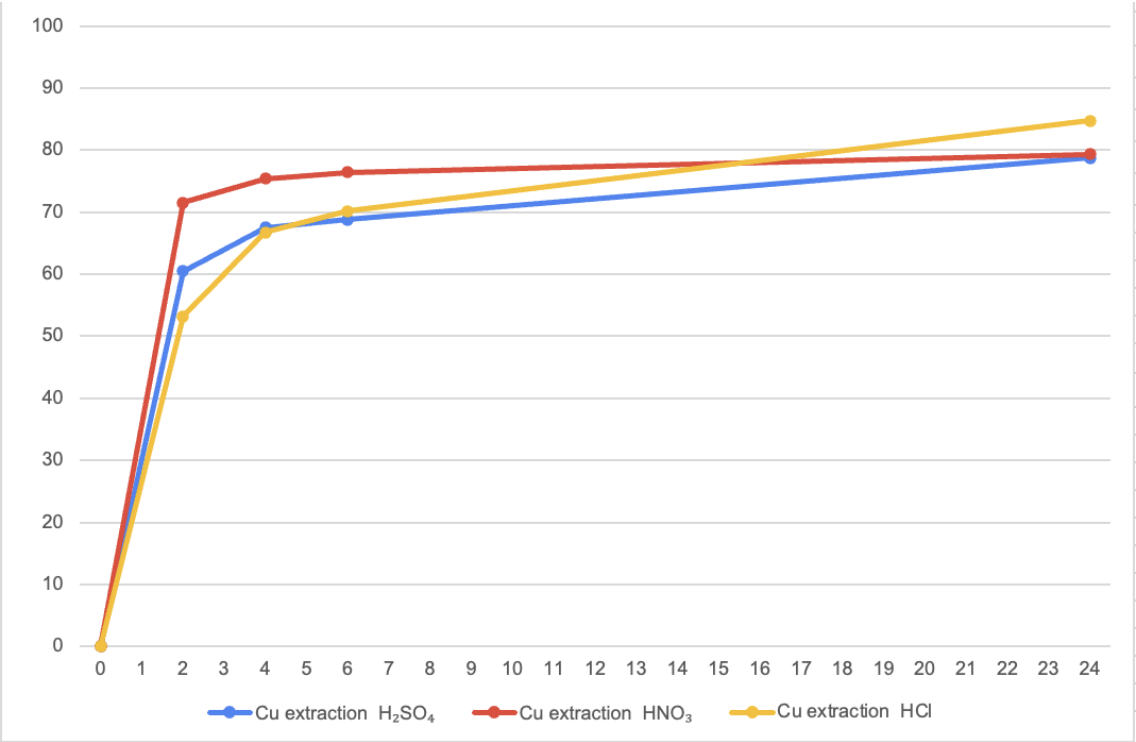


Figure 4.7 Graphic of Cu extraction in Scale-up leaching experiment (#28-30)

The colour and clarity of the PLS correlate with these extraction trends: the nitric-acid solution is the most intensely coloured, indicating a higher Cu^{2+} concentration, whereas the sulfuric-acid PLS is somewhat less intense, in line with its lower extraction. The hydrochloric-acid PLS shows an intermediate appearance that matches its intermediate Cu recovery. These observations confirm that acid medium strongly influences the efficiency of chalcopyrite dissolution in the scale-up tests.

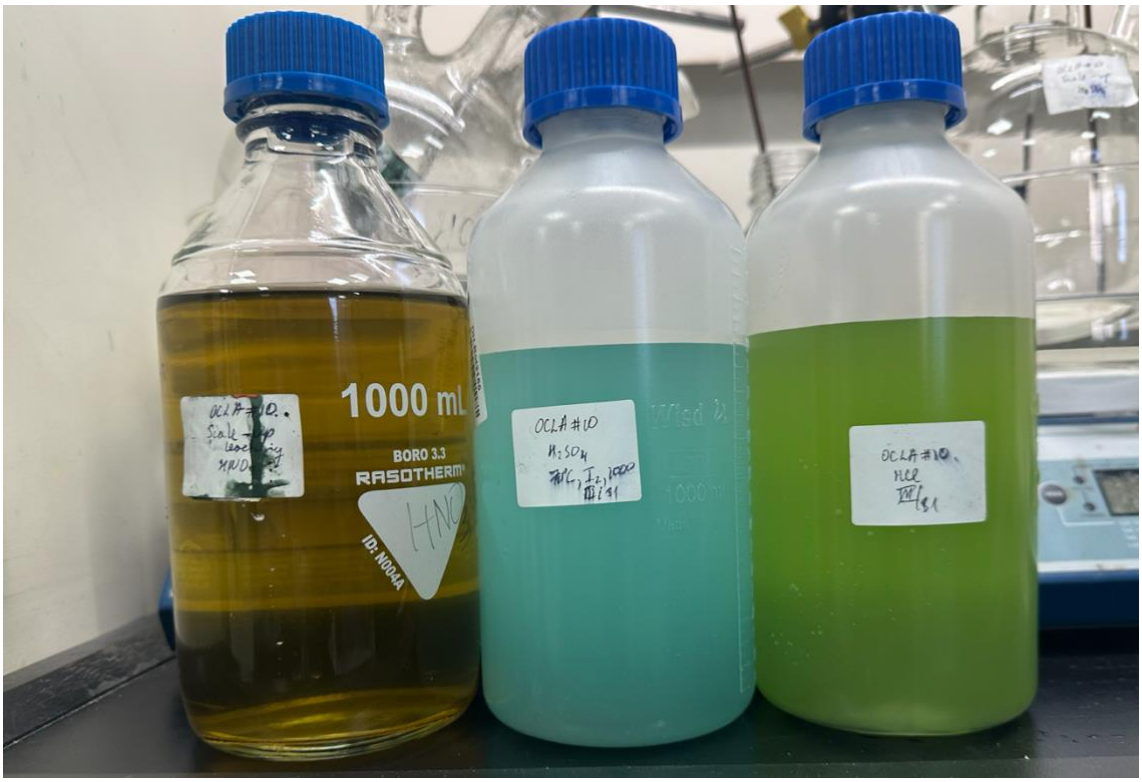


Figure 4.8 Pregnant leaching Solution (PLS) of Scale-up leaching experiment # 28-30

4.9.2 Solid residue (XRD) results

In the scale-up experiments (28–30), XRD was used to compare the mineralogy of the original OT copper concentrate with the leach residues obtained in the three acid media.In the OT concentrate pattern, strong reflections corresponding to chalcopyrite and bornite dominate the sulfide peaks, with pyrite also present, while quartz and minor feldspar represent the main gangue phases.

- In the H_2SO_4 residue, the intensities of the main chalcopyrite and bornite peaks decrease relative to the feed, while quartz peaks are comparatively enriched, indicating dissolution of copper sulfides and relative concentration of gangue.
- The HNO_3 residue shows the largest reduction in chalcopyrite/bornite peak intensity, consistent with the higher copper extraction measured in nitric acid; some broadening and/or appearance of iron-rich secondary phases may also be observed, reflecting oxidative breakdown of sulfides.
- The HCl residue exhibits intermediate attenuation of chalcopyrite peaks: copper sulfides are clearly depleted relative to the feed, but residual chalcopyrite remains, which is in line with the moderate extractions obtained in hydrochloric acid at the same conditions.

The expanded XRD view emphasizes the behaviour of individual phases: chalcopyrite and bornite peaks are progressively reduced from concentrate to H_2SO_4 to

HCl and most strongly in HNO_3, whereas quartz and other gangue reflections become more pronounced in all residues. This mineralogical evolution matches the solution-based extraction data and confirms that copper dissolution in the scale-up tests corresponds to real sulfide consumption rather than only surface alteration.

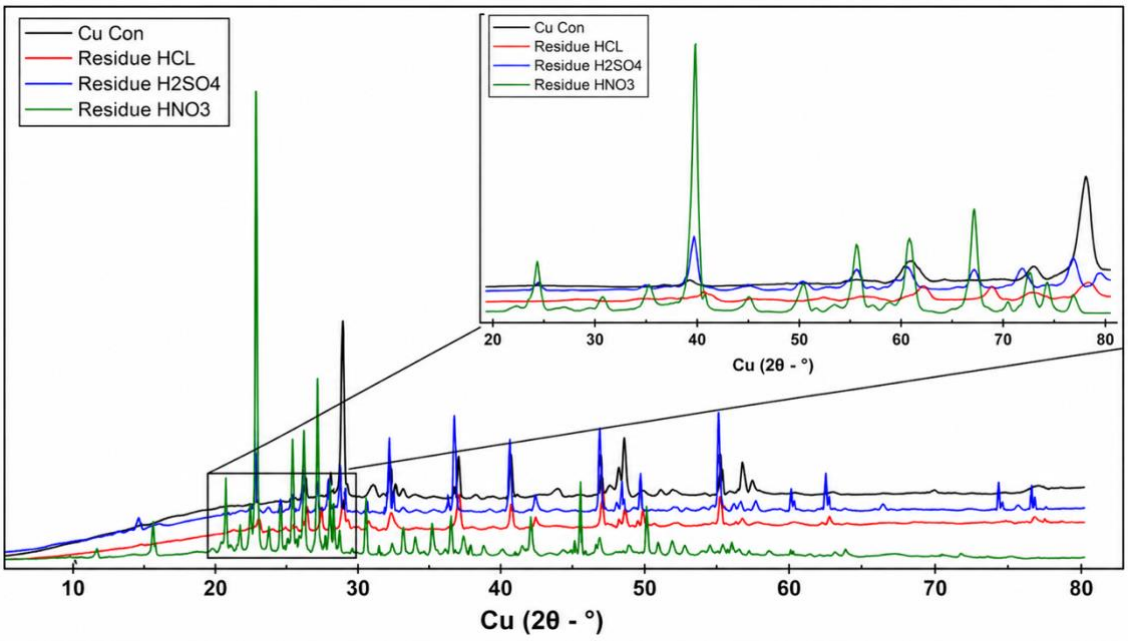


Figure 4.8 Graphic of XRD results of Scale-up leaching (Experiment # 28-30), comparison of three acid media leach residue vs OT Copper concentrate

Link to kinetic and leaching graphics: The kinetic and leaching graphics (time–extraction curves) show how fast copper enters solution under different acids and oxidizing systems.

- The time-dependent extraction curves indicate that nitric acid reaches higher copper extraction within 24 h than sulfuric or hydrochloric acid under otherwise identical conditions.
- The kinetic plots with APS and APS + I_2 show that these oxidant systems significantly increase the rate and extent of copper dissolution, particularly at elevated temperature, which is reflected in higher final extractions and steeper early-time slopes.

These kinetic trends are consistent with the XRD results from the scale-up residues: conditions that give higher extractions in the leaching curves correspond to greater attenuation of chalcopyrite and bornite peaks in the XRD patterns. Together, the solution chemistry (kinetics plots) and solid-phase mineralogy (XRD) provide a coherent

picture of how each acid system and oxidant combination affects chalcopyrite dissolution at both laboratory and scale-up levels.

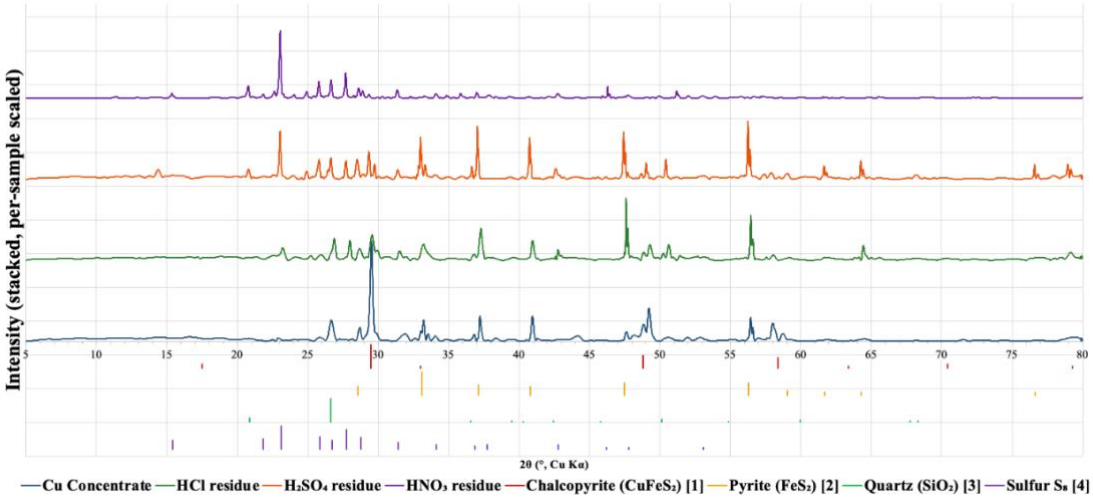


Figure 4.9 Graphic of XRD results of Scale-up leaching (Experiment # 28-30), comparison of three acid media leach residue vs OT Copper concentrate

4.9.3 Consistency between PLS and solid residue results

The PLS and XRD datasets are mutually consistent and together provide a coherent picture of the scale-up leaching behaviour. Conditions that yield higher copper concentrations in solution (especially HNO_3 and, to a lesser extent, HCl) also show the strongest attenuation of chalcopyrite and bornite peaks in the corresponding residues. Conversely, the sulfuric-acid system, which gives the lowest Cu extraction among the three acids, retains more intense sulfide reflections in the XRD patterns.

This agreement between solution chemistry and solid-phase mineralogy confirms that the observed Cu extraction in the scale-up experiments is driven by true consumption of chalcopyrite and related sulfides, rather than only superficial alteration or redistribution. It also validates the laboratory-scale kinetic trends, demonstrating that the ranking of acid systems and oxidant conditions observed in small reactors is preserved at larger volume. As a result, the selected nitric-acid-based conditions, combined with persulfate and iodine at elevated temperature, can be considered a realistic basis for future pilot-scale testing of OT chalcopyrite concentrate.

4.10. Electrowinning Results and Copper Recovery

The electrowinning experiment demonstrated that copper can be successfully recovered from the leach solution. During electrolysis, copper ions were reduced and deposited as metallic copper on the cathode surface. This was confirmed by the increase in cathode mass after the experiment. The result shows that the leach solution obtained from the hydrometallurgical process is suitable for copper recovery. This confirms the potential of combining leaching and electrowinning as an alternative route for copper production.

After completion of the scale-up leaching experiment, electrowinning was carried out using the sulfuric-acid pregnant leach solution (PLS). Electrolysis was performed at a constant applied voltage of 2 V and a current of 1.8 A in a batch cell equipped with a titanium cathode and a lead anode, which are commonly used electrode materials in sulfate media.

Prior to electrolysis, the titanium cathode mass was 18.373 g. After the electrowinning run, the cathode mass increased to 19.650 g, corresponding to a net gain of 1.277 g. This mass increase indicates that metallic copper was deposited on the cathode surface during electrolysis, consistent with the reduction of dissolved Cu^{2+} ions to Cu^0. The mass gain represents an increase of approximately 6.9% relative to the initial

cathode mass (1.277 g on 18.373 g), demonstrating substantial copper loading on the electrode.

The lead anode exhibited only a very small mass loss, decreasing from 100.948 g to 100.939 g, i.e., a loss of 0.009 g. This minimal change suggests that the lead anode remained essentially stable under the applied electrowinning conditions, with only minor anode corrosion or oxide spalling.

Overall, these electrowinning results confirm that copper ions present in the sulfuric-acid PLS generated in the scale-up leach were successfully reduced and recovered as metallic copper on the titanium cathode. This demonstrates that the copper dissolved during leaching can be effectively recovered from solution by electrowinning, thereby linking the laboratory leaching tests to a complete leach–electrowin process route.

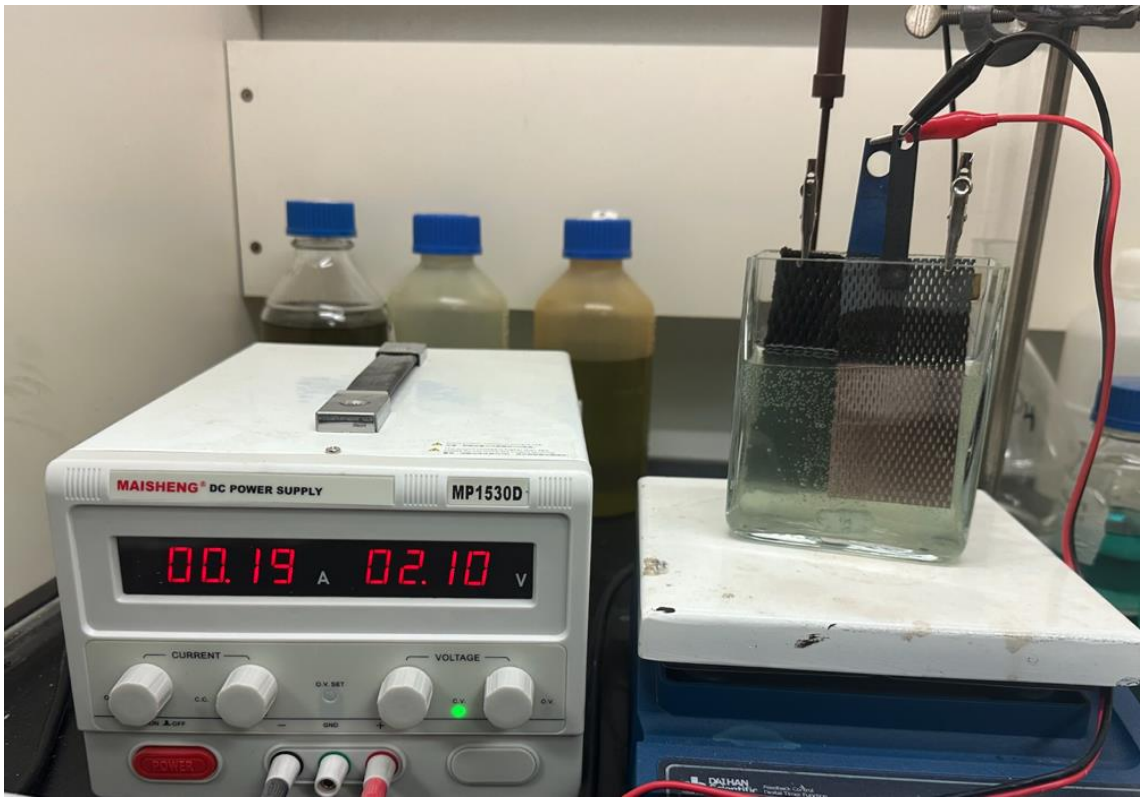


Figure 4.10 Copper electrowinning: cell voltage and current profile.

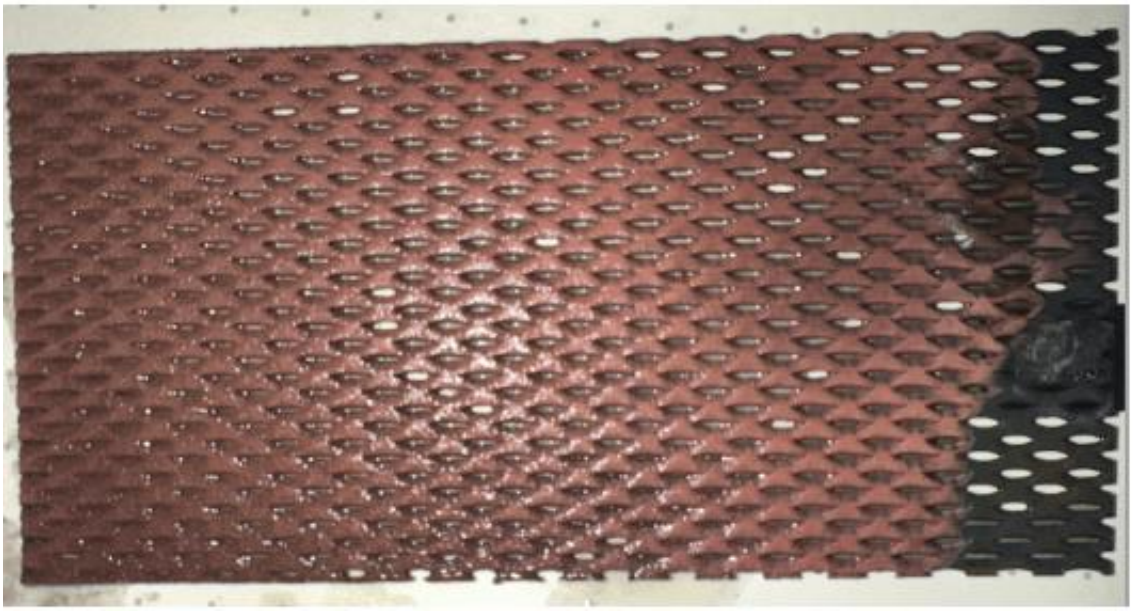


Figure 4.11 Copper cathode produced from PLS after electrowinning process

CHAPTER 5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusions

The experimental work carried out in this thesis demonstrates that temperature is the single most influential variable governing copper dissolution from the OT chalcopyrite concentrate under all conditions tested. Increasing the leaching temperature from 25 °C to 70 °C enhanced 24 h copper extraction by approximately 25–75 percentage points across the various acid types and oxidant systems, in line with the Arrhenius dependence of chalcopyrite leaching kinetics. Among the three acids investigated, nitric acid emerged as the most effective baseline lixiviant at elevated temperature, achieving high copper extraction without added oxidant (around 95% at 70 °C and 80% at 50 °C), owing to the intrinsic oxidizing power of nitrate. At 25 °C, however, this kinetic advantage largely disappears and all three acids deliver similarly low extractions in the range of roughly 17–21% after 24 h.

The addition of ammonium persulfate provided a consistent but moderate improvement in copper extraction relative to acid-only conditions, with the strongest response observed at higher temperatures in sulfuric and hydrochloric acid media and at 50 °C in nitric acid. The relatively limited effect at 25 °C is attributed to the low rate of sulfate radical generation below about 40 °C. In contrast, the combined persulfate–iodine catalytic system was found to be the most effective leaching condition identified in the Leaching experiments and constitutes the central technical result of this study. Iodine, added at 0.25 g per 100 mL and continuously regenerated via the Fe^{3+}/Fe^{2+} redox cycle sustained by persulfate, increased 24 h copper extraction by roughly 28–52 percentage points relative to persulfate-only leaches, delivering complete or near-complete extraction (>95%) at 50 °C (HNO_3 and HCl) and at 70 °C (all three acids), and raising 25 °C extraction from about 18–28% to approximately 51–66%.

A 10-fold scale-up test to 1000 mL (Scale-up) under the optimized persulfate–iodine conditions at 70 °C confirmed the reproducibility of the chemistry at larger volume, with 24 h copper extraction in the range of about 79–85% across the three acids—somewhat below the values achieved at 100 mL scale, indicating that hydrodynamics and mass-transfer require further optimization on scale-up. Overall, the results show that atmospheric-pressure hydrometallurgy using the persulfate–iodine catalytic system can achieve copper recoveries approaching those of conventional smelting, while potentially avoiding the high capital cost, SO_2 emissions, and location constraints associated with

pyrometallurgical processing. Two leaching conditions, in particular, stand out as promising candidates for further process development: (i) HNO_3 + $(NH_4)_2S_2O_8$ + I_2 at 50 °C, which achieves complete extraction at a reduced temperature, and (ii) H_2SO_4 + $(NH_4)_2S_2O_8$ + I_2 at 70 °C, which yields complete extraction in a sulfate medium directly compatible with standard SX–EW copper recovery circuits.

For Mongolia and the Oyu Tolgoi project, these findings are strategically important because they point to the technical feasibility of treating Cu–Au sulfide concentrate domestically in modular hydrometallurgical plants, thereby reducing reliance on overseas smelters and associated treatment charges. Although comprehensive pilot-scale testing and full techno-economic analysis are still required, this study provides a robust laboratory-scale foundation demonstrating that high copper extractions can be obtained under carefully optimized atmospheric leaching conditions.

5.2. Recommendations for future work

Building on the results of this thesis, several research directions are recommended:

- Detailed mineralogical characterization of leach residues from the most promising persulfate iodine tests using SEM-EDS, QEMSCAN/MLA, and quantitative XRD (Rietveld) to identify residual sulfide phases, surface passivation layers, and secondary precipitates such as elemental sulfur, jarosite, and iron oxides. This will clarify the mechanism by which iodine mitigates passivation and support predictive links between mineralogy, liberation, and extraction.
- To improve the accuracy of copper extraction calculations, future leaching studies should explicitly determine the evaporation rate of each acid medium (H_2SO_4, HNO_3, HCl) under the relevant temperatures and operating conditions. This could be done by running blank tests containing only acid solution in the leaching reactors, measuring mass or volume loss over 24 h at each temperature, and using the measured evaporation rates to correct the final solution volumes in the extraction calculations. Incorporating these corrections would eliminate apparent recoveries above 100% and provide a more reliable basis for comparing leaching performance between different acids and oxidant systems.
- Kinetic modelling of Phase 3 leaching data using shrinking-core and grain-model frameworks to determine apparent activation energies and rate-controlling steps for different acid–oxidant combinations, providing a rigorous basis for temperature and reagent optimization.

- Investigation of iodine recovery and recycling from spent leach solutions, including evaluation of oxidative precipitation, solvent extraction, and ion-exchange routes, to ensure that iodine consumption and loss do not compromise process economics.
- Pilot-scale leaching trials at volumes of 100 L and above under the two most promising conditions (HNO_3 + $(NH_4)_2S_2O_8$ + I_2 at 50 °C and H_2SO_4 + $(NH_4)_2S_2O_8$ + I_2 at 70 °C), incorporating engineering optimization of agitation, temperature control, and oxidant dosing to close the performance gap observed between 100 mL and 1000 mL tests.
- Evaluation of gold behaviour in the persulfate–iodine system, including its dissolution, association with secondary phases, and potential recovery options (e.g., adsorption onto activated carbon, alternative ligands, or direct precipitation), given the economic importance of Au in OT concentrates.
- A comparative techno-economic assessment of the persulfate–iodine hydrometallurgical flowsheet versus conventional smelting for the OT operation, incorporating realistic reagent and energy costs, capital expenditure, revenue from copper and gold, and environmental compliance obligations. Such a study would provide the commercial context needed to judge whether this project derived process merits progression to demonstration scale.

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