–PhD Thesis–

Recovery of Copper from Mine Tailing and Complex Carbonaceous Sulfide Ore by Flotation and High-Pressure Leaching

浮選および加圧浸出を用いた選鉱尾鉱と炭素質難処理銅鉱石からの銅回収

Refilwe Sandra Magwaneng

March 2019

Graduate School of International Resource Sciences

AKITA UNIVERSITY

Contents

Page No.

Abstract:

Currently, resources for copper are abundant but there are short term supply limitations due to limited technologies. In this research work, focus was made on recovery of copper from underexplored mineral resource of mine tailing and complex carbonaceous sulphide ore. These resources are potential reserve to metal production inventory that is faced with declining ore grade. The preliminary studies of copper recovery indicated that mineralogical composition was one of the main components to consider for the processing method employed. Therefore, it is essential to develop effective method for specific mineral resources of copper. The process conditions for flotation and high-pressure leaching were tested and optimized to recover copper from the two mineral resources. Hence, the two main chapters in this PhD thesis discussed the process development for each mineral resource and conclusion were drawn.

Thesis Summary

Chapter 1

This section gives an introductory to the general knowledge of copper, its significance owing its characteristics for industrial and daily use. An assessment of the current global resource and reserve for copper is also discussed. Furthermore, explanation is made on the mineral resource considered for this research and how it compares to already existing resources. The conventional metal processing and potential advanced technologies for processing copper are also explained in this chapter.

Chapter 2

A process development modelling study for recovery of copper and nickel from mine tailing by combination of flotation and high-pressure leaching was performed. This study has shown that the flotation stage is efficient in concentrating mine tailing to suitable metal grades that are ideal for further metal extraction such as high-pressure leaching process. The copper bearing minerals of chalcopyrite was able to be concentrated from 0.19 wt% copper to 6.72 wt% that is comparable with the currently mined ores. According to the results, particle size, slurry pH and to a lesser extent the collector used were the most significant parameters in the flotation of mine tailing. The fine particle indicated that, copper mineral upgrading was compromised because of reporting of fines, and at higher slurry pH (<7) iron sulfide minerals associated with copper were depressed during flotation.

Evidently, during leaching, the concentrate obtained from mine tailing flotation gave a 90 % leaching rate with maximum chalcopyrite dissolution. Chalcopyrite is not easily dissolved in aqueous solution, but temperature control showed the most influential parameter during the process. It was observed that at lower temperatures, chalcopyrite leaching was slow and formation of sulfur which was passivating resulted in poor copper concentrations and low recoveries. At high temperature, chalcopyrite leaching was spontaneous, and acid regeneration was possible for continuous leaching chalcopyrite.

The process is simple and bears potential traits of flotation and high-pressure leaching. The proposed flowsheet envisaged a suitable solution for acid generation as well as iron hydrolysis which is important in solid residue disposal.

Chapter 3

From literature survey the world reserve will increase if metal prices increase and new process technology are developed. There are limited technologies to treat the underexplored complex carbonaceous sulphide ore that have potential copper high grade. Direct pressure leaching has potential to recover the most commonly chalcopyrite mineral that is not easily dissolved in aqueous solution.

Flotation testing was undertaken and did not confirm a desirable degree for copper concentration due to the co-existence with naturally hydrophobic organic materials. On the other hand, a high pressure leaching of copper in chalcopyrite was achieved via an oxidative reaction. The kinetic analysis of the system showed that the leaching reaction are controlled by diffusion through the solid phase. SEM/EDX and XRD testing confirmed the presence of porous product layer and validity of the schematic leaching model.

According to the results over 90 % copper recovery was possible to concentrate copper in the leachate solution. The leaching reactions were found to follow shrinking core model and the parabolic leaching kinetics were established, that under the experimental conditions, led to the following model: $1-2/3\alpha-(1-\alpha)^{2/3} = k_d t$

The leaching kinetics were shown to be dependent on temperature, particle size, total pressure and acid concentration.

For the tested chalcopyrite in complex carbonaceous sulphide ore, the maximum conversion of copper to Cu^{2+} solution was obtained at high temperature conditions. Low temperatures indicated low leaching kinetics of chalcopyrite. Selective copper recovery was also possible due to the iron and calcium reaction controls.

Direct high-pressure leaching is proposed for the recovery of copper in chalcopyrite of complex carbonaceous sulfide ore that is not amendable to present-day flotation techniques. The process is competitive to the currently commercialized leaching techniques that uses higher temperatures and/or low temperatures that cannot completely dissolve copper in chalcopyrite.

Chapter 4

The chapter gives a summary of the work based on the findings by drawing the overall purpose of recovering metals from mine tailings and complex carbonaceous sulfide ore. The results indicated that the most appropriate route for processing potential copper resources in terms of recovery and concentration technique largely depends on the mineralogy of the metal resource concerned. Provided that the metal resource is secondary (mine tailing) with ore grade above mineralogical barrier, a combination of flotation and high-pressure leaching is the preferred route for copper where hydrometallurgy can be applied. However, for primary ores of complex carbonaceous characteristics, then direct pressure leaching is preferred route as the presence of naturally hydrophobic gangue minerals (organic carbon) are not amendable to present-day flotation techniques.

List of Figures

Page No.

Chapter 1: Introduction

Chapter 2: Recovery of Copper and Nickel from Mine Tailing

Chapter 3: Comparison of Flotation and Direct High Pressure Leaching of Copper from Complex Carbonaceous Sulfide Ore

List of Tables

Page No.

Chapter 1: Introduction

Chapter 2: Recovery of Copper and Nickel from Mine Tailing

Chapter 3: Comparison of Flotation and Direct High Pressure Leaching of Complex Carbonaceous Sulfide Ore

List of Abbreviations

HPL: **H**igh–**P**ressure **L**eaching

PAX: **P**otassium **A**myl **X**anthate

PLS: **P**regnant **L**each **S**olution

MIBC: **M**ethyl **I**so **B**utyl **C**arbinol

XRD: **X**–**R**ay **D**iffractometer

XRF: **X**–**R**ay **F**luorescence **S**pectrometer

ICP–OES: **I**nductively **C**oupled **P**lasma–**O**ptical **E**mission **S**pectrometry

SEM–EDS: **S**canning **E**lectron **M**icroscope **E**nergy–**D**ispersive **X**–**R**ay **S**pectroscopy

SX: **S**olvent **E**xtraction

List of Symbols

Leaching:

R_{M}: Metal leaching rate (%)

C_{L}: Metal concentration in pregnant leach solution (mg/L)

C_{F}: Metal concentration in feed (mg/kg)

V_{L}: Volume of pregnant leach solution (L)

m_{F}: Dry mass of the feed (kg)

Flotation:

Y: Yield (%)

I: Enrichment ratio

R: Recovery (%)

F: Weight of feed (g)

C: Weight of concentrate (g)

f: Metal grade in the feed (mass%)

c: Metal grade in the feed (mass%)

t: Metal grade in tailings (mass%)

Kinetics study:

α: The fraction reacted (%)

k_{r} and k_{d}: The kinetic constants

t: The reaction time (min)

k: Rate constant

A: Pre–exponential factor (s^{-1})

E_a: Activation energy (kJ/mol)

R: Gas constant ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)

T: Absolute temperature (°C)

P_{Total}: Total pressure (MPa)

1: Introduction

Copper processing and production has a long history for the development of human civilization. The name copper comes from the Latin cuprum, from the island of Cyprus and is abbreviated as Cu. The discovery of this significant metal dates back to prehistoric times and is said to have been mined more than 5000 years ago. In fact, one of the major ‘ages’ or human history is named after a copper alloy: bronze. Copper is the first metal to be used by man in almost any quantity and its continuous discovery has always been a major priority. Many great scientists such as Ampere, Faraday and Ohm in the late 18th and early 19th centuries in regards to electricity and magnetism, which helped the onset of industrial revolution, propelled the copper into a new era (Khoshkhoo, no date). Today, many textbooks and conference proceedings are written and devoted to all aspects regarding copper.

Most of the copper produced worldwide comes from sulfide minerals, and a majority of the production goes through mineral beneficiations such as crushing and flotation. It is then followed by pyrometallurgical extraction process. The aforementioned process has been widely used during the early years of discovery as many high-grade ores were present. Nowadays, the easily-accessible sulfide minerals deposits with high grade are being depleted, producers must mine low grade ore or complex sulfide ores that are more difficult to process to meet supply and demand. The concentration from these sulfides contain various impurities like carbonates which are very detrimental as they are highly reagent consuming and require a lot of energy during smelting. In other instances, producers are also forced to consider the downstream processing of secondary copper resources such as mine tailing since the inception of stringent environmental regulations. Mine tailings can be classified as low grade ores since their copper grades is relatively similar to the currently low grade mined ore.

Sicupira *et al.*, 2011 and Bogdanović *et al.*, 2016 did an assessment on the recovery of low-grade ores with copper grades as low as 0.19-0.90 wt% and found out they could be upgraded to 6 wt% by flotation. This initial metal grade is almost similar to that of mine tailings found in Bor Mine, Serbia which have a grade of 0.189 wt% (Mudd, 2009).

Commercial processing for treating copper flotation concentrates are almost exclusively by conventional smelting/converting technology despite the concerted efforts of many companies and institutions to develop hydrometallurgical process. The process has the advantage of being a well-developed and efficient technology, rendering its dominance to less likely be eroded by hydrometallurgical process. However, depletion of high-grade ores and increased complexity of existing ores pose a challenge due to the extensive energy required and the compromised copper cathode quality produced when the process is used. Furthermore, the implementation of stringent environmental regulations has made smelting unpopular technology around the world. Copper smelters are perceived as bad air polluters despite the advances made in smelting technologies for significant reductions in SO_2 emissions. An added disadvantage to pyrometallurgical processing is its high capital cost, meaning it is usually economic to build large plants to realize economies of scale. Consequently, most small copper concentrate producers are forced to sell their concentrates to toll smelters at high prices or incur shipping costs. Theoretically, the hydrometallurgical process represents an attractive alternative in that most metals can easily dissolve at reasonable temperatures, non-air polluting and potentially more cost effective on a small scale than pyrometallurgical process.

Thus, the development of a copper recovery technology by flotation and high pressure leaching for copper resources mitigate further research. An important consideration in evaluating this process is that it should be able to upgrade copper minerals during flotation and should be able to treat them during leaching to make them ideal for following solvent extraction and electrowinning process (SX-EW).

1.1 Current status of copper demand and production

Over the last decades the contemporary development of copper mining and metals industry has been characterized by:

1. Increased industrial demand for products due to improved technology, population increase and need for higher standard of living.
2. Involvement in processing primary low-grade reserves and complex ores: the grades of metallic ores are falling globally as higher-grade reserves are explored and are progressively being depleted. For example, Fig 1.1 shows the general decline in base and precious metal ore grades in Australia over time (Mudd, 2009; Norgate and Jahanshahi, 2010).
3. Increasing copper production: According to the US Geological Survey (2017) the global refined copper production is expected to rise (Fig 1.2). However, mine production was estimated to decline owing to supply disruptions at multiple leading copper mines and a general lack of new projects and expansions. Reduced mining rates are mostly affected by low copper prices caused by poor technical complications (Fig 1.3).
4. Stringent environmental policies: the effects of mining and processing low grade ores (~1%) has shown environmental impacts due to additional energy consumption that run parallel with increased mine tailing generation, storage risk and occasional disasters. Famous occasional disasters have been observed in tailings dam failure (Rico *et al.*, 2008; European Commission (EC), 2009; Larrauri, 2018). The waste products of mining have also indicated potential for acid mine drainage (AMD) due to the oxidation of sulfides in tailings that are left in open areas. The extent of AMD has a potential of affecting underground water extensively.

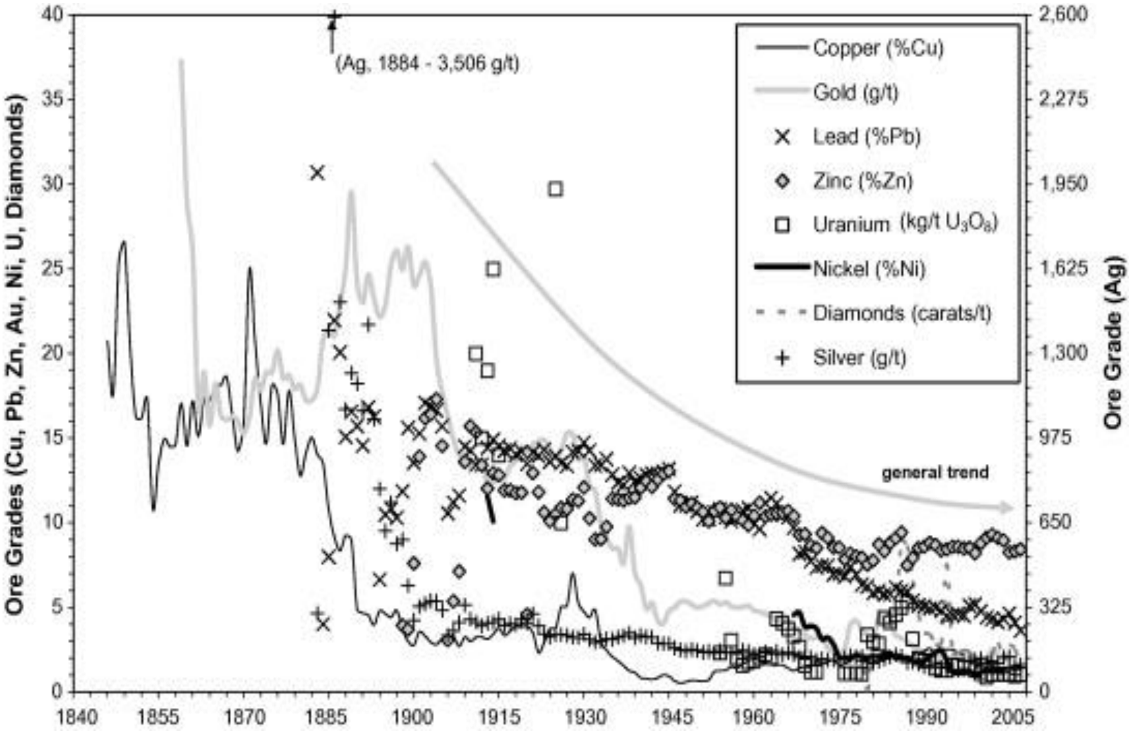


Figure 1. 1. Decline in Australia ore grades over time (Source: Mudd, 2009; Norgate and Jahanshahi, 2010).

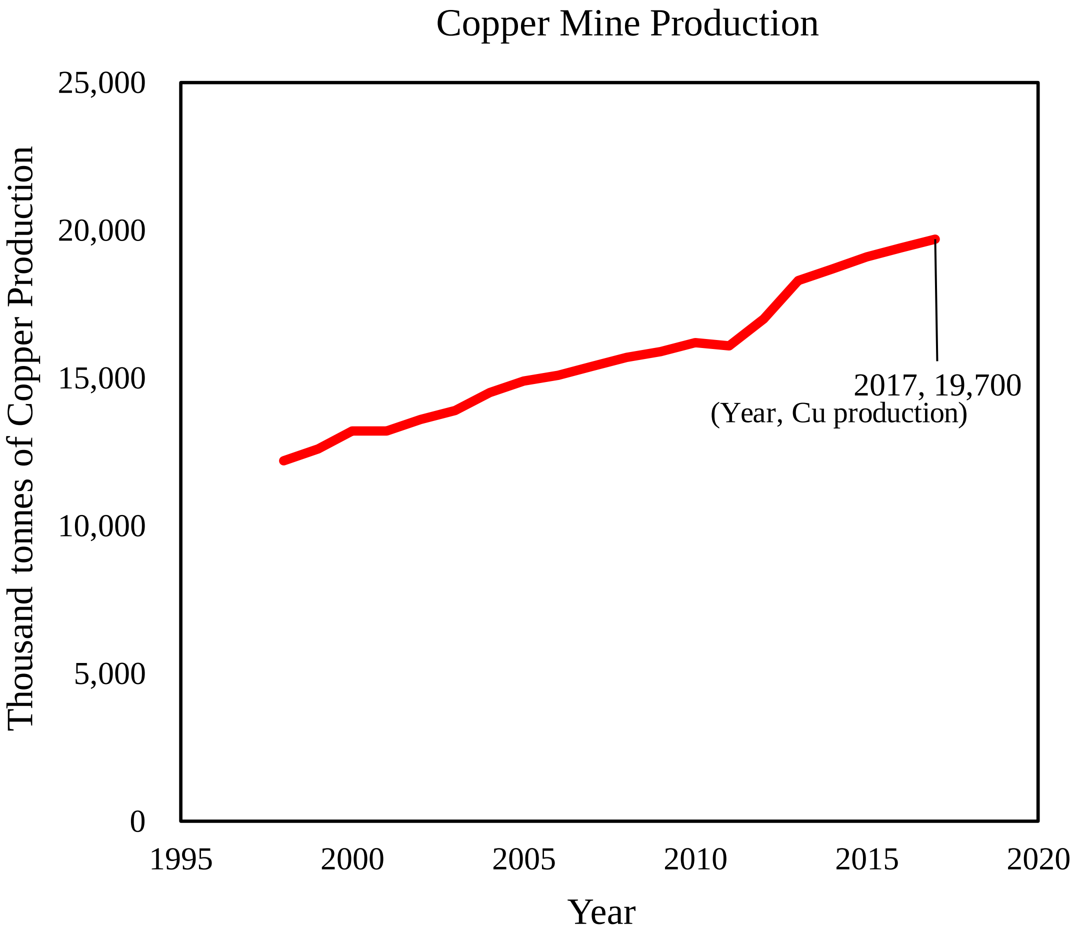


Figure 1. 2. Global copper mine production from 1995 to 2017 (Source: Lee Bray, 2017).

Figure 1. 3. Copper price trends over 5-year period from 2014-2018. (Source: InvestmentMine Mining and Markets, 2018).

1.2 Copper Background and Distribution

Sources of copper

Copper is the most abundant element in the accessible sphere of the earth and combines with a number of elements. More than 150 copper minerals have been identified, although only a small number of these are of economic importance (Table 1.1) (British Geological Survey, 2007). The copper minerals are divided into three groups (Fig. 1.4). The primary minerals are related to hydrothermal/sulfide process and include chalcopyrite (Fig. 1.5) and bornite. A second group are the copper oxides, typically formed from weathering of sulfides and include cuprite, malachite and covellite (British Geological Survey, 2007). The third group of minerals are the secondary sulfide which take up the general equation $Cu_xMe_yS_z$ where Me can be substituted by other metals such as $Cu_{12}Sb_4S_{13}$ and others may be covellite (CuS).

Table 1. 1 Common copper minerals found in deposits that have economic significance. (Source: (British Geological Survey, 2007).

Mineral Name	Chemical formula	Max. Cu content (wt%)
Native copper	Cu	100
Chalcocite	Cu_2S	79.9
Cuprite	Cu_2O	88.8
Covellite	CuS	66.4
Bornite	Cu_2FeS_4	63.3
Malachite	$Cu_2CO_3(OH)_2$	57.5
Azurite	$2CuCO_3Cu(OH)_2$	55.3
Antlerite	$Cu_3SO_4(OH)_4$	53.7
Enargite	Cu_3AsS_4	49
Chrysocolla	$CuSiO_3.2(H_2O)$	36.2
Chalcopyrite	$CuFeS_2$	34.6

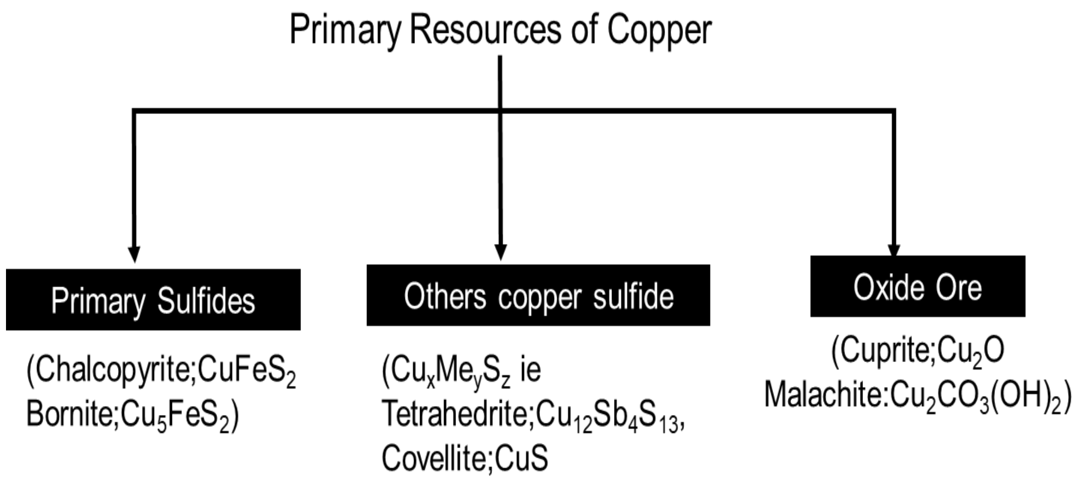


Figure 1. 4. Primary mineral resources of copper.

Figure 1. 5. Chalcopyrite ore (Source: British Geological Survey, 2007)

Generally, copper minerals are sourced from different ore deposits in different countries around the world (Fig. 1.6). The most common deposits are the porphyry deposits which constitutes 55-60 % of world copper production. They are followed by sedimentary-hosted deposits which are reported to make up at least 20 % of world production. About 80 % of the world's copper comes from sulfide and copper-iron sulfide, with chalcopyrite ($CuFeS_2$) being the most common minerals in these ores (British Geological Survey, 2007; Norgate and Jahanshahi, 2010). Other deposits are the oxide ores. A summarized table of all the different copper deposits are given in Table 1.2.

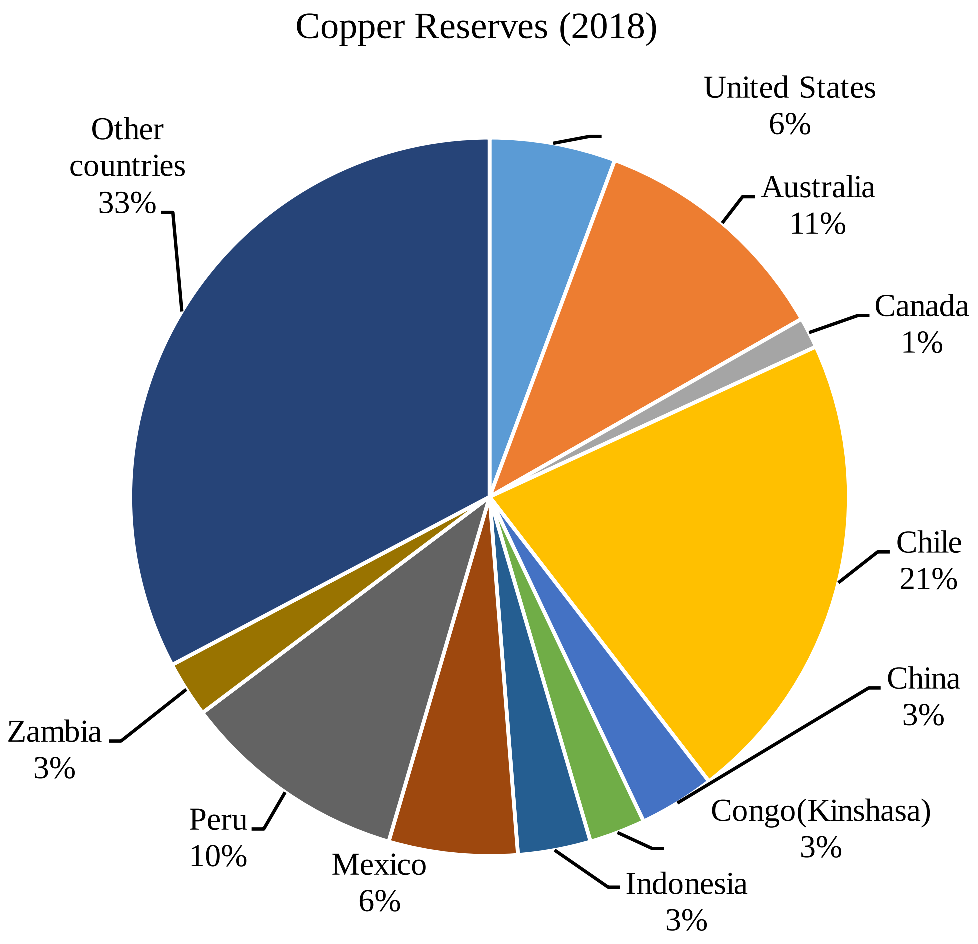


Figure 1. 6. Global major copper reserves by countries (2018). (Source: Lee Bray, 2017)

Table 1. 2 Summary of main copper deposit types. (Sources: British Geological Survey, 2007)

Deposit Type	Synonyms	Description	Examples
Porphyry		Large, relatively low-grade stockwork to disseminated deposits related to intrusion	Bingham Canyon, USA, Grasberg, Indonesia
Sediment-hosted	Shale-hosted copper, stratiform copper, Central African type	Stratabound dissemination of copper minerals	Lubin, Poland; Nchanga, Zambia
Red-bed	Sandstone-hosted, continental red-bed	Copper mineralization occurring in oxidized zones in sedimentary and volcanic rocks	Mantos Blancos, Chile; Mantos Blancos (v), Chile
Volcanogenic massive sulfide (VMS)	Volcanic-associated	Mineralization hosted by submarine volcano sedimentary sequence	Rio Tinto, Spain; Bathurst, Canada
Magmatic sulfide deposits		Sulfide concentration associated with a variety of mafic and ultramafic magmatic rocks	Sudbury, Canada; Kambalda, Australia
Sedimentary exhalative (SEDEX)		Bodies of polymetallic sulfides deposited from hydrothermal fluids vented into sedimentary basins	Broken Hill, Australia; Red Dog, Alaska
Epithermal		Veins, stockworks and breccia associated with high-level or near surface volcanic-related low temperature hydrothermal systems	El Indio, Chile; Lepanto, Philippines
Copper Skarns	Contact metasomatic copper deposits	Mineralization formed by chemical alteration associated intrusions into carbonated rocks	Ok Tedi, Papua New Guinea; Rosita, Nicaragua
Vein-style deposits	Polymetallic veins	Mineralized structures often developed along fractures	Copper Hills, Australia; Butte, USA
Supergene		In-situ natural secondary enrichment of primary mineralization	Erdenet, Mongolia; La Escondida, Chile

Although copper has been mainly sort from primary resources (those extracted from ground), the need to increase production and also technological advancement have enabled consideration of other secondary(recycled) resources such as mine tailing. These materials could be classified into the downstream processing of copper lifecycle and include mine tailing and electronic waste. Mine tailings are very significant in the copper production cycle as they contain significant amount of copper. It is estimated that more mine tailing will increase as primary resources are extracted to meet the demands of increased population and more people striving to achieve a higher standard of life.

Copper properties

Copper with an atomic number of 29 on the periodic table has a weight of 63.546 grams/mol. The metal has a freezing point of 1084.62 ^{0}C and a boiling point of 2562 ^{0}C. It has a specific gravity of 8.96 at 20 ^{0}C, a valance of +1 or +2, atomic radius of 128 pm and electronegativity of 1.90 (Conner, 2013). Copper is reddish in colour, takes on a bright metallic luster, and is malleable, ductile, and a good conductor of heat and electricity, second only to silver in electrical conductivity.

Applications and potential of copper

Copper is widely used in the electrical industry despite competition from other materials. Its alloys, brass and bronze have been used for a long time and are still very significant. A lot of countries make coins made out of copper alloys example is the Japanese yen (Fig. 1.7). Copper is also found to be contained in monel and gun alloys. Copper can also be found in different compounds of oxide and sulfate such as blue vitriol which has a wide use as an agricultural poison and an algicide in water purification. High-purity (99.99+%) is readily found available commercially.

Figure 1. 7. One of the uses of copper, Japanese yen. (Source: http://commons.wikimedia.org//)

Copper is also widely in architecture because of its durability, corrosion resistance and weatherproof architectural material. Most roofs, domes and spires and doors have been made from copper for many years.

That being said, the importance of copper shows its significance and need for improved technology. It is therefore imperative to seek out advanced technologies that would provide consistence production of copper.

1.3 Main Copper Production Process

Copper beneficiation Process

Usually, the copper minerals which are approximately 0.5 to 2 % Cu in the ore are subjected to physical separation as they are not eligible for direct smelting from an economic perspective. However, it is important to consider the copper hosting mineral that is to be subjected for physical separation (flotation) (Of, 1994; Wills and Napier-munn, 2006). As indicated in Fig. 1.8, different copper minerals undergo different processing routes.

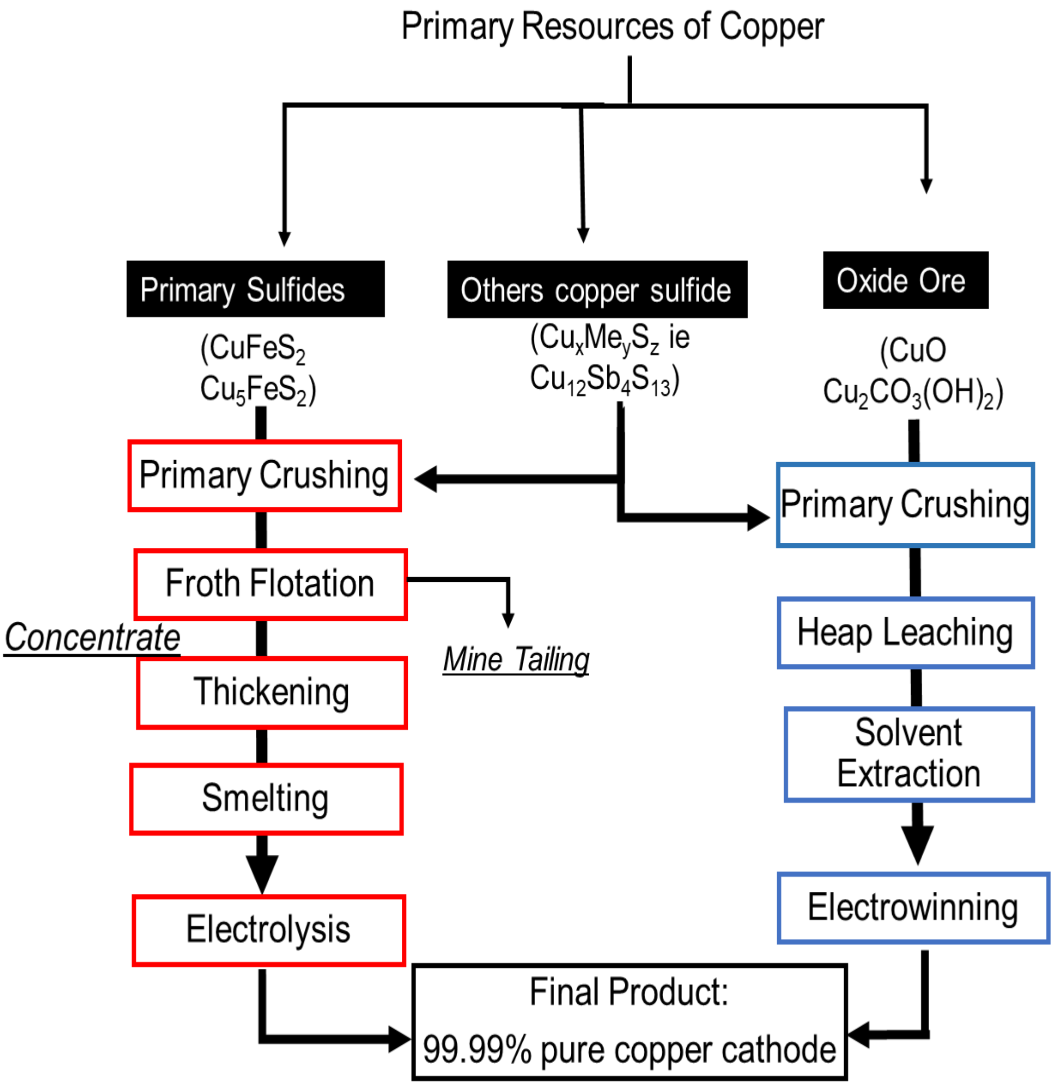


Figure 1. 8. Conventional flowsheet for different copper mineral resources.

Extraction: There are three principle techniques that are employed in the extraction of copper resources. These techniques are applied based on the characteristics and geographic location of the ore body. The most common is the open-pit mining which is generally appropriate for near surface and low-grade resources. The second type of extraction is underground mining which was most common during the 1900s. Overtime, these types of mining has become very expensive due to the higher costs and safety issues. In-situ leaching is the last type of extraction method, although not common has been practices in a few mines such as Mopani in Zambian Copperbelt (Batterham & Robinson, 2018, Robinson and Scientific, 2018).

Physical beneficiation: The concentration of ores is very important in ensuring the economic feasibility of a copper processing project. The physical beneficiation can be done in different ways such as comminution, flotation, magnetic separation and gravity separation. The mineral characteristics of the ore is very important in determining the type of physical beneficiation to take.

Comminution: is the process of breaking down large chunks of ore bodies to produce small particles consisting of individual mineral phases. These are then separated to remove gangue (rock residues), thereafter followed by a process of physical liberation. This is strongly dependent on whether the copper ore is oxide or sulfide ore.

The oxide ores are taken directly to hydrometallurgical liberation process due to their unresponsiveness to flotation chemicals (*No Title*, no date; Zhan-fang *et al.*, 2009). For sulfide ores, froth flotation is used to separate gangue minerals while special native copper bearing ores can be subjected to gravity circuits.

Flotation: The process follows crushing and grinding. It uses the concept of hydrophobic and hydrophilic properties of different minerals found in the ore (Wills, 2006). Usually, the minerals of interest (chalcopyrite) are subjected to reagents that will render them hydrophobic and allowed to float and skimmed for further processing. The rich float(concentrate) is then taken for further processing The gangue minerals which are hydrophilic are then left at the bottom and later discharged as tailing to tailing dams or stock piled. At this stage, the initial grade of Cu is improved from

0.4-3 % to 10-25 %. The process is usually carried out in large industrial cell as shown in Fig. 1.9.

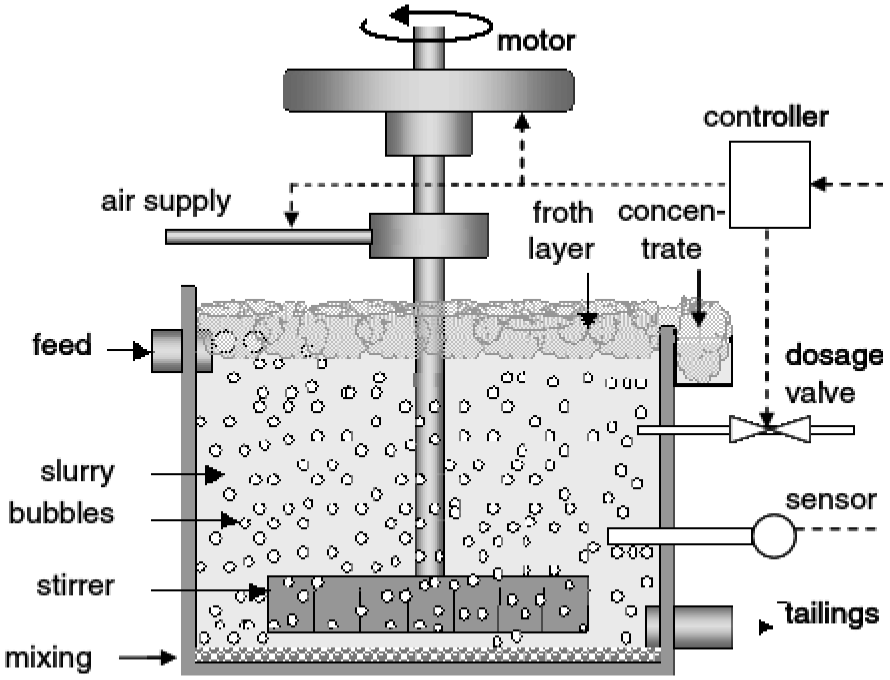


Figure 1. 9. Flotation cell for sulfide minerals. (Source: Kramer et al., 2012)

Gravity separation: The process utilizes the difference in specific weight of the mineral components in the ore to separate from gangue minerals. Here the ore may be in suspension in dry granular mixture. All the gravitational methods are common in the sense that they use gravity as the dominant force (http://en.wikipedia.org/wiki/Gravity_separation).

Copper Extraction Process

Copper is generally extracted from ores by either pyrometallurgical or hydrometallurgical processing route. The former involves smelting of the ore or concentrate at high temperatures, while the latter involves leaching the ore or concentrate at different temperature ranges. These two broad processing paths may be broken down further into the following routes as shown in Fig. 1.10 for copper ores:

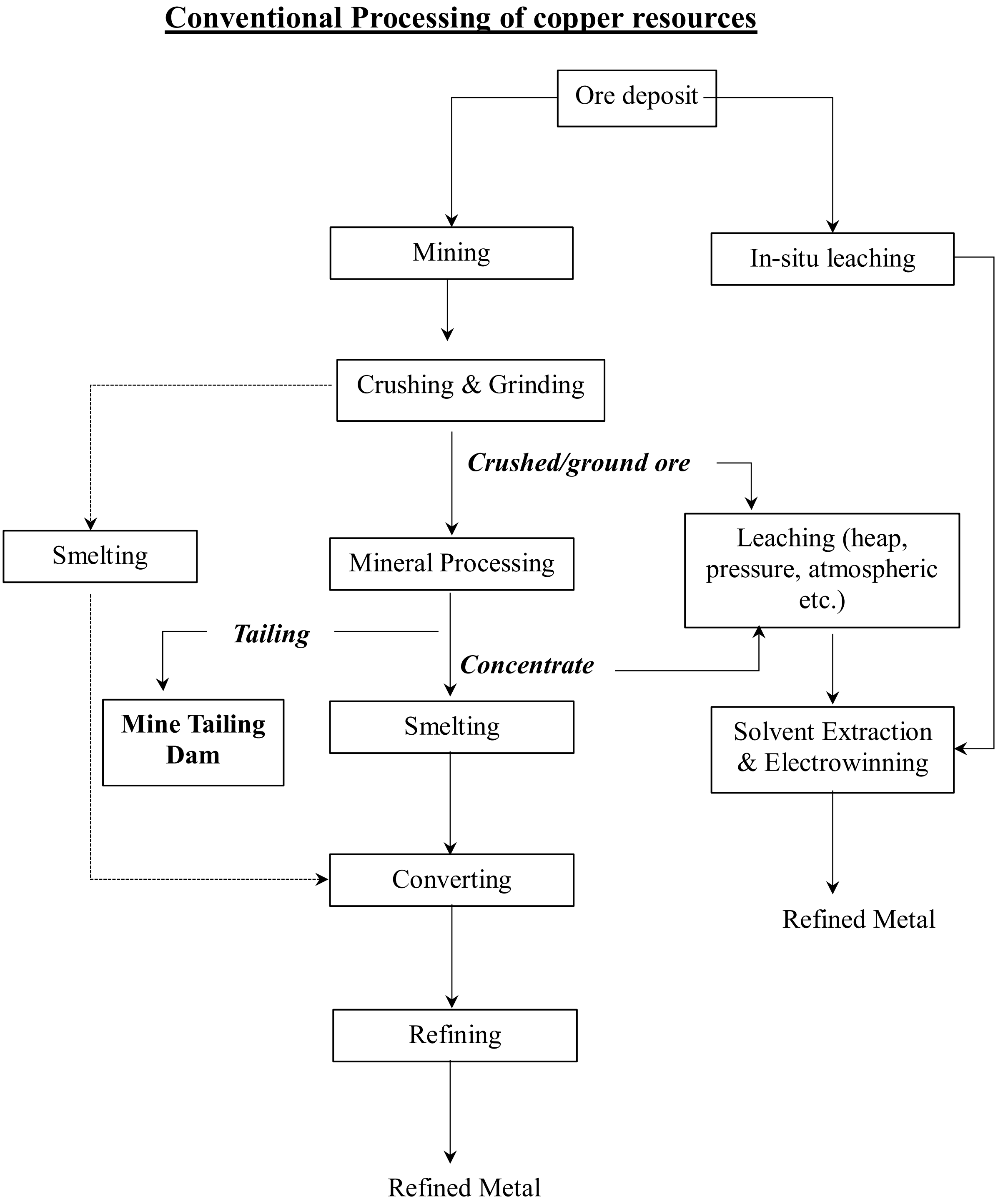
Pyrometallurgy processing

- Concentration and smelting
- Direct smelting of ore

Hydrometallurgical processing

- In situ leaching of ore
- Heap or pressure leaching of ore or concentrate

Although the direct smelting route has been shown in Fig.1.10, it is not commercially used for production of copper due to the low grade associated with ore deposits of copper. The other processing route is discussed in more detail further below.



Conventional Processing of copper resources

Figure 1. 10. Processing routes for copper ore. (Source: Bogdanović *et al.*, 2016)

Pyrometallurgical processing

After the ore has been concentrated by flotation to a final product of 20-30% Cu, it is then dried, mixed with silica and flux and fed to the flash smelter where partial roasting and smelting happens simultaneously (Fig.1.11). Sulfur dioxide is given off by the oxidation reactions. This gas is captured and used for production of sulfuric acid. At about 1200 ^{0}C the liquid matte and slag separate in the furnace. The upgraded matte (50-70% Cu) is tapped and transferred to the converter for final conversion to elemental copper. The product after the converter is called blister copper sulfide and has copper content of 99.9%. The blister copper is the fire refined to remove oxygen and cast into anodes for electrorefining. The products of electrorefining are copper cathodes assaying over 99.99 of copper (Bogdanović *et al.*, 2016).

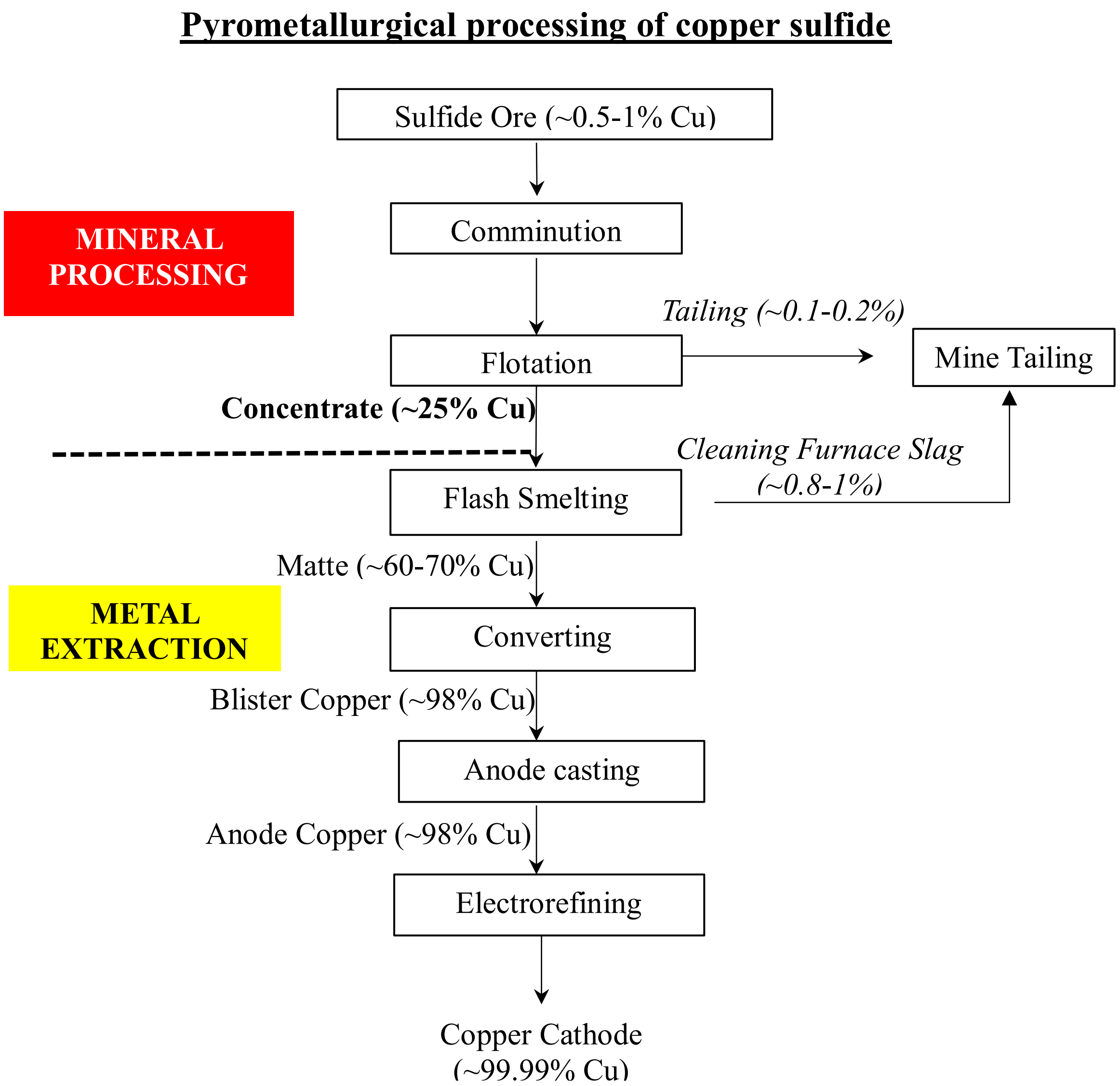


Figure 1. 11. A typical pyrometallurgical flow-sheet for copper production. (Source: Bogdanović *et al.*, 2016)

As mentioned earlier, the effects of declining ore grades, finer grind sizes and complex mineralogical assemblages on the processing route give out detrimental effect of high energy consumption and greenhouse gas emissions of copper metal product as reported by Norgate and Jahanshahi, 2010.

Hydrometallurgical processing

The conventional hydrometallurgical processing route of copper oxide and sulfide ores consist of three main processing: leaching, solvent extraction (SX) and electrowinning (EW). Fig.1.12 shows a simplified hydrometallurgical flow-sheet for copper extraction.

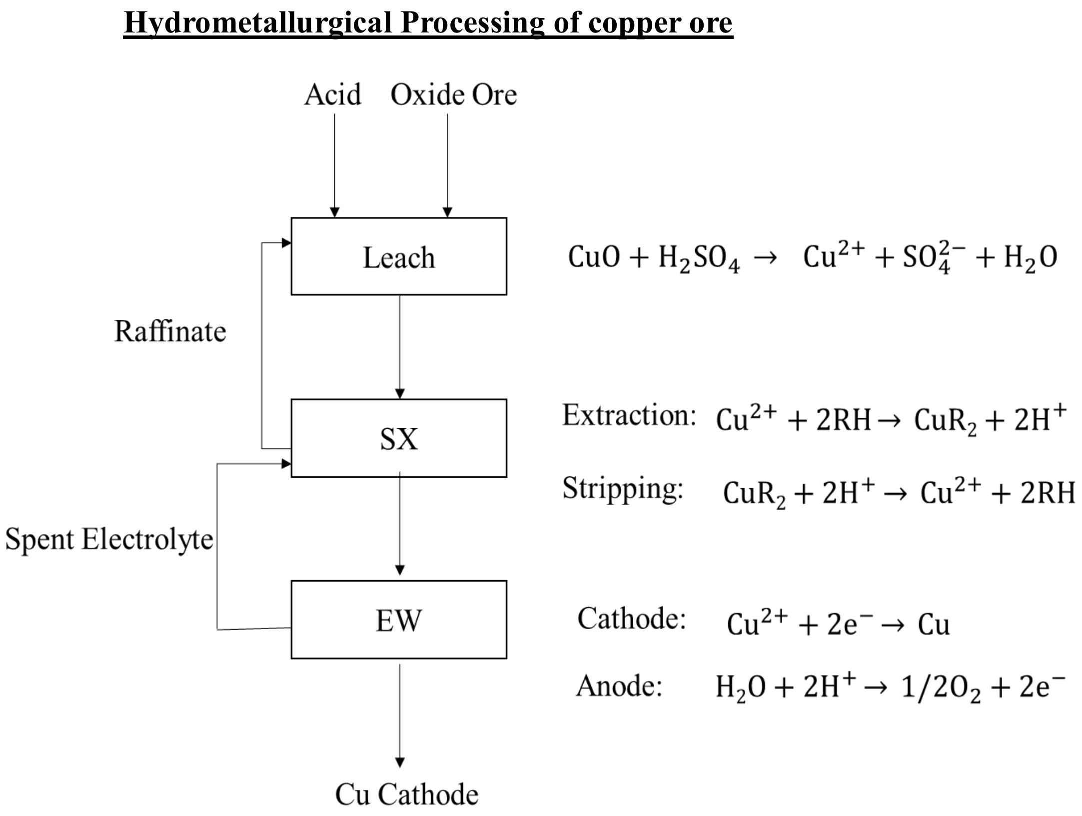


Figure 1. 12. Simplified copper production from oxide ores by hydrometallurgy. (Source: Bogdanović *et al.*, 2016)

Hydrometallurgical processing can be divided into predominantly sulfate and chloride process. Within the sulfate grouping, process can be sub-grouped as either atmospheric or super-atmospheric and chemical or biological leaching processes. There are a large number of reasons for pursuing alternatives of leaching compared to conventional processing (pyrometallurgy) and this include:

1. Capital cost. The capital cost of a smelter and refinery complexes is very high. The typical range of cost is \$3000-\$5000 (USD) investment per annual tonne of copper production (e.g \$900 Million to \$1.5 Billion per 300,000 tpy Cu production) (Dreisinger, 2006).
2. Impurity tolerance. Perhaps one of the major advantages to the processing of the complex ores found today. Smelters are limited in ability to treat concentrates that contain high levels of deleterious impurities.
3. Copper-Gold concentrates. Gold is frequently associated with copper concentrates. In some cases, high recovery of gold flotation is accompanied by high levels of pyrite flotation resulting in a low-grade copper concentrate for treatment.
4. Mine to market Optimization. It may make sense that the overall economics of a mining operation to account for (1) production of a lower grade concentrate with higher overall recovery of copper from the mine, (2) treatment of the lower grade concentrate at the mine site to make copper metal and (3) use of by-product weak acid from the copper recovery process as a reagent to leach and recover copper at the mine site. The overall economics achieved using this approach may give an advantage to an alternative to smelting.
5. Recovery of valuable by-products. Copper concentrates tend to contain many other significant base and precious metal by-products. Copper smelters are efficient at recovery of gold, silver and PGM’s but often pay poorly and with much delay for these elements.

6. Use of existing capital. In some selected cases, copper heap leach-SX-EW process plants are running out of feed. These plants have fully functional SX/EW plants available for further copper recovery as electrowon cathode. In this case, it may make sense to adopt a copper concentrate hydrometallurgical process as the "front end" of the process plant and further utilize existing capital.
7. Economics. Smelter economics are more scale sensitive than hydrometallurgical alternatives. Hydrometallurgy plants may be more suited to application of modular incremental project development if required.

Hydrometallurgical processing of copper has been studied extensively as an alternative route to chalcopyrite treatment. However, the challenge of process development for chalcopyrite leaching in sulfate media is generally to leach chalcopyrite quickly and completely with high yield of elemental sulfur. It is advantageous to have high yield of elemental sulfur as it leads to reduced costs of oxygen for mineral leaching and reduced neutralization/acid disposal costs. To overcome the slow and incomplete leaching of chalcopyrite at lower temperatures, two famous problems (1) passivating films around chalcopyrite surfaces and (2) the potential blocking and wetting of chalcopyrite by liquid elemental sulfur must be addressed (Dreisinger, 2006; Adebayo and Ajayi, 2014; Lorenzo-talla *et al.*, 2018). To date, a large number of hydrometallurgical treatment process have been developed to treat copper concentrate. These processes have failed to achieve sustained commercial production due to one or more of the following lists of challenges:

1. Low copper concentration recovery in the primary leachate.

2. Copper losses to pre-precipitation with iron hydrolysis products or other gangue minerals.
3. Difficult or incomplete precious metal recovery from leach residue.
4. Unconventional and difficult electrolysis step.
5. Difficult elemental sulfur recovery step from leach residue.
6. Excess corrosion (especially chloride circuits).
7. Difficulty in fixing toxic by-products in stable waste products.
8. Large energy requirements for mixing and oxygen dispersion.
9. Poor quality copper product that require electrorefining.

Other factors worth noting in the prevention of advancement of new technologies include:

1. New technology risk. Many of the new process have unique chemistry, processing conditions or equipment. These processes have not had adequate commercial demonstration to mitigate risk.
2. Cost of licensing. The potential cost of licensing new technology while also assuming the risk of being first to commercially practice can mitigate against new technology selection.

Against this backdrop, significant advances in improving hydrometallurgical processing have been carried out for copper minerals. Low temperature leaching that utilize fine grinding have or high temperature (>200 ^{0}C) have been employed to leach copper concentrates. Both processes require intensive energies, but an assessment in the high-pressure leaching offers a competitive consideration in the leaching of ores with chalcopyrite mineral. Table 1.3 gives a summary of the disadvantages and advantages of high-pressure leaching process.

Table 1. 3. Advantages and disadvantages of high-pressure leaching (Stopić *et al.*, 2011, https://www.sgs.com/en/mining/metallurgy-and-process-design/unit-operations-and-metallurgical-services/pressure-and-ambient-leaching).

Advantages	Disadvantage
• Highly effective for difficult and complex copper ores, ie can treat chalcopyrite which is not easily dissolved in aqueous solutions.	• Very complex chemistry
• High recovery rates at fast leaching time compared to atmospheric or bioleaching process.	• High capital cost
• Possible for selective metal extraction and iron hydrolysis control that is advantageous in waste disposal.	• Safety issues must be considered
• Provide an advantage in by-product recovery ie. Ni, Co, Zn and PGE metals	

Significant advances have been made over the last few years in advancing the use of hydrometallurgy for copper ore and concentrate treatment. The historical and current development are discussed in reference (Dreisinger, 2006; McDonald and Muir, 2007a, 2007b). Table 1.4 lists the major sulfate-based processes.

How processing of other ore compares to processing of mine tailing and complex carbonaceous sulfide ore

As already stated, most mined ores follow the conventional processing route of concentration, smelting and refining and currently by leaching. More than 67 % of the world copper production originated from the pyrometallurgical treatment of porphyry copper deposits. Pyrometallurgical technologies have been commercialized for the processing of either sulfides ore laterite containing copper metal values plus other non-ferrous metals such as nickel and cobalt. Under the oxidizing conditions, Cu tends to form metallic Cu as well as Cu oxide, as explained extensively by Yazawa: the addition of oxygen of Cu_2S yields Cu instead of Cu_2O. When the latter happens, the Cu_2O dissolves in the slag generated during copper making. The large concentration of iron in most copper concentrates creates a large amount of slag, which allow for more Cu to be lost in it. Examples of pyrometallurgical plants can be found in the article by Bellmans *et al*., (2016) and Moskalyk and Alfantazi (2003). However, in the case of carbonaceous sulfide ores, the presence of carbonaceous material makes it difficult as they report to slags and require extensive energy for processing. In the case of mine tailing, it is difficult to upgrade the copper minerals to the suitable grade of 25 % required for smelting thus rendering an alternative of hydrometallurgical processing.

The prospective processes have been successfully demonstrated around the 1990's. Hydrometallurgical leaching has been successful in the processing of Polish copper deposits which are of sedimentary origin. The Phelphs Dodge has employed high temperature pressure oxidation, albeit at pilot scale, since 2003 for the processing of chalcopyrite concentrate at Bagdad mine in Arizona.

Table 1. 4 Sulfate-based copper hydrometallurgical process for ore or concentrate (Dreisinger, 2006; McDonald and Muir, 2007a, 2007b).

Process	Status	Temperature, °C	Pressure, atm	Regrind d_{80}, µm	Significant conditions
Mt Gordon Process	Commercial	90	8	100	Pressure oxidation of chalcocite/pyrite ore or bulk concentrate in an iron sulfate rich electrolyte
BIOCOP™	Pilot plant	65-80	1	37	High T bioleach. Uses thermophilic bacteria
Anglo American/UBC	Commercial	150	1	5-20	Modest grind combined with surfactants for chalcopyrite leaching
Sepon Copper Process	Commercial	80-Copper 220-230-Pyrite	Atm 30-40	100 50	Atmospheric ferric leach for copper from chalcosite. Pressure oxidation of pyrite concentrate to make acid and ferric sulfate for copper leach
Total pressure oxidation process	Commercial	200-300	30-50	37	Extreme conditions of T and P designed to rapidly destroy chalcopyrite and other sulfide
CESL copper process	Pilot plant	140-150	10-12	37	Chloride catalyzed leach of chalcopyrite leaching producing basic copper sulfate precipitate in the autoclave
Activox process	Pilot plant	90-110	10-12	5-10	Fine grinding combined with high oxygen overpressure overcomes chalcopyrite passivation.

1.4 Problem Statement for Mine Tailing and Carbonaceous Sulfide Ore

Presently, resources for copper are abundant but there is a short-term supply limitation due to limited technologies. There is a serious consideration to outsource primary, secondary or both mineral resources to combat the global demand and supply curve, trend of falling grades of ores, rising energy demands and also ensure an environmentally secure type of processing. Considerable efforts have been made by far to ensure the sustainable developments of copper ore resources by different aspects such as:

- Extensive exploration for ore bodies which have significant copper minerals such as complex carbonaceous sulfide ores, volcanogenic massive sulfide and sea sediments (Norgate and Jahanshahi, 2010)
- Outsourcing copper minerals from mine tailing that might contain base transition metals (copper, iron, nickel, and zinc) that are of economic significance (Falagán, Grail and Johnson, 2017).
- Downstream processing of electronic waste and scraps has been seen evident in most developed countries such as Japan (Li *et al.*, 2013; Kaya, 2016). According to the World Economic Forum, Japan is reclaiming metals from end-life products to make the 2020 Olympic Medals to increase sustainability in processing.

Mine tailings and complex carbonaceous sulfide ore are considered as possible resources for copper in this research work.

1.4.1 Mine tailing

Mine tailing are products generated as waste during flotation process. They consist of ground rock and effluents that are generated in mine processing plant such as flotation process as shown in Fig 1.13. The mine tailing is disposed in the tailing dam which are usually in the vicinity of most mining towns and represent a serious environmental hotspot. One of the main directly/indirectly pollutant in the metallurgical processing of copper is the pyrite present. Pyrite is a widely spread mineral and is present in many valuable mineral raw materials as a deterrent to mineral processing and treatment. It is inevitably present in copper sulfide ores as well as smelter copper concentrates.

The exploitation of copper sulfide minerals which are associated with pyrite, lead to uncontrolled oxidation under the influence of weathering. When oxidation occurs, acid solutions are produced, enriched with heavy metal ions, solution salts and other substances, which through piercing, percolating and overflowing waters come to underground and surface waters and pollute nearer and wider areas. Among other harmful elements that can be found in mine tailings is arsenic. As naturally occurs in over 200 different mineral forms, but it is common in FeS_2, PbS and $CuFeS_2$. The most common As mineral is FeAsS. In the reaction of concentrate smelting obtained from the most spreaded arsenical pyritic copper deposits, As_2O_3 is released. The main source of As emission is copper smelting and present significant pollution problems.

With the ever-growing demand for mineral products, coupled with deterioration and depletion of high-grade mineral ore deposits and environmental concern associated with mining and metallurgical waste products, recovery of copper from mine tailing is the alternative (Crowson, 2012, Bethell, 2012, Nesbitt, 2007, Jones and Boger, 2012).

Figure 1. 13. Plant flotation circuit (Source: http://www.miningeducation.com/2016/02/flotation-cell-for-mineral-separation)

Why consideration of mine tailing for copper recovery?

As already mentioned, mine tailings are considered waste and therefore require extensive management to reduce negative impact that are associated with them. By far more issues have been raised as concern in the management of these materials and include:

- Susceptibility to acid mine drainage (AMD) and underground water pollution. Mine tailings are known to contain metals that can easily be leached when exposed to rainfall and atmospheric oxygen to produce acidic waters that leak into underground water streams.
- Mine tailing is prone to collapse and land-slides because of their instability
- Mine tailings tend to occupy more land space for storage and treatment
- There is a problem of widespread wind transportation of dry tailings to larger and distant areas that can be potentially harmful to human, animal and plant lives.

Therefore, it is important to consider specific approaches to the management of mine tailing by evaluation of three (3) factors (Fig 1.14):

- cost- a consideration on the economics of metal recovery from mine tailing to ensure optimum returns by employing a cost-effective technology is very important
- environmental performance- the basis for a successful and proper handling of mine tailing involves, proper material characterization, including an accurate prediction of their long-term behavior and a good choice of site location.
- risk of failure- ensures that in cases where storage of mine tailing is not possible there are alternative integrated where mine tailings could be reused and recycled.

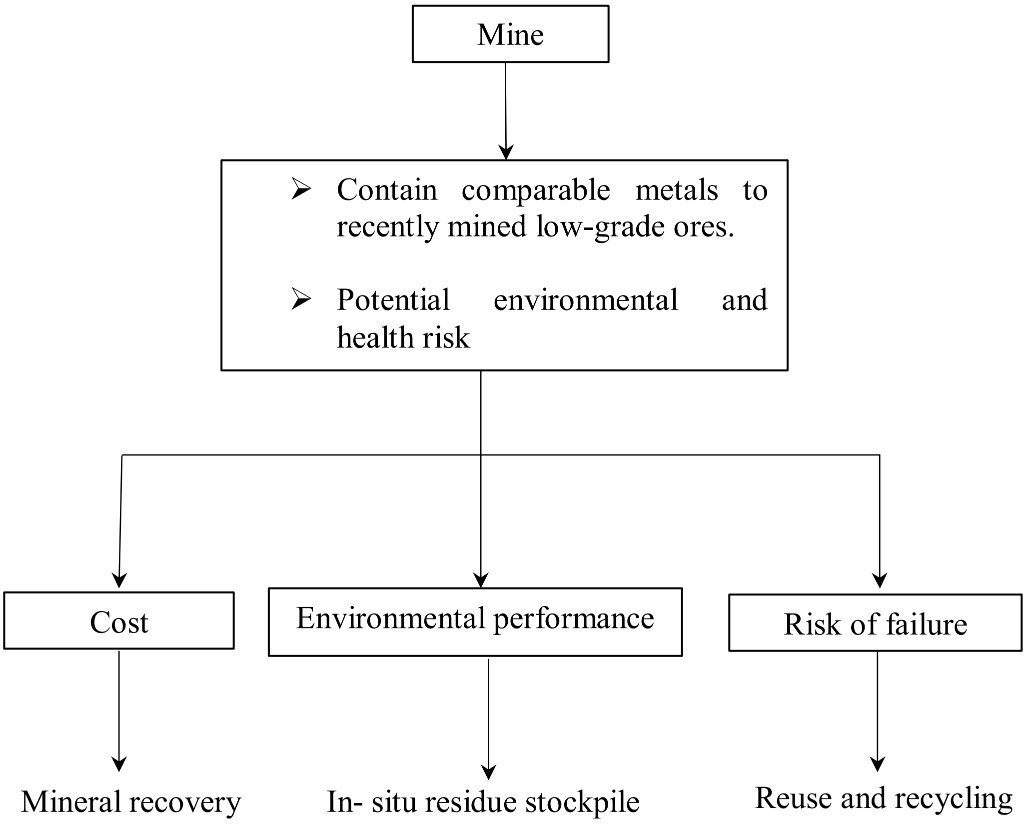


Figure 1. 14. Schematic diagram of mine tailing management strategy.

The emphasis of this research is made on the first and third option to improve technological process recovery of copper to meet demands of current status.

Recent trends have observed that these considered waste materials contain significant copper metal particularly because in many historic operations, the efficiency technology used to concentrate target minerals was not as good as those of the currently available. The mine tailing contains an average of 0.19-1.0 wt% copper which compares relatively well to the low-grade ores which are currently mined. The world production of mine tailing is expected to grow from its estimated current sitting of more than 14 billion tonnes over the next years (Garcilaso, 2009; Adiansyah *et al.*, 2015).

1.4.2 Complex carbonaceous sulfide ore

It is important to consider what special circumstances might produce economic deposit of copper in sedimentary rocks. In many cases, there are some intriguing hints about the factors important in the formation of the deposits that are not completely understood. Many authors have indicated that no one theory of genesis can explain all the ore deposit. However, most suspect that many copper deposits result from many different processes acting on sedimentary throughout their geologic history, and because many of these processes are obscured by later events and are difficult to decipher, there should be avoidance to make any classification scheme that carries the connotations of genesis with it. Hitzman *et al.*, (2010) indicated that the sedimentary rock hosted stratiform copper deposits form by movement of oxidized, copper bearing fluids across a reduction front that results in the precipitation of copper sulfide Fig. 1.15.

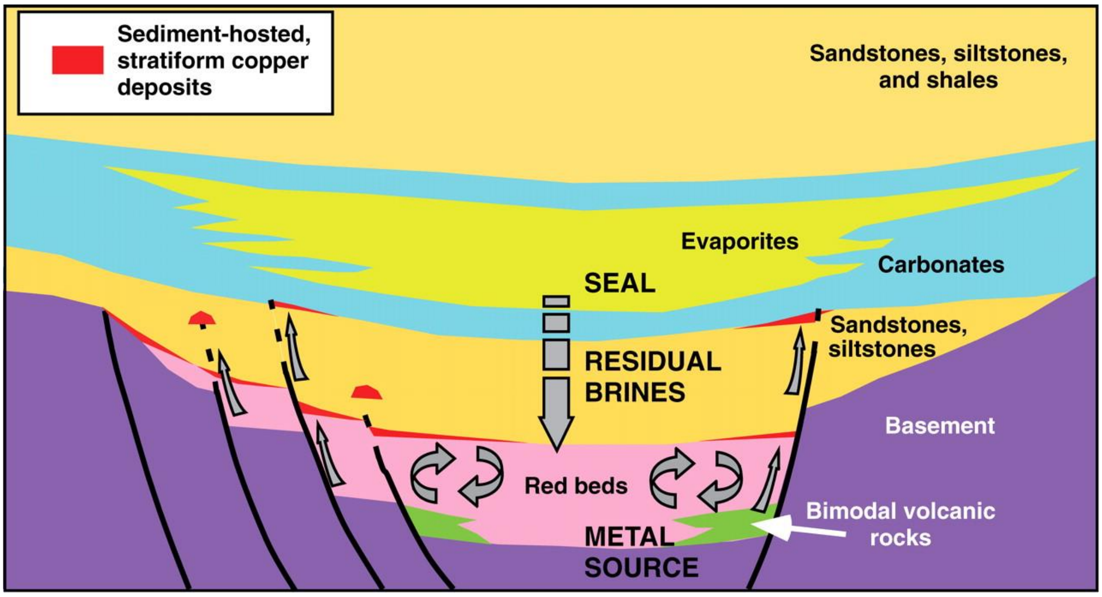


Figure 1. 15. Schematic model of sediment-hosted copper deposit. (Source: https://pubs.geoscienceworld.org/segweb)

The distribution of this deposits is widespread across different regions of the world containing significant amount of copper (Fig. 1.16). It is indicated that the deposits show deposition during the Paleoproterozoic to the Tertiary era. The deposits are found in rift-controlled basins under anoxic conditions. The (super) giant deposits formed in closed systems by overlying evaporates which contain fluid flow and superposed events in common. A general thickness >2.2-meter thickness with average of ~1-2 Cu content is observed.

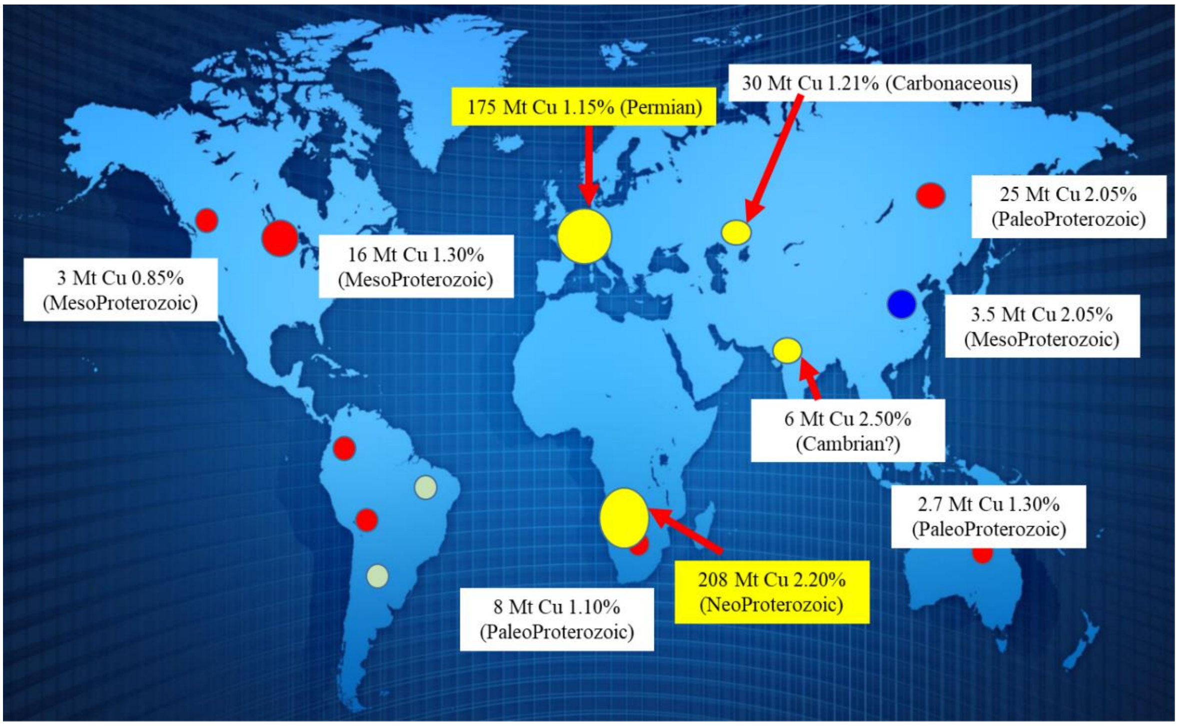


Figure 1. 16. Distribution of sediment hosted copper deposits around the world. (Source: https://pubs.geoscienceworld.org/segweb)

Why consideration of complex carbonaceous sulfide ore?

As already introduced, the copper resources are much higher but short-term limitations, which often result in upward price trends, act as a spur to the exploration of new deposits. The complex carbonaceous sulfide ore which are from sedimentary origin show that they are a potential because of their high copper content as indicated in Fig 1.16. Despite their potential metal content, there are some difficulties surrounding these deposits, which include;

- occur as polymetallic which makes mineral processing and separation very difficult.
- The deposits contain significant carbonaceous material which are detrimental to the conventional flotation process. That is, the naturally hydrophobic organic and inorganic materials present makes upgrading of concentrates difficult as it floats with the desired mineral constituents
- Carbonaceous material in the deposits are highly reagent consuming.

It is for this reason that defined economic process options for treating these complex ores should be made, considering the fact that less refractory and commonly mined deposits are being depleted.

The complex carbonaceous sulfide mineral resources fall under the 20 % of the untapped primary sedimentary-copper host rocks. The ores are an important source of many metals(polymetallic) such as lead, zinc, copper, cobalt and silver. The tonnages of carbonaceous sulfide ores (sediment-hosted) vary, with the average being 22 million tonnes grading 2.1 % Cu and 23 g/t Ag (British Geological Survey, 2007) but can be as much as several hundred million tonnes. For example, the enormous Lubin orebody in south-west Poland contains 2600 million tonnes with >2.0 % Cu and 30-80 g/t Ag.

It is difficult to follow the conventional pyrometallurgical methods due to the high energy requirements that would be required to process these ores. The hydrometallurgical routes are becoming more active and growing worldwide. Many studies of hydrometallurgy are central to atmospheric leaching and biological leaching from these ore deposits. However, leaching by this method is slow and require large amounts of acid reagents to leach copper. Despite that, an effective flotation process following removal of organic carbon and carbonate materials may provide the best alternative to include the concentrate to hydrometallurgical leaching. Alternatively, direct high-pressure leaching studies are a potential to chemically concentrate copper that can go on to subsequent process such as solvent extraction (SX) and electrowinning (EW) if all copper pregnant solution content is over 2 g/L. For those reasons, it becomes necessary to recover copper from complex carbonaceous sulfide ore by developing the production technologies efficient to face the demand and supply in the world.

1.5 Aim and Objective

The project research thus had two major focus:

1. Defining a set of parameters to recover copper by flotation and high-pressure leaching process or combination of both processes.
2. Develop a simpler, economic and environmentally friendly process for copper recovery with consideration to different mineralogical properties of two different copper mineral resources.

Additionally, it is also considered important to gain sufficient knowledge regarding the behavior of copper flotation and dissolution of the mine tailing and complex carbonaceous sulfide ore, thus enabling proper education of future process operators.

Mineral processing and extraction process employed in thesis: A flowsheet development was therefore planned by carrying out experimental work by flotation, direct high-pressure leaching, atmospheric leaching and combined flotation and high-pressure leaching. According to the preliminary results, mine tailings yielded better upgrading results as compared to complex carbonaceous sulfide ore. The results of this mainly points to the different mineralogical composition of the materials. This observation indicated the necessity of considering the mineralogical characterization of the mineral resource considered.

Atmospheric leaching was also employed for leaching mine tailings and complex carbonaceous sulfide ore, and the results yielded poor leaching efficiencies. It is reflected that chalcopyrite in the samples cannot be leached at low temperatures, let alone without oxidizing agents because of its refectory properties.

Different parameters where considered to study the recovery and extraction of copper from the aforementioned mineral resources. In the case of flotation, slurry pH, different collectors and their dosage such as potassium amyl xanthate $C_5H_{11}OCSSK$, Aerofloat 208, sodium oleate, particle size and frother (MIBC) dosage were studied. For high pressure leaching, the leaching medium concentration, time, stirring speed, solid/liquid ratio and temperature were extensively studied.

There is mounting evidence that increased copper metal demand will increase while parallel decline of grade ores will continue. Therefore, studies of alternative resources, mine tailing and complex carbonaceous ore will enhance in the efficient extraction of copper and therefore add to the existing inventory of metals. The hypotheses for this study are that there is potential to develop effective method by considering suitable parameters to recover copper from different mineral resources.

1.6 Mineral Resources Used in the Study

Mine tailings

The mine tailings used in this study were obtained from BCL mine, Selebi Phikwe, Botswana (Fig.1.17). The mine is famously known as a Ni-Cu mine and had a smelter that has since ceased operations and is under liquidation since 2016 (http://mmegi.bw//).The mine closed in 2016 siting reduction in metal prices and increased operational cost to keep the underground mining operation afloat.

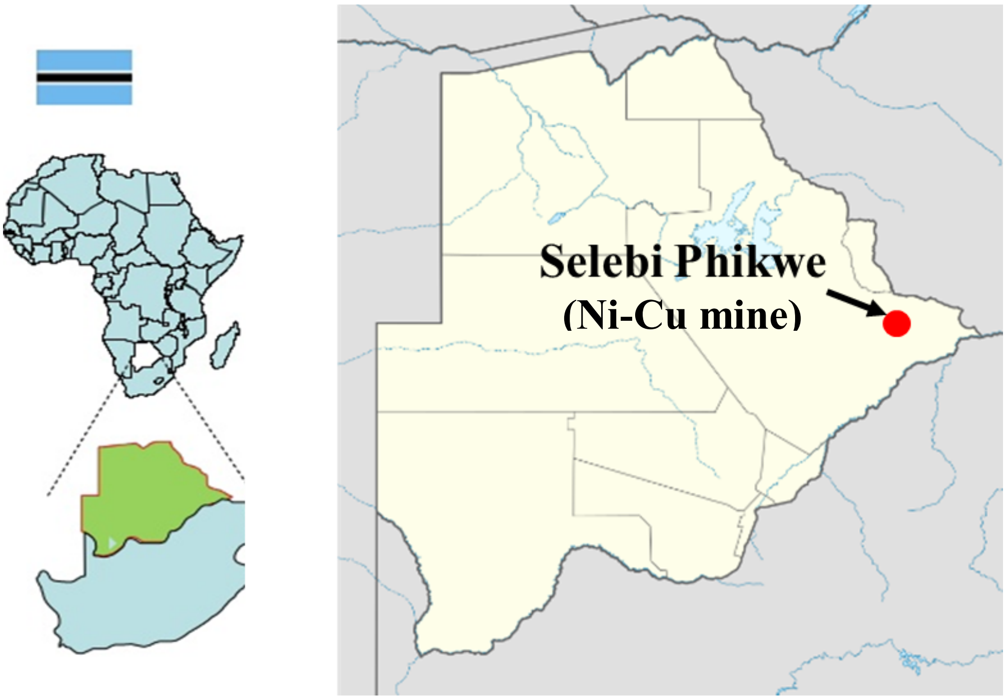


Figure 1. 17. Map of Botswana showing location of Selebi Phikwe. (Source: (Schwartz, Schippers and Hahn, 2005)

According to different sources the BCL mine are estimated to have over 100 million tonnes of tailing resource (http://mmegi.bw//, Schwartz, Schippers and Hahn, 2005). The tailing consists of waste on Ni-, Cu-, Zn-, and Co-sulfidic processing. The solids contain about 11% pyrrhotite, 1,5% other metal sulfide and hornblende and feldspar as major gangue minerals (Schippers, Schwartz, 2005; Schwartz, Schippers and Hahn, 2005). The mine tailing dam, which has neither surface barrier nor bottom seal, covers an area of approximately 1 km^2, with a height close to 50 m (Schippers, Schwartz, 2005; Schwartz, Schippers and Hahn, 2005). Because of this characterization of the tailing site, the area phases possible threats of acid mine drainage (AMD), which is already evident by the reddish color observations made (Fig.1.18). AMD occurs when sulfide minerals in the mine tailing are chemically and biologically oxidized to yield high amounts of heavy metals that are a threat to groundwater quality. The rate of oxidation especially for pyritic minerals found in the mine tailing is strongly dependent on temperature, pH, humidity and availability of oxygen. Consequently, the oxidation rate strongly depends on the abundance of acidophilic Fe(II)- and metal sulfide oxidizing micro-organisms, which accelerate the kinetics of pyrite by 30-300 fold (Edwards *et al.*, 2000; Schippers *et al.*, 2007).

Potential for Selebi Phikwe Mine Tailing Processing

According to the Mmegi online report (http://www.mmegi.bw/ 2010/July/Friday23) the Selebi Phikwe mine had an estimated 145 million tonnes of tailing in year 2010. The initial grade, that will later be discussed, of Cu and Ni were 0.19 and 0.23 wt%. This is comparable to the currently mined low grade ores. Additionally, as observed in Fig. 1.18 the current surrounding of the tailing dam, the environment has some reddish discoloration. This observation indicates the onset oxidation of sulfides that could potentially lead to acid mine drainage.

Figure 1. 18. Selebi Phikwe Mine tailing showing signs of pyrite oxidation reaction which result in AMD. (Source: Schippers, Schwartz, 2005).

Complex carbonaceous sulfide ore

The complex carbonaceous sulfide ore were sourced from South East Asia and were provided by Nittetsu Mining company. Previous confidential reports and cursory mineralogical characteristics of the ore indicate that the major copper host mineral was chalcopyrite with small traces of bornite. These results were also confirmed by in-house laboratory studies using X-ray diffractometer and SEM-EDS analysis.

The sample contain organic and carbonaceous material (inorganic material) as gangue minerals. This material is a major hindrance to the concentration of the ore by flotation, as they are naturally hydrophobic and reagent consuming. Numerous studies on the elimination of organic carbon had been carried out by using different flotation equipment such as at Jameson cell and separating concentrates into two concentrates to send to different smelting furnaces (Smith, Metallurgist and Lin, no date; Wieniewski and Skorupska, 2016; Problems, 2017). Due to the complexity of the mineralogical complexity of these ore resources it becomes very difficult to carry out the conventional sulfide processing of the ore through to pyrometallurgical route (Fig. 1.19).

Potential for Complex Carbonaceous Sulfide Ore

The complex carbonaceous sulfide ore falls under the sedimentary copper-hosted deposits which account for 20 % of the world deposits. Interestingly, despite their distribution, not a lot of processing has been done on them due to their mineralogical complexity and lack of technologies. A few commonly worked deposits of this nature such as Kupshciefier in Poland have been processed but challenges of carbonates presence hinder the process of flotation as the gangue minerals contaminate the concentrates. The samples supplied by Nittetsu company contained only copper metal with a high grade of 2.08 wt% compared to the usually polymetallic deposits of similar nature. Therefore, a comparison study between two stage flotation and direct pressure leaching was carried out to recover copper and also consider the influence of the gangue organic carbon and carbonaceous material in both processes.

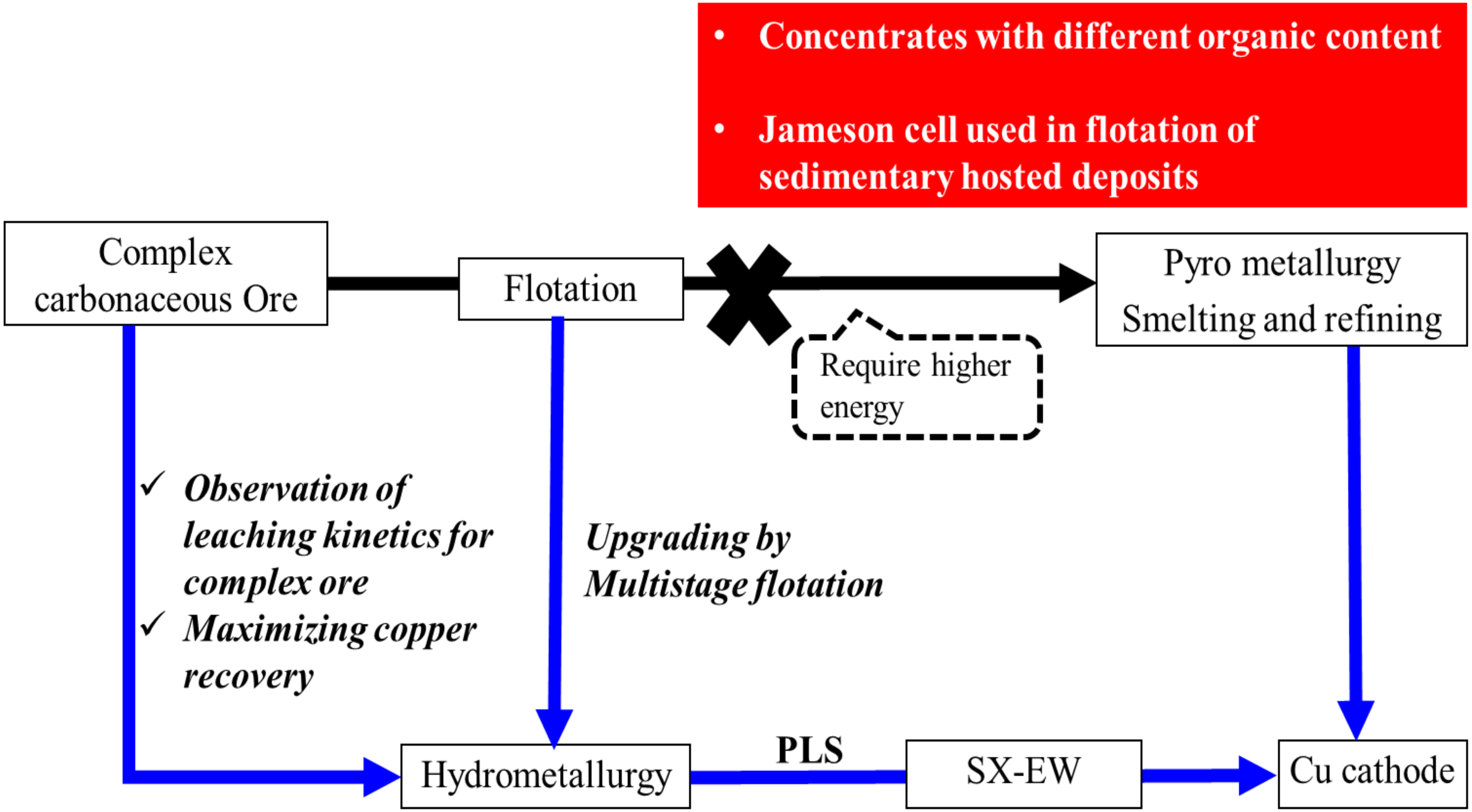


Figure 1. 19. Application of mineral beneficiation and extraction of copper from carbonaceous sulfide ore.

Significance of the study

The findings of this study will redound to the increased copper production and meet current demands of the metal required to increase standard of living. The considerations of untapped mineral resources either primary (complex carbonaceous sulfide ore) and secondary (mine tailing) processing justifies the need to construct effective mineral processes to combat the lingering problem of depletion of high-grade ores. Additionally, the process and choice of mineral resource i.e. mine tailing also helps to combat the environmental concerns associated with mineral processing. Thus, industrial sites that apply the recommended approach derived from the results of this study will be able to increase recovery efficiency of copper and increase production. The process will be guided on the exact parameters that emphasized maximum recoveries to improve recovery efficiency. For the researcher, the study will help uncover critical areas of the mechanisms involved in the separation and recoveries of copper that other researchers have not explores.

1.7 Organization of thesis

This PhD thesis is organized into four (4) chapters, each dealing with different aspects of metal recovery development process from different mineral resources.

Chapter 1

This section gives an introductory to the general knowledge of copper, significance of copper owing its characteristics for industrial and daily use, global resource and reserve is made. Further explanation is made on the mineral resource considered for this research. Moreover, the conventional metal processing and advanced technologies for copper recovery in mine tailing and complex carbonaceous sulfide ore were explained.

Chapter 2

This chapter focused on re-processing of copper and nickel from mine tailings from BCL mine, Selebi Phikwe, Botswana. The mine tailing had a grade of 0.19 wt% and 0.23 wt% copper and nickel respectively. The grade is comparable to low-grade mined deposits in Chile. The applications of mineral separation process involving flotation followed by high pressure leaching were applied to concentrate copper and nickel. The effect of collector type, dosage, pH and particle size were considered for the flotation of copper and nickel in a two-stage flotation process. Results indicated that >81.50 % recovery of copper was achieved while nickel recoveries were lower at 30% at optimum condition of 75 g/L Aerofloat 208 collector, natural slurry pH 4-6, 100 μm averaging D_{50} 75 μm, 10% pulp density, 100 g/t MIBC for 10 minutes flotation. The concentrates were upgraded to 6.72 wt% and 2.39 wt% copper and nickel respectively. The leaching of the concentrates indicated leaching rates of

97.04 % and 96.10 % of copper and nickel respectively. A combined process of flotation and high pressure leaching for the recovery of copper and nickel by flotation and high-pressure leaching is proposed for the BCL mine tailing.

Chapter 3

The main objective of this chapter was to compare the physical and chemical concentration of copper by flotation and high pressure leaching from the underexplored complex carbonaceous sulfide ore from South East Asia. The ore had copper grade of 2.08 wt% and contained 0.67 % of organic carbon. Typically, the presence of organic carbon makes conventional flotation process difficult owing to their natural hydrophobicity that affect quality of concentrate and reagent consumption. As such a two-stage flotation process was compared with direct pressure leaching for recovery of copper. The first process was a two-stage flotation process that comprised of pre-flotation followed by rougher flotation. In the pre-flotation stage, the intention was to separate organic carbon from copper minerals by considering the particle size and addition of frother (MIBC) only. A separation efficiency of 65.75 % of organic carbon from copper minerals was achieved when using the particle size averaging D_{50} 4 μm with addition of 200 g/t MIBC. In the rougher flotation stage, copper was upgraded to 6.49 wt% following a 160 g/t sodium oleate addition (NaOL), 700 rpm stirring speed, 10 minutes flotation and using D_{50} 4 μm particle size fractions. The average recovery for copper was low at 59.95 % when applying the flotation process.

Another process, direct leaching, was employed by considering effects of particle size, sulfuric acid concentration, temperature, pulp density and time. In this case, the average leaching rate of copper was observed at >95 % with a concentration of 2.47

g/L concentration. The leaching kinetics of copper where studied with respect to time and under optimum conditions the dissolution of copper in chalcopyrite was represented by the shrinking core model with diffusion mechanism given as $1- 2/3\alpha - (1- \alpha)^{2/3}$. The activation energy was calculated to be 18.89 kJ/mol. According to the results, particle size and temperature were the most significant parameters. Finally, it was concluded that the application of direct pressure leaching was best suited for the recovery of copper from complex carbonaceous sulfide ore compared to flotation. Direct high pressure leaching yielded maximum leaching efficiency with high concentration of copper at >95% and 2.47 g/L respectively, while recovery and grade of flotation products were 59.95 % and 6.49 wt% respectively.

Chapter 4

The chapter gives a summary of the work based on the findings by drawing the overall purpose of recovering metals from mine tailings and complex carbonaceous sulfide ore. Two process are suggested for the recovery of copper from two different ores by considering their mineralogical characterization with associated grade and gangue minerals. A brief economic evaluation of the two process is given on the chapter. Finally, the process for copper recovery with the same mineralogical composition as those studied is suggested to industrial application. Furthermore, future work required to extend the outcomes of the current findings were included.

REFERENCES

[1] Adebayo, A. and Ajayi, O. O. (2014) ‘Dissolution Kinetics of Chalcopyrite with Hydrogen Peroxide in Sulphuric Acid Dissolution Kinetics of Chalcopyrite with Hydrogen Peroxide in Sulphuric acid Medium’, (March 2003).

[2] Bobadilla-fazzini, R. A. *et al.* (2016) ‘Hydrometallurgy Primary copper sul fi des bioleaching vs . chloride leaching : Advantages and drawbacks’, *Hydrometallurgy*, 168, pp. 26–31. doi: 10.1016/j.hydromet.2016.08.008.

[3] Chmielewski, K. T. and Among, I. (2008) ‘Search for a New Technology’, (122), pp. 94–100.

[4] Chmielewski, T. (2015) ‘Development of a hydrometallurgical technology for production of metals from kghm polska miedz S.A. concentrates’, *Physicochemical Problems of Mineral Processing*, 51(1), pp. 335–350. doi: 10.5277/ppmp150120.

[5] Davis, E. M. and Davis, R. J. (2003) *Fundamentals of Chemical Reaction Engineering, McGraw-Hili chemical engineering series*. doi: 10.1021/ed043pA758.1.

[6] Dimitrijević, M. *et al.* (2009) ‘Influence of pyrometallurgical copper production on the environment’, *Journal of Hazardous Materials*, 164(2–3), pp. 892–899. doi: 10.1016/j.jhazmat.2008.08.099.

[7] Do, H. and Use, W. (2009) ‘Copper — A Metal for the Ages How Do We Use Copper ? Where Does Copper Come From ?’, (May).

[8] Dreisinger, D. (2006) ‘Copper leaching from primary sulfides : Options for biological and chemical extraction of copper’, 83, pp. 10–20. doi: 10.1016/j.hydromet.2006.03.032.

[9] Eisener, C. G. W., Mart, R. S. T. C. S. and Erson, A. R. G. (2003) ‘Kinetics and mechanisms of the leaching of low Fe sphalerite’, 67(5), pp. 823–830. doi: 10.1016/S0016-7037(02)01276-0.

[10] European Commission (EC) (2009) ‘Report. Reference document on the best available techniques. Management of tailings and waste-rock in mining activities’, *Reference Documents on Best Available Techniques*, (January), p. 511. Available at: http://eippcb.jrc.ec.europa.eu/reference/BREF/mmr_adopted_0109.pdf.

[11] Flanagan, D. M. *et al.* (2018) ‘Mineral Industry Surveys’, (2), pp. 1–13.

[12] Han, B. *et al.* (2017) ‘Leaching and Kinetic Study on Pressure Oxidation of Chalcopyrite in H2SO4 Solution and the Effect of Pyrite on Chalcopyrite Leaching Leaching and Kinetic Study on Pressure Oxidation of Chalcopyrite in H 2 SO 4 Solution and the Effect of Pyrite on Chalcopy’, *Journal of Sustainable Metallurgy*. Springer International Publishing, (November). doi: 10.1007/s40831-017-0135-3.

[13] Hidalgo, T. *et al.* (2018) ‘Kinetic study of chalcopyrite dissolution with iron (III) chloride in methanesulfonic acid’, *Minerals Engineering*. Elsevier, 125(May), pp. 66–74. doi: 10.1016/j.mineng.2018.05.025.

[14] Lane, D. J. *et al.* (2016) ‘Selective leaching of penalty elements from copper concentrates: A review’, *Minerals Engineering*, 98, pp. 110–121. doi: 10.1016/j.mineng.2016.08.006.

[15] Larrauri, P. C. (2018) ‘Tailings Dams Failures : Updated Statistical Model for Discharge Volume and Runout’, pp. 1–10. doi: 10.3390/environments5020028.

[16] Li, W. and Adachi, T. (2017) ‘Quantitative estimation of resource

nationalism by binary choice logit model for panel data’, *Resources Policy*. Elsevier Ltd, 53(January), pp. 247–258. doi: 10.1016/j.resourpol.2017.07.002.

[17] Lorenzo-talla, J. *et al.* (2018) ‘Ferric leaching of the sphalerite contained in a bulk concentrate : Kinetic study’, 125(May), pp. 50–59. doi: 10.1016/j.mineng.2018.05.026.

[18] McDonald, R. G. and Muir, D. M. (2007a) ‘Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products’, *Hydrometallurgy,* 86(3–4), pp. 191–205. doi: 10.1016/j.hydromet.2006.11.015.

[19] McDonald, R. G. and Muir, D. M. (2007b) ‘Pressure oxidation leaching of chalcopyrite. Part II: Comparison of medium temperature kinetics and products and effect of chloride ion’, *Hydrometallurgy*, 86(3–4), pp. 206–220. doi: 10.1016/j.hydromet.2006.11.016.

[20] Montenegro, V., Sano, H. and Fujisawa, T. (2013) ‘Recirculation of high arsenic content copper smelting dust to smelting and converting processes’, *Minerals Engineering*. Elsevier Ltd, 49, pp. 184–189. doi: 10.1016/j.mineng.2010.03.020.

[21] Moskalyk, R. R. and Alfantazi, A. M. (2003) ‘Review of copper pyrometallurgical practice: Today and tomorrow’, *Minerals Engineering*, 16(10), pp. 893–919. doi: 10.1016/j.mineng.2003.08.002.

[22] Muszer, A. *et al.* (2013) ‘Covellinisation of copper sulphide minerals under pressure leaching conditions’, *Hydrometallurgy*, 137(2013), pp. 1–7. doi: 10.1016/j.hydromet.2013.03.010.

[23] Najdenov, I., Raić, K. T. and Kokeza, G. (2012) ‘Aspects of energy

reduction by autogenous copper production in the copper smelting plant Bor', *Energy*, 43(1), pp. 376–384. doi: 10.1016/j.energy.2012.04.007.

[24] Norgate, T. and Jahanshahi, S. (2010) 'Low grade ores - Smelt, leach or concentrate?', *Minerals Engineering*, 23(2), pp. 65–73. doi: 10.1016/j.mineng.2009.10.002.

[25] Of, B. (1994) 'T ECHNICAL R ESOURCE D OCUMENT EXTRACTION AND BENEFICIATION OF ORES AND MINERALS', (August).

[26] Paper, C. (2015) 'Hydrometallurgy – an Alternative and a', (November).

[27] Problems, P. (2017) 'SELECTIVITY AND POWER OF FROTHERS IN COPPER ORE FLOTATION * Abstract ':, 53(202), pp. 515–523.

[28] Production, D. (2016) 'No Title', (703), pp. 2016–2017.

[29] Rico, M. *et al.* (2008) 'Reported tailings dam failures . A review of the European incidents in the Reported tailings dam failures A review of the European incidents in the worldwide context', (August 2018). doi: 10.1016/j.jhazmat.2007.07.050.

[30] Robinson, D. J. and Scientific, T. C. (2018) 'Special Feature: Mineral Processing, In situ recovery – a move toward "keyhole mining".', (August).

[31] Smith, T., Metallurgist, P. and Lin, D. (no date) 'PAPER 21 Removal of Organic Carbon with a Jameson Cell at Red Dog Mine', pp. 333–346.

[32] Watling, H. R. (2014) 'Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options', *Hydrometallurgy*, 146, pp. 96–110. doi: 10.1016/j.hydromet.2014.03.013.

[33] Wieniewski, A. and Skorupska, B. (2016) 'Technology of Polish copper ore beneficiation – perspectives', 4, pp. 0–10.

[34] Wills, B. A. and Napier-munn, T. (2006) *Preface to 7th Edition*.

[35] Zhan-fang, C. A. O. *et al.* (2009) 'Techniques of copper recovery from Mexican copper oxide ore', 19(August 2008), pp. 45–48.

2: Recovery of Copper and Nickel from Mine Tailing by Flotation and High-Pressure Leaching

2.1 Introduction

Flotation is of interesting topic in recycling ions by using surficial reactors. Its efficiency is dependent on the hydrophobic and hydrophilic properties of mineral sample (Lutandula and Maloba, 2013; Chen *et al.*, 2014; Babel *et al.*, 2018). Improving recovery of minerals by studying their relationship between different parameters of flotation and floatability has been a long-standing goal within the mineral processing industry. However, some of the minerals are not fully recovered during this process and end up reporting to the ever increasing mine tailings that occupy a wide area in a many mining country.

It is an axiomatic approach that qualitative chemical and mineralogical composition of flotation tailings has to be, as expectable, very similar to the composition of ores processed by flotation. Such waste contains similar minerals at low concentration and predominately have high percentages of gangue minerals, mainly SiO_2 and Al_2O_3 and other various alumina-silicates, as well as considerable amounts of iron minerals, commonly pyrite with lesser extent hematite, limonite (Babel *et al.*, 2018). Toxic elements, such as arsenic, may also be present in elevated concentrations (e.g. Nguyen *et al.*, 2015). The appearance of secondary minerals formed due to weathering are found in a greater extent in older tailing ponds (Falagán *et al.*, 2017). This increase in tailings presents environmental problems in many regions (Chen *et al.*, 2014; Evdokimov and Evdokimov, 2014; Fosso-kankeu, 2015; Paper *et al.*, 2016).

In the case that the mine tailings are exposed to weathering, chemical percolation, some heavy metals become more soluble and mobile (Molecular and Biology, 1995; Cruz *et al.*, 2015; Fosso-kankeu, 2015; Cao *et al.*, 2016; Paper *et al.*, 2016; Babel *et al.*, 2018). The metals that had been leached into the ground act as sources of contamination, which extends to the underground water reserves and soil. An excellent review on the effects of mine tailing has been done in Bor mine tailings in Serbia, describing the potential risk associated for acid mine drainage (AMD) (Dimitrijevi´c *et al.*, 2009). Until recently, more researches surrounding the aforementioned mine tailing has been revisited to find alternatives of reclaiming and accessing the potential of this mine tailing (Hans *et al.*, 2014; 2018). On the other hand, catastrophic environmental pollution has occurd due to the failing of the system used to store mine waste. One such example is the failure of the retaining dam of a tailing impoundment at Aznalcóllar-Los Frailes mine (in south-west Spain) which resulted in the release of vast amounts of acid waters and tailing slurries into the catchment of a local major river nearby with Doñana National Park in April 1998 (Falagán *et al.*, 2017, Grimalt *et al.*, 1999, Ericksson and Adamek, 2000). However, in order to address these problems, many researches have been made, aiming at metal recovery through improving separation methods, such as flotation, pyrometallurgy and hydrometallurgy (Huang, Li and Chen, 2007; Evdokimov and Evdokimov, 2014; S. Yin, Wang, Wu, Free, *et al.*, 2018; S. Yin, Wang, Wu, Kabwe, *et al.*, 2018; Z. Yin *et al.*, 2018). An added advantage to their consideration is the fact that over time, increasing demand for metal, coupled with depleting reserves of high-grade ores, has meant that some the waste materials may contain significant metals comparable to the currently mined ores. Since the mine tailing have already been pre-processed, the cost of extracting residual metals from them is often economically more attractive than mining deep ore bodies. Consequently, other by-product metals may be contained that had not been previously worth extracting before. This was the case with the cobalt-rich tailing pond produced at a former copper mine in Kasese, Uganda, which were reprocessed by bioleaching decades before mining at the site ended, both to extract cobalt and to remove the environmental threat posed by the tailing deposits (Falagán *et al*., 2017, Morin and D'Hugues, 2007).

Harnessing the fast and potential to extract metals from low grade/ mine tailing, high pressure leaching presents a better to option as it is operationally economic for such small-scale processing. In the leaching process, metals from the flotation concentrates are enriched into a pregnant leached solution with aid of acid reagent. It is therefore important that mineral interactions at flotation and leaching are quantified to understand effective recoveries of minerals and ways of rejecting iron gangue minerals (Ally *et al.*, 2001; Fleming, Brown and Botha, 2010; Lv *et al.*, 2017; Mackay *et al.*, 2018).

The BCL mine tailing site description

As a typical base metal mine in Botswana, BCL Limited mine has been storing its tailing from flotation since commencement in 1973 (Ally *et al.*, 2001; Schippers *et al.*, 2007; Fleming, Brown and Botha, 2010; Lv *et al.*, 2017; Mackay *et al.*, 2018). The reservoir contains large volumes of tailings that contain significant amount of copper and nickel minerals due to poor liberation or mechanical faults associated with mining operations. According to Ekosse et al. (2005) the height of the mine tailing was projected to reach 50 m by 2014 with the tailing dam covering over 1 km^2 by 2003. The tailing dam hosts waste of mafic rocks that metamorphosed under amphibolite-facies conditions covered in water in the central part with the periphery of the damn surface dry (Fig 2.1). Very few studies carried out in this location and are only limited to the geomicrobiological and geochemical studies of the area.

Figure 2. 1. Deposition of BCL mine tailing into dam

Potential for Selebi Phikwe Mine Tailing Processing

As already indicated in Chapter 1, mine tailing have pose a potential risk to human and environment wellbeing. The BCL mine tailing in Selebi Phikwe, Botswana are no exception. The geochemical studies carried out by Ekosse *et al.*, (2005) and Shemang *et al.,* (2011) indicated that the area is susceptible to acid mine drainage as indicated by the change in discoloration around the area (Chapter 1, Fig 1.18). An even greater risk to the area lurks, as the mine closed in 2016, leaving it with minimal maintenance (http://www.thepatriot.co.bw/analysis-opinions/item/6078-lies-are-at-the-centre-of-bcl-mine-closure.html).

In the present study, the metal extraction of copper is strongly considered as a remedial strategy within the mine closure plan. The Selebi Phikwe mine has an estimated tailing resource of over 100 million tonnes, and almost 300, 000 tonnes of copper and nickel could be recovered. According to preliminary chemical analysis the ore contain 0.19 wt% of copper, 0.21 wt% of Ni which are very comparable to the low-grade ores mined today. The consideration of these resource is an important contributor to the copper inventory considering the increase in demand in metal despite the decline in low grade ores. Additionally, the reprocessing of the mine tailing will be beneficial to reducing the already prevalent environmental impact associated with the mine tailing.

Because of their metal content a process design concept for copper and nickel recovery was suggested as indicated in Fig. 2.2. Instead of carrying out flotation and sending for pyrometallurgical extraction the mine tailing underwent a two-stage flotation and high pressure leaching to establish a metal recovery protocol. The proposed flowsheet was chosen because it is difficult to produce high-quality copper concentrates of Cu>25 % that are required for smelting and refining. Furthermore, there more energy is required to extract the metal in this way. On the other hand, it is very feasible to concentrate the mine tailing to a desirable Cu content to make it economically feasible for high pressure leaching. An initial Cu metal content of >2 wt% is possible to be leached and later sent for solvent extraction and electrowinning.

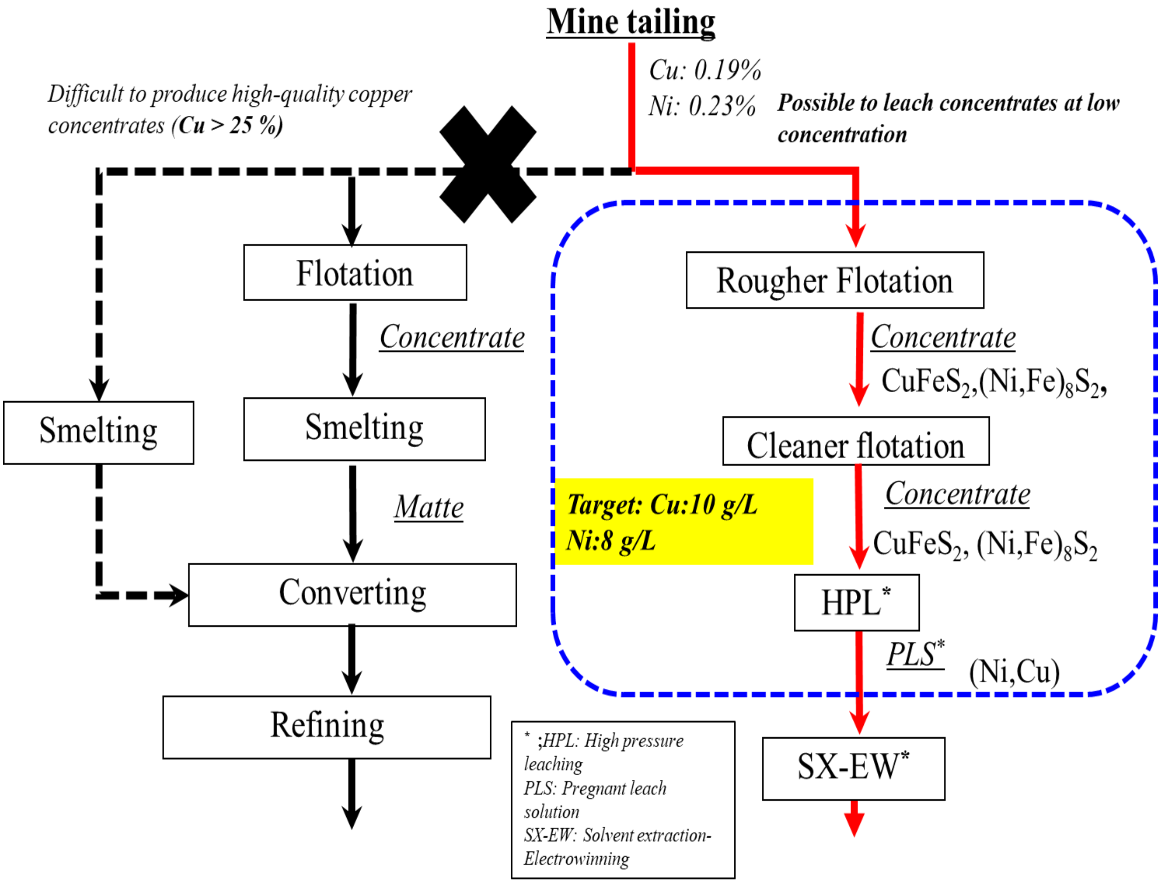


Figure 2. 2. Process design concept for Cu and Ni recovery from BCL mine tailing.

Aims and Objectives

The main objective of this study was to assess an efficient approach for recovery of copper and nickel from the BCL Limited mine tailings of Botswana. For this purpose, influences of parameters in flotation and high-pressure oxidative leaching processes on the recovery of copper and nickel from the mine tailings were discussed. Positive results of the research would help in ascertaining their feasibility for secondary resources.

2.2 Experimental

Sample

Mine tailings sample from BCL mine (Botswana) was used in this study (Fig.2.3). The sample was firstly finely crushed to under 106 µm by ball milling to make an average particle size of 45 µm (D_{50}) which was estimated by a wet type size distribution analyser (Microtrac MT3300II) as shown on Fig.2.4. The chemical composition of the mine tailing sample was determined using X-ray fluorescence (XRF, Rigaku ZSX Primus II) and an inductively coupled plasma optical emission spectrometer (ICP-OES, SII NanoTechnology Inc., Chiba, Japan). The results showed grade value of Cu at 0.19 wt. % and Ni at 0.23 wt. % (Table 2.1).

Figure 2. 3. Photo of original mine tailing as received

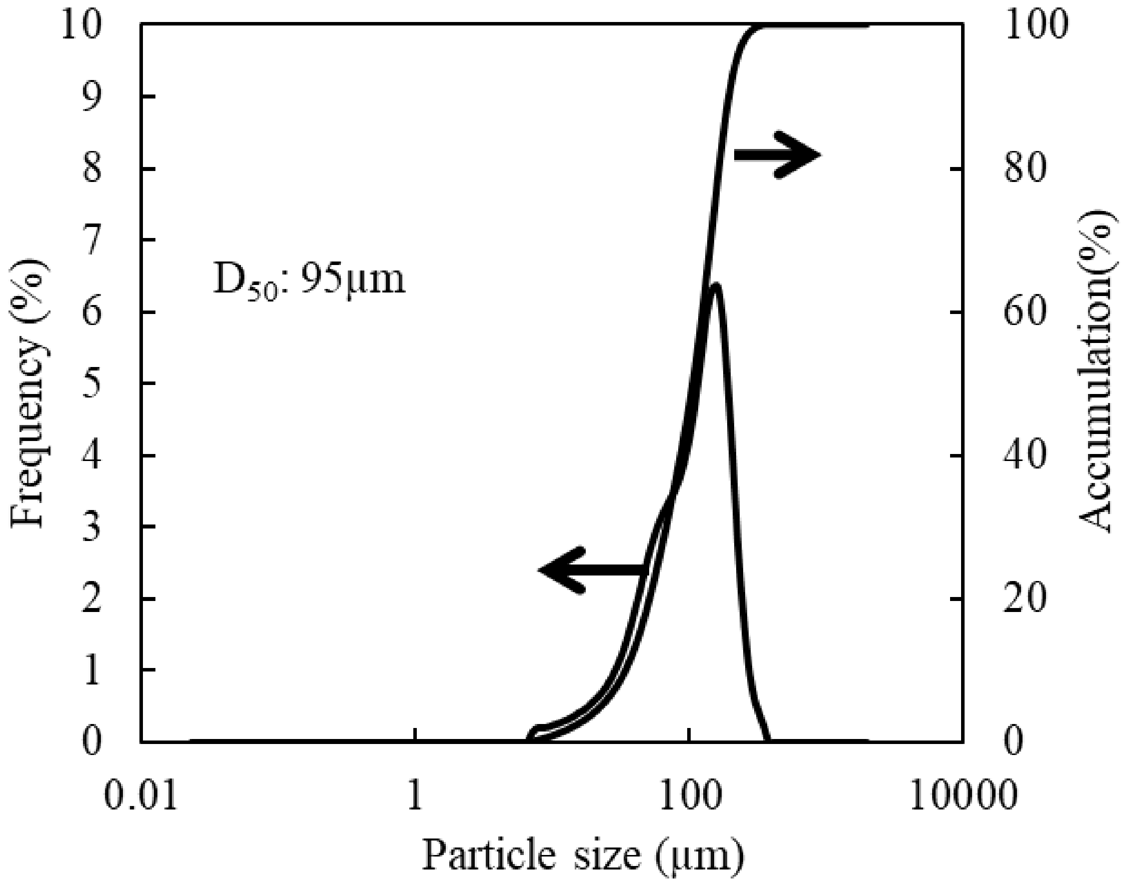


Figure 2. 4. Particle size distribution of mine tailing

Table 2. 1. ICP-OES and XRF analysis of mine tailing

Elements	Cu	Ni	Fe
wt %	0.19	0.23	10.38
Elements	Al	Mg	SiO_2
wt %	1.91	1.32	31.11

The mineralogical characterization was analysed by X-ray diffraction (XRD, Rigaku RINT-2200V) pattern and indicated the composition to be of quartz, kaolinite, pyrite and pyrrhotite as major minerals in the sample (Fig. 2.5).

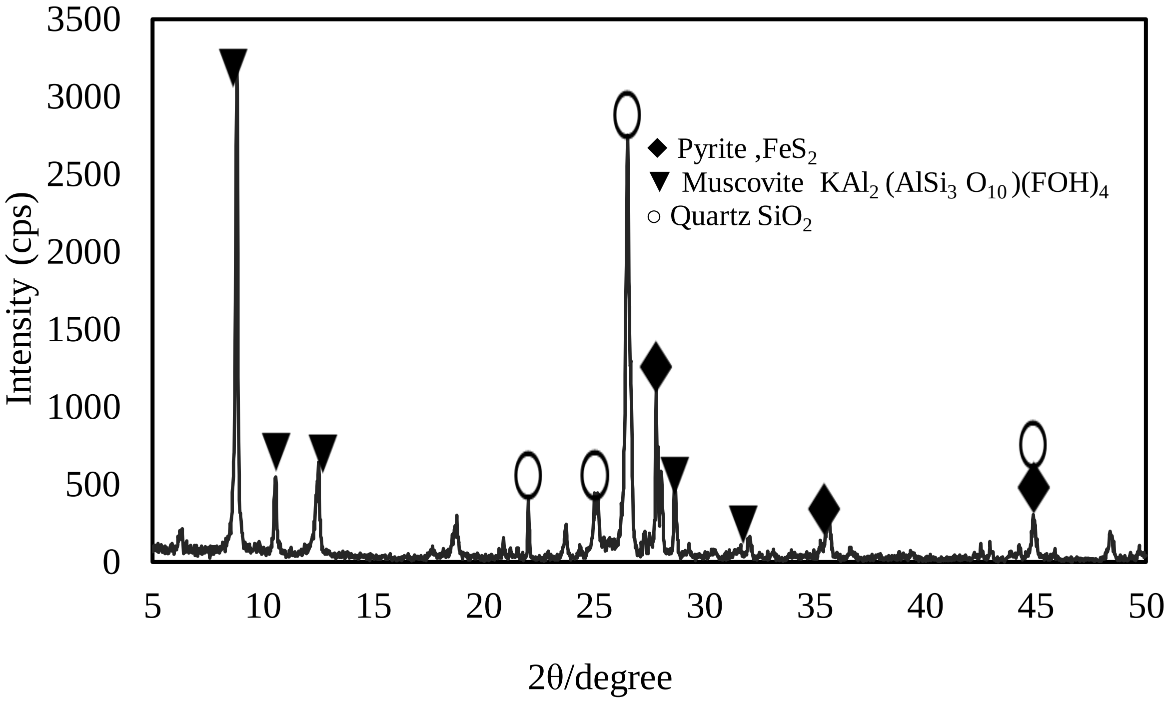


Figure 2. 5. XRD pattern analysis of mine tailing

The presence of copper mineral was confirmed by scanning electron microscope energy dispersive X-ray spectrometry (SEM-EDS). According to the analysis, copper and nickel were in close association with iron and sulphur. The mineral constituents of the sample are given in (Table 2.2).

Table 2. 2. Mineralogical constituents of mine tailing

Mineral	**Chemical Formula**
Pyrite (Py)	FeS_2
Chalcopyrite (Cpx)	$CuFeS_2$
Pyrrhotite (Po)	$Fe_{1-x}S$
Pentlandite (Pn)	$(FeNi)_9S_8$

Chemical Reagents

The chemical reagents used for the processing of mine tailings by flotation and high-pressure leaching are listed in Table. For the flotation process, calcium hydroxide ($Ca\ (OH)_2$), potassium amyl xanthate (PAX, $C_5H11OCSSK$) and Aerofloat 208 (AF 208,) and methyl isobutyl carbinol (MIBC, $C_6H_{14}O$) were used. In the high-pressure leaching process, sulfuric acid (H_2SO_4) was used as a leachate while oxygen was supplied by oxygen (O_2) tank.

Procedure

Flotation of mine tailing

Flotation experiment was carried out in a 0.5 L mineral separation flotation machine (MS, 237FL, Mekhanobr-tekhnika Corp.) cell that comprises of two sections (mixing and froth formation) and a tube connected to generator for air supply (Fig. 2.6). A 50g sample was charged into the cell with distilled water to obtain pulp densities of 10%. The slurry pH was kept at a natural pH of 4 and either adjusted by adding calcium hydroxide ($Ca\ (OH)_2$). Collectors used were potassium amyl xanthate (PAX, $C_5H11OCSSK$) and Aerofloat 208 (AF 208,) while frother used was methyl isobutyl carbinol (MIBC, $C_6H_{14}O$). In all flotation test MIBC addition was fixed at 200 g/t while PAX was carried. Air injection and slurry stirring speed were kept constant at 40 unit and 1600 rpm respectively.

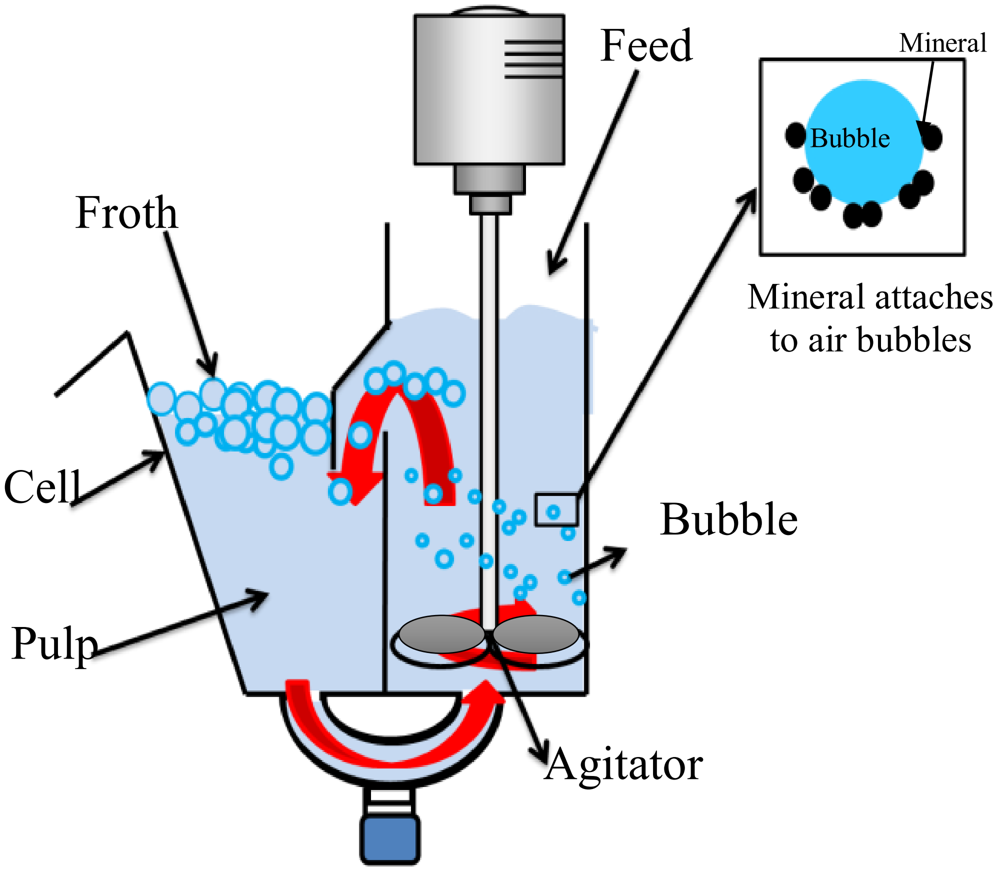


Figure 2. 6. Illustration of the 0.50L laboratory MS flotation machine used in the study.

A general process for Cu and Ni recovery was performed in two stage flotation shown in (Fig. 2.7). The effects of critical parameters which are particle size, different collector, and collector dosage, pulp density, pH value and sulfurizing agent were examined at different conditions (Table 2.3). Attrition ball milling was carried out for 30minutes. As a result of optimum flotation conditions, concentrate obtained was used further for leaching experiment.

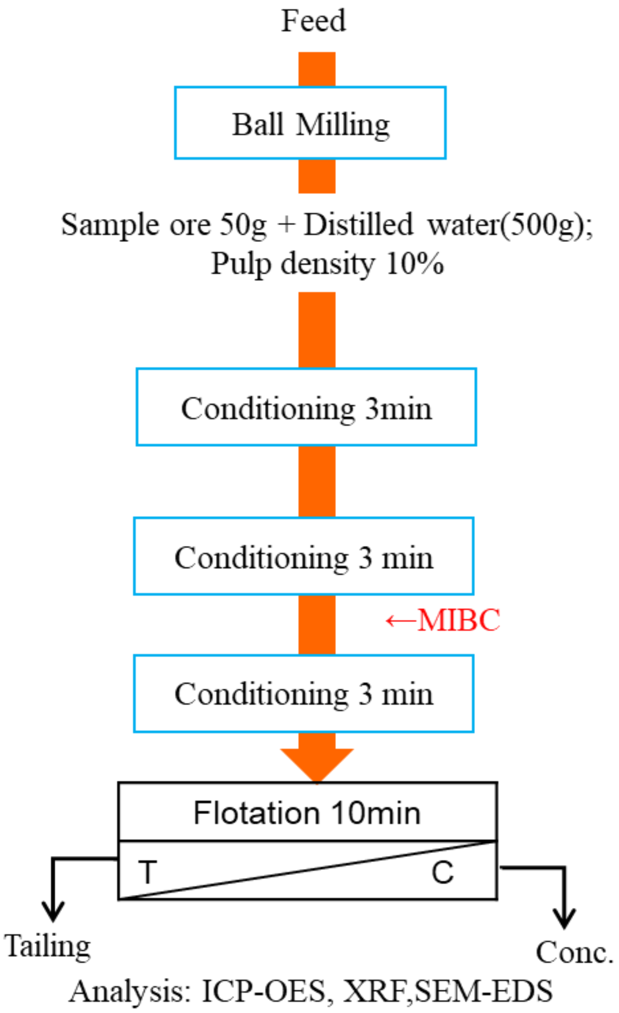


Figure 2. 7. Flotation procedure for mine tailing

Table 2. 3. Experimental conditions for flotation process

Parameter	**Condition**
Flotation Time	10 min
Pulp density	10%
pH	1-12
Collector(PAX,$C_5H_{11}OCSSK$ and Aerofloat 208)	0-100 g/t-ore
Frother(MIBC)	200g/t
Particle size (µm)	<53,+53-100,+100-180,+180-250,+250 µm
Flotation equipment	500 ml ML cell
Stirring speed	1800 rpm

High-pressure leaching of mine tailing concentrates

Dissolution (leaching) of Cu and Ni was carried in an autoclave machine with a reaction container placed inside (Fig. 2.8). The leaching media used was sulfuric acid (H_2SO_4) with varying concentration from 0-3 mol dm^{-3}. Sample weight for all leaching experiments was kept at 1:10 (solid: liquid) ratio and leaching was conducted at leaching temperatures; 160-200 ^{0}C for different periods ranging from 30 to 150 minutes. The reaction container was placed inside the autoclave and stirring was set to 700 rpm. Pressure in the system was done between 0.5-2.5 MPa.

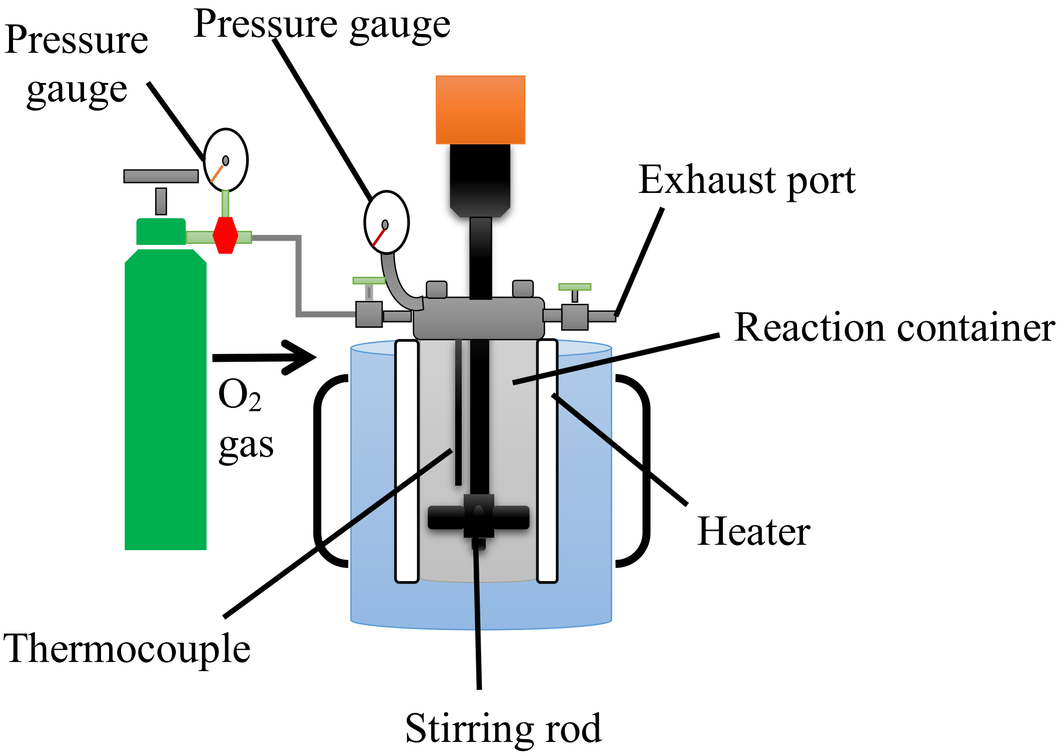
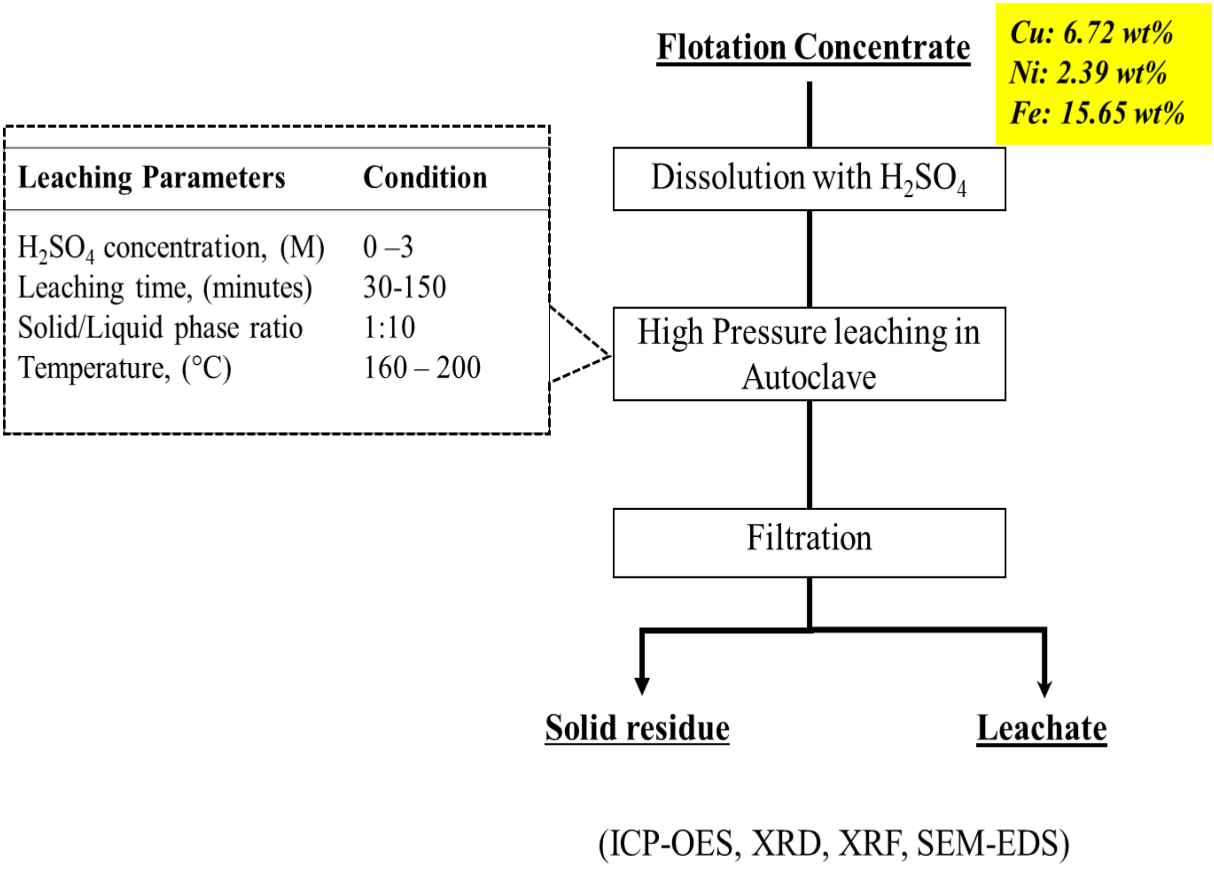


Figure 2. 8. Illustration of the autoclave machine used in the study.

The procedure for leaching involved placing the required amount of sample in a Teflon vessel, recording the pH, ORP and temperature and placing into the autoclave

(Fig. 2.9). The temperature was set to the required set point and when it reached the point, leaching was started by first allowing the required amount of oxygen required for leaching. After leaching, the gas supply was switched off while autoclave equipment was allowed to cool. The pH, ORP and temperature of leachate were recorded before filtering the solid residue from leachate solution. The solid residue was placed in a 60 ^{0}C oven overnight to dry.



Leaching Parameters	**Condition**
H_2SO_4 concentration, (M)	0 –3
Leaching time, (minutes)	30-150
Solid/Liquid phase ratio	1:10
Temperature, (°C)	160 – 200

Figure 2. 9. Leaching procedure for high pressure leaching.

Analysis of process products

The mineralogical characterization of all solid samples was performed by using X-ray diffraction (XRD) analysis equipment (Rigaku Co., Japan), X-ray fluorescence (XRF) analyser and Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS). Chemical composition for all liquids and solids samples dissolved in aqua-regia were analysed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, SPS-5500, Seiko Instrument Inc.).

In this chapter the recovery (R), yield (Y) and enrichment ratio (ER) of each metal from mine tailing was calculated as follows **Eqs. 2.1-2.3**:

$$R = \frac{c(f - t)}{f(c - t)} \times 100 \tag{2.1}$$

$$Y = \frac{C}{F} \times 100 \tag{2.2}$$

$$ER = \frac{c}{f} \tag{2.3}$$

Where R is recovery, Y is yield and ER is enrichment of each metal. C and F are the weight of the concentrates and feed, c, t and f are the metal grades in the concentrates, tailing and feed respectively.

The leaching efficiency (y) is used to evaluate the leaching results of mine tailing concentrates, as expressed in **Equation 2.4** as follows:

$$y = \frac{Q \times a - m \times \beta}{Q \times a} \times 100 \tag{2.4}$$

Where Q is the weight of the concentrate, m is the weight of the leaching residue, a is the metal grade of the concentrate, and β is the metal grade of the leaching residue.

2.3 Results and Discussion

2.3.1 Flotation

Effect of particle size

A series of floatation experiments were performed at different particle size for the bulk concentration of Cu and Ni. The particle size ranges investigated were < 53 µm to +250 µm. The other conditions were fixed as follows: slurry pH 4-5, flotation time 10 minutes, MIBC 200 g/t, PAX 50 g/t and pulp density 10%. It is clear that the upgrading of concentrates is almost the same in the particle size range of +100 to +250 µm at 1.44-1.43 wt%. A general upgrade is seen with an increase in particle size (Fig. 2.10).

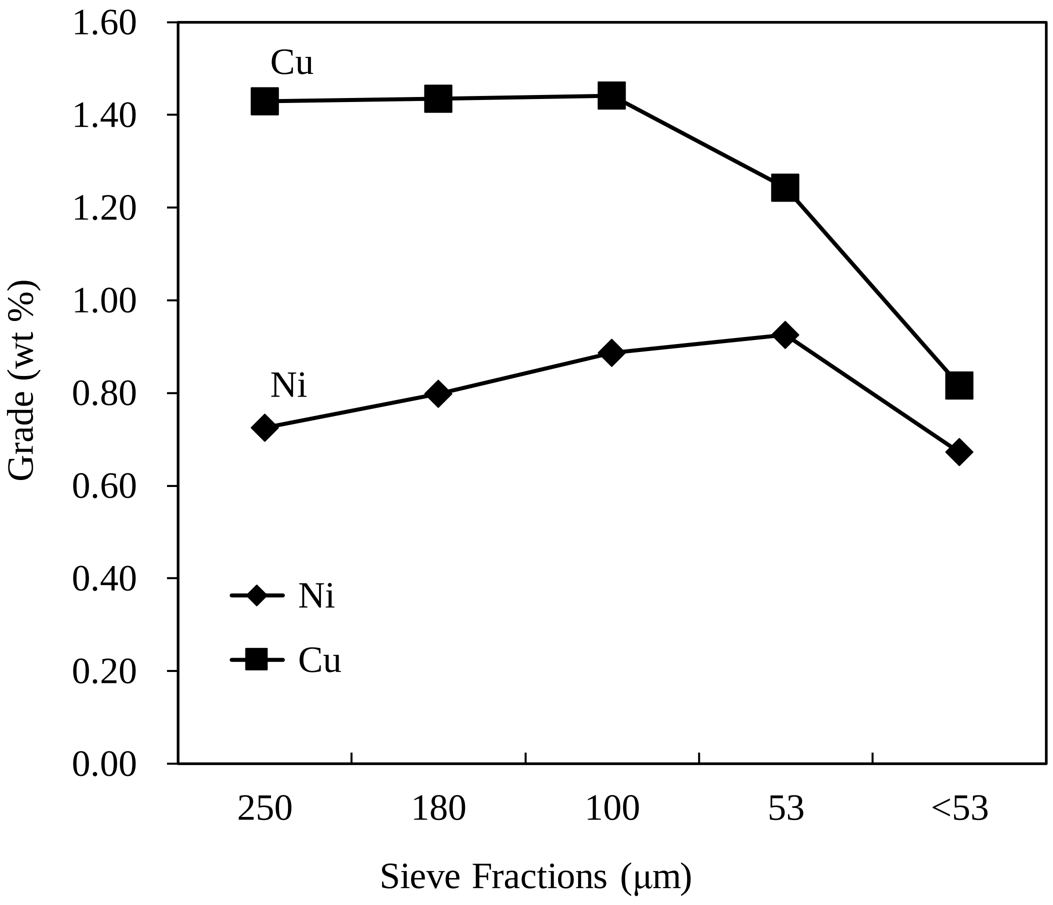


Figure 2. 10. Effect of particle size on the flotation upgrade of mine tailing.

It is clear that the recovery of Cu is highest above 80% in all size fractions compared to Ni which had a gradual increase in recovery from large particle size to low particle size ranging between 35% to 50 % (Fig. 2.11). A clear difference in the direction of grade and recovery is expected, as the gangue minerals subsequently floated with minerals of interest (chalcopyrite and pentlandite) therefore compromising the quality of the concentrate but increasing recovery.

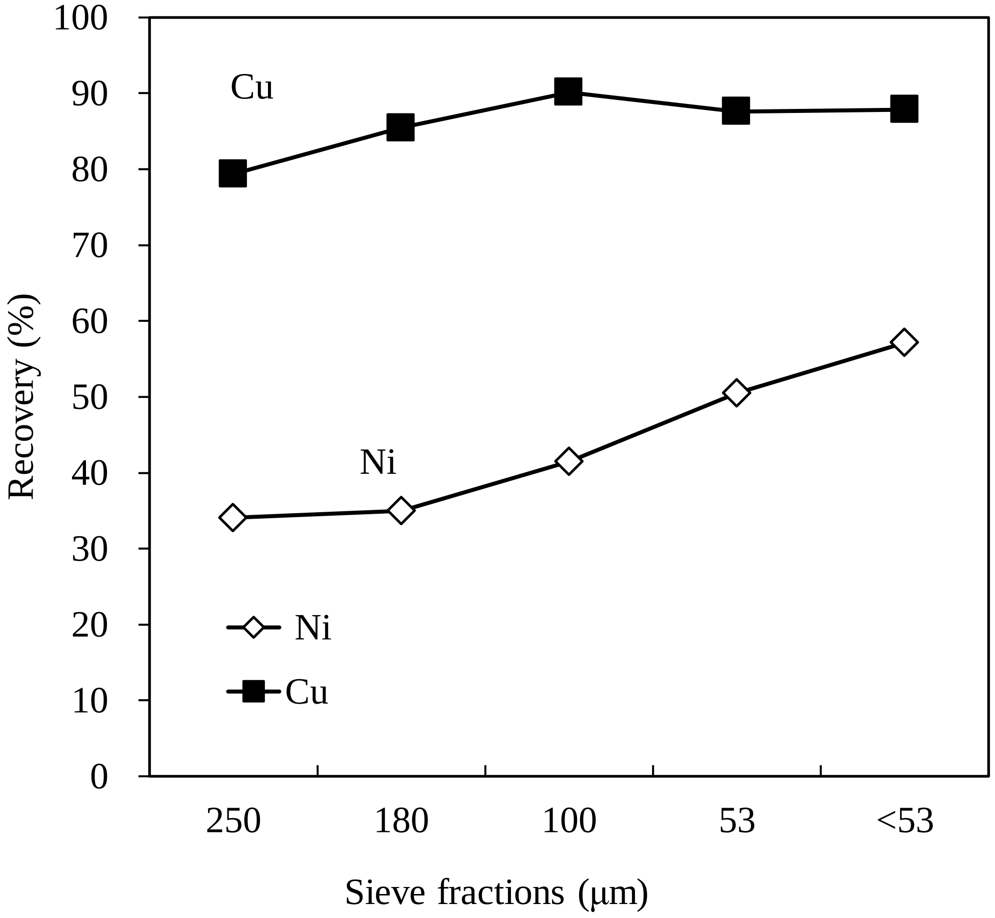


Figure 2. 11. Effect of particle size flotation on the recovery of mine tailing.

It was decided that the particle size fraction between +53 to +250 µm would be mixed and ball milled to an average D_{50} particle size of 95 μm.

Effect of PAX on floatability of Cu and Ni bearing minerals

The influence of increasing concentrations of PAX from 0 g/t to 100 g/t was investigated in the flotation of Cu and Ni from mine tailing. MIBC dosage was kept constant at 200 g/t, slurry pH at 4 and pulp density at 10 %. The results obtained for grade and recovery are summarised in Fig. 2.12.

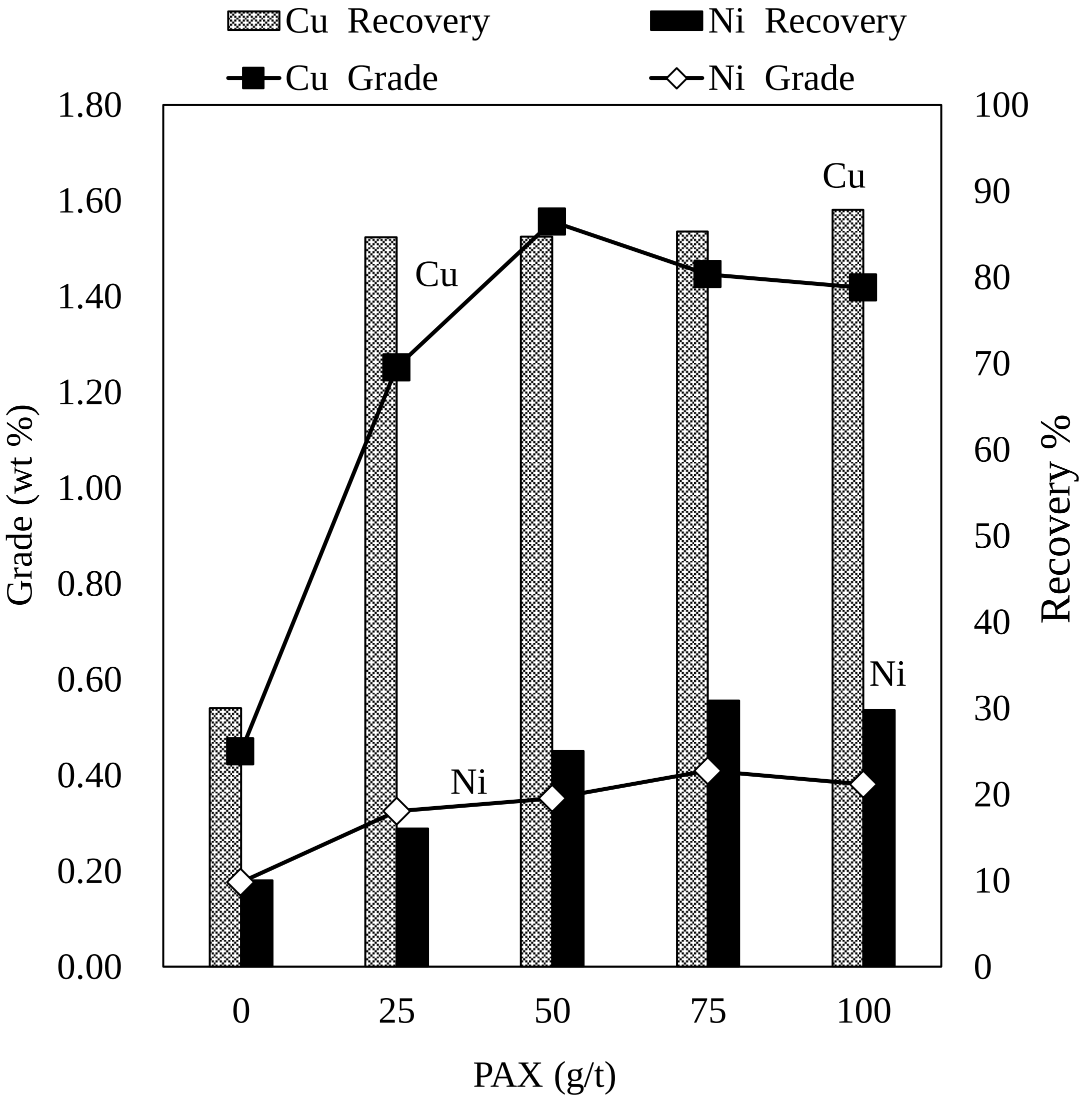


Figure 2. 12. Effect of PAX flotation on the recovery of mine tailing.

Copper showed the most interesting results as its grade reached 1.60 wt. % and recoveries about 80 %. Nickel showed the lowest grade and recoveries, respectively grades for Ni gradually increased with increase in PAX and reached maximum at 0.78 wt. % and recoveries were below 50 %. Recovered concentrates showed increased amount of pyrite (FeS_2) and pyrrhotite (Fe_{1-x} S) indicating association with Cu and Ni. Generally, FeS_2 and $Fe_{1-x}S$ recoveries are low and independent of their percentage, however when a collector addition is scaled to the amount of Cu and Ni in the mixture then optimum recoveries could be achieved. The optimum condition for PAX addition was selected as 50 g/t.

Effect of AF208 on floatability of Cu and Ni bearing minerals

Aerofloat 208 as a collector and MIBC as frother was used to investigate its dosage on Cu and Ni recovery and grade. Results from flotation with AF208 concentration ranging from 0 to 100 g/t and MIBC addition fixed at 200 g/t, pulp density at 10 %, slurry pH 4-5 and time of 10 minutes are presented in Fig. 2.13. The grades of Cu showed no improvement above 1.86 wt. % and those for Ni were below 0.48 wt. %. Copper recovery reported were above 70 % for all AF208 concentrations range however Ni recoveries were below 22.43 %. AF208 addition does not favour Ni recovery in bulk flotation with Cu.

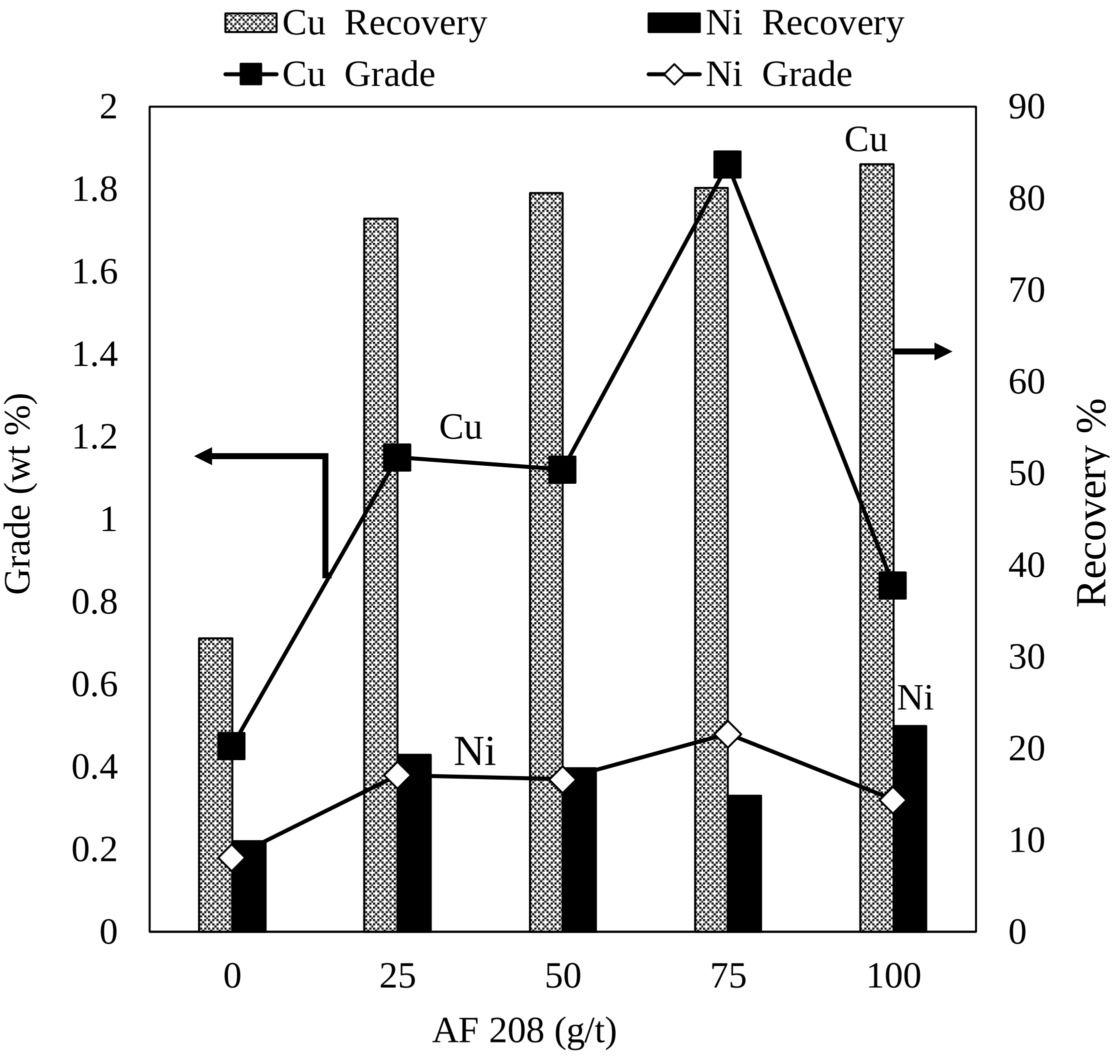


Figure 2. 13. Effect of AF208 flotation on the recovery of mine tailing.

Comparison of collectors

The bulk flotation for upgrading and recovery of Cu and Ni from mine tailing was effectively achieved by addition of PAX. Although recovery of Ni is lower, it was most appropriate that with PAX, addition better results are obtained. AF208 showed no favourable outcomes for recovery and upgrading of Ni. As such PAX addition was opted for the optimum bulk flotation for Cu and Ni.

Effect of pH on flotation

Maintaining PAX and MIBC concentrations at 50g/t and 200 g/t respectively, flotation behaviours of Cu and Ni were investigated at varying pH ranging from 4-12 and the results are presented in Fig. 2.14 and 2.15. Pulp density was maintained at 10 % and flotation was performed for 10 min. The slurry pH was adjusted by adding $Ca(OH)_2$. The grades of both Cu and Ni showed a gradual decrease with an increased pH value. Their corresponding recoveries also showed the same behaviour. Naturally Fe-bearing minerals such as pyrite are depressed at more alkaline conditions while chalcopyrite is rarely not affected by pH value. But, the association between the Fe-bearing minerals with Cu and Ni shows a decline as pyrite. It was concluded that optimum slurry pH was better kept natural at 4.

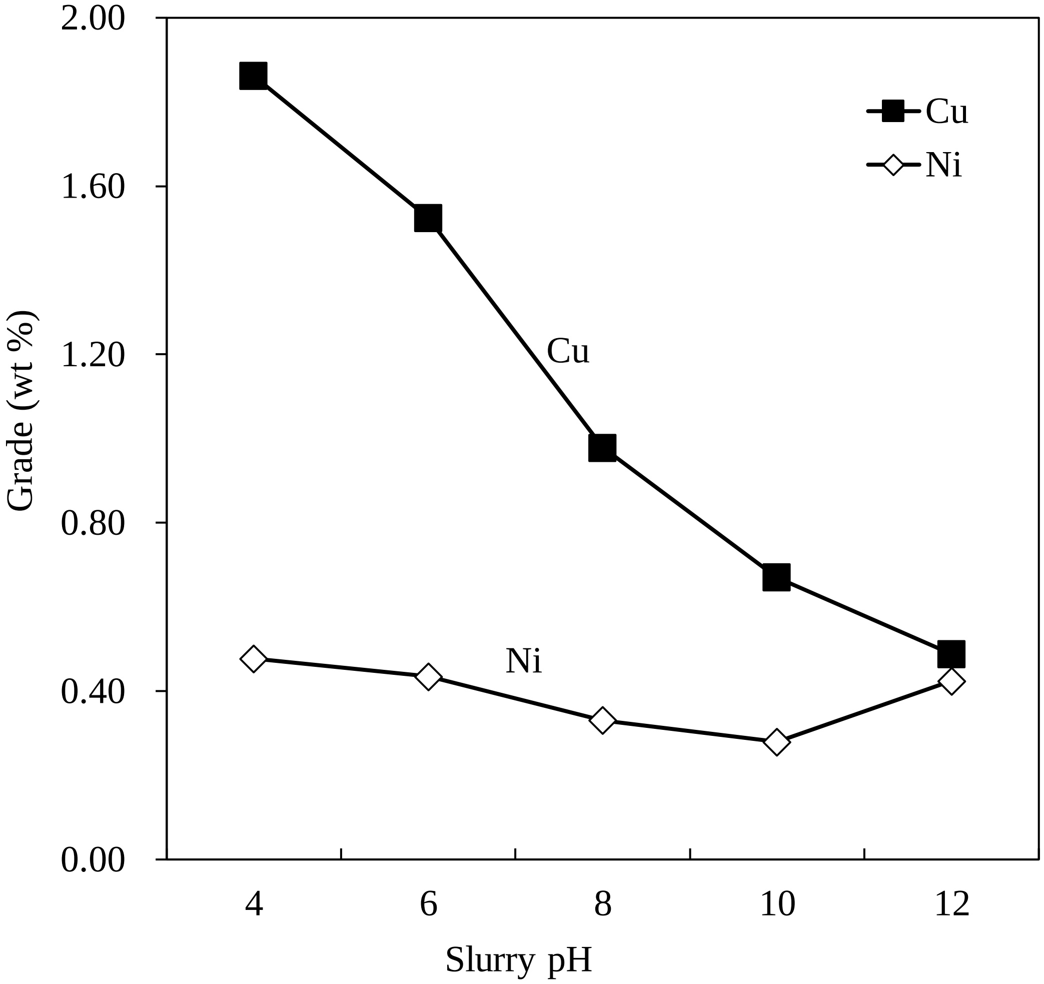


Figure 2. 14. Effect of slurry pH flotation on the grade of mine tailing.

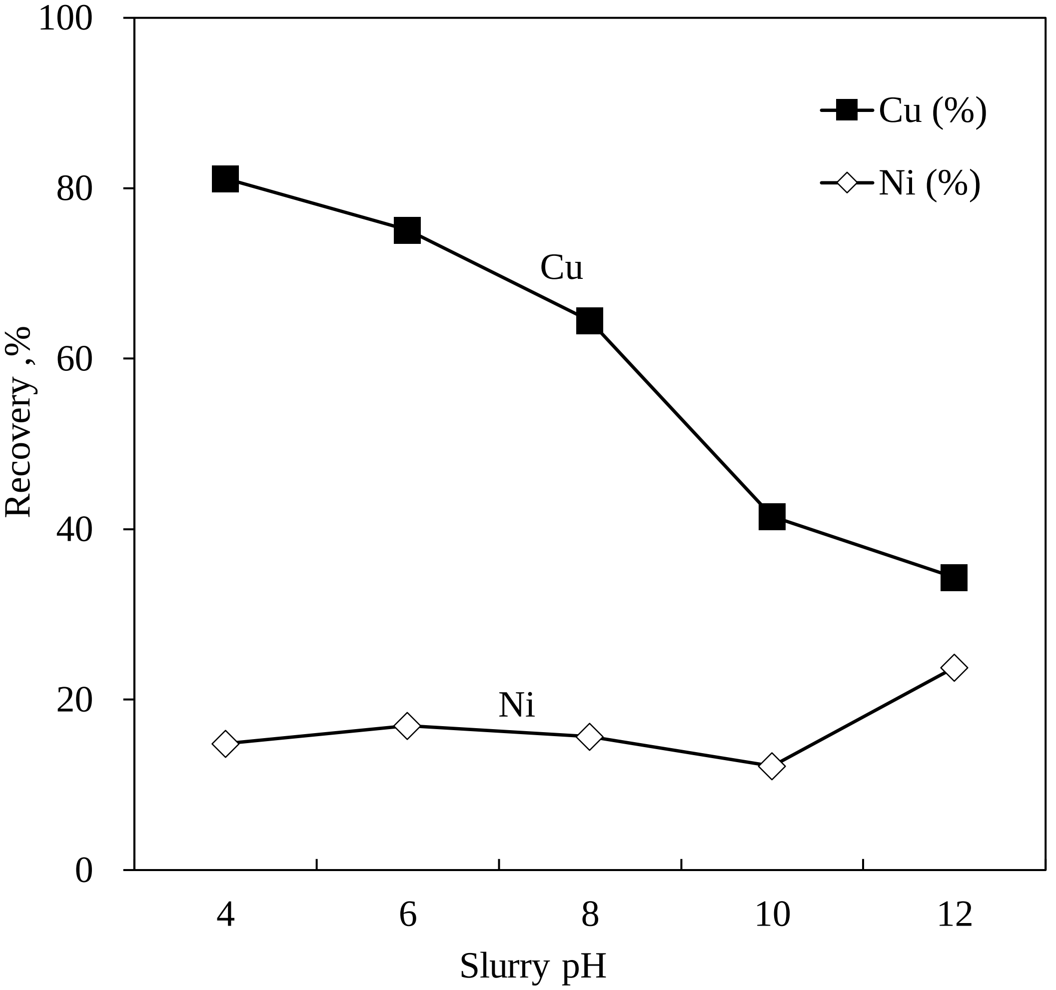


Figure 2. 15. Effect of slurry pH flotation on the recovery of mine tailing.

Optimization conditions for the first stage flotation

Upgrading and recovery of Cu and Ni from the mine tailing achieved efficient value by flotation with addition of PAX collector at 50 g/t. The slurry pulp density was 10% for flotation of Cu and Ni, a particle size distribution at D_{50}: 180μm is most ideal and MIBC was kept constant at 200 g/t. The concentrate obtained at these optimized conditions was then taken for second stage flotation.

Second stage flotation

A sequential flotation for the recovery of Cu and Ni from the first flotation concentration was performed using the optimized obtained from the first stage of flotation process. A mineralogical characterization was done on the final tailing and Ni minerals were found to present indicating Fig. 2.16.

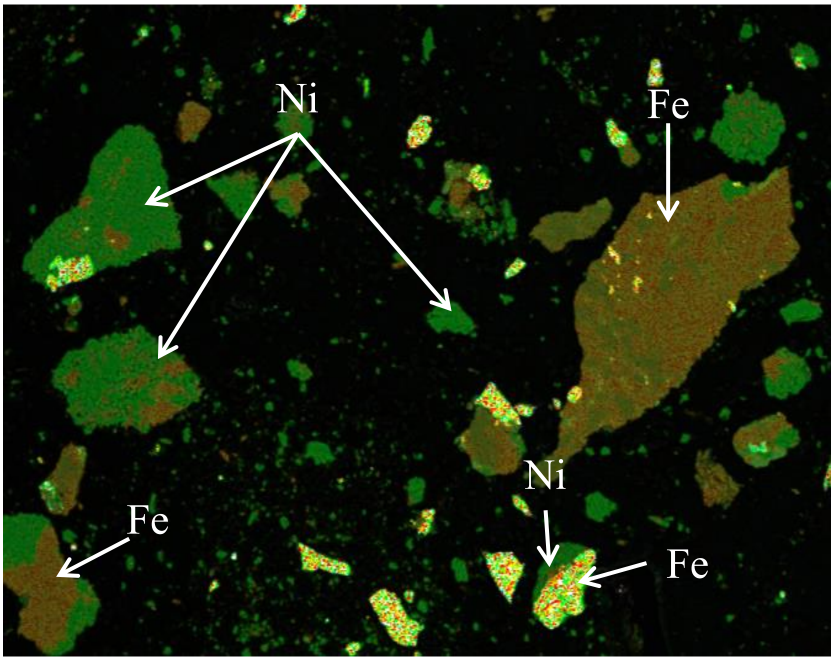
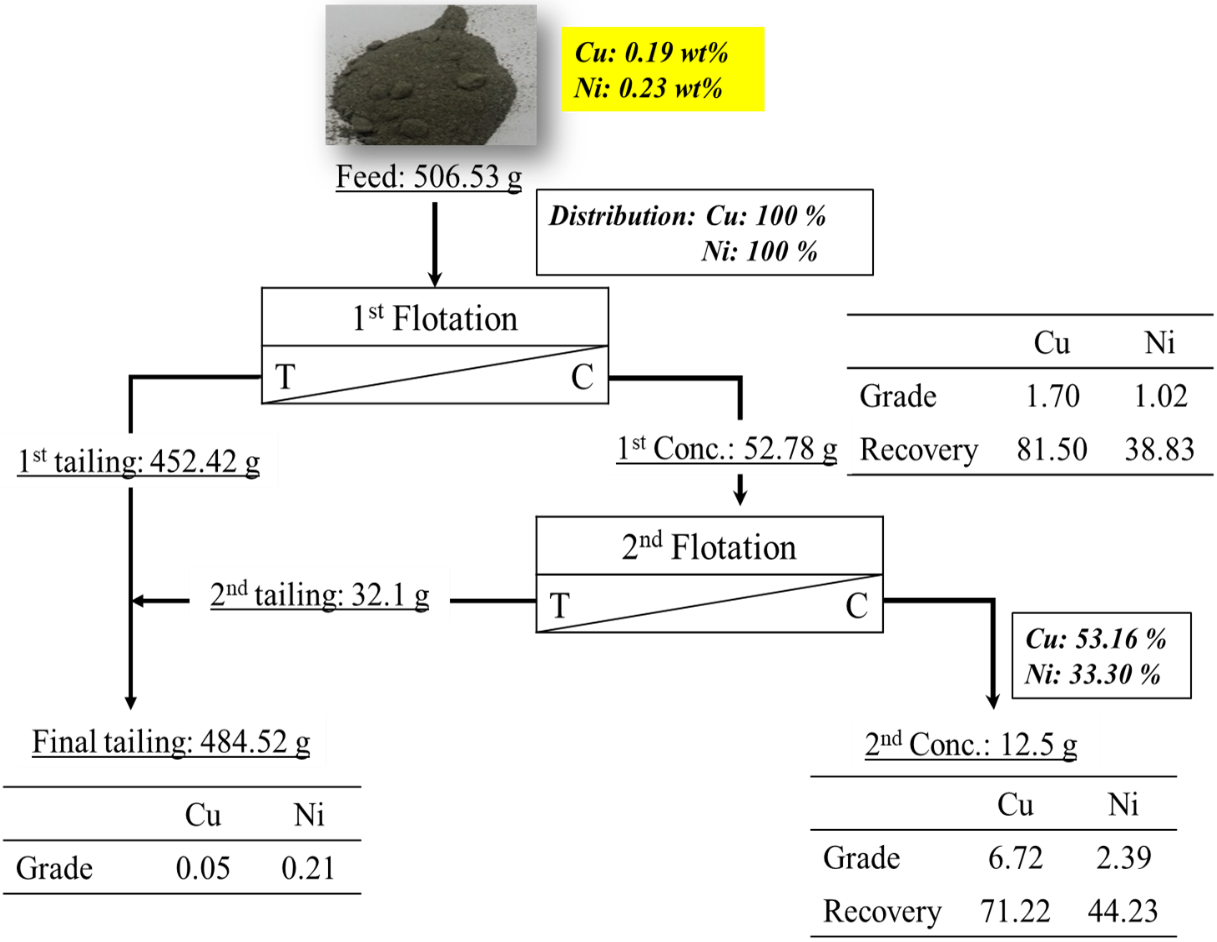


Figure 2. 16. SEM-EDS analysis of final tailing indicating presence of Ni.

General flow sheet

A process flow sheet based on the experimental procedure and results obtained in the flotation experiment is given in Fig.2.17. The process mainly consists of two-stage flotation designed to obtain optimum parameters for Cu and Ni recovery and upgrading. The second stage was to further upgrade and remove gangue minerals in the concentrate. An upgrade of 6.72 wt. % for Cu and 2.39 wt. % for Ni is achieved. Reduction of Fe-gangue minerals associated with Cu and Ni in the concentrate was achieved and were viable for high pressure leaching.



	Cu	Ni
Grade	1.70	1.02
Recovery	81.50	38.83

	Cu	Ni
Grade	0.05	0.21

	Cu	Ni
Grade	6.72	2.39
Recovery	71.22	44.23

Figure 2. 17. Summarized two-stage flotation process for copper and nickel recovery from mine tailing.

2.3.2 High pressure leaching

Effect of sulphuric acid (H_2SO_4)

Leaching experiments were carried out to investigate the dissolution of metals from the flotation concentrate by varying concentrations of sulphuric acid. A 5g sample (concentrate) introduced into the reaction vessel containing a 50 ml of H_2SO_4 with concentration ranging from 0 to 2.5 mol dm^{-3} and set up in an autoclave. The pH, ORP and temperatures were measured and agitation speed, of 200 rpm temperature and leaching times set at 170 ^{0}C for 1 hour respectively. The results obtained are presented in Figure 2.18. The dissolution of Cu into 1 mol dm^{-3} sulphuric acid solution was mostly 70% and gradually decreased with increasing the H_2SO_4 concentration.

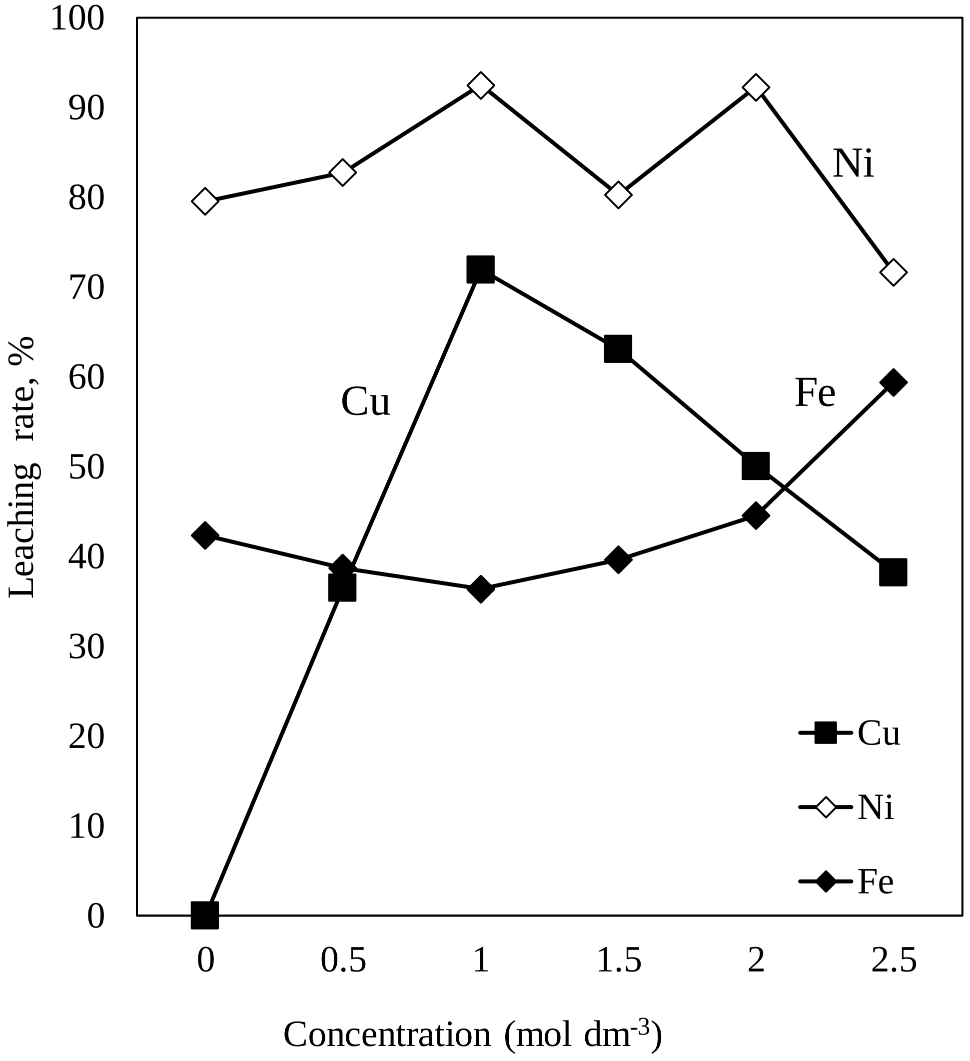


Figure 2. 18. Effect of sulfuric acid on leaching of Cu, Ni and Fe.

Effect of temperature on Cu and Ni leaching

Leaching of the flotation tailing concentrate was carried out at temperature range between 160-200 ^{0}C in 1 mol dm^{-3} H_2SO_4 concentration, 1.5 MPa pressure and S/L ratio of 1:10. The results are presented in Fig 2.19. Evidently copper and iron dissolution increases with temperature.

The data in Fig.2.19 show that leaching with sulphuric acid gave 20% higher copper dissolution values at 170 ^{0}C. It was also observed that nickel dissolution was slightly higher 96.3 %. It is also noticeable in Fig 2.19, that the dissolution of iron was low. Temperature is a crucial parameter in the leaching of chalcopyrite. It allows for control of products such as elemental sulphur and acid production. It can be concluded that, at medium temperature (170 ^{0}C) some of the iron was precipitated and consequently some of the sulphur was converted to elemental sulphur (S^0) Fig 2.20.

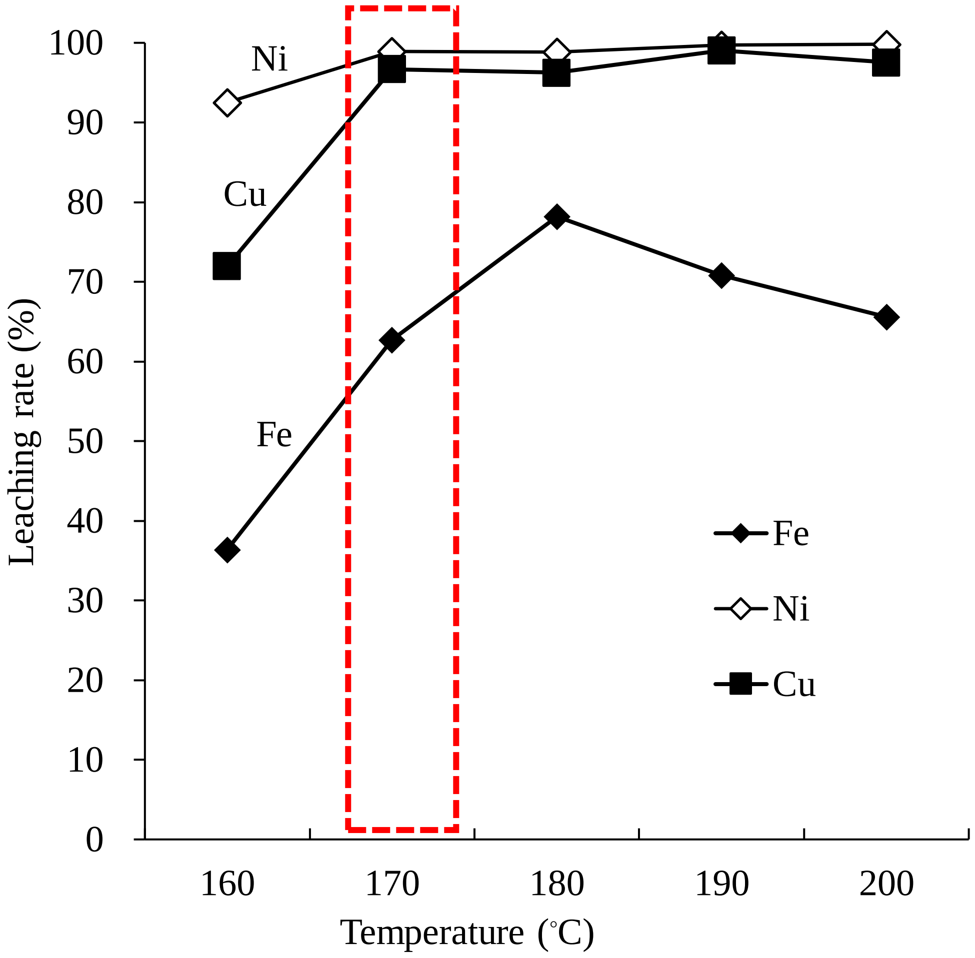


Figure 2. 19. Effect of sulfuric acid concentration on leaching of Cu, Fe and Ni.

The results obtained from XRD analysis showed that the sulphide in Cu-Ni ore may take reactions as follows:

$$2CuFeS_2 + H_2SO_4 + 8.5\ O_2 \rightarrow 2CuSO_4 + Fe(SO_4)_3 + H_2O \qquad (2.5)$$

$$2CuFeS_2 + 16\ Fe(SO_4)_3 + 16H_2O \rightarrow 2CuSO_4 + 34FeSO_4 + 16\ H_2SO_4 \qquad (2.6)$$

$$2FeSO_4 + 16\ H_2SO_4 + 0.5\ O_2 \rightarrow 2CuSO_4 + H_2O + Fe_2(SO_4)_3 \qquad (2.7)$$

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow 3\,H_2SO_4 + \; + Fe_2O_3 \qquad (2.8)$$

$$2FeS_2 + H_2O + \frac{7}{2}O_2 \rightarrow 2FeSO_4 + + H_2SO_4 + S^0 \qquad (2.9)$$

$$2FeS_2 + 2H_2O \rightarrow Fe_2O_3 + S^0 \qquad (2.10)$$

The chemical reaction in Eq. 2.5-2.8 are the most significant in maintaining acid supply and increased dissolution of Cu into sulphate solution. The observation on the solid residue indicated that ferrous sulphate converted to ferric sulphate with increased temperature under oxidation in the acidic solution. It was also observed that pyrite oxidation resulted in the formation of elemental sulphur according to Eq. 2.9-2.10 the elemental sulphur is stable at temperature above 150 ^{0}C in acid solution under an oxygen pressure.

(B)

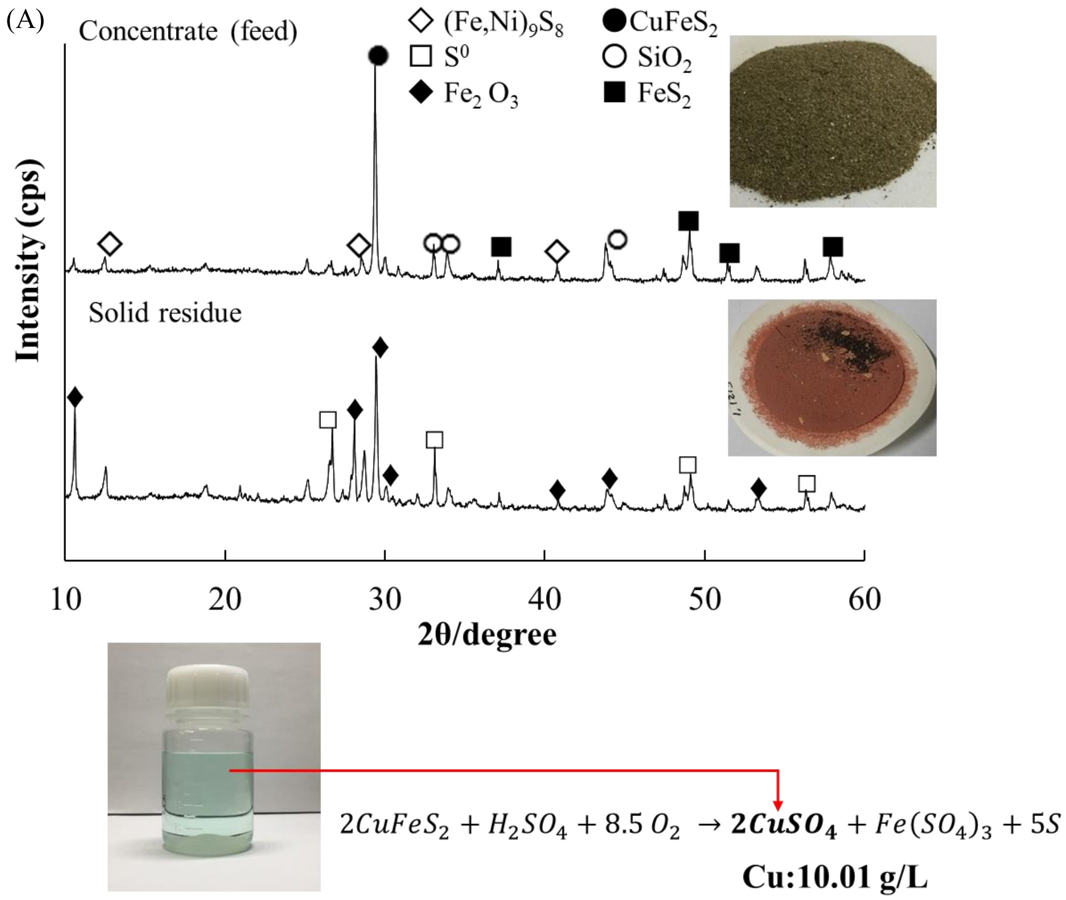


Figure 2. 20. XRD pattern (A) and PLS solution (B) from leaching of concentrates of mine tailing.

Effect of time on Cu and Ni leaching

Leaching experiments for dissolution of Cu and Ni from the mine tailing concentrate were conducted at varying time changing from 30 to 150 minutes. Other conditions were kept constant at 1 M concentration of H_2SO_4, solid to liquid (S: L) phase ratio of 1:10, agitation speed of 200 rpm and temperature at 170 ^{0}C. The results showed that extending the time up to 60 minutes has a significant on the dissolution of Cu and Ni and the increase in leaching time has no further effect (Figure 2.21).

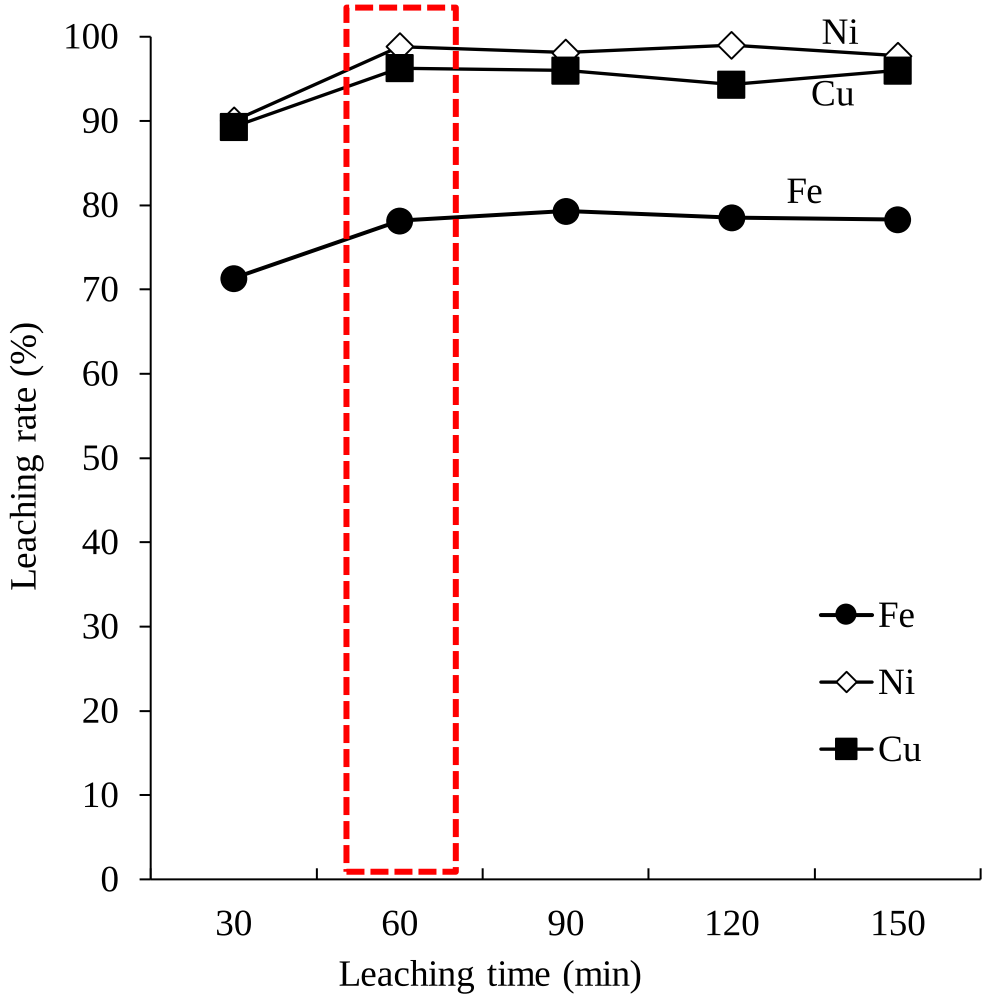
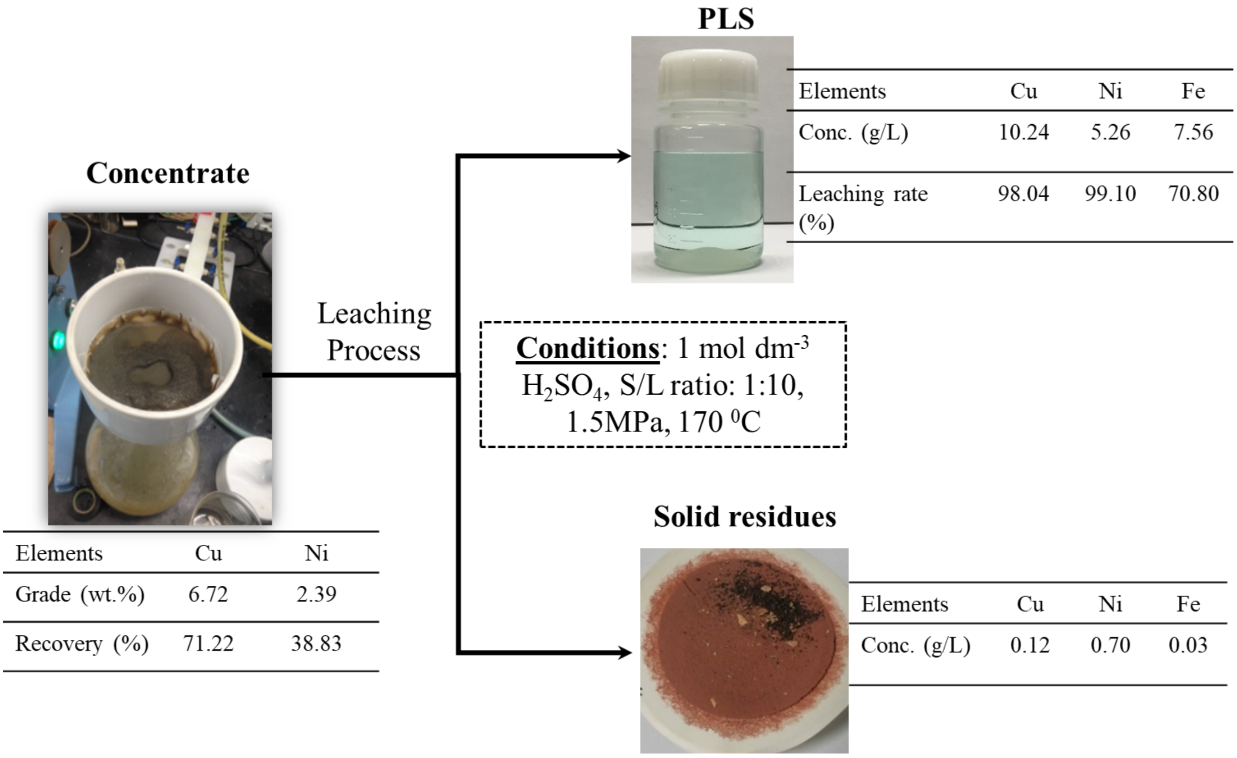


Figure 2. 21. Effect of leaching time on leaching of Cu, Fe and Ni.

Characterization of solid residue after leaching

The solid residues obtained from leaching experiments under optimum conditions were analysed by XRF, XRD and ICP-OES. The leaching experiments under optimum conditions are shown as indicated in (Figure 2.22). XRD pattern of the residue indicate that there was a complete dissolving of Cu and Ni into the leachate and formation of hematite in the system resulted as hydrolysis of Fe (Figure 2.23). Despite these observations some Fe still dissolved in the leached and its concentration higher than the Ni (Figure 2.19). Therefore, it is important that further separation method be considered for separating and obtaining pure metals in future.



Conditions: 1 mol dm^{-3} H_2SO_4, S/L ratio: 1:10, 1.5MPa, 170 ^{0}C

Elements	Cu	Ni
Grade (wt.%)	6.72	2.39
Recovery (%)	71.22	38.83

Elements	Cu	Ni	Fe
Conc. (g/L)	10.24	5.26	7.56
Leaching rate (%)	98.04	99.10	70.80

Elements	Cu	Ni	Fe
Conc. (g/L)	0.12	0.70	0.03

Figure 2. 22. High pressure leaching for concentrates from mine tailing flotation.

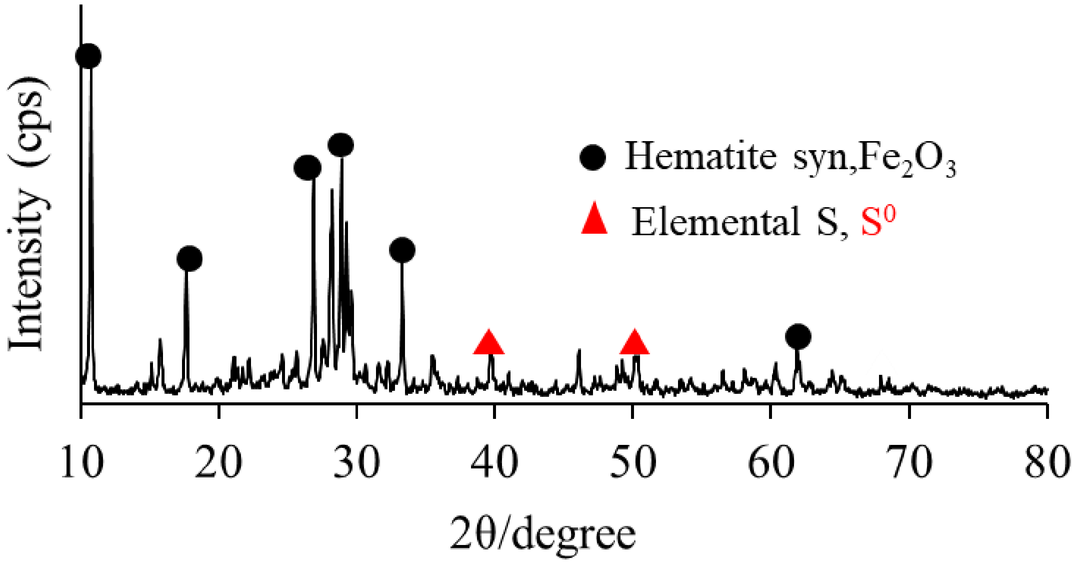
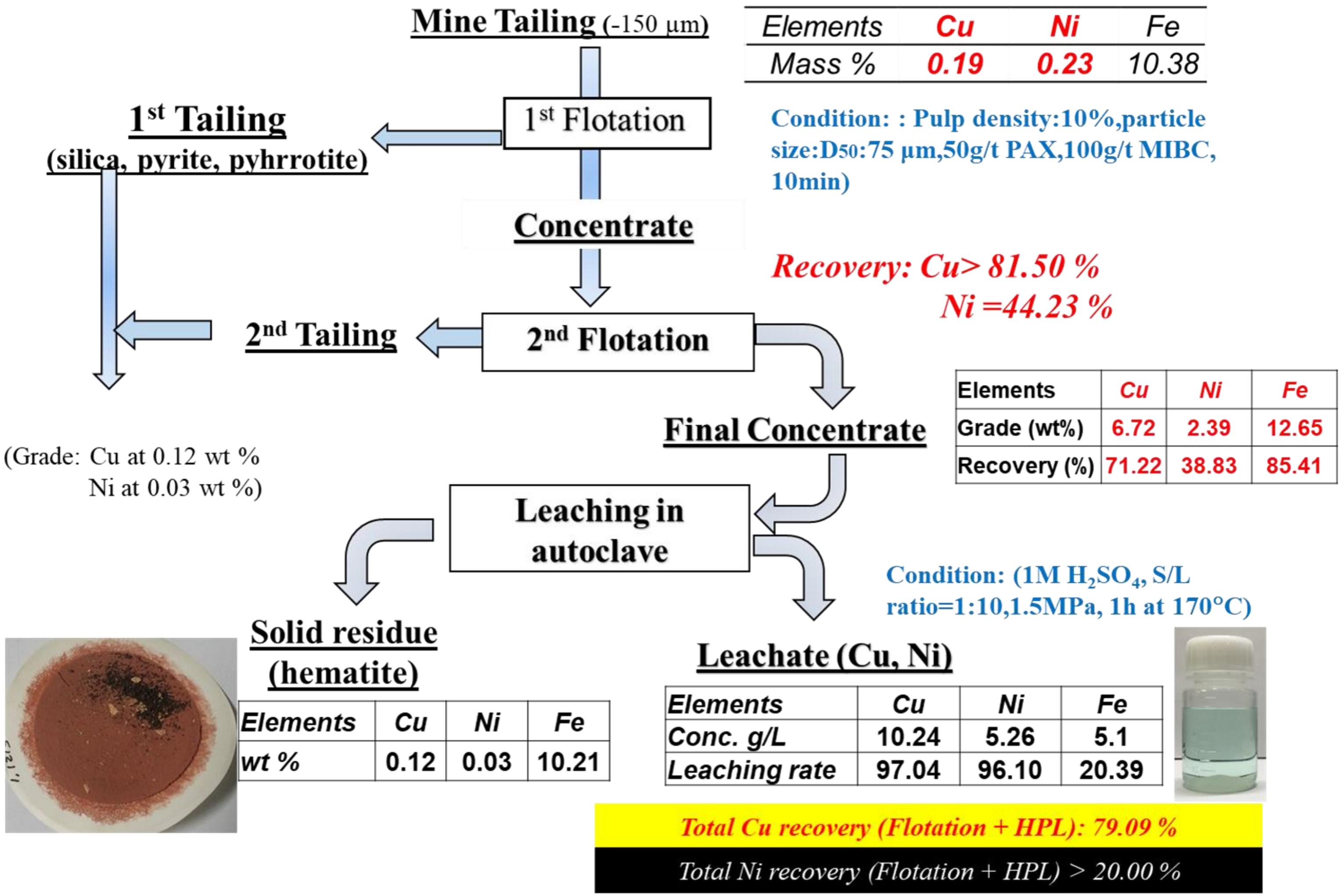


Figure 2. 23. XRD pattern for the solid residue obtained at optimized leaching condition of 1 mol dm^{-3} H_2SO_4, solid-liquid ratio (S: L) 1:10, temperature 180 ^{0}C, stirring speed 200 rpm.

Process evaluation

The main objective in this study was to investigate a process or combination of flotation and high-pressure leaching (HPL) process to improve the grade and recovery of Cu and Ni in the mine tailings. A process flow sheet based on the experimental procedure and results obtained from this work is shown in Figure 2.24. The process mainly consists of sequential first/two stage flotation and HPL designed to remove gangue minerals and upgrade Cu and Ni recovery. The second stage was to upgrade the grade of the Cu and Ni concentrate with optimized conditions obtained from 1st flotation experiments. Cu and Ni in the concentrate were upgraded to 6.72 wt. % and 2.39 wt. % respectively and the concentrate underwent high pressure leaching as shown in the flowsheet (Figure 2.24). Under high pressure leaching high dissolution of Cu and Ni were achieved at 98.04 % and 99.10 % respectively. Their concentrations in the leachate were 10.24 g/L for Cu and 5.26 g/L for Ni. However, the leachate contained a significant amount of Fe (7.56 g/L) and its leaching rate was 70.8 %. Some of the Fe however hydrolysed to hematite in the solid residue obtained.



Elements	Cu	Ni	Fe
Mass %	0.19	0.23	10.38

Condition: : Pulp density:10%,particle size:D50:75 µm,50g/t PAX,100g/t MIBC, 10min)

Recovery: Cu> 81.50 %
Ni =44.23 %

Elements	Cu	Ni	Fe
Grade (wt%)	6.72	2.39	12.65
Recovery (%)	71.22	38.83	85.41

(Grade: Cu at 0.12 wt %
Ni at 0.03 wt %)

Condition: (1M H_2SO_4, S/L ratio=1:10,1.5MPa, 1h at 170°C)

Elements	Cu	Ni	Fe
wt %	0.12	0.03	10.21

Elements	Cu	Ni	Fe
Conc. g/L	10.24	5.26	5.1
Leaching rate	97.04	96.10	20.39

Total Cu recovery (Flotation + HPL): 79.09 %

Total Ni recovery (Flotation + HPL) > 20.00 %

Figure 2. 24. Flowsheet design for the flotation and high pressure leaching of mine tailing.

2.4 Conclusion

A process development modelling study for recovery of copper and nickel from mine tailing by combination of flotation and high-pressure leaching was performed. This study has shown that the flotation stage is efficient in concentrating mine tailing to suitable metal grades that are ideal for further metal extraction such as high-pressure leaching process. The copper bearing minerals of chalcopyrite was able to be concentrated from 0.19 wt% copper to 6.72 wt% that is comparable with the currently mined ores. According to the results, particle size, slurry pH and to a lesser extent the collector used were the most significant parameters in the flotation of mine tailing. The fine particle indicated that, copper mineral upgrading was compromised because of reporting of fines, and at higher slurry pH (<7) iron sulfide minerals associated with copper were depressed during flotation.

Evidently, during leaching, the concentrate obtained from mine tailing flotation gave a 90 % leaching rate with maximum chalcopyrite dissolution. Chalcopyrite is not easily dissolved in aqueous solution, but temperature control showed the most influential parameter during the process. It was observed that at lower temperatures, chalcopyrite leaching was slow and formation of sulfur which was passivating resulted in poor copper concentrations and low recoveries. At high temperature, chalcopyrite leaching was spontaneous, and acid regeneration was possible for continuous leaching chalcopyrite.

The proposed combined process showed that a 79.9 % copper recovery is attainable from the 100 million tonnes of mine tailings in Selebi Phikwe BCL mine. The process is simple and bears potential traits of flotation and high-pressure leaching.

The proposed flowsheet envisaged a suitable solution for acid generation as well as iron hydrolysis which is important in solid residue disposal.

More investigation is required toward the complete development of copper and extraction of accompanying nickel from Selebi Phikwe mine tailing.

REFERENCES

[1] Adiansyah, J. S. *et al.* (2015) 'A framework for a sustainable approach to mine tailings management: Disposal strategies', *Journal of Cleaner Production*. Elsevier Ltd, 108, pp. 1–13. doi: 10.1016/j.jclepro.2015.07.139.

[2] Ahmadi, A. *et al.* (2011) 'Conventional and electrochemical bioleaching of chalcopyrite concentrates by moderately thermophilic bacteria at high pulp density', *Hydrometallurgy*, 106(1–2), pp. 84–92. doi: 10.1016/j.hydromet.2010.12.007.

[3] Ally, M. R. *et al.* (2001) *Economical Recovery of By-products in the Mining Industry*.

[4] Antonijević, M. M. and Bogdanović, G. D. (2004) 'Investigation of the leaching of chalcopyritic ore in acidic solutions', *Hydrometallurgy*, 73(3–4), pp. 245–256. doi: 10.1016/j.hydromet.2003.11.003.

[5] Antonijević, M. M., Janković, Z. D. and Dimitrijević, M. D. (2004) 'Kinetics of chalcopyrite dissolution by hydrogen peroxide in sulphuric acid', *Hydrometallurgy*, 71(3–4), pp. 329–334. doi: 10.1016/S0304-386X(03)00082-3.

[6] Babel, B. *et al.* (2018) 'Reprocessing of a Southern Chilean Zn Tailing by Flotation—A Case Study', *Minerals*, 8(7), p. 295. doi: 10.3390/min8070295.

[7] Bogdanović, G. D. *et al.* (2016) 'Leaching of Low-Grade Copper Ores: a Case Study for " Kraku Bugaresku-Cementacija " Deposits (Eastern Serbia)', *Journal of Mining and Metallurgy*, 52(1), pp. 45–56.

[8] British Geological Survey (2007) ‘Copper’, *mineralsUK*, (June), p. 1. Available at: http://www.bgs.ac.uk/downloads/start.cfm?id=1410.

[9] Cao, J. *et al.* (2016) ‘Colloids and Surfaces A : Physicochemical and Engineering Aspects The role of some special ions in the flotation separation of pentlandite from lizardite’, 490, pp. 173–181.

[10] Chen, T. *et al.* (2014) ‘Hydrometallurgy Pollution control and metal resource recovery for acid mine drainage’, *Hydrometallurgy*, 147–148, pp. 112–119. doi: 10.1016/j.hydromet.2014.04.024.

[11] Conner, K. D. (2013) ‘Pressure Oxidation of Enargite Concentrates Containing Gold and Silver’.

[12] Crundwell, F. K. (2013) ‘The dissolution and leaching of minerals: Mechanisms, myths and misunderstandings’, *Hydrometallurgy*. Elsevier B.V., 139, pp. 132–148. doi: 10.1016/j.hydromet.2013.08.003.

[13] Cruz, N. *et al.* (2015) ‘The interaction of pH modifiers with kaolinite in copper-gold flotation’, *Minerals Engineering*, 84, pp. 27–33. doi: 10.1016/j.mineng.2015.09.019.

[14] Dreisinger, D. (2006) ‘Copper leaching from primary sulfides : Options for biological and chemical extraction of copper’, 83, pp. 10–20. doi: 10.1016/j.hydromet.2006.03.032.

[15] Edwards, K. J. *et al.* (2000) ‘Geochemical and biological aspects of sulfide mineral dissolution: Lessons from Iron Mountain, California’, *Chemical Geology*, 169(3–4), pp. 383–397. doi: 10.1016/S0009-2541(00)00216-3.

[16] European Commission (EC) (2009) ‘Report. Reference document on the best available techniques. Management of tailings and waste-rock in mining activities’, *Reference Documents on Best Available Techniques*, (January),

p. 511. Available at: http://eippcb.jrc.ec.europa.eu/reference/BREF/mmr_adopted_0109.pdf.

[17] Evdokimov, S. I. and Evdokimov, V. S. (2014) ‘Metal recovery from old tailings’, *Journal of Mining Science*, 50(4), pp. 800–808. doi: 10.1134/S1062739114040206.

[18] Falagán, C., Grail, B. M. and Johnson, D. B. (2017) ‘New approaches for extracting and recovering metals from mine tailings’, *Minerals Engineering*, 106, pp. 71–78. doi: 10.1016/j.mineng.2016.10.008.

[19] Fleming, C. A., Brown, J. A. and Botha, M. (2010) ‘An economic and environmental case for re-processing gold tailings in South Africa’, *42nd Annual Meeting of the Canadian Mineral Processors*, pp. 365–388. Available at: http://www.sgs.com/-/media/global/documents/technical-documents/sgs-technical-papers/sgs-min-tp2010-03-a-case-for-re-processing-gold-tailings-in-south-africa.pdf.

[20] Fosso-kankeu, E. (2015) ‘Recovery of Base Metals from Mine Tailings Dumps collected in the Vicinity of Potchefstroom : Leaching assisted by Complexing Agent’, *7th International Conference on Latest Trends in Engineering & Technology (ICLTET’2015)*, pp. 103–106.

[21] Garcilaso, I. (2009) ‘Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities’, (January), p. 557.

[22] Gok, O. *et al.* (2014) ‘Leaching kinetics of copper from chalcopyrite concentrate in nitrous-sulfuric acid’, *Physicochemical Problems of Mineral Processing*, 50(1), pp. 399–413. doi: 10.5277/ppmp140133.

[23] Han, B. *et al.* (2017) 'Leaching and Kinetic Study on Pressure Oxidation of Chalcopyrite in H2SO4 Solution and the Effect of Pyrite on Chalcopyrite Leaching', *Journal of Sustainable Metallurgy*. Springer International Publishing, 3(3), pp. 528–542. doi: 10.1007/s40831-017-0135-3.

[24] Han, B. *et al.* (2018) 'Development of copper recovery process from flotation tailings by a combined method of high–pressure leaching–solvent extraction', *Journal of Hazardous Materials*, 352(August 2017), pp. 192–203. doi: 10.1016/j.jhazmat.2018.03.014.

[25] Huang, K., Li, Q. wei and Chen, J. (2007) 'Recovery of copper, nickel and cobalt from acidic pressure leaching solutions of low-grade sulfide flotation concentrates', *Minerals Engineering*, 20(7), pp. 722–728. doi: 10.1016/j.mineng.2007.01.011.

[26] Kaskiala, T. (2002) 'Determination of oxygen solubility in aqueous sulphuric acid media', *Minerals Engineering*, 15(11), pp. 853–857. doi: 10.1016/S0892-6875(02)00089-4.

[27] Kaya, M. (2016) 'Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes', *Waste Management*. Elsevier Ltd, 57, pp. 64–90. doi: 10.1016/j.wasman.2016.08.004.

[28] Khoshkhoo, M. (no date) *Chalcopyrite Dissolution in Sulphate-Based Leaching and Bioleaching Systems*.

[29] Koleini, S. M. J., Aghazadeh, V. and Sandström, Å.˚ (2011) 'Acidic sulphate leaching of chalcopyrite concentrates in presence of pyrite', *Minerals Engineering*. Elsevier Ltd, 24(5), pp. 381–386. doi: 10.1016/j.mineng.2010.11.008.

[30] Kramer, A. *et al.* (2012) ‘Surface tension measurement for optimization of flotation control’, *Procedia Engineering*, 46(December), pp. 111–118. doi: 10.1016/j.proeng.2012.09.453.

[31] Lampinen, M., Laari, A. and Turunen, I. (2015) ‘Kinetic model for direct leaching of zinc sulfide concentrates at high slurry and solute concentration’, *Hydrometallurgy*. Elsevier B.V., 153, pp. 160–169. doi: 10.1016/j.hydromet.2015.02.012.

[32] Larrauri, P. C. (2018) ‘Tailings Dams Failures : Updated Statistical Model for Discharge Volume and Runout’, pp. 1–10. doi: 10.3390/environments5020028.

[33] Lee Bray, E. (2017) *Mineral Commodity Summaries 2017*. doi: http://dx.doi.org/10.3133/70140094.

[34] Li, J. *et al.* (2013) ‘Regional or global WEEE recycling. Where to go?’, *Waste Management*, 33(4), pp. 923–934. doi: 10.1016/j.wasman.2012.11.011.

[35] Liao, Y. *et al.* (2015) ‘Leaching kinetics of calcification roasting calcinate from multimetallic sulfide copper concentrate containing high content of lead and iron’, *Separation and Purification Technology*. Elsevier B.V., 149, pp. 190–196. doi: 10.1016/j.seppur.2015.05.042.

[36] Liu, Z. X. *et al.* (2016) ‘Oxidative leaching behavior of metalliferous black shale in acidic solution using persulfate as oxidant’, *Transactions of Nonferrous Metals Society of China (English Edition)*. The Nonferrous Metals Society of China, 26(2), pp. 565–574. doi: 10.1016/S1003-6326(16)64145-6.

[37] Look, A. N. E. W. *et al.* (1998) 'Pergamon l)', *Science*, 11(11), pp. 1011–1024.

[38] Lorenzo-talla, J. *et al.* (2018) 'Ferric leaching of the sphalerite contained in a bulk concentrate : Kinetic study', 125(May), pp. 50–59. doi: 10.1016/j.mineng.2018.05.026.

[39] Lutandula, M. S. and Maloba, B. (2013) 'Recovery of cobalt and copper through reprocessing of tailings from flotation of oxidised ores', *Journal of Environmental Chemical Engineering*, 1(4), pp. 1085–1090. doi: 10.1016/j.jece.2013.08.025.

[40] Lv, C. C. *et al.* (2017) 'Characterization of a Copper Mine Tailing and Comprehensive Recovery of Cu and S from the Tailing 1', 14(2). doi: 10.12783/issn.1544-8053/14/2/15.

[41] Mackay, I. *et al.* (2018) 'Dynamic froth stability of copper flotation tailings', *Minerals Engineering*, 124(May), pp. 103–107. doi: 10.1016/j.mineng.2018.05.005.

[42] McDonald, R. G. and Muir, D. M. (2007a) 'Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products', *Hydrometallurgy*, 86(3–4), pp. 191–205. doi: 10.1016/j.hydromet.2006.11.015.

[43] McDonald, R. G. and Muir, D. M. (2007b) 'Pressure oxidation leaching of chalcopyrite. Part II: Comparison of medium temperature kinetics and products and effect of chloride ion', *Hydrometallurgy*, 86(3–4), pp. 206–220. doi: 10.1016/j.hydromet.2006.11.016.

[44] Mesa, D. and Brito-Parada, P. R. (2019) ‘Scale-up in froth flotation: A state-of-the-art review’, *Separation and Purification Technology*, 210(September 2018), pp. 950–962. doi: 10.1016/j.seppur.2018.08.076.

[45] Molecular, K. L. and Biology, C. (1995) ‘IIHIII United States Patent (19)’, (19).

[46] Moradi, S. and Monhemius, A. J. (2011) ‘Mixed sulphide-oxide lead and zinc ores: Problems and solutions’, *Minerals Engineering*. Elsevier Ltd, 24(10), pp. 1062–1076. doi: 10.1016/j.mineng.2011.05.014.

[47] Mudd, G. M. (2009) *The Sustainability of Mining in Australia: Key Production Trends and Their Environmental Implications for the Future, Research Report No RR5, Department of Civil Engineering, Monash University and Mineral Policy Institute*. doi: 978-0-9803199-4-1.

[48] NMP2-CT-2004-505710 / BIOSHALE (2007) *Publishable Activity Report of Bioshale Project*. Available at: http://bioshale.brgm.fr/Documents/ResultsProducts/Publishable_Activity_Report-Bioshale.pdf.

[49] Norgate, T. and Jahanshahi, S. (2010) ‘Low grade ores - Smelt, leach or concentrate?’, *Minerals Engineering*. Elsevier Ltd, 23(2), pp. 65–73. doi: 10.1016/j.mineng.2009.10.002.

[50] Of, B. (1994) ‘T ECHNICAL R ESOURCE D OCUMENT EXTRACTION AND BENEFICIATION OF ORES AND MINERALS’, (August).

[51] Panda, S. *et al.* (2015) ‘Current scenario of chalcopyrite bioleaching: A review on the recent advances to its heap-leach technology’, *Bioresource Technology*. Elsevier Ltd, 196, pp. 694–706. doi: 10.1016/j.biortech.2015.08.064.

[52] Paper, C. *et al.* (2016) 'Nanofiltration – A new separation pathway in secondary mining', (August), pp. 1356–1363.

[53] Problems, P. (2017) 'SELECTIVITY AND POWER OF FROTHERS IN COPPER ORE FLOTATION * Abstract ':, 53(202), pp. 515–523.

[54] Rico, M. *et al.* (2008) 'Reported tailings dam failures . A review of the European incidents in the Reported tailings dam failures A review of the European incidents in the worldwide context', (August 2018). doi: 10.1016/j.jhazmat.2007.07.050.

[55] Robinson, D. J. and Scientific, T. C. (2018) 'Special Feature: Mineral Processing, In situ recovery – a move toward "keyhole mining".', (August).

[56] Schippers, A. *et al.* (2007) 'Geomicrobiological and geochemical investigation of a pyrrhotite-containing mine waste tailings dam near Selebi-Phikwe in Botswana', *Journal of Geochemical Exploration*, 92(2–3), pp. 151–158. doi: 10.1016/j.gexplo.2006.08.003.

[57] Schippers, A., Schwartz, M. and Cknowledgements, A. (2005) 'Geomicrobiological and geochemical investigation of the BCL mine waste tailings dam at Selebi-Phikwe', (April).

[58] Schwartz, M. O., Schippers, a. and Hahn, L. (2005) 'Hydrochemical models of the sulphidic tailings dumps at Matchless (Namibia) and Selebi-Phikwe (Botswana)', *Environmental Geology*, 49(4), pp. 504–510. doi: 10.1007/s00254-005-0033-z.

[59] Sicupira, L. *et al.* (2011) 'Assessing metal recovery from low-grade copper ores containing fluoride', *Hydrometallurgy*. Elsevier B.V., 109(3–4), pp. 202–210. doi: 10.1016/j.hydromet.2011.07.003.

[60] Smith, T., Metallurgist, P. and Lin, D. (no date) ‘PAPER 21 Removal of Organic Carbon with a Jameson Cell at Red Dog Mine’, pp. 333–346.

[61] Sokić, M. D., Marković, B. and Živković, D. (2009) ‘Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid’, *Hydrometallurgy*, 95(3–4), pp. 273–279. doi: 10.1016/j.hydromet.2008.06.012.

[62] Sun, L. *et al.* (2009) ‘Adsorption of NO and NH3 over CuO/γ-Al2O3 catalyst by DRIFTS’, *Huagong Xuebao/CIESC Journal*, 60(2), pp. 444–449. doi: 10.1007/s11771.

[63] Tindall, G. P. and Muir, D. M. (1998) ‘Effect of Eh on the rate and mechanism of the transformation of goethite into hematite in a high temperature acid leach process’, *Hydrometallurgy*, 47(2–3), pp. 377–381. doi: 10.1016/S0304-386X(97)00047-9.

[64] Tshilombo, K. G. and Mulaba-Bafubiandi, A. F. (2013) ‘Ammonia / nitric Acid Leaching of Copper- Cobalt Oxidized Ore’, *International Conference on Mining, Mineral Processing and Metallurgical Engineering (ICMMME)*, pp. 120–122. Available at: https://pdfs.semanticscholar.org/aec0/5ae93a6194aca6e05eb8f94a4ee0f2f60adc.pdf.

[65] Watling, H. R. (2006) ‘The bioleaching of sulphide minerals with emphasis on copper sulphides - A review’, *Hydrometallurgy*, 84(1–2), pp. 81–108. doi: 10.1016/j.hydromet.2006.05.001.

[66] Wieniewski, A. and Skorupska, B. (2016) ‘Technology of Polish copper ore beneficiation – perspectives’, 4, pp. 0–10.

[67] Wills, B. A. and Napier-munn, T. (2006) *Preface to 7th Edition*.

[68] Yin, S., Wang, L., Wu, A., Kabwe, E., *et al.* (2018) ‘Copper recycle from sulfide tailings using combined leaching of ammonia’, *Journal of Cleaner Production*, 189, pp. 746–753. doi: 10.1016/j.jclepro.2018.04.116.

[69] Yin, S., Wang, L., Wu, A., Free, M. L., *et al.* (2018) ‘Enhancement of copper recovery by acid leaching of high-mud copper oxides: A case study at Yangla Copper Mine, China’, *Journal of Cleaner Production*, 202, pp. 321–331. doi: 10.1016/j.jclepro.2018.08.122.

[70] Yin, Z. *et al.* (2018) ‘Evaluation of the possibility of copper recovery from tailings by flotation through bench-scale, commissioning, and industrial tests’, *Journal of Cleaner Production*, 171, pp. 1039–1048. doi: 10.1016/j.jclepro.2017.10.020.

[71] Yu, P. H., Hansen, C. K. and Wadsworth, M. E. (1973) ‘A kinetic study of the leaching of chalcopyrite at elevated temperatures’, *Metallurgical Transactions*, 4(September), pp. 2137–2144. doi: 10.1007/BF02643279.

[72] Zhan-fang, C. A. O. *et al.* (2009) ‘Techniques of copper recovery from Mexican copper oxide ore’, 19(August 2008), pp. 45–48.

3: Comparison of Flotation and Direct High Pressure Leaching of Complex Carbonaceous Sulfide Ore

3.1 Introduction

Copper is naturally present in the earth's crust, at a concentration of about 67 parts per million (https://courses.lumenlearning.com/geology). The modern society's need to produce goods has resulted in dramatical demand for copper over the last decades. Between 1995-2017 the copper production has increased from 12,000 to 19,000 thousand million tonnes (USGS, 2018). It is thus no doubt that the demand for copper will continue to increase as forecasted by different authors. Research and development for the extraction of copper has been centered around the depletion and declining of ore grades (Prior *et al.*, 2012; Henckens *et al.*, 2016). On the contrary, the USGS,2018 documented that over 680 million tonnes of reserves are present worldwide with higher resources that are affected by short term supply limitations, which often result in upward price trends. The limited technology and energy intensity required for the metallurgical processing of these resources have also been noted (Krausmann *et al.*, 2009; Mudd, 2012; Calvo *et al.*, 2016). Both of these issues, either together or in isolation, have significant implication for primary metal production. For this reason, the development of energy intensive technologies is required for efficient processing of the ores.

Carbonaceous sulfide ores host a wealth of polymetallic minerals characterized by organic and carbonaceous material. Currently, exploitation is limited to the Lubin plant of KGHM in Poland, Kupferschiefer in SE Germany, Red Dog mine in Alaska, Mount Isa mine in the north-west part of Queensland and Zinifex Century mine in Australia. Although the mineralogical assemblage of economic minerals varies, they contain substantial amounts of high-grade mineralogy. For example, the Kupferschiefer-tpye mineralization is characterized by high-grades (average grades of ca. 1.5 wt% are currently exploited), with Ag (50-100 g/t) as the most important by-product. However, beneficiation of these deposits is extremely difficult owing to their complex mineralogy with close association to harmful impurities of organic carbon and carbonates and fine grain sizes.

The floatability of carbonaceous sulfide ore is a challenge due to their fined-grained intergrowth of valuable minerals and special carbonaceous composition. In the past years, several mineral processes have been tested for treating carbonaceous sulfide ore, such as flotation, gravity separation combined with flotation. Smith *et al.* (2008) investigated the flotation of zinc-lead ore processing from red Dog mine in Alaska near the Arctic Circle to remove organic carbon. The idea behind the process he used was to channel the material, after grinding and classification in hydrocyclones, to pre-flotation, which results in two concentration products using the Jameson cells. Gredelj *et al.* (2009) reported a setback in the approach to increase recovery of sulfides which contained organic matter up to -3%. His approach to increase the effectiveness of the process is by conditioning by application of the methyl isobutyl carbinol (MIBC) frother. Koniecyzny *et al.*(2012) paid close attention to determine the possibility of organic carbon separation during pre-flotation stage, to be sent to be sent to flash smelting process. His interest lay in the fact that the KGHM Polska Miedz S.A strategy, was to completely replace the shaft furnace for flash smelting technology. The analysis of the obtained results showed that there is a possibility of separating significant amount of organic carbon at pre-flotation stage by applying only the frother and as such is investigated in this study. An extra flotation treatment is also added by including collector to increase quality of the concentrate in this research.

The volatile price developments on the metal markets and increasing cost of production for complex ores (low/high grade) require efficiency in the establishment process chain or introduction of alternative-energy and resource efficient processing technologies (Chmielewski, 2015). Such new processing options can aim at the adaptation and improvement of existing protocols e.g. replacing pyrometallurgy by hydrometallurgy process. The conventional copper extraction via smelting is extremely energy consuming. For this reason, other researchers have resort to hydrometallurgical process. Bio-hydrometallurgy has been used extensively, particularly, for carbonaceous sulfide ores and has been considered a strong point of extracting metals (Watling, 2006; NMP2-CT-2004-505710 / BIOSHALE, 2007; Ahmadi *et al.*, 2011; Kamradt *et al.*, 2012; Kostudis *et al.*, 2015; Panda *et al.*, 2015). However, this technology still has some limitations because of the abundance of organic carbon and is still rich in carbonates such as dolomite and calcite. These carbonates material readily decompose in an acidic solution and are likely to increase acid consumption and also expected to result in collapse of the original ore fabric, thus decreasing leachability (Kostudis *et al.*, 2015). Additionally, the incomplete dissolution of chalcopyrite has been confirmed and remains a key issue for copper bioleaching improvement (Watling, 2006; Panda *et al.*, 2015).

Hydrometallurgical processing in pressure oxidative environments such as in autoclaves are gaining more attraction. By subjecting chalcopyrite minerals to high temperatures under oxidizing environments, increased leaching kinetics have been achieved (Look *et al.*, 1998; Huang, Li and Chen, 2007; Chmielewski, Wodka and Iwachow, 2009; Tshilombo and Mulaba-Bafubiandi, 2013). Han *et al.* (2017, 2018) investigated the leaching of chalcopyrite concentrate under sulfuric acid in an autoclave and had 94.5% leaching rate efficiency. He confirmed that the chalcopyrite dissolution was controlled by the chemical reaction model. (Gok *et al.*, 2014) found that higher leaching efficiency of up to 98% from chalcopyrite concentrate was achieved under conditions of 120 ^{0}C at 6 atm pressure for 2hours. Overall though, the sulfuric leaching of chalcopyrite is mostly preferred because of it is cost effective, environmentally friendly and can be regenerated during electro-winning. Furthermore, the process can easily be combined with solvent-extraction-electrowinning methods (SX-EW) (Han *et al.*, 2018).

Aims and Objectives

In a word, it is necessary to develop a novel metallurgical process for the recovery of copper from complex carbonaceous sulfide ore. The process could be characterized as environmentally friendly and may be high recovery/extraction of copper at low-cost. Separation efficiency between associated gangue minerals is highly desirable.

The aim of this work chapter, was to carry out a comparative experimental study in the effective recovery of copper from complex carbonaceous sulfide ore by flotation and direct high-pressure leaching method (Fig 3.1). The flotation processes considered two (2) stages of recovery. At the first, organic carbon is to be separated from the sulfide by application of frother only (MIBC). The second stage follows the addition of collector to upgrade the ore to a target greater than 10 wt%.

The direct pressure leaching of complex carbonaceous sulfide ore considers an important selection leaching environment for these ores. Even though the application of leaching using sulfuric acid is currently used in other stages of development (Table 3.1) none can be considered as directly applicable to the complex carbonaceous ore. A high organic carbon content and carbonate materials of dolomite and calcite marks the pinnacle of marking effective parameters suitable for efficient dissolution. Additionally, the separation efficiency of copper and iron is highly considered in this process.

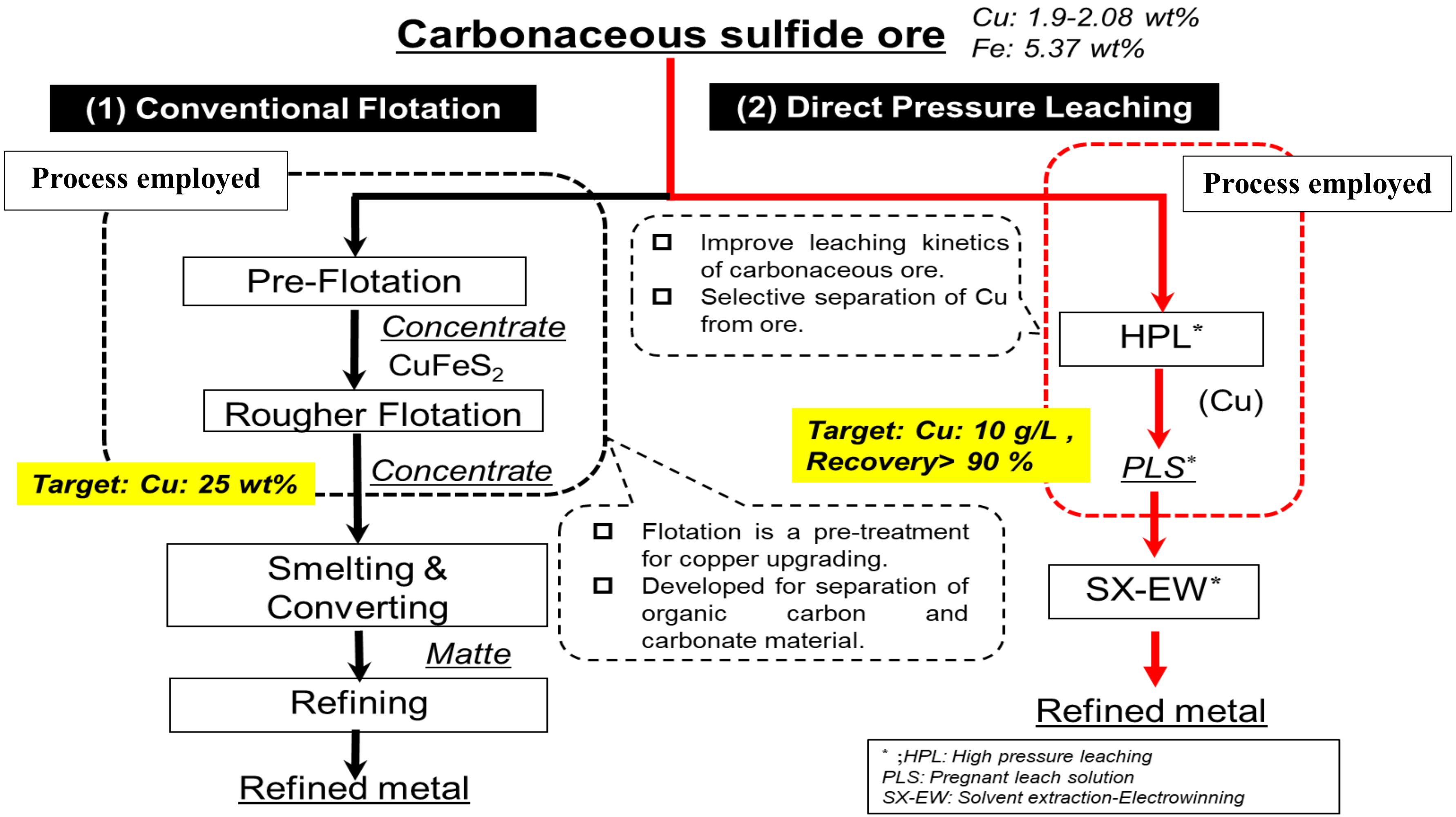


Figure 3. 1. Conceptual design plan to recover carbonaceous sulfide.

Table 3. 1. Application of hydrometallurgical leaching at different companies.

Process	**Status**	**Temp. ^0C**	**Pressure, atm**	**Regrind d_{80}, µm**	**Special conditions**
AA-UBS Process	Pilot plant	150	10-12	10-15	Reground chalcopyrite pressure leaching with addition of surfactant
CESL Copper Process	Demo plant	140-150	10-12	37	Chloride assisted pressure sulfate leaching of chalcopyrite
Dynatec Process	Pilot plant	150	10-12	37	Pressure leaching of chalcopyrite using low grade coal additive
Mt.Gordon Process	Commercial	90	8	100	Pressure leaching of chalcocite/pyrite ore in Fe(III) solution
Platsol Process	Pilot plant	220-230	30-40	15	Total pressure oxidation in the presence of 10-20 g/dm^3 NaCl.Precious metal leached in one step
Sepon Copper Process	Commercial	80 ^0C-Cu 230 ^0C-FeS_2	1 atm 30-40	100 50	Atmospheric leach for copper from Cu_2S. Pressure leaching of FeS_2 to produce H_2SO_4 and Fe^{3+} for copper leaching
Total Pressure Oxidation Process	Commercial	200-230	30-40	100	Extreme conditions of T and p designed to rapidly destroy chalcopyrite and other sulfides
Las Cruces Copper Process	Commercial	90	1	37	Atmospheric leach of copper from sulphide ore using oxygenated and acidified Fe(III)

3.2 Experimental

Sample Material

Complex ore from South East Asia, supplied by Nittetsu Mining Co. Ltd was used for leaching and direct leaching studies. The sample was firstly finely crushed to under 106 µm by ball milling to make an average particle size of 50 µm (D_{50}) which was estimated by a wet type size distribution analyser (Microtrac MT3300II) as shown on Figure 3.2. The chemical analysis of the sample was determined by digestion in hydrochloric acid and nitric acid in the ratio 4:1 and subsequent analysis were performed using X-ray fluorescence (XRF, Rigaku ZSX Primus II) and an inductively coupled plasma optical emission spectrometer (ICP-OES, SII NanoTechnology Inc., Chiba, Japan). The results showed grade value of Cu 2.50 wt % (Table 3.2).

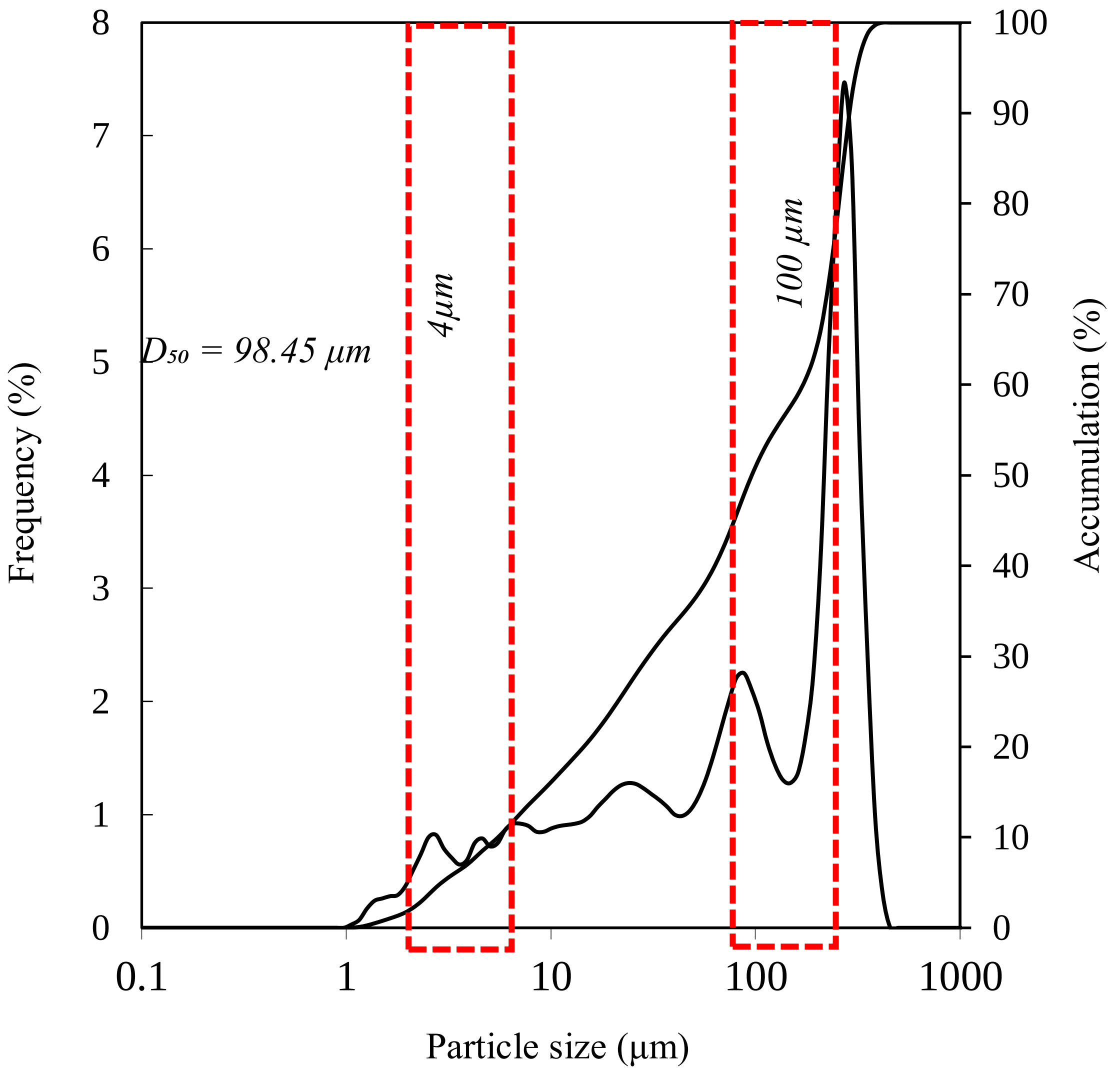


Figure 3. 2. Particle size distribution of complex carbonaceous sulphide ore.

Table 3. 2. Chemical analysis of complex carbonaceous sulphide ore.

Element	Ca	Cu	Fe	Mg	Al	OC	IC
Grade(wt%)	12.16	2.08	5.37	4.03	1.84	0.98	4.55

The mineralogical characterization was analysed by X-ray diffraction (XRD, Rigaku RINT-2200V) pattern and indicated the gangue composition to be of quartz, kaolinite, calcite, dolomite and traces of chlorite (Figure 3.3). It can also be seen that the sample contained organic carbon which was determined by combustion in Nittetsu

Mining Co. Ltd laboratory. The presence of copper mineral was confirmed by scanning electron microscope energy dispersive X-ray spectrometry (SEM-EDS).

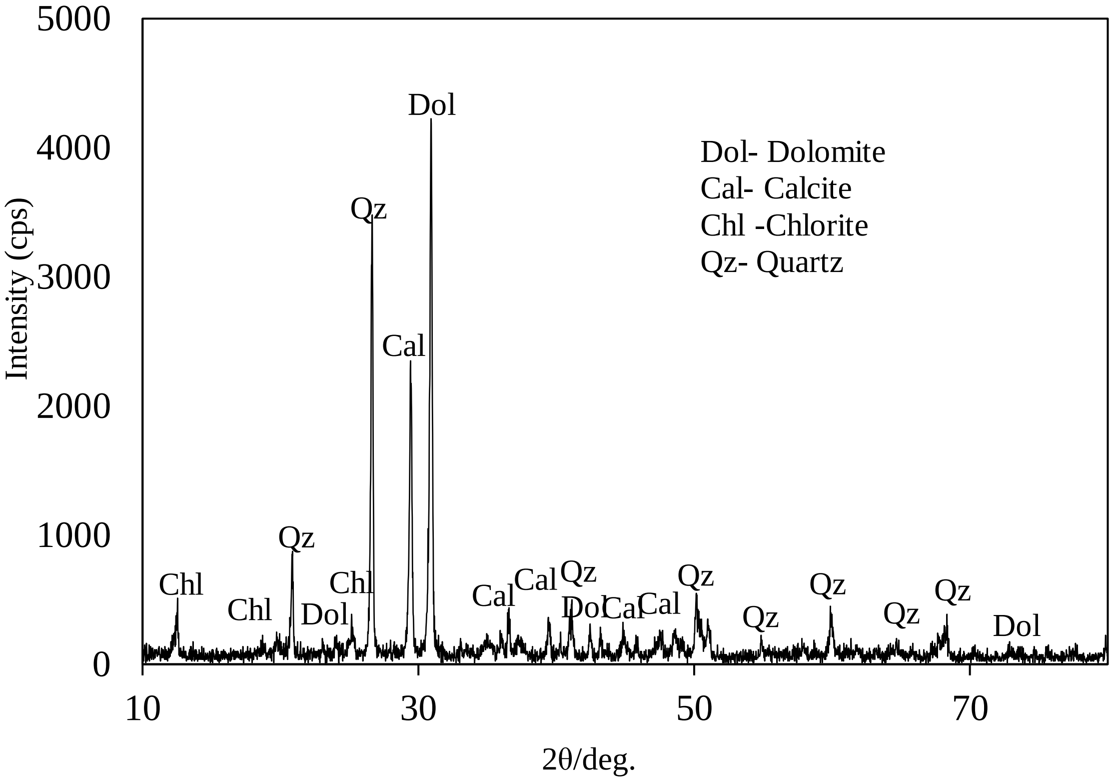


Figure 3. 3. XRD pattern of original complex carbonaceous sulphide ore.

Chemical Reagents

The chemical reagents used for the processing of mine tailings by flotation and high-pressure leaching are listed in Table 3.3. For the flotation process, potassium amyl xanthate (PAX, C_5H11OCSSK) and sodium oleate (NaOL) and methyl isobutyl carbinol (MIBC, $C_6H_{14}O$) were used. In the high-pressure leaching process, sulfuric acid (H_2SO_4) was used as a leachate while oxygen was supplied by oxygen (O_2) tank. Table 3.3.

Table 3. 3. Chemical reagents used in the study.

Experiments	Type	Name	Maker	Formula
Flotation	Collector	Potassium Amyl Xanthate (PAX)	Kanto Chemical	$KC_6H_{11}OS_2$
		Sodium Oleate (NaOL)		
	Frother	Methyl Iso Butyl Carbinol (MIBC)	–	$C_6H_{13}O$
		Sulfuric acid	Kanto Chemical	H_2SO_4
High pressure leaching (HPL)		Sulfuric acid	Kanto Chemical	H_2SO_4
		Oxygen	Aiba Shouten	O_2

Procedure

Flotation of complex carbonaceous sulphide ore

Flotation experiment was carried out in a 0.5 L mineral separation flotation machine (MS, 237FL, Mekhanobr-tekhnika Corp.) cell that comprises of two sections (mixing and froth formation) and a tube connected to generator for air supply. A 50g sample was charged into the cell with distilled water to obtain pulp densities of 10%. The slurry pH was kept at a natural pH of 6. Collectors used were potassium amyl xanthate (PAX, $C_5H11OCSSK$) and sodium oleate (NaOL) while frother used was methyl isobutyl carbinol (MIBC, $C_6H_{14}O$). In all flotation test MIBC addition was fixed at 200 g/t. Air injection and slurry stirring speed were kept constant at 40 unit and 1600 rpm respectively.

A general process for Cu recovery was performed in two stage flotation shown in (Figure 3.4). In the first stage, pre-flotation was carried out with the objective of removing organic carbon that is a major hindrance to concentrate quality. Here, MIBC frother was the only reagent used to target the organic carbon. A mixture of MIBC and kerosene was also considered in the experiment. On the second stage, the concentrates were sent to the rougher cell to target copper minerals and here the application of different collectors was considered to examine the most effective. In all experiments two average particle size were used, D_{50}: 4 and 100 µm.

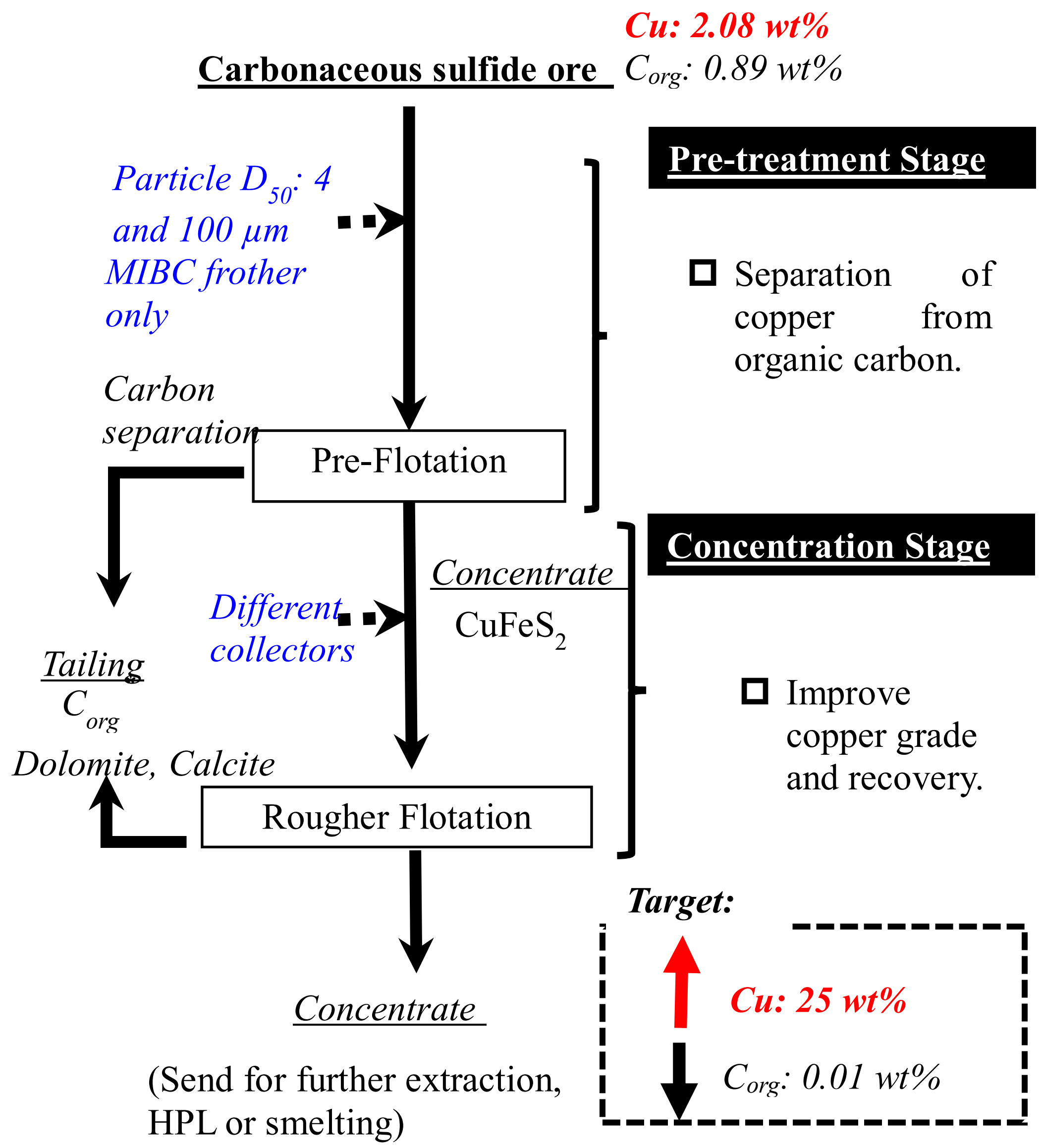


Figure 3. 4. Flotation procedure for complex carbonaceous sulphide ore

High-pressure leaching of complex carbonaceous sulphide ore

The leaching experiments were carried out using a stainless-steel autoclave (Nitto Koatu, Japan) equipped with a Teflon vessel (200 mL), heating mantle, temperature controller and variable stirrer. The procedure consisted of mixing the sample with a sulfuric acid solution and heating to the desired set temperatures; once at the intended temperature, the leaching time was recorded while keeping stirring speed constant (700 rpm) and total pressure (2.5 MPa) constant (Figure 3.5). After set reaction time, the autoclave was cooled and the solution was filtered. The obtained solid residue (S.R) was dried overnight in an oven (60 ºC) and later analyzed by XRD and scanning electron microscope-energy dispersive X-ray spectroscopy. The pregnant leached S.R was chemically analyzed by ICP-OES.

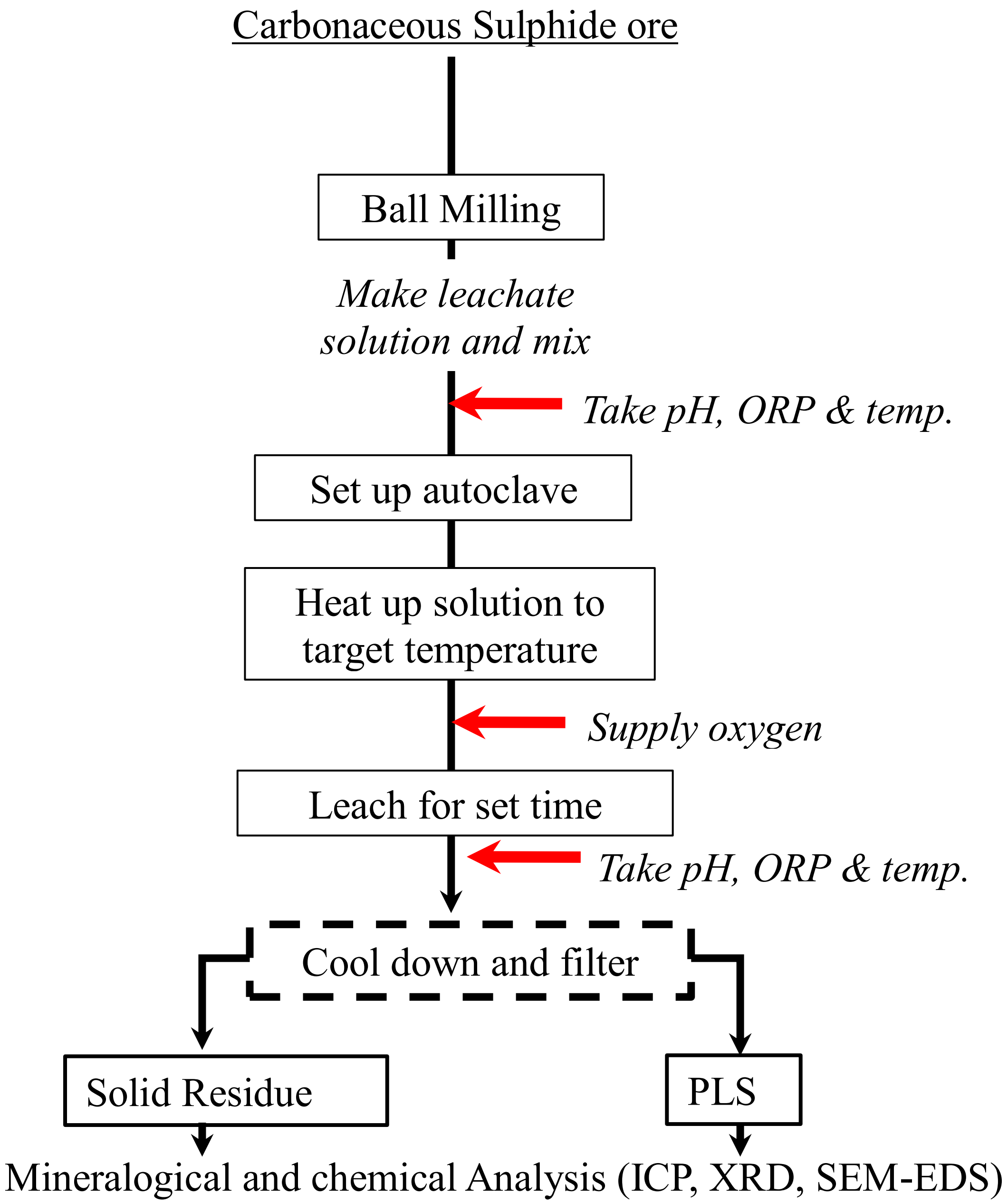


Figure 3. 5. HPL procedure for complex carbonaceous sulphide ore

Atmospheric leaching of atmospheric leaching

The application of atmospheric leaching of the carbonaceous sulphide ore was also considered at different sulfuric acid concentrations (0-1 mol dm^{-3}). The complex sulphide ore were placed in a beaker above a heating pan. The experimental procedure for atmospheric leaching followed initial measurement of pH, ORP and temperature. The solution allowed to heat to a fixed temperature of 95 ^{0}C and leached for one hour. The pulp density, stirring speed were kept constant at 10% and 800 rpm respectively. After leaching the solution was cooled, and pH, ORP and temperature were recorded before filtering. The solid residue was dried by placing in an oven at 60 ^{0}C overnight before being taken for analysis. The atmospheric leaching was used to examine the leaching kinetics of copper.

Analysis of process products

The mineralogical characterization of all solid samples was performed by using X-ray diffraction (XRD) analysis equipment (Rigaku Co., Japan), X-ray fluorescence (XRF) analyser and Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS). Chemical composition for all liquids and solids samples dissolved in aqua-regia were analysed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, SPS-5500, Seiko Instrument Inc.).

In this chapter the recovery (R), yield (Y) and enrichment ratio (ER) of each metal from mine tailing was calculated as follows Eqs.: 3.1-3.3:

$$R = \frac{c(f-t)}{f(c-t)} \times 100 \tag{3.11}$$

$$Y = \frac{C}{F} \times 100 \tag{3.12}$$

$$ER = \frac{c}{f} \tag{3.13}$$

Where R is recovery, Y is yield and ER is enrichment of each metal. C and F are the weight of the concentrates and feed, c, t and f are the metal grades in the concentrates, tailing and feed respectively.

The leaching efficiency (y) is used to evaluate the leaching results of mine tailing concentrates, as expressed in Eq. 3.4 as follows:

$$y = \frac{Q \times a - m \times \beta}{Q \times a} \times 100 \tag{3.14}$$

Where Q is the weight of the concentrate, m is the weight of the leaching residue, a is the metal grade of the concentrate, and β is the metal grade of the leaching residue.

3.3 Results and Discussion

3.3.1 Flotation Process

Pre-flotation

The sized separation of organic carbon from complex carbonaceous sulphide ore was investigated and results presented in (Figure 3.6). Additionally, for the purpose of ensuring frother optimization an emulsion of MIBC and kerosene was carried out. The importance of kerosene acts as a supportive aid to determine it influence on the control adsorption of MIBC on the organic carbon and carbonate minerals under investigation. In this case, the tailings obtained are fundamentally important in ascertaining that more sulphide is contained after flotation. The recovery and grade determinations aid in determining the efficiency of carrying out pre-flotation experiments.

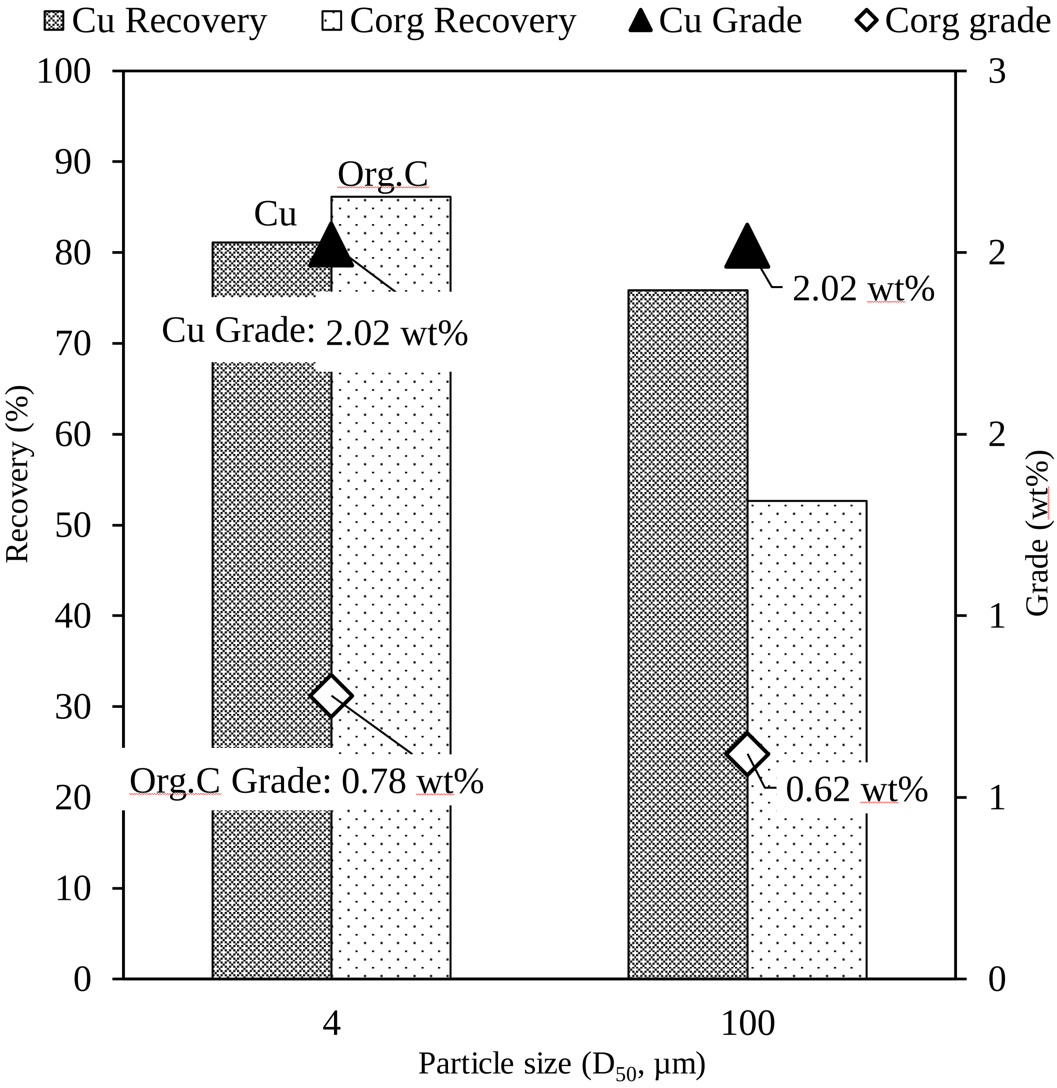


Figure 3. 6. Effect of MIBC on the pre-flotation of organic carbon.

According to the concentrates obtained from flotation of complex carbonaceous sulphide ore, particle size played a significant role in the separation of organic carbon from the feed. The results indicate a 50% recovery of organic carbon in the average particle size of D_{50}: 100 µm. The grade of the organic carbon was also reported the least at 0.62 wt% in the concentrates. It is possible that the highest number of organic carbons that is reported in the smallest fraction size made it easier for frother consumption therefore rendering the separation of organic carbon from feed.

Rougher flotation circuit

Here, the concentrates from pre-flotation separation circuit were used as feed. The experiment was carried out under slurry pH 6-7, flotation time 10 minutes, 5 minutes conditioning, 200 g/t MIBC frother at 700 r/min stirring speed. The rougher flotation circuit was directed at maximising Cu recovery and upgrade. Henceforth, the performed experiments were intended to investigate the role of different collector in the reduced carbonate concentrates.

The results for the effect of PAX are shown in (Figure 3.7). According to the graph plotting specified, the lowest average particle size D_{50}:4 µm showed the most optimum upgrade and recovery at 6.15 wt% and 66.49 % recovery. Although organic carbon also upgraded, it was also reported the least in this fraction at 2.07 wt%. In the higher average particle size organic carbon flotation was significantly lower at almost 15% recovery and that of copper did not exceed beyond 50%.

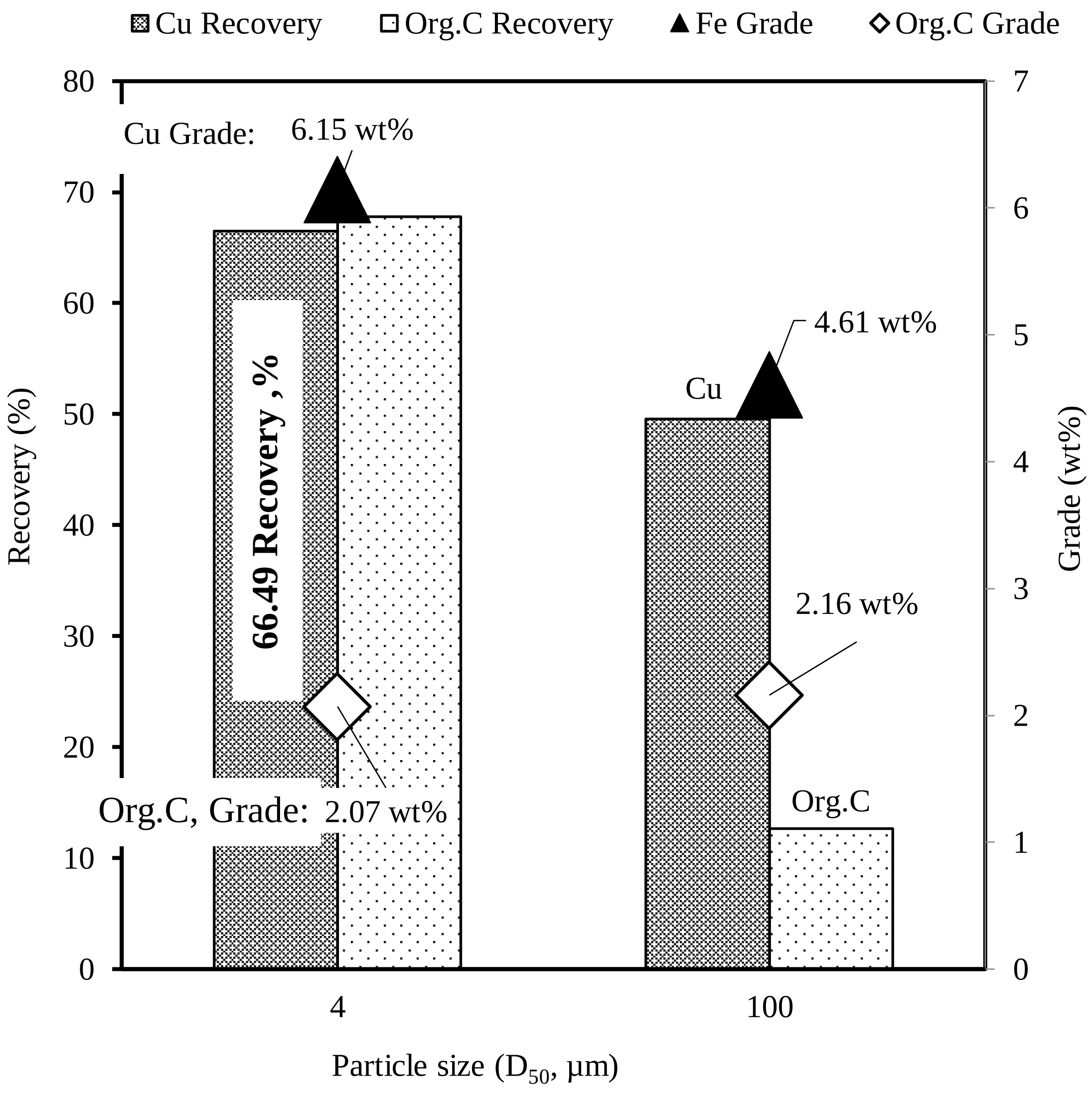


Figure 3. 7. Effect of PAX on the concentration of chalcopyrite.

Figure 3.8 shows the influence of sodium oleate (NaOL) on the recovery of Cu and the response of organic carbon in the flotation process. Here, the grade of the copper was most improved in the larger average particle size, D_{50}: 100 µm at 9.33 wt%. The recovery of Cu was reported at 52.97 % while organic carbon was 38.41 % with a grade of 0.49 wt%. The recovery of Cu in D_{50}: 4 µm was 59.95 % with an upgrade of 6.49 wt%. The organic carbon was also higher in this fraction at 53.36 wt% with a

0.62 wt% grade. It can be clearly noted that NaOL did not favour the upgrading of organic carbon which is most favourable in the recovery of Cu from carbonaceous sulphide ore.

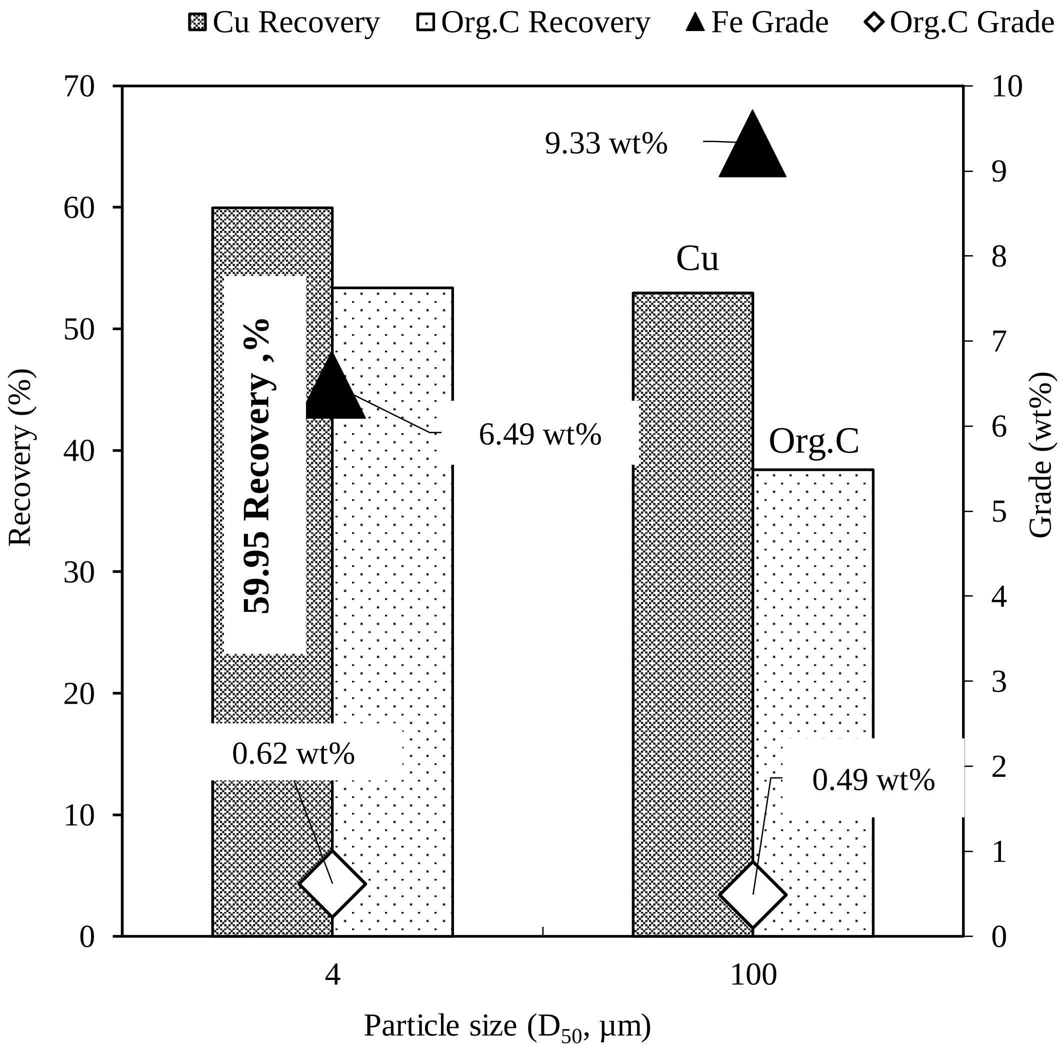


Figure 3. 8. Effect of NaOL on the concentration of chalcopyrite.

Optimization of flotation process

The optimized flotation conditions for Cu from complex carbonaceous sulphide ore were summarized in Table 3.4 following a two-stage flotation circuit. At optimal conditions, average particle size D_{50}: 100 μm at pre-flotation was chosen with 200 g/t of MIBC addition, and at rougher flotation circuit the same average size particle size was chosen and NaOL selected as the collector. A flow sheet was proposed and showed that an average 65.75 % organic carbon was achieved during pre-flotation stage. The difficulty to separate organic carbon is especially difficult because the material tends to be reagent consuming, therefore requiring more for efficiency. Furthermore, the organic carbon showed to have existed with copper bearing minerals making it difficult to separate. At the rougher flotation stage, a higher upgrade of Cu was achieved when NaOL was used to 9.33 wt% with a recovery of 52.97 % under the same average particle size. A better demonstration of organic carbon is most reflected in the use of NaOL at 100 g/t dosage. A flowsheet is given in Figure 3.9.

Table 3. 4. Summary of optimal conditions for flotation of carbonaceous sulphide ore

Parameters	Conditions	Cu recovery (%)	Cu grade (mass%)
Pulp density	10 %	59.95	3.25
NaOL dosage	160 g/t–ore		
MIBC dosage	200 g/t–ore		
pH	10		
Particle size	4 µm		
Flotation time	10 min		

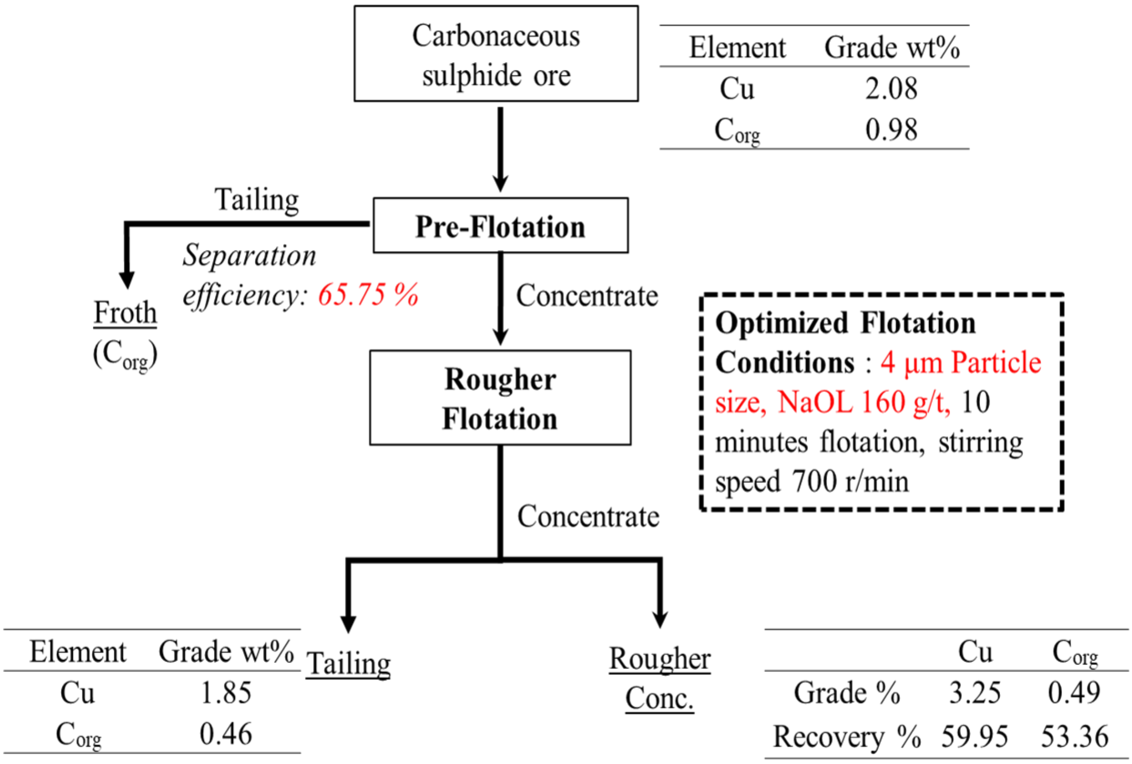


Figure 3. 9. Summarized flowsheet for flotation process of complex carbonaceous sulphide ore

Mineralogical composition analysis was performed by XRD and SEM-EDS. The chalcopyrite intensity was detected on the concentrate after flotation Figure 3.10 and 3.11. The mineral constituent observed in other products was calcite, dolomite and quartz. The SEM-ED showed the presence of calcium in the concentrates indicating that separation efficiency was low. The two-stage process of flotation is difficulties organic carbon is competitively naturally hydrophobic therefore rendering the concentration of copper minerals.

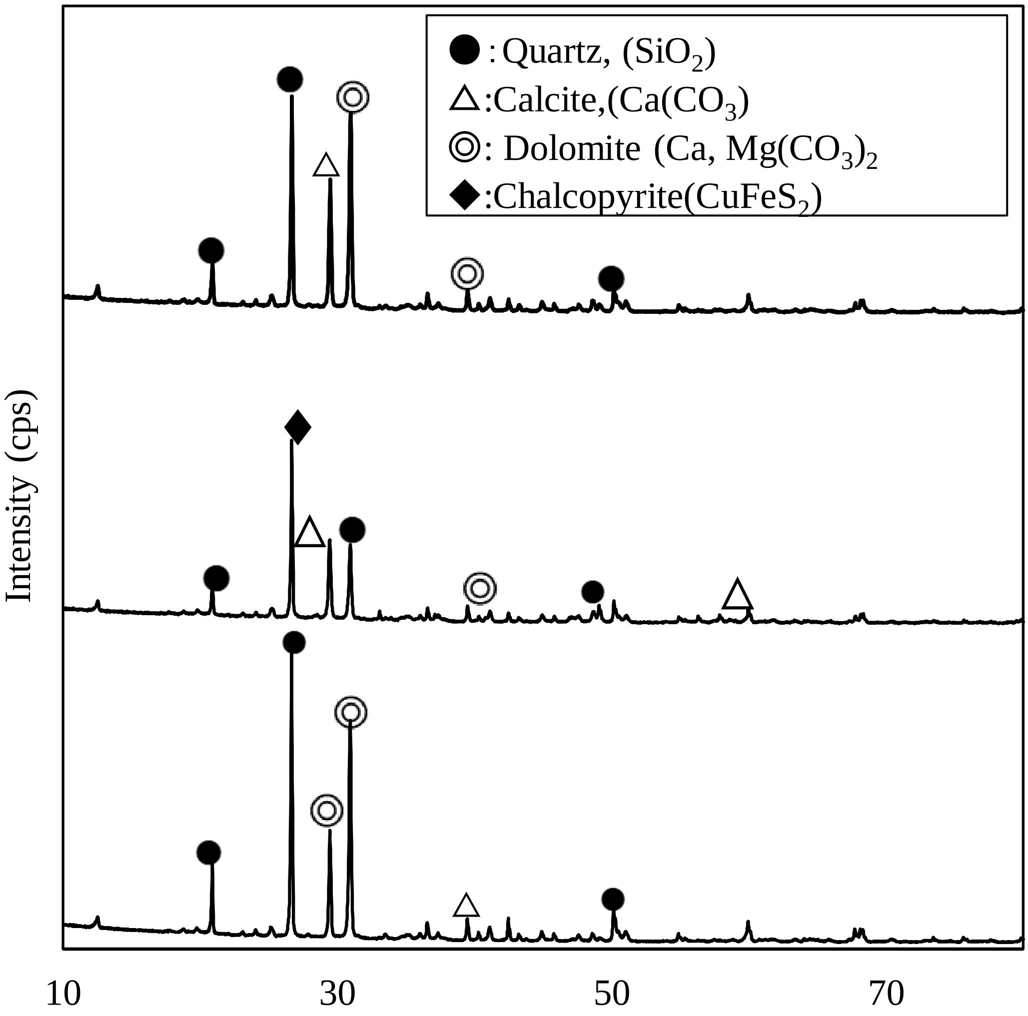


Figure 3. 10. XRD pattern for complex carbonaceous flotation products.

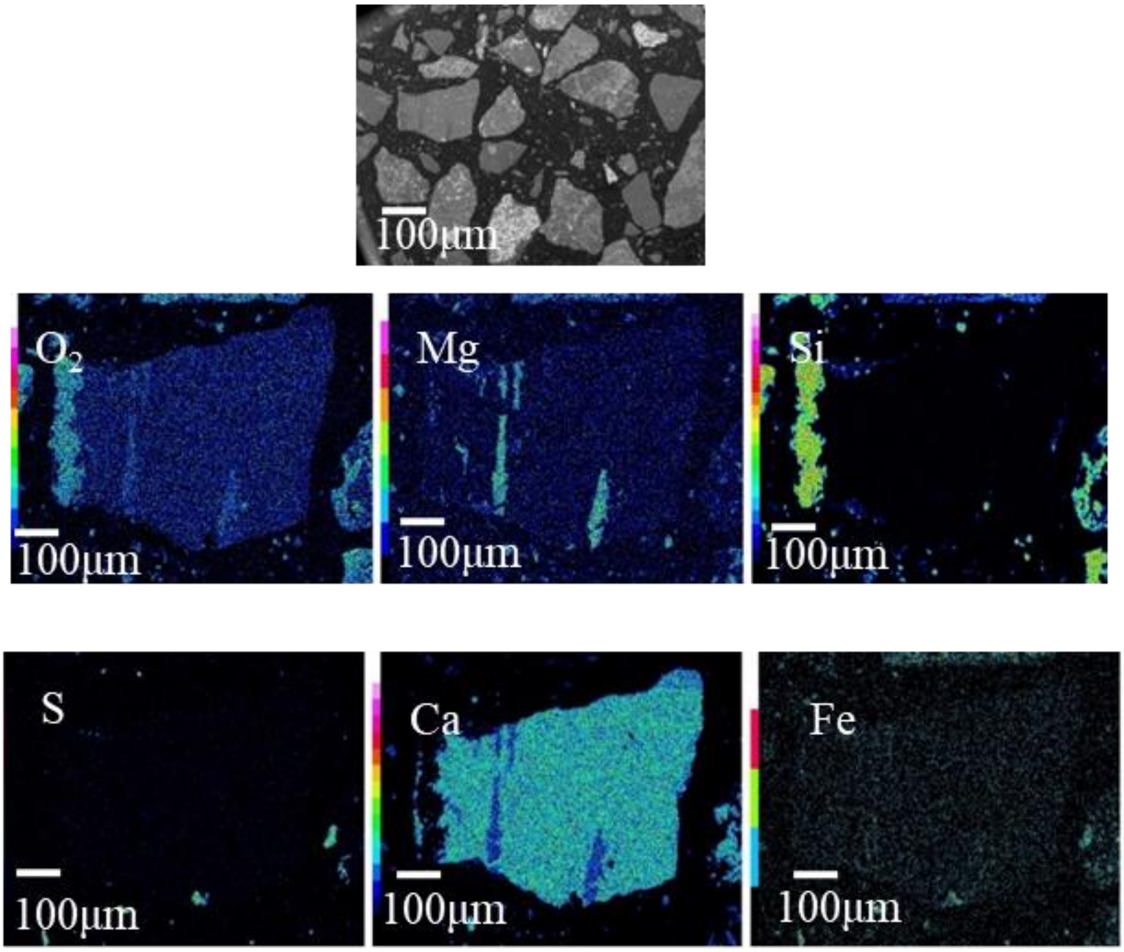


Figure 3. 11. SEM-EDS pattern for complex carbonaceous flotation products.

3.3.2 Leaching Process Experiments

3.3.2.1 Atmospheric Leaching

Direct atmospheric leaching of carbonaceous sulphide ore was carried out in a beaker set up as shown on Figure 3.12. The leaching of carbonaceous sulphide ore was carried out under different sulfuric acid concentration (H_2SO_4, 0.2-1 mol dm^{-3}) at 95 ^{0}C, agitation speed of 700 rpm for one hour. As indicated in the leaching efficiency of Cu did not exceed 10 %. Fe dissolution was also considered because it is closely related to the leaching of copper. The dissolution of iron was very low as well. It is understandable that the leaching kinetics would be so low, given the presence of carbonate minerals. The carbonate minerals are detrimental as they are acid consuming therefore making it difficult to leach the Cu minerals. For this reason, it was concluded that leaching of Cu in complex carbonaceous sulphide ore at a longer time with increased acid concentration would be an alternative during atmospheric leaching.

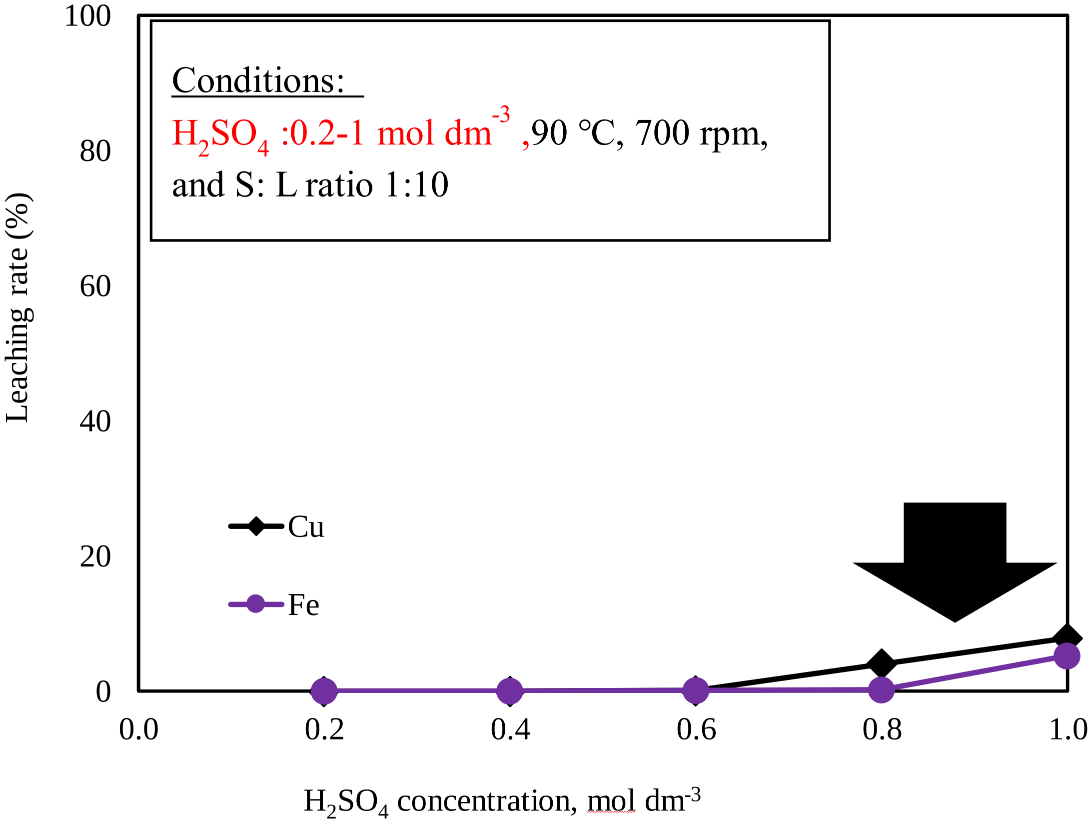


Figure 3. 12. Atmospheric pressure leaching of complex carbonaceous flotation products.

3.3.2.2 Direct High-Pressure Leaching

Effect of sulphuric acid concentration

The effect of sulfuric acid concentration on the rate of copper and iron leaching was examined under two separate conditions of atmospheric leaching (AL) and high-pressure leaching (HPL). Sulfuric acid concentration was tested in the range of 0-1 M while other leaching parameters of temperature and stirring speed were kept constant at 160 ^{0}C and 700 rpm for one hour. In the case of high-pressure leaching, total pressure was controlled to 1 MPa. From the results presented in Fig. 3.13 it can be concluded that the leaching recovery of Cu was greater with increasing sulfuric acid concentration by high pressure leaching compared to atmospheric pressure leaching. In high pressure leaching, copper dissolution was highest at 91.08 % whereas in atmospheric leaching it was 79.58 % at 1.0 M sulfuric acid concentration.

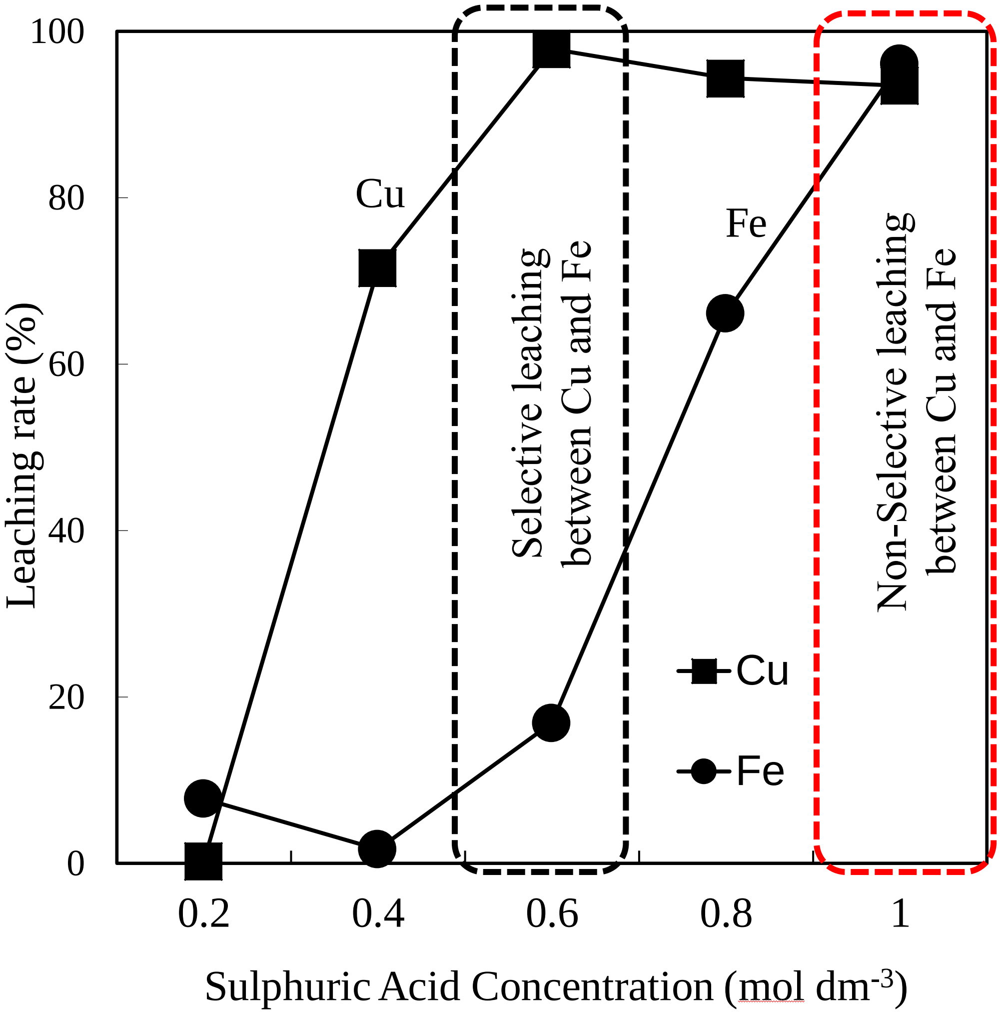


Figure 3. 13. Effect of sulphuric acid of leaching rate of copper in complex carbonaceous ore.

A relatively high leaching rate of Cu is observed in HPL at 0.6 M H_2SO_4 compared to AL. These results are attributed to the variable design consideration for autoclave machine used in the leaching experiments. In an autoclave, oxygen mass transfer from gas into solution greatly enhances the oxygen utilization in dissolution of sulfide even with no acid addition.

Similarly, a higher increase in iron recovery is seen with increasing H_2SO_4 concentration during high pressure leaching experiment compared to atmospheric pressure Fig. 3.13.

Despite the increased Cu and Fe recoveries observed in high pressure leaching, the concentration of the metal was considerably low. For copper, concentration of metal in pregnant leached solution was highest at 3.69 g/L in 1 M H_2SO_4. Low reporting of these concentration level could be attributed to the presence of acid consuming components of calcium and magnesium dolomite. Additionally, from previous mineralogical observations, copper minerals were seen disseminated in an unreacted mineral phase in the solid residue. In order to address this problem a non-oxidative leaching to decompose these components is highly suggested and will be considered for further experimental work.

Furthermore, the low concentrations of Cu and Fe reported in the pregnant leached solutions could be the result of un-leached minerals that are highly disseminated in the copper ore. A further liberation is suggested to reduce particle size for effective leaching.

Effect of temperature

A series of leaching experiments were performed at different temperatures of 90, 110,130,150 and 170 ^{0}C. The other leaching conditions were fixed as follows: S/L ratio of 1:5, sulfuric acid concentration of 0.5 mol L^{-3}, particle size fraction of 75 μm for 60 minutes. The influence of temperature on leaching of copper, iron and calcium is shown in Fig. 3.14. It indicates that an increase in temperature increases the leaching rate of copper and iron. The change in leaching rate of copper increased from 38.95 % to 92.36 %.

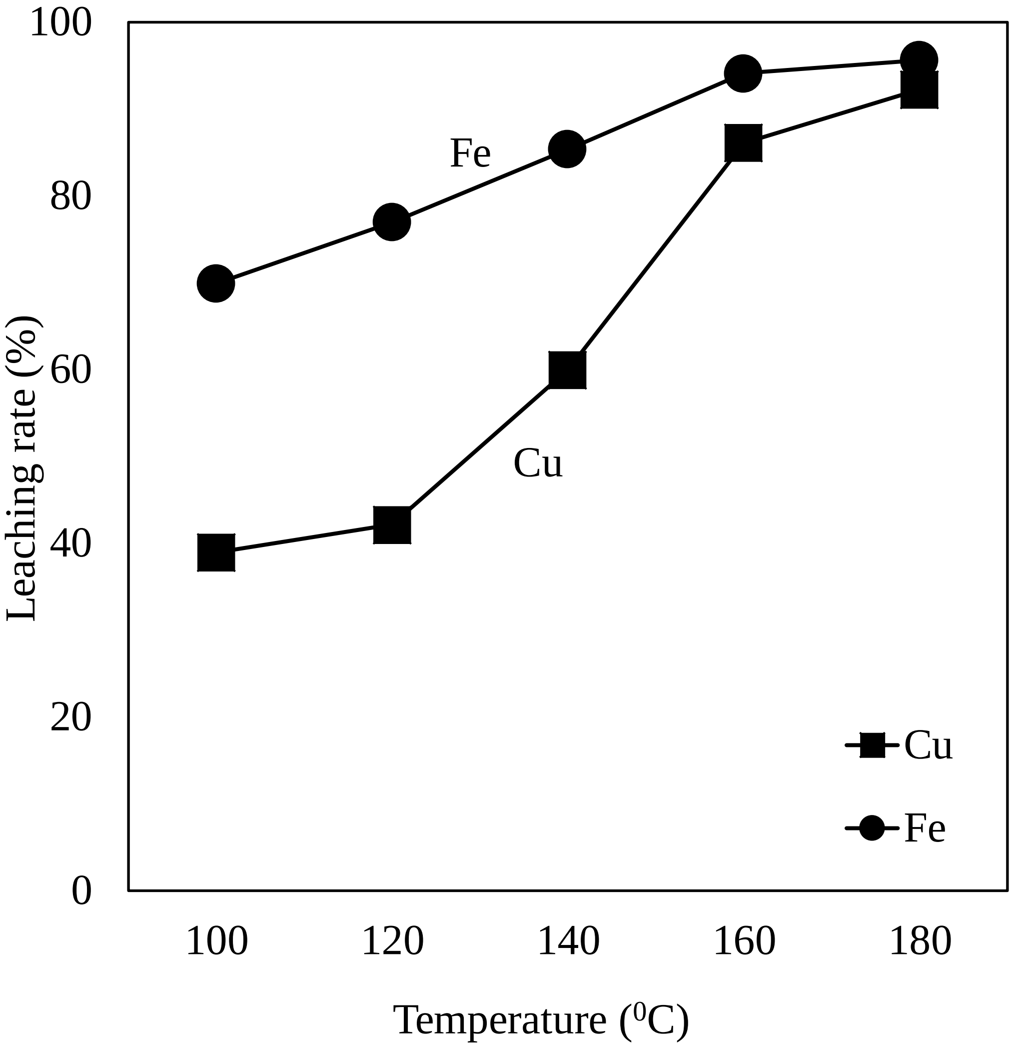


Figure 3. 14. Effect of Temperature of leaching rate of copper in complex carbonaceous ore.

The summarized metal concentrations in the leachate are presented in Fig. 3.15. An increase in temperature resulted in the formation of iron from dissolution of iron minerals and subsequently presented an increased oxidation of copper minerals (Antonijević and Bogdanović, 2004). With an increase in temperature, leaching of iron reached a plateau, which can be explained that increases in iron concentration resulted in appearance of iron oxide precipitate Fig. 3.16. According to other literatures, this observation could result in the passivation of copper metal. This observation was not made as copper concentration in the leachate increased with temperature. The kinetic studies observed suggested that, copper dissolution was not completely dependent on iron concentration.

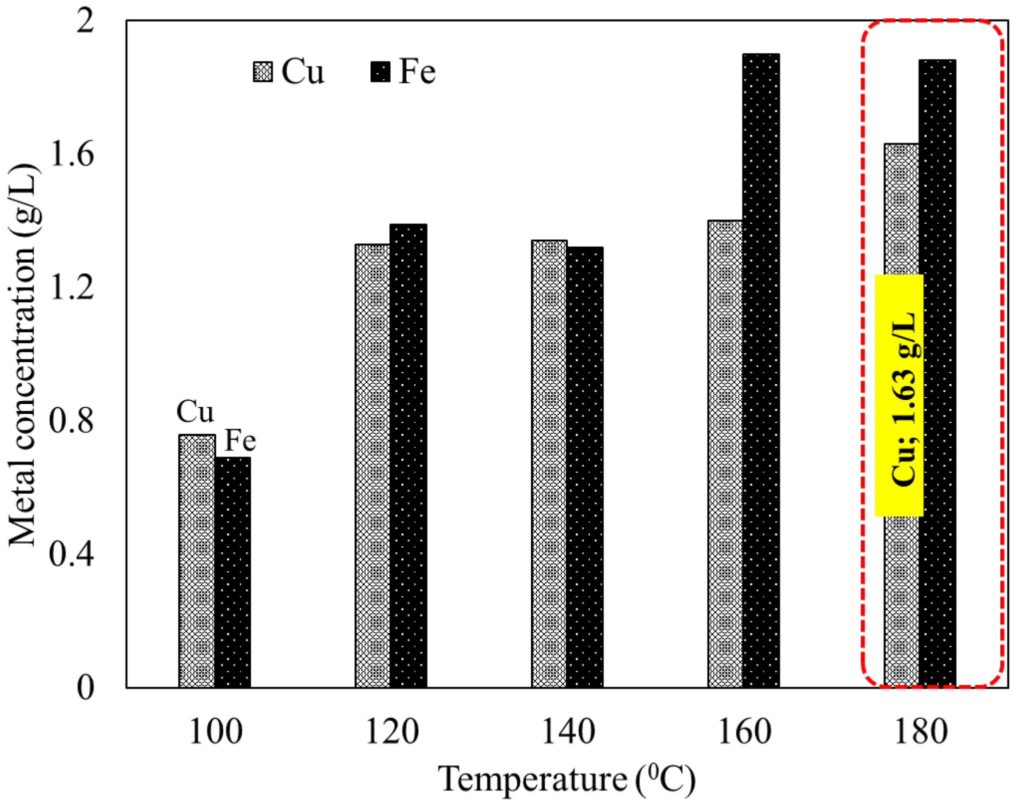


Figure 3. 15. Effect of Temperature of leaching concentration of copper in complex carbonaceous ore.

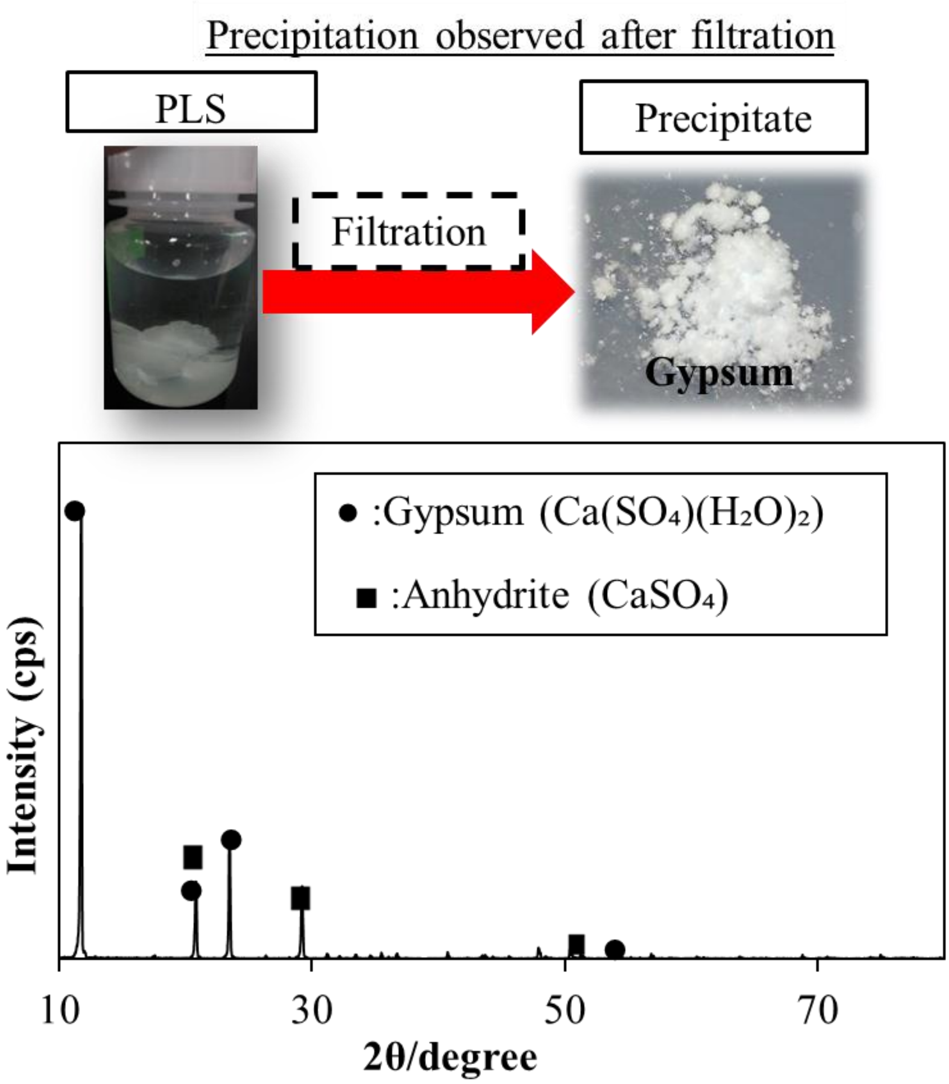


Figure 3. 16. Solid residue precipitates observations by XRD analysis.

Effect of solid/liquid ratio

The effect of S/L ratio in the range, 1:10,1:5,1:3 and 1:1 was investigated in the leaching of carbonaceous sulfide ore. The experiment was carried out using sulfuric acid of concentration of 0.5 mol L^{-1} at 150 ^{0}C and experimental results are shown in Fig. 3.17.

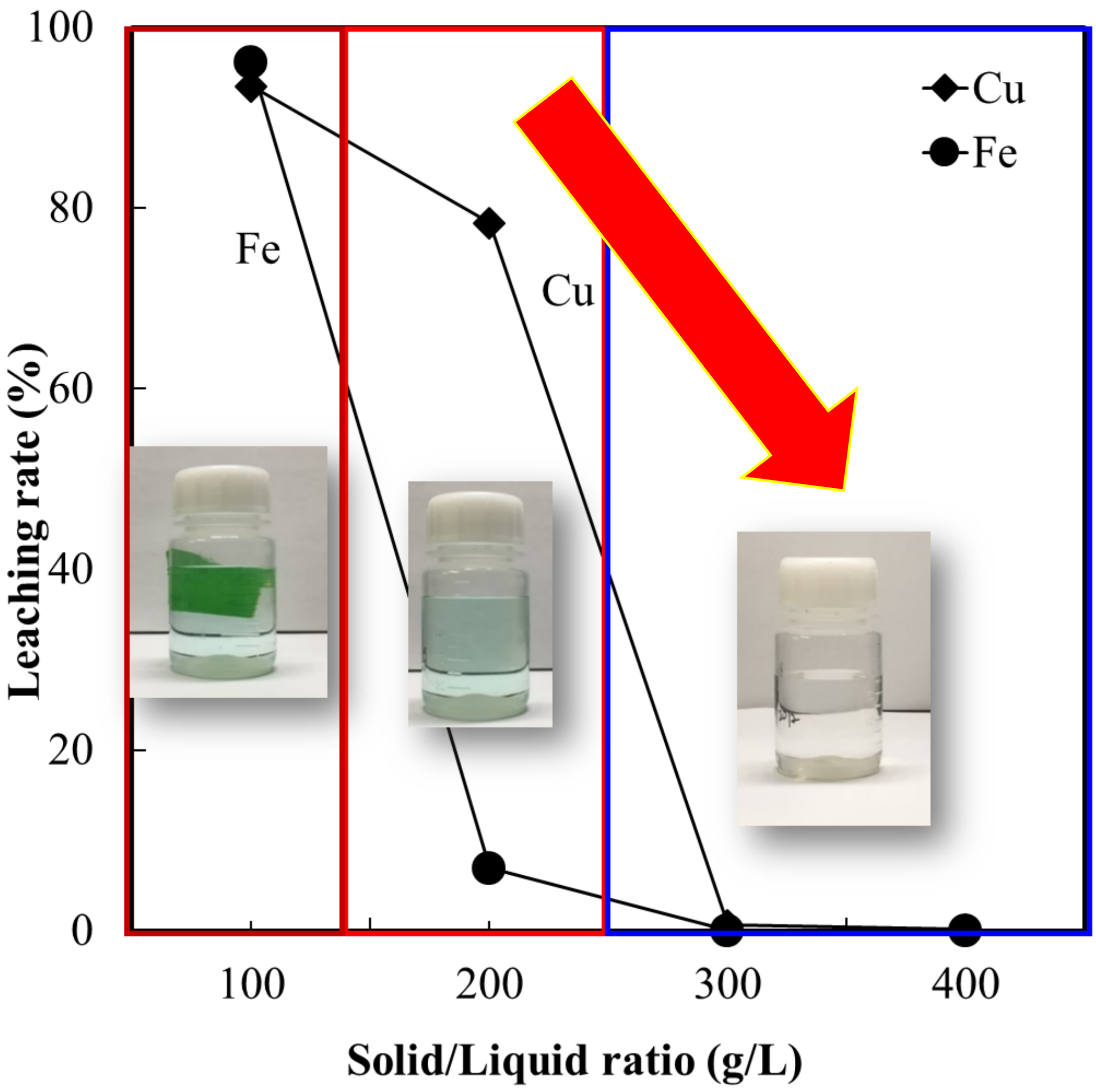


Figure 3. 17. Effect of solid/liquid ratio of leaching rate of copper in complex carbonaceous ore.

The observed effect of pulp density shows a gradual decrease of Cu and Fe concentrations with increase in solid: liquid ratio (Fig. 3.18). The dissolution of calcium in the leachate is recorded in the range below 10 % for all experiments carried out. This work is in agreement with the work of McDonald and Muir (2007) who found out that an increment of solid/liquid ratio decreased the leaching rate of Cu. This phenomenon is ascribed to the fact that an increment in solid/liquid ratio effect the viscosity of particles due to probable difficulties in agitation. Furthermore, the reaction became rate-limited by oxygen transfer into the liquor which is essential to the dissolution of Cu. Additionally, solid/liquid ratio could reduce the leaching rate of copper by reducing the production of acid because of the low concentrations of Cu minerals in the ore but high acid consuming carbonaceous minerals. However, Antonijevic *et al.* (2008) found that a change in the solid/liquid ratio did not affect the leaching rate of copper and iron as the dissolution rate was consistent for various pulp densities. A detailed study on the kinetic mechanism of copper leaching rate and iron dissolution involving the solid/liquid obtained by fractional factorial analysis will help in understanding the process better.

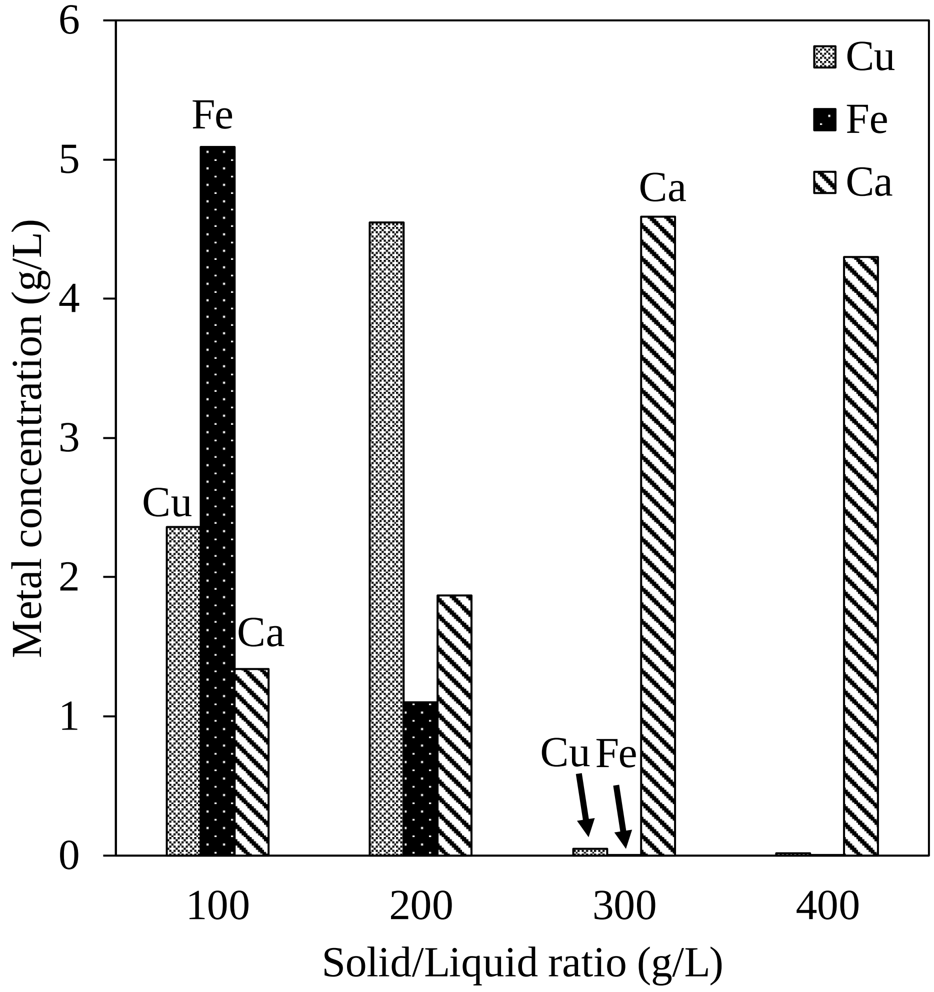


Figure 3. 18. Effect of solid/liquid ratio of leaching concentration of copper in complex carbonaceous ore.

3.3.3 Principles of the chemical modification and kinetic leaching of complex carbonaceous sulfide ore

According to various literature review, a fair amount of chemical reactions can be used to study the chemical reactions occurring in different ores. In this study we considered the $CuFeS_2$-H_2SO_4-H_2O-O_2 system (McDonald and Muir, 2007b, 2007a).

$$CuFeS_2 + O_2 + H_2SO_4 \rightarrow CuSO_4 + Fe_2(SO_4)_3 + H_2O + S^0 \qquad (3.15)$$

$$CuFeS_2 + \ Fe_2(SO_4)_3 \rightarrow CuSO_4 + +Fe_2SO_4 + S^0 \qquad (3.16)$$

The leaching of chalcopyrite at high temperature is described following the equation below:

$$2CuFeS_2 + 8.5O_2 + H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + H_2O + S^0 \qquad (3.17)$$

$$\begin{aligned} &2CuFeS_2 + 16Fe_2(SO_4)_3 + 16H_2O \\ &\qquad \rightarrow 2CuSO_4 + 34FeSO_4 + 16H_2SO_4 \end{aligned} \qquad (3.18)$$

Consequently, during the reaction, sulfuric acid is generated following the reaction of elemental sulfur that might have formed (dependent on temperature or amount of oxygen), while the ferrous sulfate converts to ferric sulfate as described below:

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (3.19)$$

$$2FeSO_4 + 0.5O_2 + 2H_2SO_4 \rightarrow H_2SO_4 + Fe_2(SO_4)_3 \qquad (3.20)$$

The hydrolysis of iron in the ferric sulfate proceeds depending on different conditions such as the amount of free acidity in the system. This reaction strongly affects the oxidation of chalcopyrite and hence occurs in different pathways upon the presence of Fe^{3+}, Fe^{2+}, H^+ and O_2. The hydrolysis occurs as follows:

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3 + 3H_2SO_4 \tag{3.21}$$

$$Fe_2(SO_4)_3 + 14H_2O \rightarrow 2(H_3O)Fe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \tag{3.22}$$

$$Fe_2(SO_4)_3 + 2H_2O \rightarrow 2Fe(OH)SO_4 + H_2SO_4 \tag{3.23}$$

When low-acidities are present in the system, the inter-conversion of iron containing residues occur as follows:

$$2(H_3O)Fe_3(SO_4)_2(OH)_6 \leftrightarrow 5H_2O + 3Fe_2O_3 + 4H_2SO_4 \tag{3.24}$$

$$2Fe(OH)SO_4 + H_2O \leftrightarrow Fe_2O_3 + 2H_2SO_4 \tag{3.25}$$

Additionally, due to the presence of acid consuming minerals such as calcite and dolomite we considered the phase changes according to new crystal formations following $CaCO_3$ /$MgCO_3$-H_2SO_4-H_2O system (Tindall and Muir, 1998; Moradi and Monhemius, 2011; Liu *et al.*, 2016):

$$CaCO_3 + H_2O + H_2SO_4 \rightarrow CaSO_4.2H_2O \downarrow + CO_2 \uparrow \tag{3.26}$$

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4.2H_2O \downarrow + 2CO_2 \uparrow + MgSO_4 \tag{3.27}$$

3.3.4 Intrinsic kinetics of reaction on complex carbonaceous sulfide surface

Kinetic modelling control

To control the leaching process, it is important to establish quantitative measurements of the leaching kinetics to assist in making interpretation to the nature of the process taking place. The slowest step controls the whole leaching kinetics and is regarded as the rate-limiting step. Therefore the rate of the leaching was considered with respect to time (t) and fraction reacted (α) (Liu *et al.*, 2016).

Generally, the leaching of chalcopyrite includes a number of simple steps, which often require separate evaluation such as the reaction rate. The rate of reaction shown in Eq. 3.25 is commonly used to ascribe the number of reactants and the transformed reaction products as follows:

$$aA + bB \rightarrow Products \tag{3.28}$$

Fig 3.19 illustrates the course of possible reactions in a system following Eq. 3.26-3.27. The overall process can be classified into three types of process namely, chemical, diffusion or mixed reaction systems. Here, the reaction of particles differs according to different factors such as the type of ore and liquid reagent used. When the process has taken place, the interface of the particle may be characterized by the formation of either soluble or insoluble reaction products transferred into the surrounding medium or they remain on the surface. In the reaction of the conversion of the particle there are three possible cases of the rate controlling step of the reaction (Havlik, 2008):

- Transference of the reactant mass through the layer of the liquid reagent adjacent to the surface
- Heterogeneous chemical reactions on the surface of the shrinking unreacted core

- Diffusion through layer of the reaction product.

There are also three possible cases for extraction:

- Mass transfer in the boundary layer
- Heterogeneous reaction on the internal surfaces of the particles
- Internal diffusion in the pores.

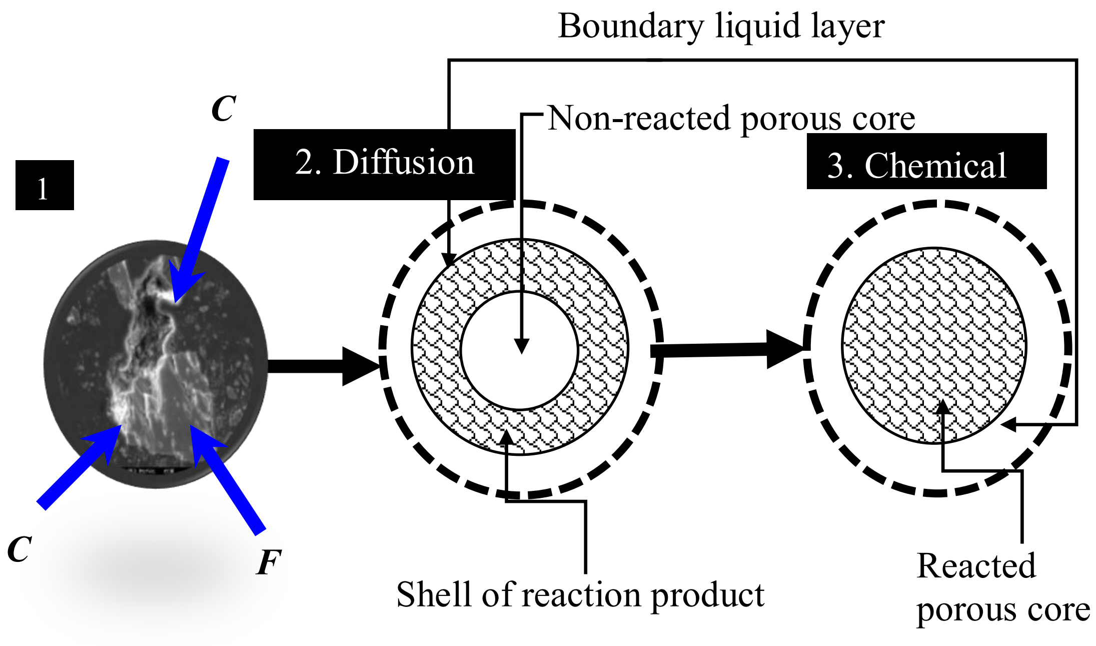


Figure 3. 19. Illustration of leaching kinetic model of copper dissolution.

The aforementioned cases of the rate-controlling steps must be considered in deriving the kinetic equations of the reacting particles. It is equally important to note that the interfacial area may not change in a regular manner. Therefore, practically, we consider the presence of a grain of specific form which the leached particle originates during the reaction and substitution of the results into these equations shows whether the reaction follows the proposed course or whether it deviates from it. This procedure therefore uses the kinetic modelling equations for determination of the course and mechanism in the leaching system.

Kinetic modelling equations for determination of mechanism

As already mentioned, the kinetic dependences are based on the kinetic curves of the time dependence of the amount of leached metal which can either be controlled by diffusion, chemical or the chemical reaction. The controlling mechanism are usually not known in advance therefore two approximations can be made (Havlik, 2008):

- the first approximation may be the shape of the curve: if the curves are parabolic then it signifies the diffusion reaction
- a linear form of the kinetic dependences indicates a chemical reaction system since the chemical reaction is defined by equation of a straight line.

In order to determine the mechanism of leaching copper in complex carbonaceous ore under sulfuric acid conditions, it is important to use the shrinking core models. The shrinking core model is one of the most useful hydrometallurgical reaction models to explain clearly how a reaction is affected by different process. In particular, the mechanism can either be surface/chemical controlled, diffusion-controlled or a mixed controlled containing diffusion and surface reaction components, which simultaneously take place.

If the reaction is controlled by a diffusion through a product layer, the integrated rate equation is as follows (Eq. 3.26):

$$1-\frac{2}{3a}-(1-\alpha)^{\frac{2}{3}}=k_d t \qquad (3.29)$$

where α is the fraction reacting, $k_d=c/d_0^2$ are the pore diffusion rate constant and the chemical rate constant, respectively, c is constant, t is leaching time and d_0 denotes the initial particle diameter.

When the reaction is controlled by surface/chemical reaction, then the rate expression is as follows (Fig 3.18 (3)):

$$1 - (1 - \alpha)^{\frac{1}{3}} = k_c t \tag{3.30}$$

where α is the fraction reacting, $k_c = c/d_0$ are the pore diffusion rate constant and the chemical rate constant, respectively, c is constant, t is leaching time and d_0 denotes the initial particle diameter.

Activation energy

The reactions in a leaching process occur when molecules collide with sufficient energy. Thus, reaction rates are related to collision frequency. Similarly, the rates are also related to collision energy. The reaction rate constant is proportional to the reaction rate. Therefore, the rate constant can be expressed in terms of collision frequent factor, v, and the probability that the reaction collision has sufficient energy (Havlik, 2008). The relationship is described by the Arrhenius equation Eq. 3.17 (Havlik, 2008):

$$\ln k = \ln A - E_a/(RT) \tag{3.31}$$

where k is the apparent rate constant, A is the pre-exponential factor, R is the mole gas constant and T is the thermodynamic temperature.

The Arrhenius equation can provide valuable information in designing hydrometallurgical process. In particular, the activation energy can be used to predict the rate responses to a change in temperature. Simply put, the Arrhenius equation can be used to determine the rate as a function of temperature if the constants are known.

It is worth noting that one of the most important parameters, the effect of temperature on the leaching of chalcopyrite, is not defined unambiguously. Particularly, this is given by the difference in leaching conditions such as the mineralogical characterization of the leaching feed. The diffusion-controlled process is not greatly affected by temperature while the chemical controlled process is strongly depended in temperature. According to Havlik, 2008, this is due to the diffusion co-effiecient being lineraly independent on temperature according to Stokes-Einstein equation, whereas the rate costant of the chemical reaction depends exponentially on temperature as expressed by the Arrhenius dependence. In other words, this means that the value of coefficient D increases in units but the coefficient k increaes by orders of magnitude. For this reason the diffusion controlled-process are low and in the range of 4-13 kJ/mol while those in a chemical reaction are higher than 42 kJ/mol (Havlik, 2008). The reactions for a mixed system vary in the range 15-38 kJ/mol. The calculations of activation energy have resulted in the scatter of different activation energies found by different authors as indicated in Table 3.5.

Table 3. 5. Different activation energies observed by different authors in leaching.

Material	**Medium**	**E_a (kJ/mol)**	**Temp. (^{0}C)**	**Rate-controlling step**	**Reference**
$CuFeS_2$(natural)	$NaNO_2$+H_2SO_4	34.06	80-120	Diffusion	(Gok *et al.*, 2014)
$CuFeS_2$(natural)	H_2SO_4	42.4	160-180	Chemical reaction	(Han *et al.*, 2017)
$CuFeS_2$(natural)	$NaNO_3$+H_2SO_4	83	70-90	Mixed controlled	(Sokić, Marković and Živković, 2009)
$CuFeS_2$(natural)	H_2O_2+H_2SO_4	60	24.85-49.85	Chemical reaction	(Antonijević, Janković and Dimitrijević, 2004)
$CuFeS_2$(natural)	H_2SO_4	16.08	29.85-94.85	Mixed controlled	(Sun *et al.*, 2009)

As already mentioned, the kinetic study of leaching of chalcopyrite in complex carbonaceous sulfide ore involves two stages. At first, the degree of transformation in relation to the parameters investigated with respect to time. The parameters that was studied included stirring speed, particle size, sulfuric acid concentration and temperature. The kinetic parameters of the reaction were evaluated and interpretation were made in relation to the nature of the process that occurred in the system.

Determination of leaching variables in leaching of carbonaceous sulfide ore

Effect of stirring speed

Figure 3.20 shows the kinetic curves of leaching of copper at different stirring speed of 450, 600, 750 and 900 rpm. The other parameters were fixed at pulp density of 100 g/L, temperature of 160 ^{0}C, sulphuric acid concentration of 1.0 mol/dm^{-3}, average particle size of d_{50} ~106 µm, total pressure of 2.5 MPa for 1 hour. The leaching efficiency of copper increased from 80.15 % to 86.32% when stirring speed was increased from minimum 450 rpm to 900 rpm. The other ranges of 600 and 750 rpm did not show any substantial influence for leaching copper. Sun *et al.*, (2009) also discussed that usually an increase in stirring speed increased the rate of leaching due to the suspension of mineral particles and the decreasing thickness of the mass transfer boundary layer on the surface of the particles. However, his results indicated that there was no significant rise in the copper extraction with increase in stirring speed from 500 to 600 r/min. These observations were also identical to the current study therefore it would seem pointless to increase the stirring speed above 750 rpm in terms of raising the extraction of copper. An average 700 rpm stirring speed was chosen for further experiments.

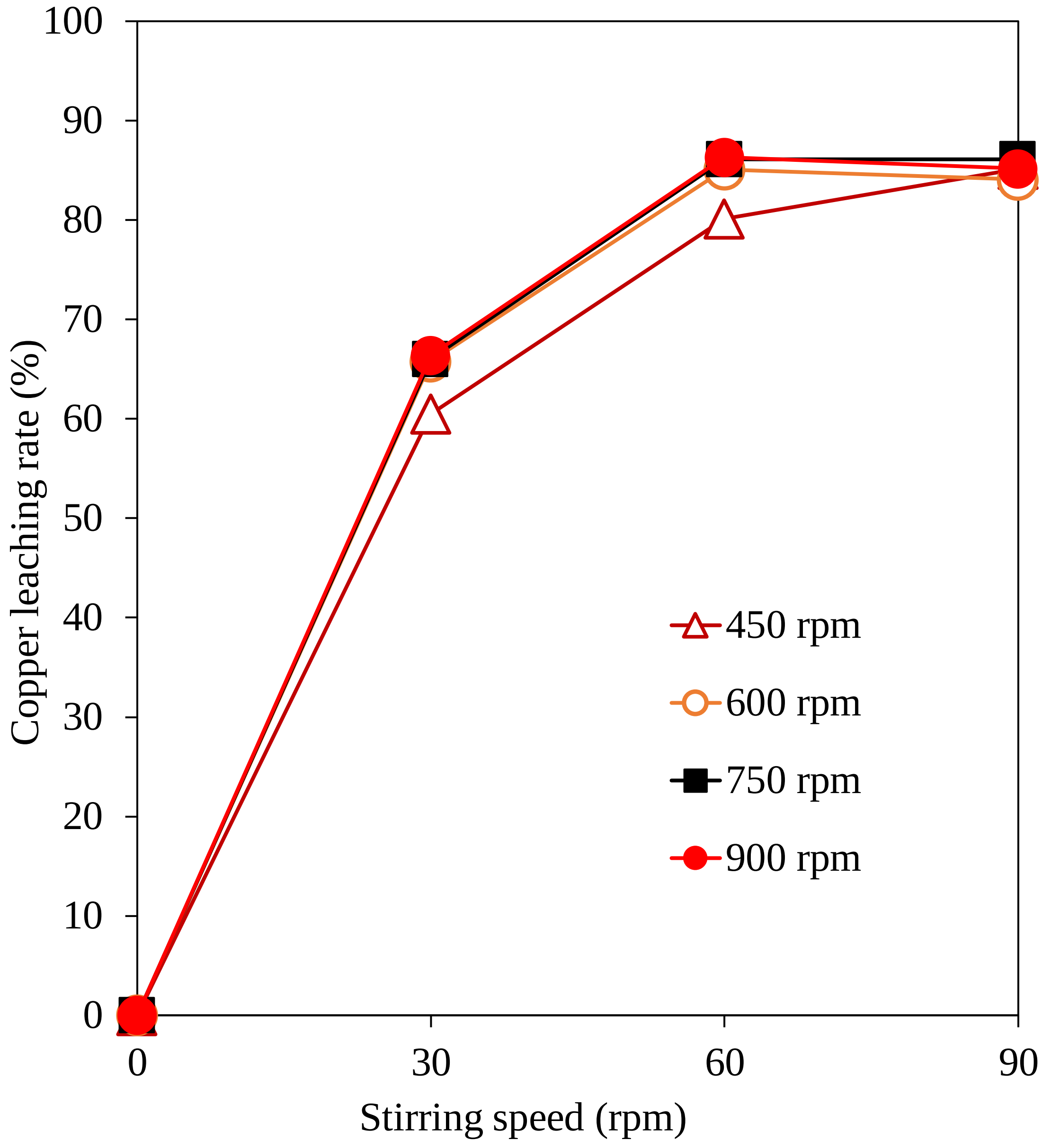


Figure 3. 20. Effect of stirring speed of leaching rate of copper in complex carbonaceous ore.

Effect of particle size

To investigate the effect of temperature, the ore was slightly ground and sieved to particle size ranges of 200-160 μm, 160-106 μm, 106-75 μm, 75-32 μm and -32 μm. The experiments were performed at pulp density of 100 g/L, total pressure of 2.5 MP, H_2SO_4 concentration of 1 mol/dm^{-3}, stirring speed of 700 rpm and temperature of

160 ^{0}C. The results are indicated in Fig 3.21. It can be seen that reduction of the particle produced remarkable results in the leaching rate of copper. The findings indicated that the leaching rate was enhanced when particle size reduced therefore increasing the active surface area for reaction. Similar results have been observed in other literatures.

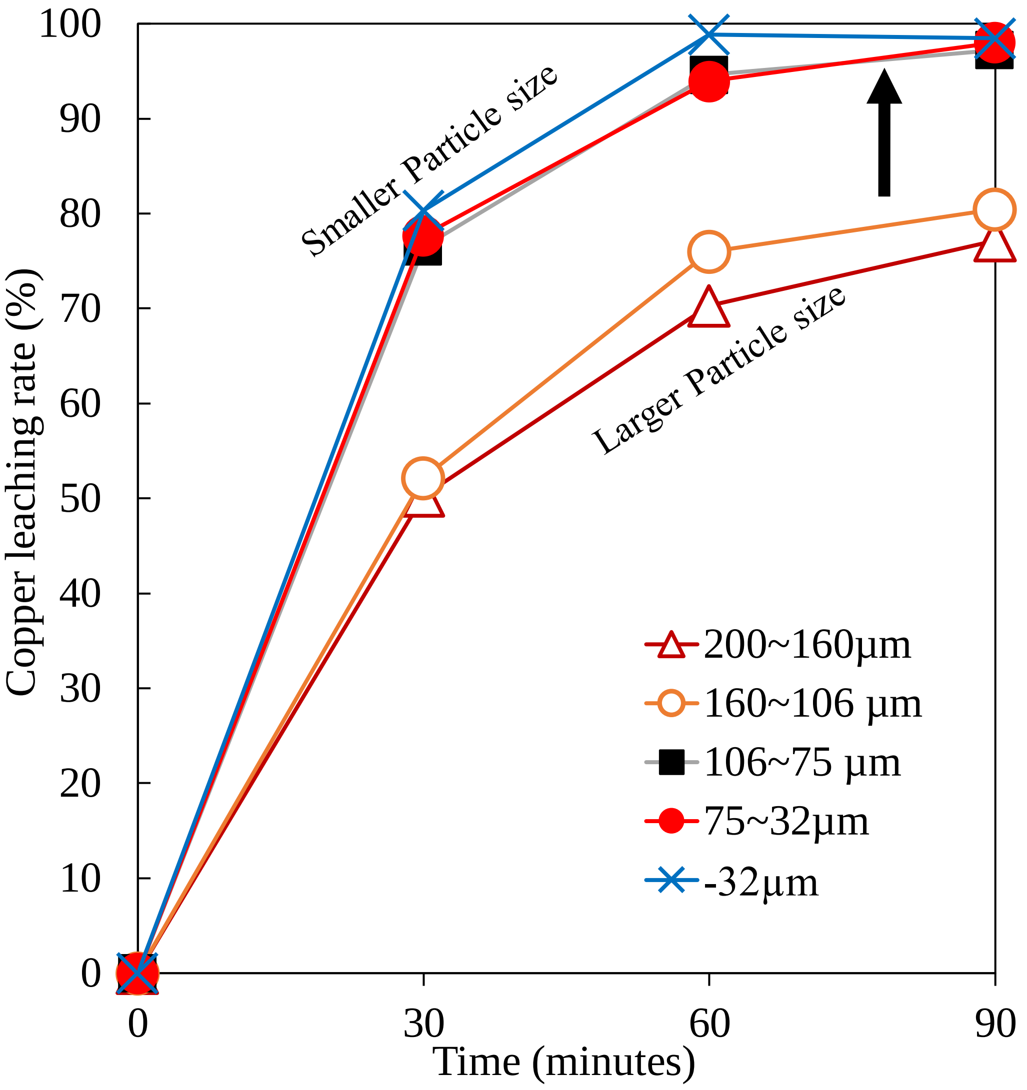


Figure 3. 21. Effect of particle size of leaching rate of copper in complex carbonaceous ore.

Effect of H_2SO_4 concentration

The effect of sulphuric acid concentration on copper dissolution was studied at various concentrations ranging from 0.2-1.0 mol dm^{-3}. From Fig. 3.22 it can be see that raising the sulphuric acid concentration from 0.2 mol dm^{-3} to 1.0 mol dm^{-3} increased the leaching rate of copper. The leaching efficiency of copper increased from <10 % to 93.46 %. It was expected that lower leaching rates would be low due to the presence of carbonate minerals. The calcite and dolomite are acid consuming minerals. At the highest concentration, an increase in time shows a steady dissolution which indicated that the system had reached saturation. The leaching efficiency of copper by sulphuric acid has produced conflicting results. Han *et al.*, (2017) presented that an increase in sulphuric acid concentration had a negative effect in the dissolution of chalcopyrite. (Liao *et al.*, 2015) and Koleini, Aghazadeh and Sandström, (2011) had conflicting results as to the role of sulphuric effect, the former indicated that copper leaching was increasing the acid concentration from 0.80 mol dm^{-3}. The latter indicated that no dependence was observed in copper dissolution due to the difficulties of controlling the redox potential.

Crundwell, (2013) argued that the acid attack mechanism should be rejected and presented that the first step of the reaction is not fast enough and it does not successfully describe the kinetic parameters. McDonald and Muir, (2007a, 2007b) presented that the dissolution reaction goes entirely through the acid attack. The equation presented earlier (Eq. 3.1 and 3.3) shows the action of acid in the system with the chalcopyrite mineral. These observations agree well with our findings. However, the role of sulphuric acid remains not authoritatively answered because if acid attack occurs, then the expectation would be that the reaction rate would be strongly dependent on the acid concentration as (Crundwell, 2013) argued.

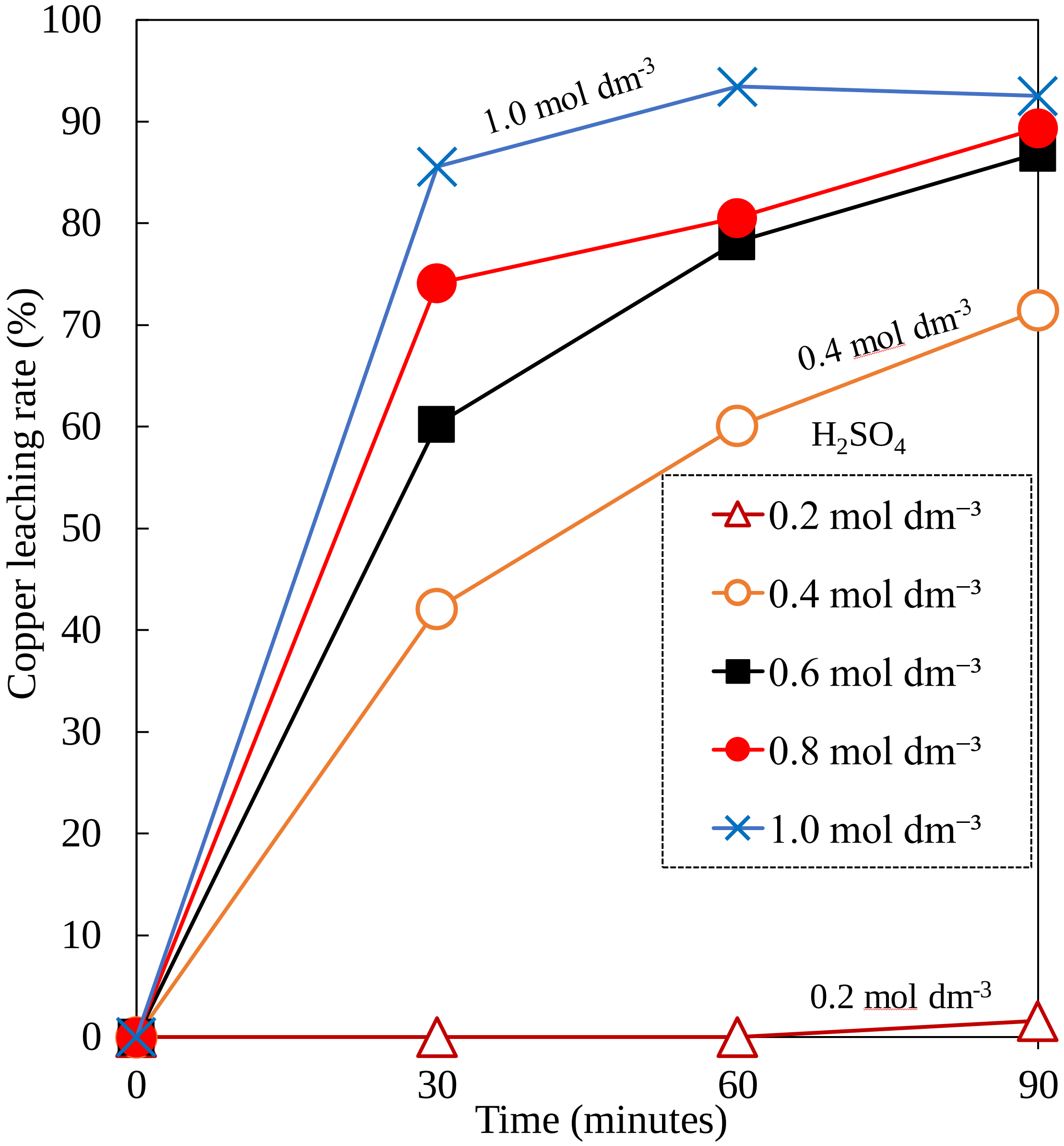


Figure 3. 22. Effect of sulphuric acid of leaching rate of copper in complex carbonaceous ore.

The leaching rate of iron with respect to acid concentration have an intertwined relationship. As seen in Fig. 3.23 the leaching rate of iron shows an increase in leaching rate when acid concentration occurs. The result may be due to the high solubility of ferric sulphate in high acidic environments. The hydrolysis of iron in solution is clearly depicted by the amount of acid concentration in the system. Equation 3.7-3.8 depicts the iron dissolution of iron in the system, Interestingly, when there is no precipitation of iron minerals, the iron remains as solution form in the system.

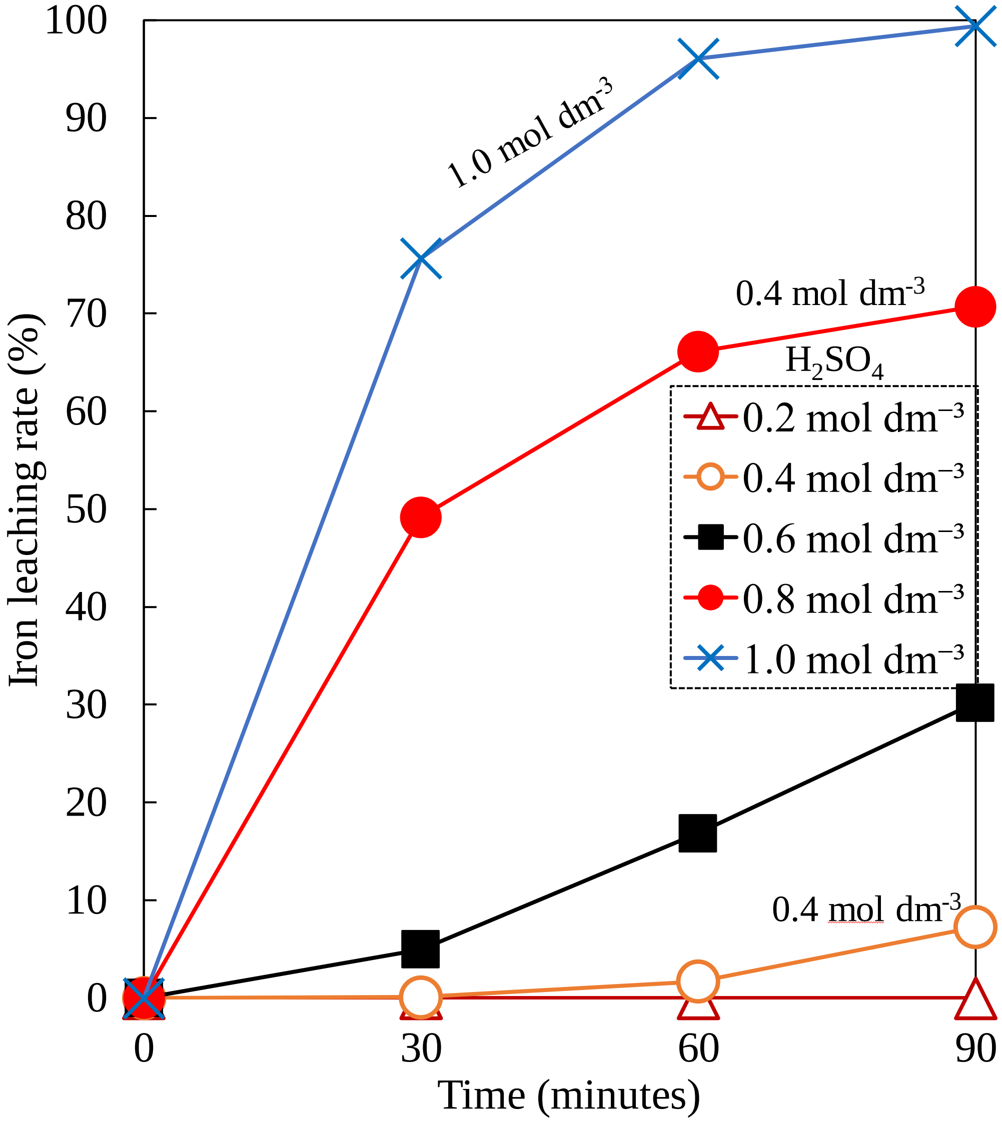


Figure 3. 23. Effect of sulphuric acid of leaching rate of iron in complex carbonaceous ore.

Effect of temperature

A series of experiments were carried out at T=100,120,140,160, and 180 ^{0}C to investigate the effect of temperature on leaching rate. The sulphuric acid concentration, stirring speed, particle size, pulp density was kept constant as 1 mol dm^{-3}, 700 rpm, -106 µm and 100 g/L, respectively.

As presented in Fig. 3.24, the increase in temperature greatly improved the leaching efficiency of copper. When reaction temperatures increased from 100 0C to 180 0, the leaching of copper in complex carbonaceous sulphide ore rose from 45.26 % to 98.45 %. The temperature increase proves to be a significant factor into leaching rate because it accelerated the molecules thermal motion and increased the contact surface between single particle and leaching reagent. Liao *et al.*, (2015) also observed that an increase in temperature increased the leaching efficiency of minerals, attributing this to the fact that reaction takes place among effective colliding particles, and it is in line that particles which obtain more kinetic energy collide more frequently when a substance is heated. Other researchers have affirmed the observed positive results of increasing temperature to leach metals (Yu, Hansen and Wadsworth, 1973; Kaskiala, 2002; McDonald and Muir, 2007b, 2007a; Lampinen, Laari and Turunen, 2015; Liao *et al.*, 2015; Han *et al.*, 2017) .

According to the results 180 ^{0}C was chosen as the optimum temperature for leaching copper.

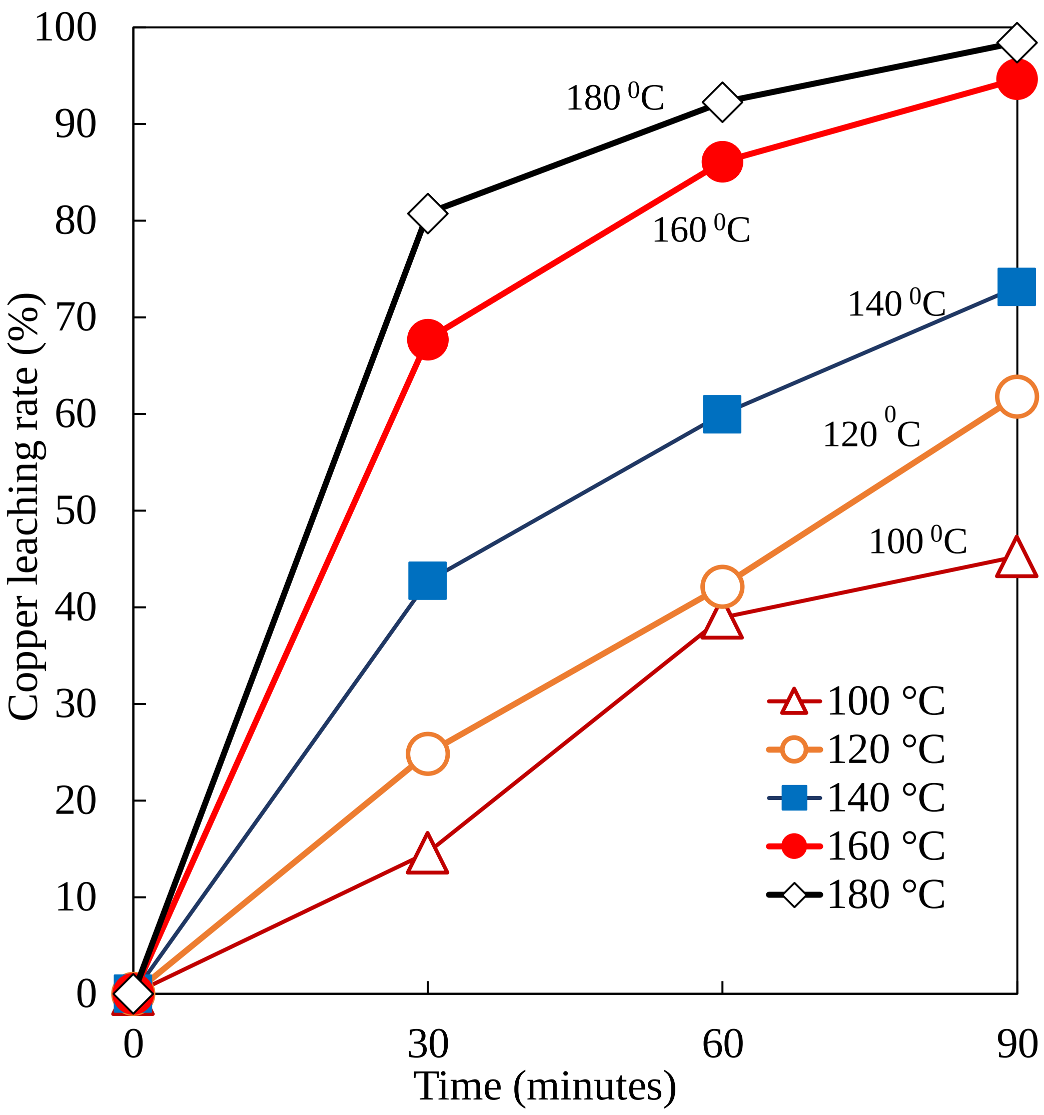


Figure 3. 24. Effect of temperature on leaching rate of copper in complex carbonaceous ore.

The SEM-EDS of the leaching residue results are shown in Fig. 3.25. It indicates that the micrograph of the leaching residues indicates a progressive increase in the roughness of the solid. After 60 min leaching, the particles present some degree of degradation, which gradually increases along the progress of leaching to 90 min. The EDS of the micro areas show that some copper was not completely dissolved and the sulphur assembled on to the mineral surface. Fig. 3.26. The results indicated that an interchanging dissolution reaction between the carbonaceous material resulted in the release of species that cause by-products such as jarosite to form. This occurrence is beneficial to the process as it can restrict consumption as well as release acid thereby altering the acid balance. The results indicate that the minerals in complex carbonaceous sulphide ore may take reactions as follows:

$$2FeS_2 + \frac{11}{2} O_2 + H_2O \rightarrow 2FeSO_4 + H_2SO_4 \tag{3.32}$$

$$2CuFeS_2 + 2.5\, O_2 + 5H_2SO_4 \rightarrow 2CuSO_4 + 5H_2O + Fe_2\,(\mathrm{SO_4})_3 + 4\mathrm{S}^0 \tag{3.33}$$

$$CaCO_3 + H_2SO_4 = CO_2 + CaSO_4 \cdot 2H_2O + H_2O \tag{3.34}$$

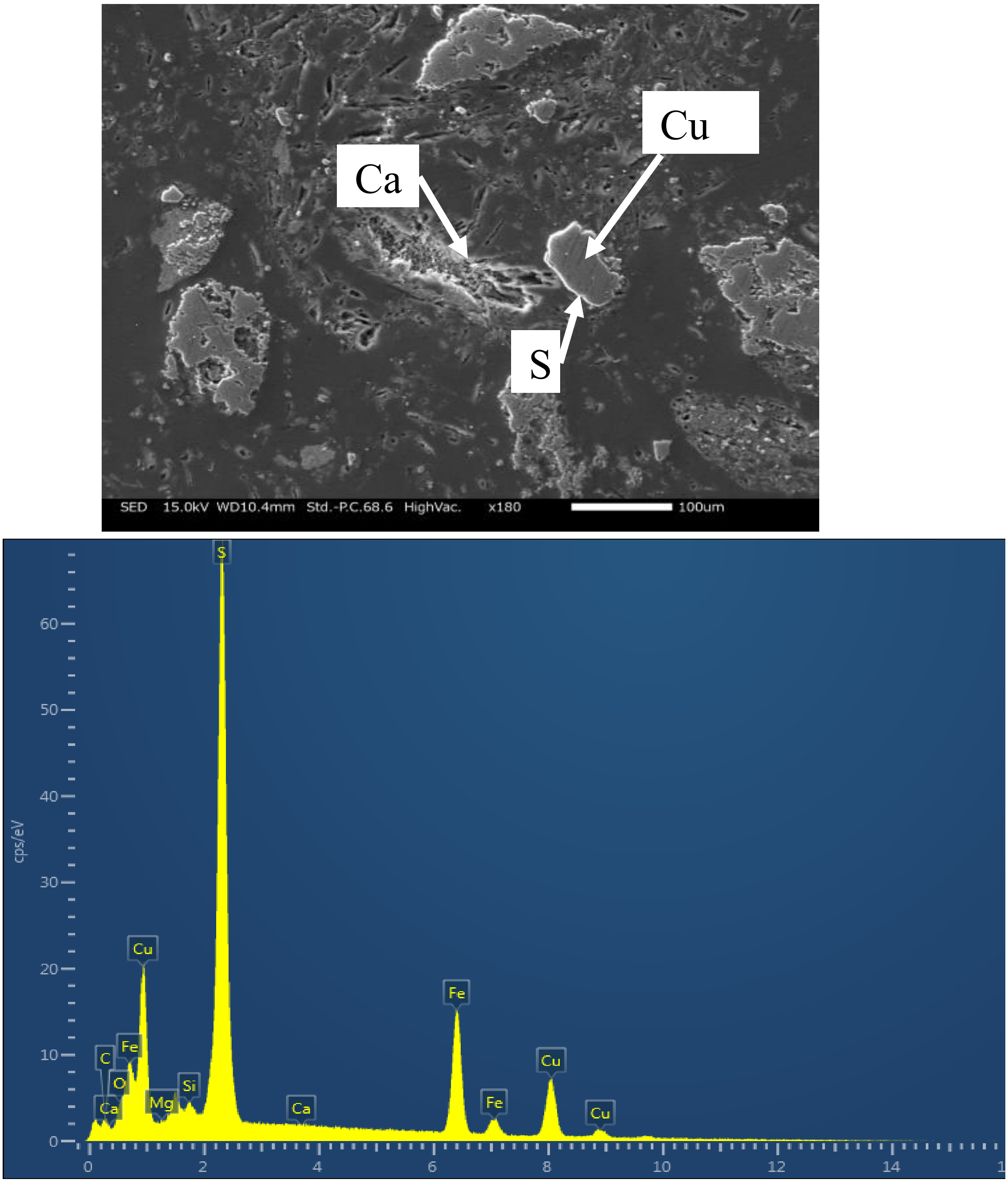


Figure 3. 25. SEM-EDS images of solid residue

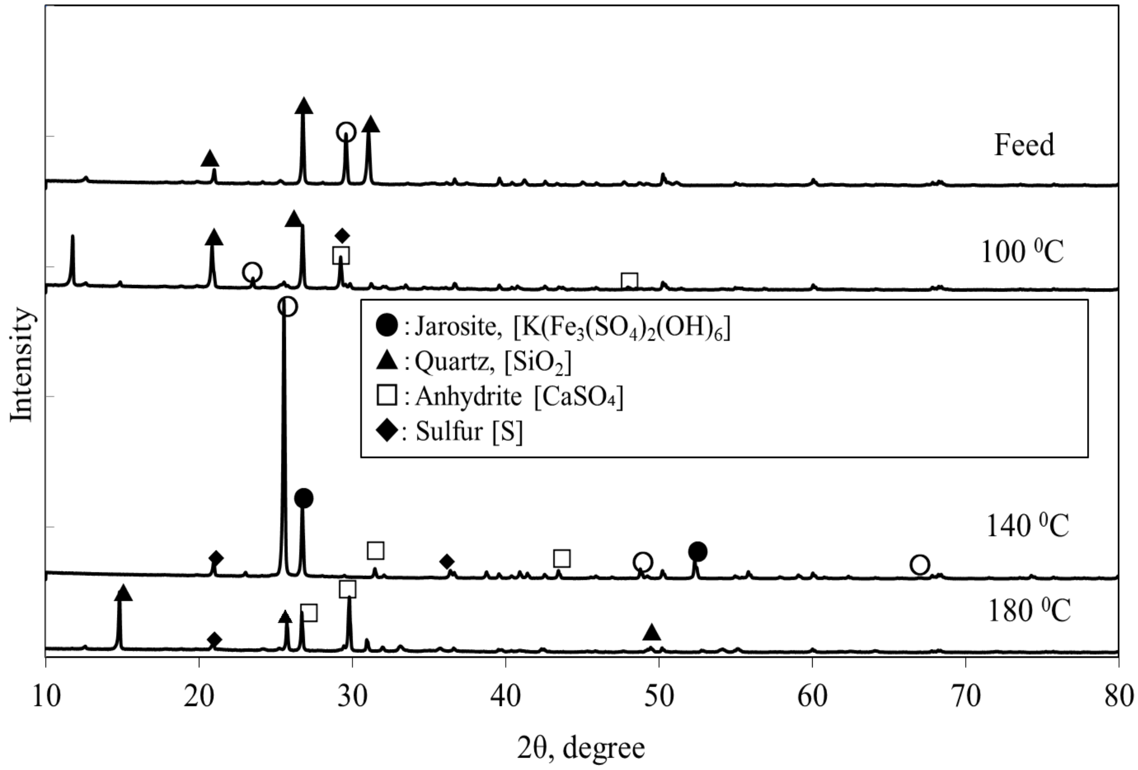


Figure 3. 26. XRD pattern of solid residue.

Effect of pressure

The influence of total pressure ($P_{total}= P_{vapor} + P_{oxygen}$) on copper dissolution from complex carbonaceous sulfide ore was evaluated with varying P_{total} ranges between 0.5 (without oxygen supply) to 2.0 MPa. Other parameters were kept constant at stirring speed: 750 rpm, particle size: -106 μm, pulp density: 100 g/L and H_2SO_4 concentration of 1.0 mol dm^{-3}.

It is evident from Fig. 3.27 that an increase in total pressure from 0.5 to 2.0 MPa a significant increase on the rate of copper leaching rate was obtained. We can observe that at the highest total pressure (2.0 MPa) over 90 % of copper was dissolved within 60 minutes. Several authors have suggested that the role of oxygen in the process seems to be as direct oxidizing agent whether to chalcopyrite or of the Fe^{2+} in solution (Dutrizac, 1994; Antonijević, Janković and Dimitrijević, 2004; Córdoba *et al.*, 2009).

On the other hand, it was observed that slight copper dissolution occurred (less than 5%) in the absence of oxidizing reagent according to Eq. 11 (Nicol, Miki and Velásquez-Yévenes, 2010):

$$CuFeS_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2H_2S \qquad (3.26)$$

According to different sources the first option for role of oxygen is unlikely, given the incapacity of low oxygen to oxidize chalcopyrite directly under ambient conditions. Córdoba *et al.*, 2009 and Lu, Jeffrey and Lawson, 2000 suggested that the most probable action of oxygen in the copper leaching from chalcopyrite is possible because of the regeneration of Fe^{3+}. Han *et al.*, 2017b suggested that the lower dissolution rate of copper with pyrite is associated with the slow oxidation of chalcopyrite after observing <1% leaching rate at P_{total} of 0.8 MPa. Similarly, the aforementioned researcher concluded that the importance of oxygen in the process resides with the oxidation of ferrous to ferric ion after observing the diffraction peaks of hematite (Fe_2O_3) and jarosite ($H_3O(Fe_3(SO_4)_2(OH)_6)$) on the XRD patterns of the solid residues.

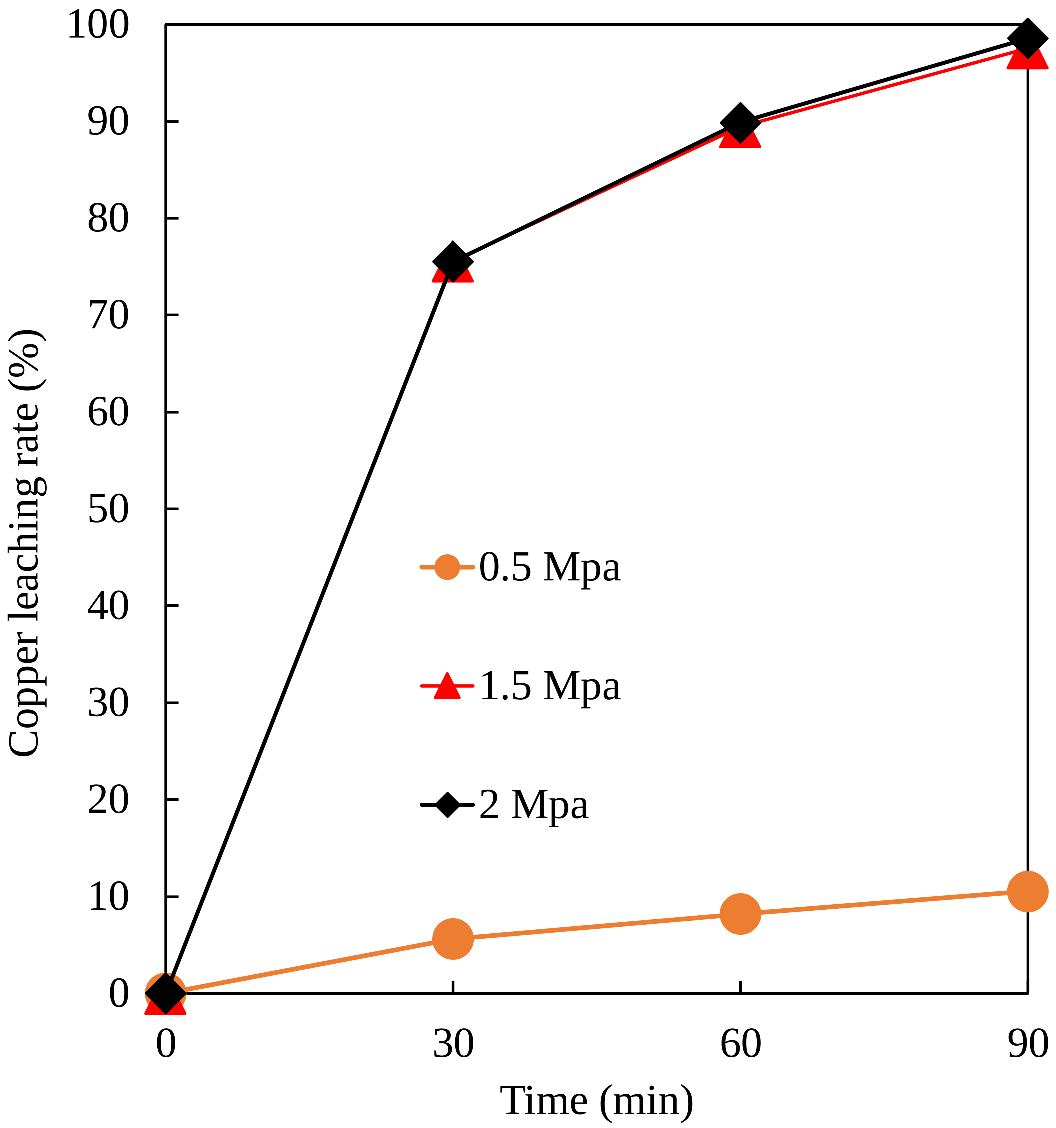


Figure 3. 27 Effect of pressure on the leaching of copper. (Temperature:180 ^{0}C, H_2SO_4 1.0 mol dm^{-3})

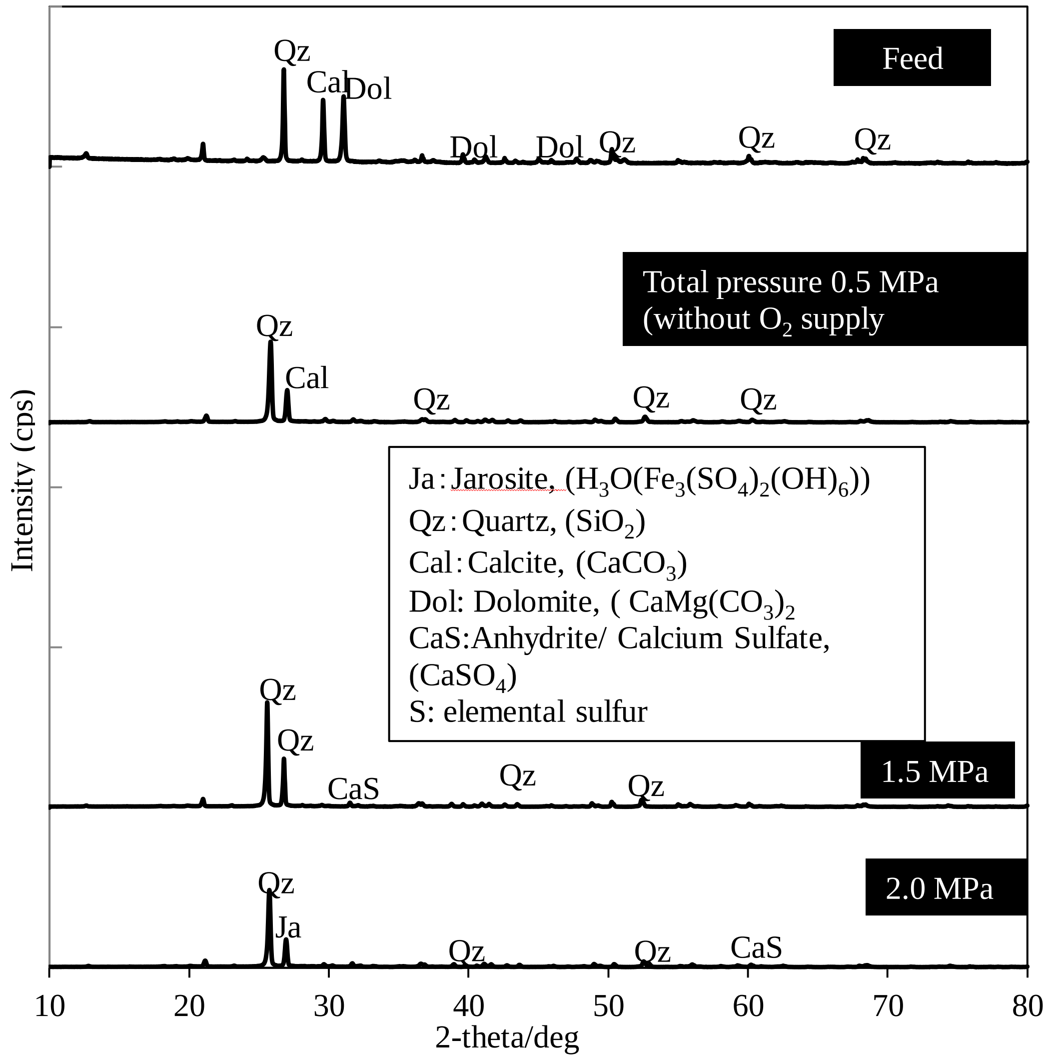


Figure 3. 28 XRD diffractograms of the feed and solid residues obtained at different total pressure leaching conditions. (Temperature:180 ^{0}C, H_2SO_4 :1.0 mol dm^{-3})

The XRD diffractograms of the residues Fig 3.28 did not show large difference between the leaching products formed under different total pressure conditions. The formation of the non-crystalline iron precipitates observed in the test explain the iron precipitation in the test. Therefore, the positive effect of oxygen during copper leaching would be related to the regeneration of oxidizing agent.

Effect of pulp density

To observe the effect of pulp density on the extraction rate, batch experiments were performed at 180 ^{0}C with four pulp density variations ranging from 100 to 400 g/L under the conditions of particle size under -106 µm, H_2SO_4 concentration of1.0 mol dm^{-3}, total pressure of 1.5 MPa and stirring speed of 750 rpm. The results plotted in Fig.3.29 illustrated that the leaching rate is unfavorable with increase in pulp density. The dissolution curve indicated that the highest final copper leaching rate (92.76 % Cu) was obtained in the smallest pulp density (i.e., at pulp density of 100 g/L). An increase in pulp density from 200 to 400 g/L copper extraction was reduced from 83.65 to 36.12 % Cu, respectively. These results indicate that high pulp density reduced the viscosity of reactant to facilitate the well mixing of reactant and contributed to the reduction of mass transfer in diffusion. The results are in accordance with those reported in reference (Liao *et al.*, 2015). Therefore, the pulp density of 100 g/L remained constant for further experimental work.

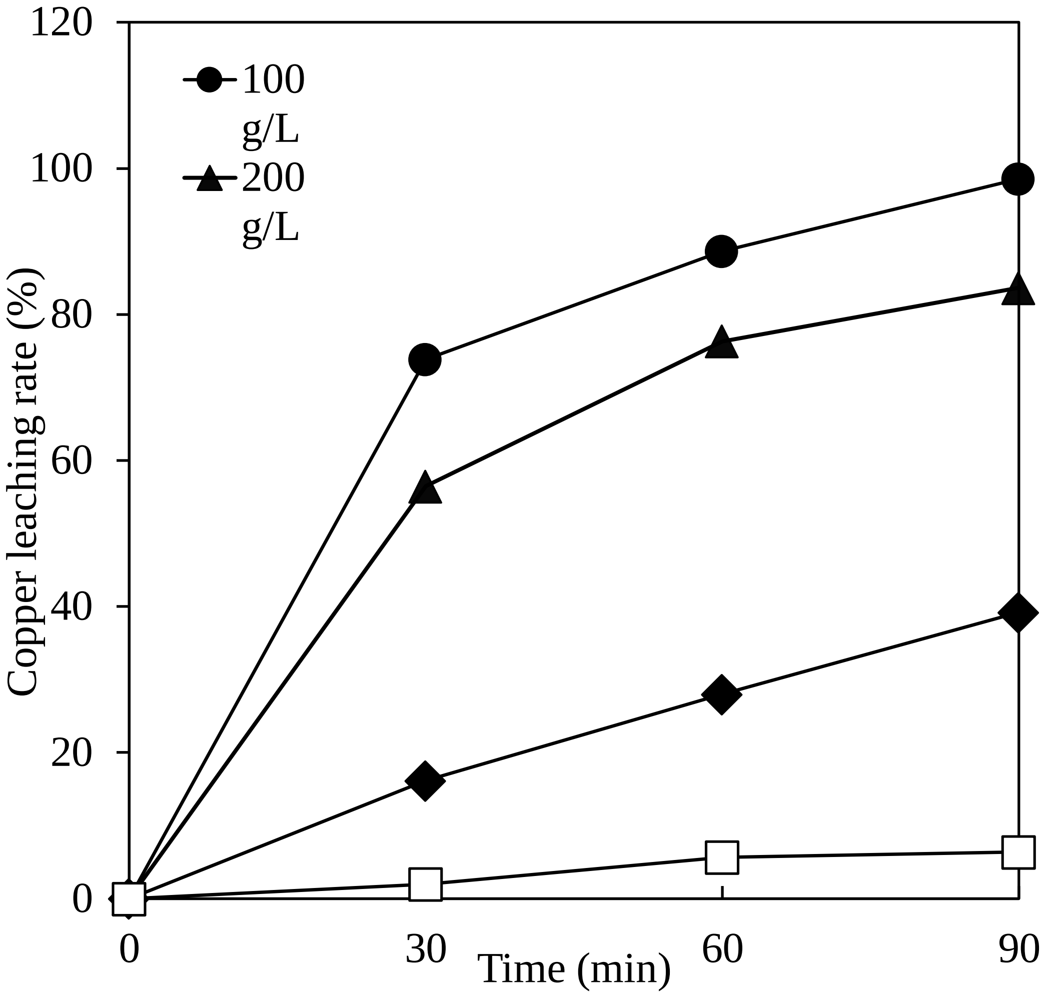


Figure 3. 29. Effect of pulp density on the leaching of copper from complex carbonaceous sulfide ore (180 ^{0}C and 1.5 MPa total pressure of oxygen).

Leaching Kinetic of Cu in complex carbonaceous sulphide ore under direct pressure leaching

The dissolution of chalcopyrite in complex carbonaceous sulphide ore may be described by a number of reaction models of heterogeneous solid-liquid reactions already proposed in literature (Antonijević, Janković and Dimitrijević, 2004; Sokić, Marković and Živković, 2009; Gok *et al.*, 2014; Lampinen, Laari and Turunen, 2015; Han *et al.*, 2017). Generally, the dissolution mechanism is based on three main kinetic models namely, chemical surface, diffusion model or through the product layer and mixed kinetic model of chemical surface and diffusion. There is usually a positive effect on the reaction kinetics when temperature rises when the system is chemically controlled. On the other end, when the reaction kinetics is slightly affected by temperature together with a mild effect of agitation then it is concluded that the leaching is controlled by diffusion. At an activation value less than 15 kJ/mol, the system is said to be controlled by diffusion while those over 40 kJ/mol signify a chemical reaction.

The obtained experimental results of the chalcopyrite oxidation in the present work were used in the process of choosing the appropriate kinetic model. The apparent rate constants and correlation coefficients were calculated using Eq 3.15 and 3.16 by the best fit of experiments data obtained from the leaching parametric studies under different temperature, stirring speed, particle size and sulphuric acid concentration (Fig. 3.20-3.29), respectively. The results obtained from the regression correlation coefficient analysis using the leaching kinetics models is summarized in Table 3.6. Results show that the linear correlation between temperature, particle size, pulp density, total pressure and H_2SO_4 concentration against the time period of leaching had correlation coefficients high over 0.97, 0.95, 0.96, 0.97 and 0.90 when fitted to the diffusion-controlled from Eq. 3.29. On the other hand, the regression correlation coefficient of temperature differed massively between 0.002 and 0.945 when the line of fit was used in the surface chemical-controlled model Fig. 3.30. Similarly, results indicated a no fit of line other parameters signifying a large difference between chemical reaction and diffusion-controlled models. In order to determine the significance of temperature the activation energy (E_a) of the chalcopyrite dissolution to estimate the Arrhenius equation (Eq.3.17) using the apparent rate constants of the diffusion (k_d) and chemical (k_c) controlled models as previously (Table 3.6). Fig. 3.31 displays the Arrhenius plot of ln k versus 1/T for copper leaching dissolution fitted into a diffusion-controlled reaction model. The result obtained indicated an activation energy of 51.44 kJ/mol which indicate that the leaching rate was controlled by diffusion. The linear dependence of the rate constant on the inverse particle size is in fact in favour of the proposed diffusion shrinking core model.

Table 3. 6. Apparent rate constant and correlation coefficients for shrinking core model under different conditions

Conditions		Chemical reaction control $1-(1-\alpha)^{1/3}$		Diffusion control $1-2/3\alpha-(1-\alpha)^{2/3}$	
		R^2	k_r (min^{-1})	R^2	k_d (min^{-1})
Temperature (°C)	100	0.9727	0.004	0.9902	0.0002
	200	0.9628	0.0058	0.9791	0.0005
	140	0.9207	0.0079	0.9911	0.0011
	160	0.8273	0.0101	0.9991	0.0025
	180	0.7664	0.0104	0.9956	0.0034
Particle size (µm)	200~160	0.9351	0.0043	0.9769	0.0031
	160~106	0.9266	0.0047	0.9557	0.003
	106~75	0.9193	0.0078	0.9642	0.0015
	75~32	0.9385	0.008	0.9875	0.0013
	-32	0.8633	0.0087	0.9552	0.0001
Pulp density (g/L)	100	0.9741	0.0081	0.9875	0.0013
	200	0.9389	0.005	0.9642	0.0015
	300	0.9982	0.0017	0.9557	0.0031
	400	0.9481	0.0003	0.9769	0.003
H_2SO_4 (mol dm^{-3})	0.2	0.9132	0.0009	0.9747	0.00008
	0.4	0.9615	0.0037	0.9958	0.001
	0.6	0.9752	0.0014	0.9906	0.0019
	0.8	0.9791	0.0005	0.9064	0.0022
	1	0.9804	0.0002	0.9322	0.0029
Pressure (MPa)	0.5	0.954	0.0004	0.9747	0.00008
	1.5	0.9071	0.0052	0.9958	0.001
	2	0.8681	0.0068	0.9906	0.0019

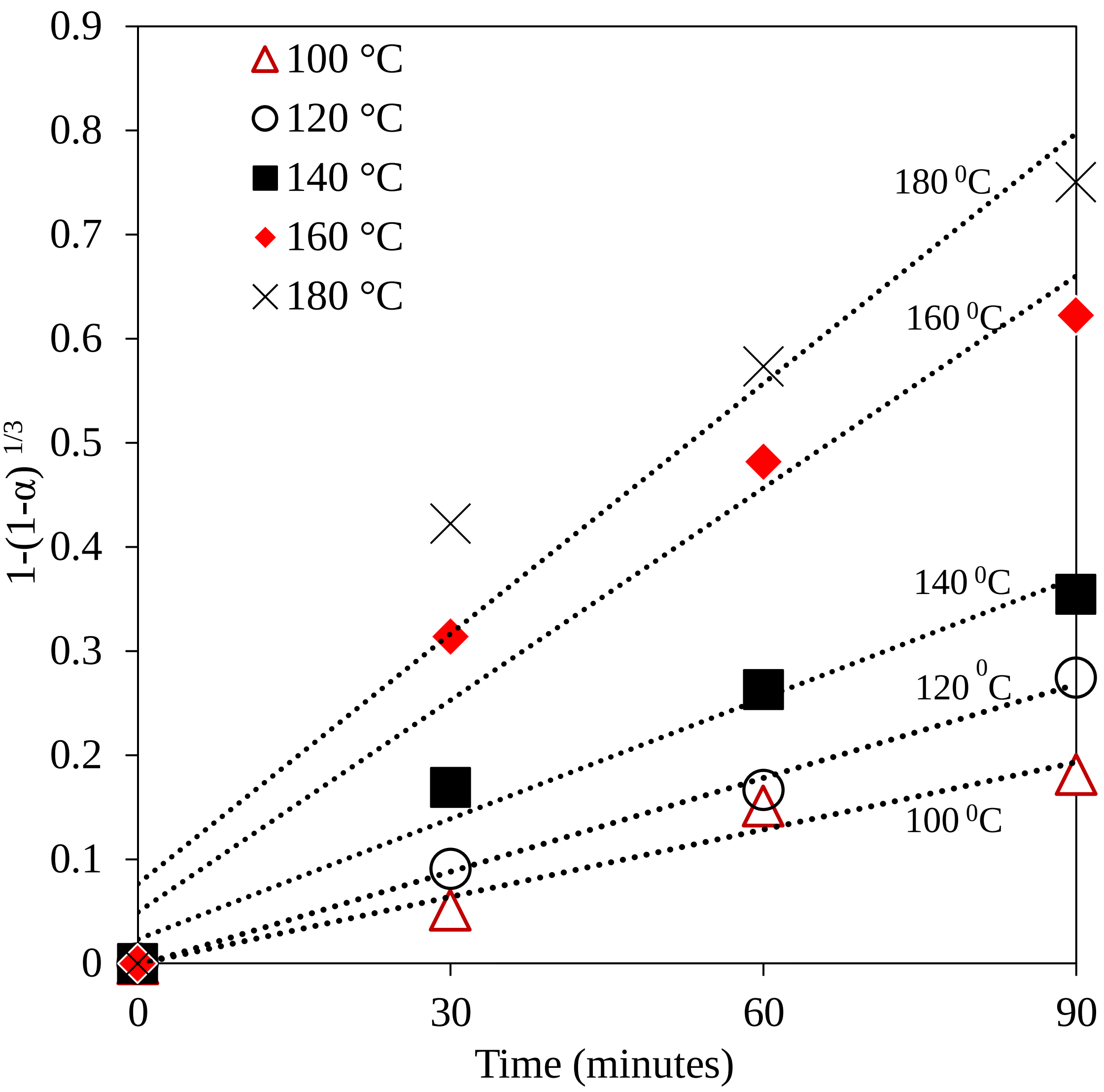


Figure 3. 30. Plot of effect temperature according to (Eq.3.30).

Effect of Temperature

According to the results in the present work, the leaching kinetics were affected by temperature. The experimental results from Fig. 3.5 were plotted against Eq. 29 and are shown in Fig. 3.31. Examination of plots in Fig. 3.31 indicated that good linearization existed and that this model could be used to describe the kinetics of copper leaching for given experimental conditions with satisfying correlation coefficients values that are greater than 0.93 (Table 3.6). Apparent activation constants (k_d) for various temperatures were determined from slopes of the lines in Fig. 3.31 and used to determine the activation energy (E_a).

The relation between the overall rate constant from Table 3.6 and temperature may be expressed by the Arrhenius equation:

$$\ln k = \ln A - E_a/(RT) \tag{3.27}$$

where, k is the overall rate constant, A is the frequency factor, Ea is the activation energy R is the universal gas constant and T is the reaction temperature. The activation energy was calculated to be 51.44 kJ/mol from the diagram ln k_d versus 1/T as shown in Fig. 3.32. Although the activation value seem to suggest a chemical reaction control (Liao *et al.*, 2015; Havlik, 2008), other studies have shown that diffusion controlled reactions have unusually high activation energy. For instance, the activation energy for the diffusion-controlled titanium and iron from ilmenite in hydrochloric acid was reported as 67.1 and 62.4 kJ/mol, respectively (Olanipekun ,1999). Similarly, the activation energy for product diffusion layer controlled HCL-H_3PO_4 leaching media of potassium from phosphorus-potassium associated ore was 54.67 kJ/mol (MA *et al.*, 2017). It appears that the rate controlling mechanism for heterogeneous dissolution reactions is better predicted from plots of the kinetic equations rather than activation energies value although in some instances the same mechanism information is derivable from both variables. Crundwell, 2013, also argued that although the activation energy is important, it does not convey any more information that is useful in determining the mechanism of dissolution than its value. Therefore, the leaching of copper in chalcopyrite contained in complex carbonaceous sulfide ore by sulfuric acid could be classified as a diffusion-controlled process.

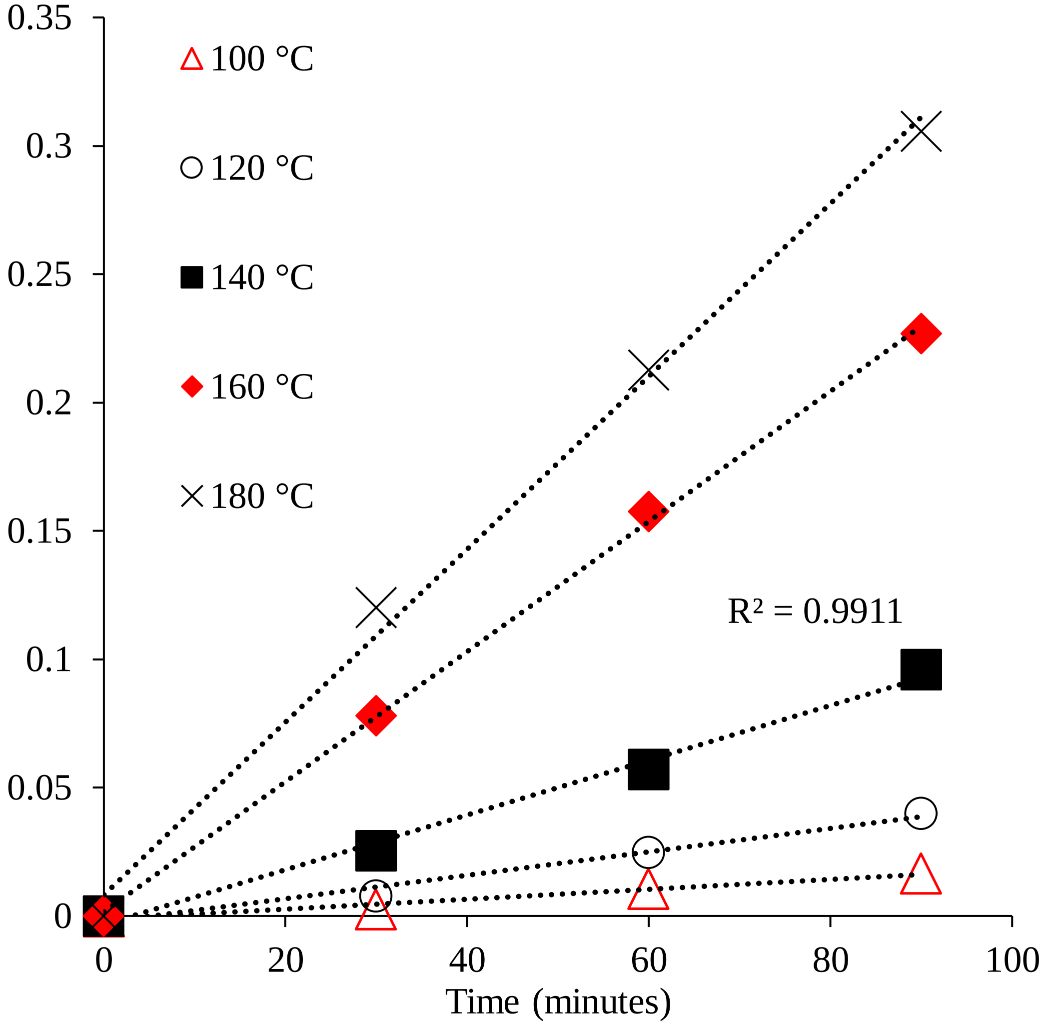


Figure 3. 31. Linear fit of 1- 2/3α- (1-α)$^{2/3}$ versus *t* for the dissolution of copper from complex carbonaceous ore.

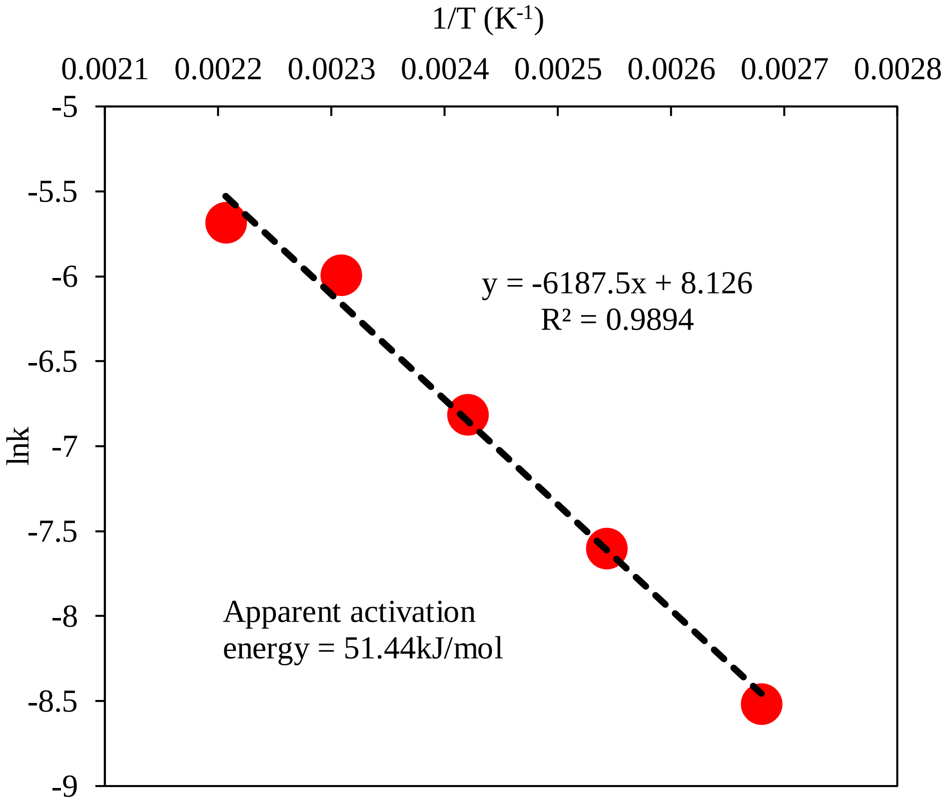


Figure 3. 32. Arrhenius plot for copper leaching from complex carbonaceous sulphide ore in H_2SO_4.

Effect of H_2SO_4 concentration and total pressure

The kinetic model for copper leaching is additionally supported by a good linear dependency of the experimental kinetic constants for effect of H_2SO_4 concentration and total pressure (P_{total}) in Fig 3.33 and 3.34 respectively. This result confirms that the leaching proceeds according to Eq. 3.29.

The dependence of the kinetic constants of H_2SO_4 concentration and total pressure (P_{total}) can also be determined from the slopes of Fig. 10 and 11. Logarithms of these values were drawn as a function of $\ln[H_2SO_4]$ versus $\ln k_d$ for acid concentration, while $\ln P_{total}$ versus $\ln k_d$ for total pressure were shown in Fig 3.35 and 3.36

respectively. The empirical reaction orders with respect to different H_2SO_4 and P_{total} were determined as 2.2 and 4.4 respectively. This result indicate that sulfuric acid and total pressure are important factors for copper leaching copper in complex carbonaceous sulfide ore.

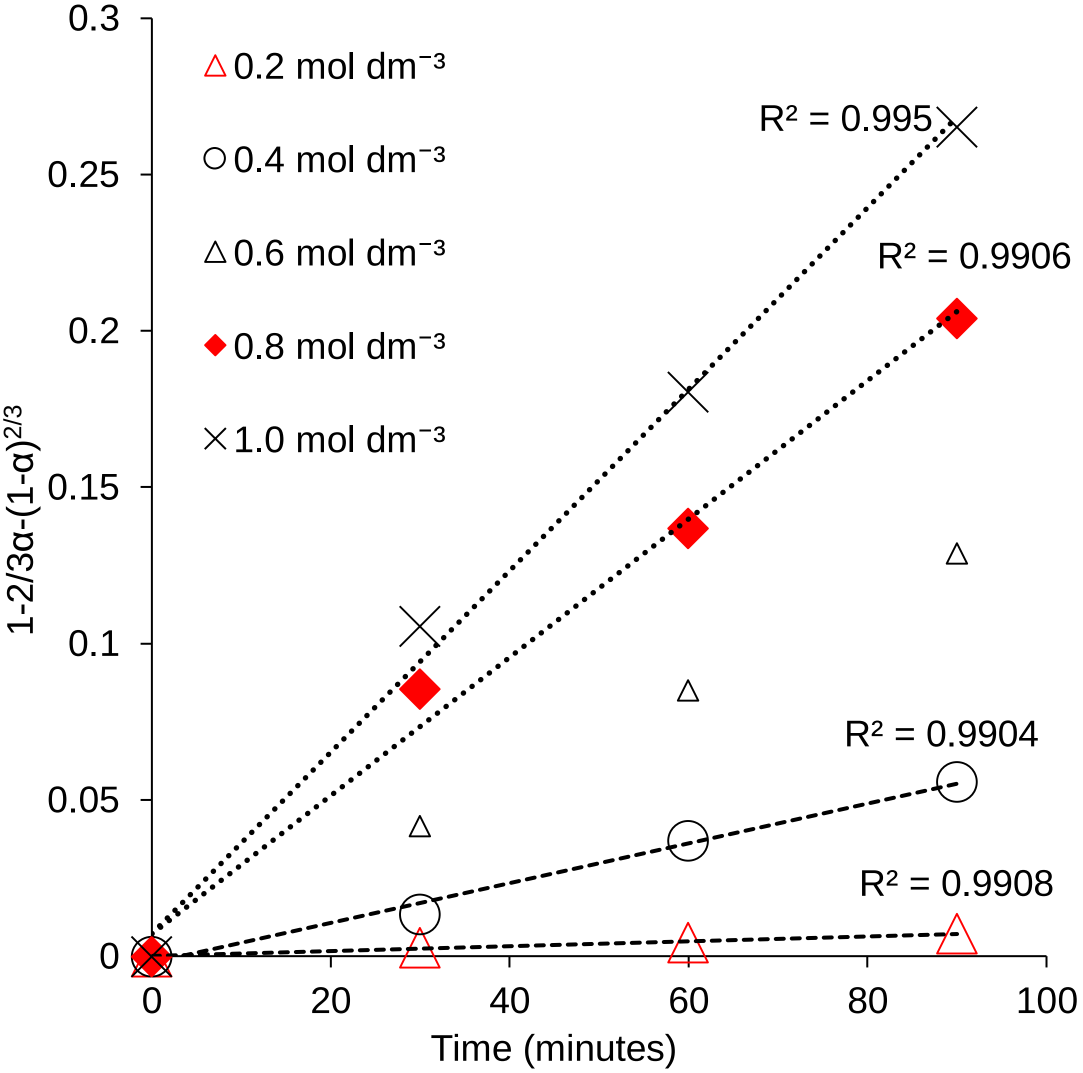


Figure 3. 33. Plot of data extracted from Fig. 3.23.

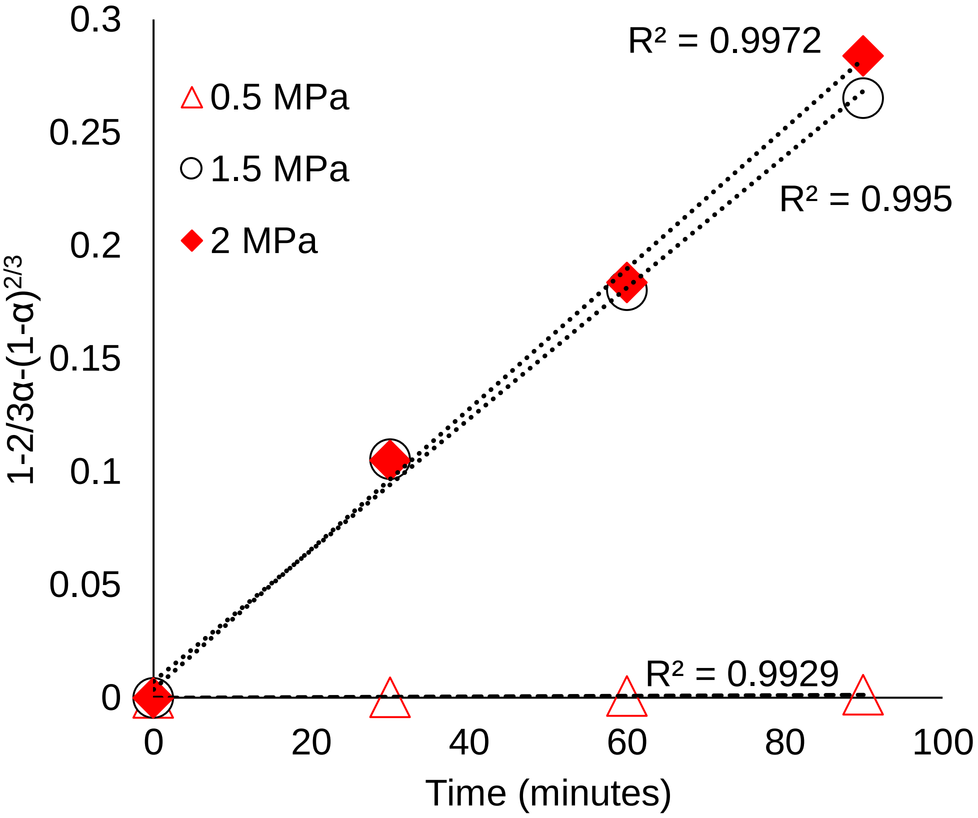


Figure 3. 34. Plot of data extracted from Fig. 3.27.

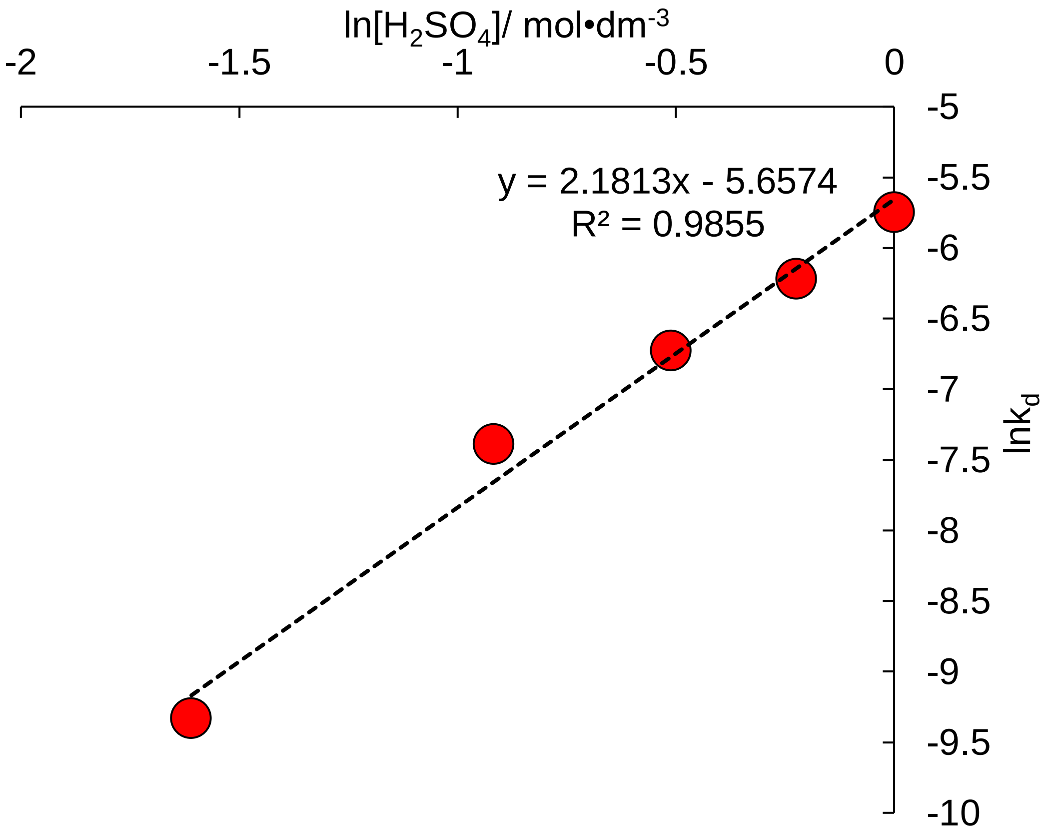


Figure 3. 35. Plot of ln k_d versus ln[H_2SO_4].

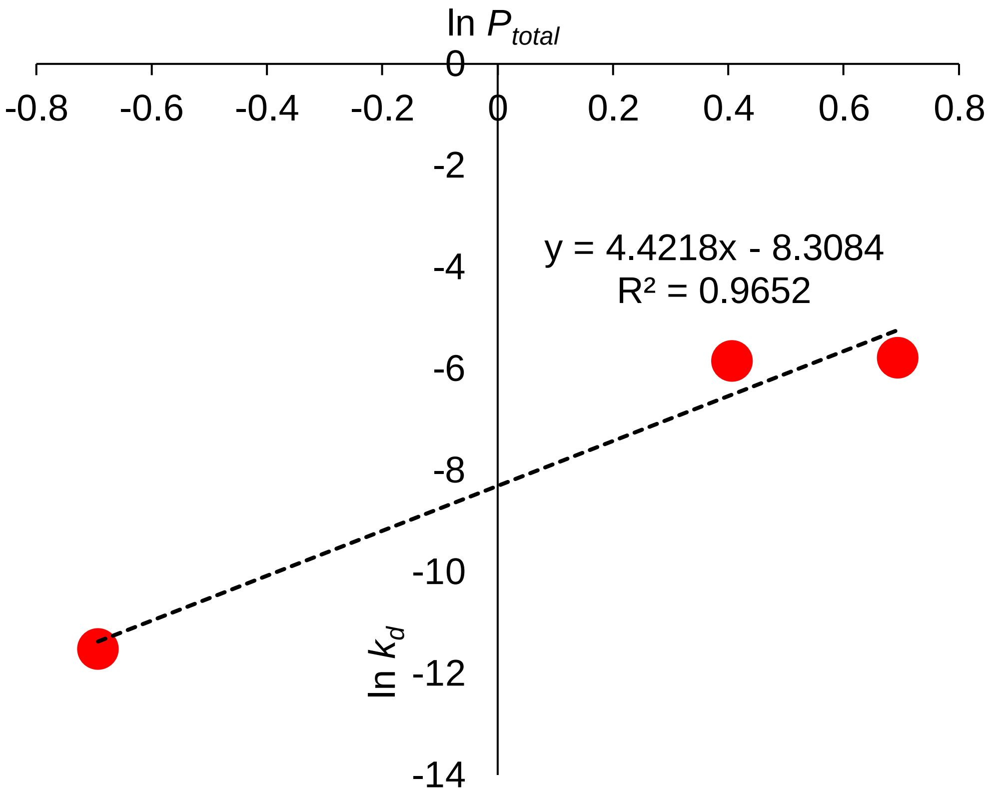


Figure 3. 36. Plot of ln k_d versus ln P_{total}.

Characterization of solid residue

It should be recalled from chemical reactions, Eq. 7-10, that during leaching of copper in sulfate-oxygenated media, acid consuming minerals such as calcite in the ore can play a detrimental role in recovery. At least two general scenarios are depicted for leaching of complex carbonaceous sulfide ore, 1) some minerals dissolve and rapidly form a precipitate at the surface that restrict further leaching or produce species that can restrict acid consumption as well as release acid thereby altering acid balance (Fig. 3.37). Some minerals gradually transform into secondary minerals resulting in a secondary mineral layer. To verify this assumption, XRD analysis were carried out at different H_2SO_4 concentrations (0.2-1.0 mol dm^{-3}) while keeping other parameters constant at temperature of 180^{0}C, pressure of 1.5

MPa, stirring speed of 750 rpm, and pulp density of 100 g/L for 60 min (Fig. 3.38). Results showed that at concentrations lower than 0.4 mol dm^{-3} calcite and dolomite contained did not alter. Consequently, low copper leaching rates were observed. It suggests that at low acid concentrations acid consumption was rapid and limited copper extraction. Free, 2010 noted that acid concentration is a key factor in determining the acid consumption and is closely tied to copper extractions. This factor is very important in determining the economical and feasibility of applying direct leaching of complex carbonaceous sulfide ore.

The results concerning the dissolution of iron are also noted. Traces of jarosite and other non-crystalline iron precipitates were observed in Fig. 3.38 at 0.6-0.8 mol dm^{-3}. Iron dissolution is also compared to the copper leaching at 0.8 and 1.0 mol dm^{-3} as shown in Fig.3.39. The results show that an increase in acid concentration aided in the continuous supply of acid and we can also observe that the copper/iron selectivity is good only at 0.8 mol dm^{-3} at shorter leaching time (<60 %). In spite of the appreciable amount of iron dissolved at 1.0, the direct leaching of copper in complex carbonaceous sulfide ore is still a viable option because of the high copper dissolution rate quickly.

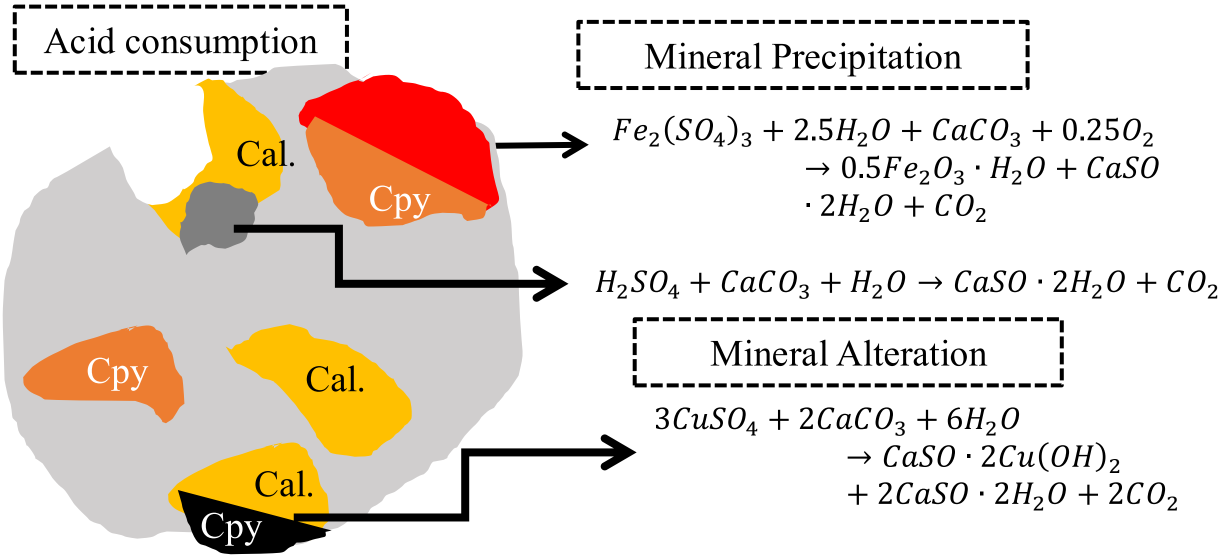


Figure 3. 37. Leaching mechanism of complex carbonaceous sulfide ore in sulfate-oxygenated leading media by direct high-pressure leaching.

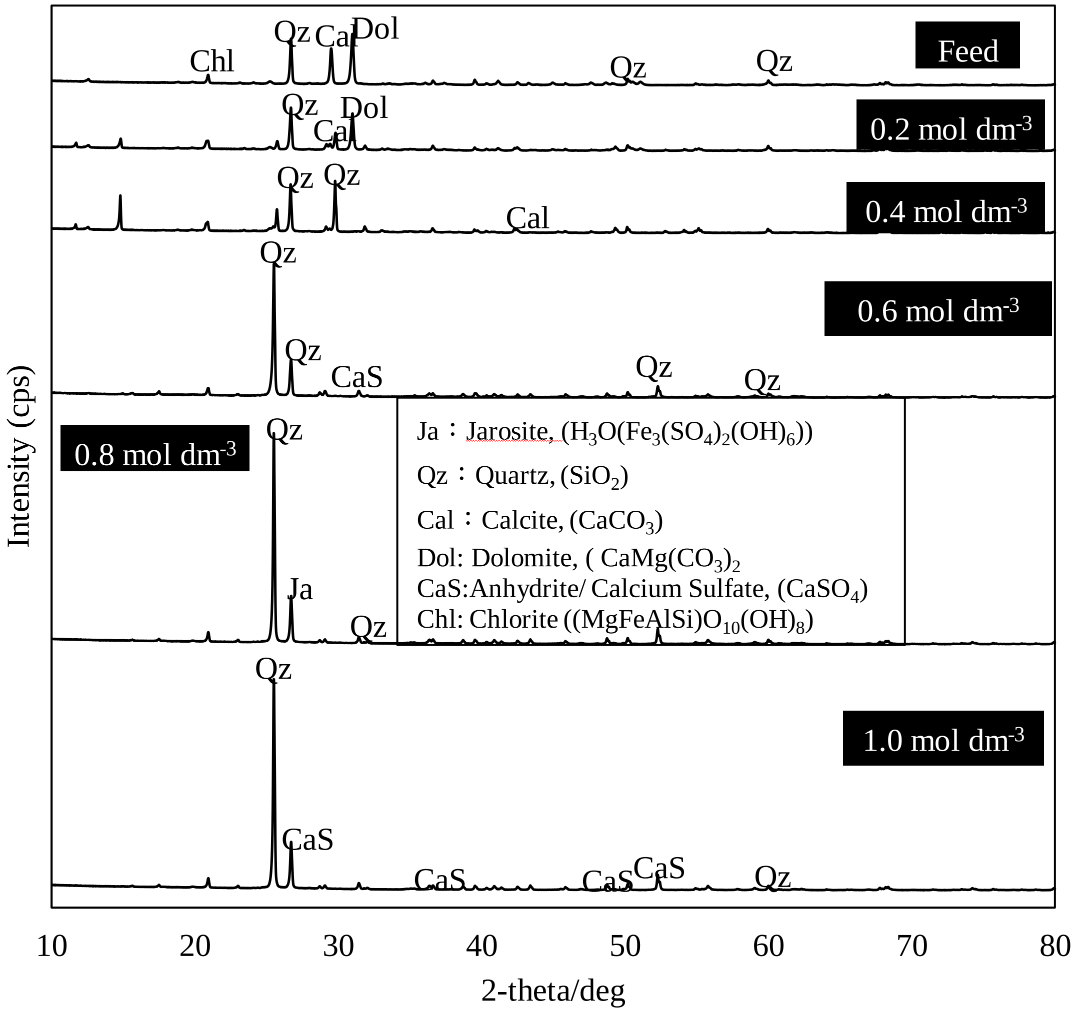


Figure 3. 38. XRD patterns (Cu Kα, Ni filter) of solid residues at different temperature.

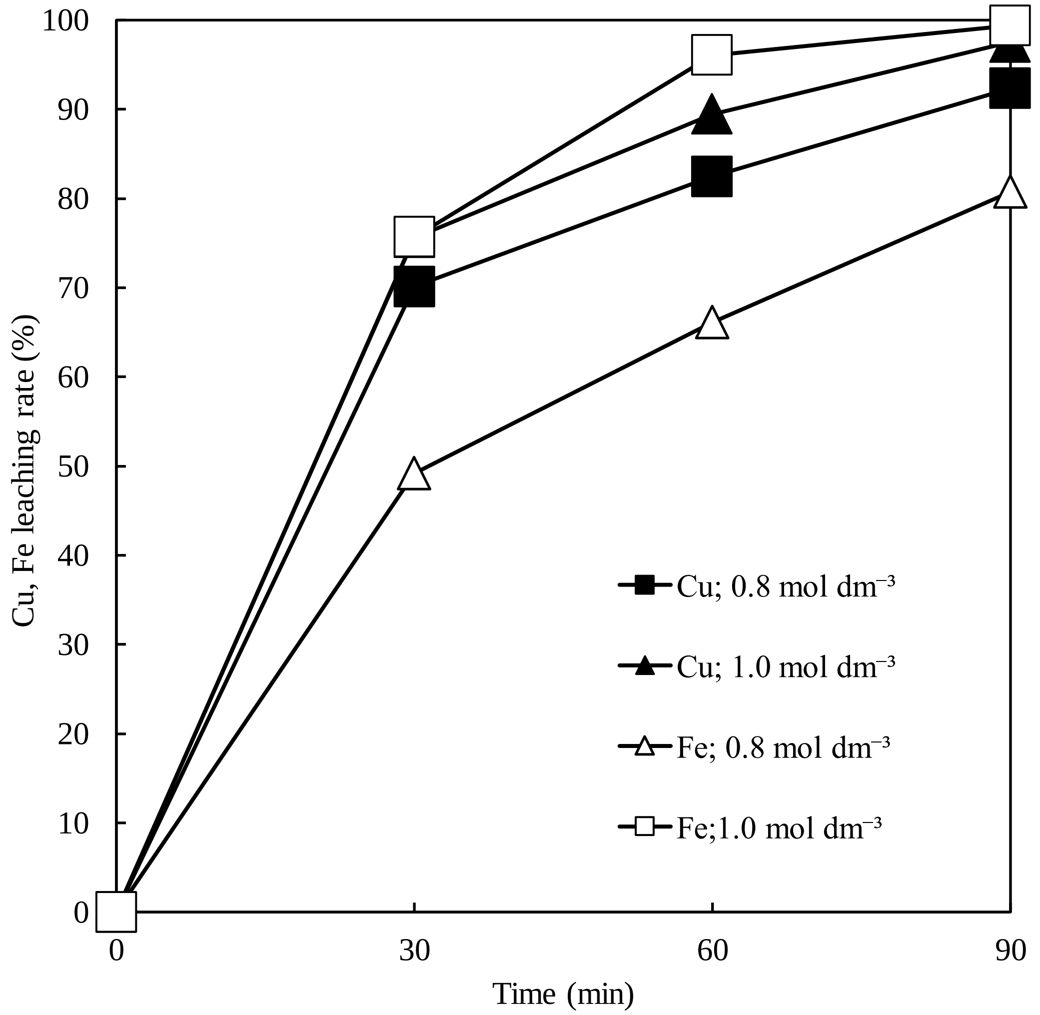


Figure 3. 39. Iron leaching rate from complex carbonaceous sulfide ore as compared to the leaching of copper at H_2SO_4 concentrations of 0.8 and 1.0 mol dm^{-3}. (Total pressure of 1.0 MPa, temperature of 180^0C, stirring speed of 750 rpm, and pulp density of 100 g/L)

Key parameters of kinetic leaching and mechanism of complex carbonaceous ore

The kinetics of leaching reaction of complex carbonaceous sulphide ore are important in investigating the rate of reaction. This process is as simple, and is affected by a large number of external factors, so that it may generally be classified as the function of multiple variables. When studying the leaching kinetics, the variables under investigation are studied with respect to time, such that the leaching rate is the amount of reacted initial substances per unit time. Usually, the dependences expressing the change of concentrations are empirical, but could be forecasted theoretically, if reaction mechanism is known (Havlik, 2008). In this research, four parameters were studied to investigate their significance and the results were evaluated from.

- **Stirring speed:** The stirring speed did not have any significant influence as observed in Fig. 3.20 therefore an average 700 rpm was used throughout the experiments.
- **Particle size:** The obtained results from Fig 3.21 are logical considering the fact that when particle size is smaller, the surface area is greater therefore enabling efficient copper dissolution.
- **Sulphuric acid concentration:** According to Fig 3.22 and 3.23. The presence of acid had a significant effect on the leaching rate. This is expected as the role of the acid is to prevent the hydrolytic precipitation of iron in the solution. Consequently, it kept acid balances when acid consuming minerals, calcite, precipitated in the solution.
- **Temperature:** The strong effect of higher temperature in leaching complex carbonaceous sulphide ore is significant in discussing the necessity of applying heat to the reaction (Fig 3.24). For examining the effect of temperature on the leaching process it is sufficient to use the Arrhenius equation and plot according to Eq. 3.17 and Fig 3.32 respectively. This plot is significant in characterizing the reaction from the viewpoint of their rate-controlling stage. As mentioned earlier, the values of activation in the range 4-19 kJ/mol are classified as diffusion-controlled process, while those

above 42 kJ/mol are the chemically controlled reactions. The results indicated an activation energy of 51.44 kJ/mol, indicating that the process falls in between and therefore a mixed/intermediate controlled reaction process.

Process evaluation

A two-stage flotation process comprising, pre-flotation stage and rougher stage was used to compare recovery of copper from complex carbonaceous sulphide ore with direct pressure leaching. Fig 3.40 gives a summary outline of copper recovered in each process. When carbonaceous ore of 2.08 wt% Cu was taken for flotation, only an average of >59.95 % Cu recovery was recovered. The separation efficiency between Cu and C_{org} was 65.75%. On the other hand, direct leaching showed better separation /recovery of copper when >95 % was able to be leached with a maximum concentration of 2.47 g/L. A very interesting observation made in the analysis was the post precipitation of some of the pregnant leached solution after a few minutes of filtration. The implications of that is beyond this current study and therefore recommended to be evaluated in further process. Additionally, the solid residues contained different phases of iron precipitates. It is important to evaluate the type of iron that formed in this process to ensure safe environmental discharge of the solid residue or alternatively recover iron from them.

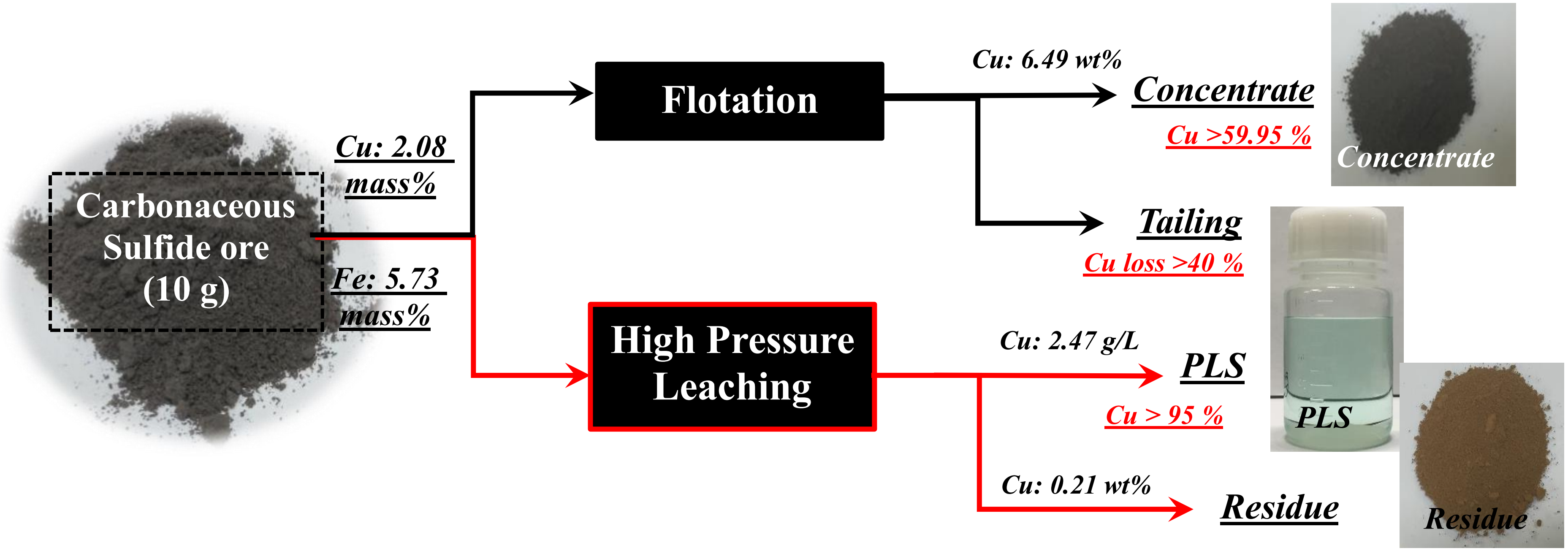


Figure 3. 40. Flowsheet for copper recovery from carbonaceous sulphide ore by direct pressure leaching.

3.4 Conclusion

From literature survey the world reserve will increase if metal prices increase and new process technology are developed. There are limited technologies to treat the underexplored complex carbonaceous sulphide ore that have potential copper high grade. The use of direct pressure leaching has potential to recover the most commonly chalcopyrite mineral that is not easily dissolved in aqueous solution.

Flotation testing was undertaken and did not confirm a desirable degree for copper concentration due to the co-existence with naturally hydrophobic organic materials. On the other hand, a high pressure leaching of copper in chalcopyrite was achieved via an oxidative reaction. The kinetic analysis of the system showed that the leaching reaction are controlled by diffusion through the solid phase. SEM/EDX and XRD testing confirmed the presence of porous product layer and validity of the schematic leaching model.

According to the results over 90 % copper recovery was possible to concentrate copper in the leachate solution. The leaching reactions were found to follow shrinking core model and the parabolic leaching kinetics were established, that under the experimental conditions, led to the following model: $1\text{-}2/3\alpha\text{-}(1\text{-}\alpha)^{2/3} = \mathrm{k}d\mathrm{t}$

The leaching kinetics were shown to be dependent on temperature, particle size and acid concentration.

For the tested chalcopyrite in complex carbonaceous sulphide ore, the maximum conversion of copper to Cu2+ solution was obtained at high temperature conditions. Low temperatures indicated low leaching kinetics of chalcopyrite. Selective copper recovery was also possible due to the iron and calcium reaction controls.

Direct high-pressure leaching is proposed for the recovery of copper in chalcopyrite of complex carbonaceous sulfide ore that is not amendable to present-day flotation techniques. The process is competitive to the currently commercialized leaching techniques that uses higher temperatures and/or low temperatures that cannot completely dissolve copper in chalcopyrite.

REFERENCE

[1] Adebayo, A. and Ajayi, O. O. (2014) 'Dissolution Kinetics of Chalcopyrite with Hydrogen Peroxide in Sulphuric Acid Dissolution Kinetics of Chalcopyrite with Hydrogen Peroxide in Sulphuric acid Medium', (March 2003).

[2] Antonijević, M. M. and Bogdanović, G. D. (2004) 'Investigation of the leaching of chalcopyritic ore in acidic solutions', *Hydrometallurgy*, 73(3–4), pp. 245–256. doi: 10.1016/j.hydromet.2003.11.003.

[3] Antonijević, M. M., Janković, Z. D. and Dimitrijević, M. D. (2004) 'Kinetics of chalcopyrite dissolution by hydrogen peroxide in sulphuric acid', *Hydrometallurgy*, 71(3–4), pp. 329–334. doi: 10.1016/S0304-386X(03)00082-3.

[4] Bogdanović, G. D. *et al.* (2016) 'Leaching of Low-Grade Copper Ores: a Case Study for " Kraku Bugaresku-Cementacija " Deposits (Eastern Serbia)', *Journal of Mining and Metallurgy*, 52(1), pp. 45–56.

[5] British Geological Survey (2007) 'Copper', *mineralsUK*, (June), p. 1. Available at: http://www.bgs.ac.uk/downloads/start.cfm?id=1410.

[6] Cao, J. *et al.* (2016) 'Colloids and Surfaces A : Physicochemical and Engineering Aspects The role of some special ions in the flotation separation of pentlandite from lizardite', 490, pp. 173–181.

[7] Chmielewski, T. (2015) 'Development of a hydrometallurgical technology for production of metals from kghm polska miedz S.A. concentrates', *Physicochemical Problems of Mineral Processing*, 51(1), pp. 335–350. doi: 10.5277/ppmp150120.

[8] Chmielewski, T., Wodka, J. and Iwachow, L. (2009) 'Ammonia Pressure Leaching for Lubin Shale Middlings', 43(January 2009), pp. 5–20.

[9] Conner, K. D. (2013) 'Pressure Oxidation of Enargite Concentrates Containing Gold and Silver'.

[10] Crundwell, F. K. (2013) 'The dissolution and leaching of minerals: Mechanisms, myths and misunderstandings', *Hydrometallurgy*. Elsevier B.V., 139, pp. 132–148. doi: 10.1016/j.hydromet.2013.08.003.

[11] Dreisinger, D. (2006) 'Copper leaching from primary sulfides : Options for biological and chemical extraction of copper', 83, pp. 10–20. doi: 10.1016/j.hydromet.2006.03.032.

[12] Gok, O. *et al.* (2014) 'Leaching kinetics of copper from chalcopyrite concentrate in nitrous-sulfuric acid', *Physicochemical Problems of Mineral Processing*, 50(1), pp. 399–413. doi: 10.5277/ppmp140133.

[13] Han, B. *et al.* (2017) 'Leaching and Kinetic Study on Pressure Oxidation of Chalcopyrite in H2SO4 Solution and the Effect of Pyrite on Chalcopyrite Leaching', *Journal of Sustainable Metallurgy*. Springer International Publishing, 3(3), pp. 528–542. doi: 10.1007/s40831-017-0135-3.

[14] Han, B. *et al.* (2018) 'Development of copper recovery process from flotation tailings by a combined method of high–pressure leaching–solvent extraction', *Journal of Hazardous Materials*, 352(August 2017), pp. 192–203. doi: 10.1016/j.jhazmat.2018.03.014.

[15] Kamradt, A. *et al.* (2012) 'An integrated process for innovative extraction of metals from Kupferschiefer mine dumps, Germany', *Chemie-Ingenieur-Technik*, 84(10), pp. 1694–1703. doi: 10.1002/cite.201200070.

[16]Kaskiala, T. (2002) ‘Determination of oxygen solubility in aqueous sulphuric acid media’, *Minerals Engineering*, 15(11), pp. 853–857. doi: 10.1016/S0892-6875(02)00089-4.

[17] Khoshkhoo, M. (no date) *Chalcopyrite Dissolution in Sulphate-Based Leaching and Bioleaching Systems*.

[18] Kostudis, S. *et al.* (2015) ‘Leaching of copper from Kupferschiefer by glutamic acid and heterotrophic bacteria’, *Minerals Engineering*. Elsevier Ltd, 75, pp. 38–44. doi: 10.1016/j.mineng.2014.12.035.

[19] Kramer, A. *et al.* (2012) ‘Surface tension measurement for optimization of flotation control’, *Procedia Engineering*, 46(December), pp. 111–118. doi: 10.1016/j.proeng.2012.09.453.

[20] Lampinen, M., Laari, A. and Turunen, I. (2015) ‘Kinetic model for direct leaching of zinc sulfide concentrates at high slurry and solute concentration’, *Hydrometallurgy*. Elsevier B.V., 153, pp. 160–169. doi: 10.1016/j.hydromet.2015.02.012.

[21] Liao, Y. *et al.* (2015) ‘Leaching kinetics of calcification roasting calcinate from multimetallic sulfide copper concentrate containing high content of lead and iron’, *Separation and Purification Technology*. Elsevier B.V., 149, pp. 190–196. doi: 10.1016/j.seppur.2015.05.042.

[22] Liu, Z. X. *et al.* (2016) ‘Oxidative leaching behavior of metalliferous black shale in acidic solution using persulfate as oxidant’, *Transactions of Nonferrous Metals Society of China (English Edition)*. The Nonferrous Metals Society of China, 26(2), pp. 565–574. doi: 10.1016/S1003-6326(16)64145-6.

[23] Lorenzo-talla, J. *et al.* (2018) 'Ferric leaching of the sphalerite contained in a bulk concentrate : Kinetic study', 125(May), pp. 50–59. doi: 10.1016/j.mineng.2018.05.026.

[24] Lutandula, M. S. and Maloba, B. (2013) 'Recovery of cobalt and copper through reprocessing of tailings from flotation of oxidised ores', *Journal of Environmental Chemical Engineering*, 1(4), pp. 1085–1090. doi: 10.1016/j.jece.2013.08.025.

[25] McDonald, R. G. and Muir, D. M. (2007a) 'Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products', *Hydrometallurgy*, 86(3–4), pp. 191–205. doi: 10.1016/j.hydromet.2006.11.015.

[26] McDonald, R. G. and Muir, D. M. (2007b) 'Pressure oxidation leaching of chalcopyrite. Part II: Comparison of medium temperature kinetics and products and effect of chloride ion', *Hydrometallurgy*, 86(3–4), pp. 206–220. doi: 10.1016/j.hydromet.2006.11.016.

[27] Mesa, D. and Brito-Parada, P. R. (2019) 'Scale-up in froth flotation: A state-of-the-art review', *Separation and Purification Technology*, 210(September 2018), pp. 950–962. doi: 10.1016/j.seppur.2018.08.076.

[28] Moradi, S. and Monhemius, A. J. (2011) 'Mixed sulphide-oxide lead and zinc ores: Problems and solutions', *Minerals Engineering*. Elsevier Ltd, 24(10), pp. 1062–1076. doi: 10.1016/j.mineng.2011.05.014.

[29] Mudd, G. M. (2009) *The Sustainability of Mining in Australia: Key Production Trends and Their Environmental Implications for the Future, Research Report No RR5, Department of Civil Engineering, Monash University and Mineral Policy Institute*. doi: 978-0-9803199-4-1.

[30] NMP2-CT-2004-505710 / BIOSHALE (2007) *Publishable Activity Report of Bioshale Project*. Available at: http://bioshale.brgm.fr/Documents/ResultsProducts/Publishable_Activity_Report-Bioshale.pdf.

[31] Norgate, T. and Jahanshahi, S. (2010) 'Low grade ores - Smelt, leach or concentrate?', *Minerals Engineering*. Elsevier Ltd, 23(2), pp. 65–73. doi: 10.1016/j.mineng.2009.10.002.

[32] Panda, S. *et al.* (2015) 'Current scenario of chalcopyrite bioleaching: A review on the recent advances to its heap-leach technology', *Bioresource Technology*. Elsevier Ltd, 196, pp. 694–706. doi: 10.1016/j.biortech.2015.08.064.

[33] Rico, M. *et al.* (2008) 'Reported tailings dam failures . A review of the European incidents in the Reported tailings dam failures A review of the European incidents in the worldwide context', (August 2018). doi: 10.1016/j.jhazmat.2007.07.050.

[34] Robinson, D. J. and Scientific, T. C. (2018) 'Special Feature: Mineral Processing, In situ recovery – a move toward "keyhole mining".', (August).

[35] Sicupira, L. *et al.* (2011) 'Assessing metal recovery from low-grade copper ores containing fluoride', *Hydrometallurgy*. Elsevier B.V., 109(3–4), pp. 202–210. doi: 10.1016/j.hydromet.2011.07.003.

[36] Smith, T., Metallurgist, P. and Lin, D. (no date) 'PAPER 21 Removal of Organic Carbon with a Jameson Cell at Red Dog Mine', pp. 333–346.

[37] Sokić, M. D., Marković, B. and Živković, D. (2009) 'Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid', *Hydrometallurgy*, 95(3–4), pp. 273–279. doi: 10.1016/j.hydromet.2008.06.012.

[38] Tindall, G. P. and Muir, D. M. (1998) ‘Effect of Eh on the rate and mechanism of the transformation of goethite into hematite in a high temperature acid leach process’, *Hydrometallurgy*, 47(2–3), pp. 377–381. doi: 10.1016/S0304-386X(97)00047-9.

[39] Watling, H. R. (2006) ‘The bioleaching of sulphide minerals with emphasis on copper sulphides - A review’, *Hydrometallurgy*, 84(1–2), pp. 81–108. doi: 10.1016/j.hydromet.2006.05.001.

[40] Wieniewski, A. and Skorupska, B. (2016) ‘Technology of Polish copper ore beneficiation – perspectives’, 4, pp. 0–10.

[41] Wills, B. A. and Napier-munn, T. (2006) *Preface to 7th Edition*.

[42] Yin, S., Wang, L., Wu, A., Kabwe, E., *et al.* (2018) ‘Copper recycle from sulfide tailings using combined leaching of ammonia’, *Journal of Cleaner Production*, 189, pp. 746–753. doi: 10.1016/j.jclepro.2018.04.116.

[43] Yin, S., Wang, L., Wu, A., Free, M. L., *et al.* (2018) ‘Enhancement of copper recovery by acid leaching of high-mud copper oxides: A case study at Yangla Copper Mine, China’, *Journal of Cleaner Production*, 202, pp. 321–331. doi: 10.1016/j.jclepro.2018.08.122.

[44] Yu, P. H., Hansen, C. K. and Wadsworth, M. E. (1973) ‘A kinetic study of the leaching of chalcopyrite at elevated temperatures’, *Metallurgical Transactions*, 4(September), pp. 2137–2144. doi: 10.1007/BF02643279.

[45] Zhan-fang, C. A. O. *et al.* (2009) ‘Techniques of copper recovery from Mexican copper oxide ore’, 19(August 2008), pp. 45–48.

4: Conclusion

4.1Summary of thesis

This research was aimed at developing a flowsheet for two copper resources by application of flotation and high-pressure leaching process. The copper resources followed those of downstream and were mine tailings from BCL mine in Botswana and the upstream were complex carbonaceous sulfide ore from South East Asia and supplied by Nittetsu Mining Co.Ltd. This PhD is composed of four (4) chapters each dealing with different aspects of developing a recovery process for copper from low grade ores and complex carbonaceous sulfide ore.

Chapter 1 Introduction

This section gives an introductory to the general knowledge of copper, significance of copper owing its characteristics for industrial and daily use, global resource and reserve is made. Further explanation is made on the mineral resource considered for this research. Moreover, the conventional metal processing and advanced technologies for copper recovery in mine tailing and complex carbonaceous sulfide ore were explained.

Chapter 2 Recovery of Copper and Nickel from Mine Tailing by Flotation and High-Pressure Leaching

A process development modelling study for recovery of copper and nickel from mine tailing by combination of flotation and high-pressure leaching was performed. This study has shown that the flotation stage is efficient in concentrating mine tailing to suitable metal grades that are ideal for further metal extraction such as high-pressure leaching process. The copper bearing minerals of chalcopyrite was able to be concentrated from 0.19 wt% copper to 6.72 wt% that is comparable with the currently mined ores. According to the results, particle size, slurry pH and to a lesser extent the collector used were the most significant parameters in the flotation of mine tailing. The fine particle indicated that, copper mineral upgrading was compromised because of reporting of fines, and at higher slurry pH (<7) iron sulfide minerals associated with copper were depressed during flotation.

Evidently, during leaching, the concentrate obtained from mine tailing flotation gave a 90 % leaching rate with maximum chalcopyrite dissolution. Chalcopyrite is not easily dissolved in aqueous solution, but temperature control showed the most influential parameter during the process. It was observed that at lower temperatures, chalcopyrite leaching was slow and formation of sulfur which was passivating resulted in poor copper concentrations and low recoveries. At high temperature, chalcopyrite leaching was spontaneous, and acid regeneration was possible for continuous leaching chalcopyrite.

The proposed combined process showed that a 79.9 % copper recovery is attainable from the 100 million tonnes of mine tailings in Selebi Phikwe BCL mine. The process is simple and bears potential traits of flotation and high-pressure leaching. The proposed flowsheet envisaged a suitable solution for acid generation as well as iron hydrolysis which is important in solid residue disposal.

More investigation is required toward the complete development of copper and extraction of accompanying nickel from Selebi Phikwe mine tailing.

Chapter 3 Comparison of Flotation and Direct High Pressure Leaching of Complex Carbonaceous Sulfide Ore

From literature survey the world reserve will increase if metal prices increase and new process technology are developed. There are limited technologies to treat the underexplored complex carbonaceous sulphide ore that have potential copper high grade. The use of direct pressure leaching has potential to recover the most commonly chalcopyrite mineral that is not easily dissolved in aqueous solution.

Flotation testing was undertaken and did not confirm a desirable degree for copper concentration due to the co-existence with naturally hydrophobic organic materials. On the other hand, a high pressure leaching of copper in chalcopyrite was achieved via an oxidative reaction. The kinetic analysis of the system showed that the leaching reaction are controlled by diffusion through the solid phase. SEM/EDX and XRD testing confirmed the presence of porous product layer and validity of the schematic leaching model.

According to the results over 90 % copper recovery was possible to concentrate copper in the leachate solution. The leaching reactions were found to follow shrinking core model and the parabolic leaching kinetics were established, that under the experimental conditions, led to the following model: $1-2/3\alpha-(1-\alpha)^{2/3}=k_dt$

The leaching kinetics were shown to be dependent on temperature, particle size and acid concentration.

For the tested chalcopyrite in complex carbonaceous sulphide ore, the maximum conversion of copper to Cu^{2+} solution was obtained at high temperature conditions. Low temperatures indicated low leaching kinetics of chalcopyrite. Selective copper recovery was also possible due to the iron and calcium reaction controls.

Direct high-pressure leaching is proposed for the recovery of copper in chalcopyrite of complex carbonaceous sulfide ore that is not amendable to present-day flotation techniques. The process is competitive to the currently commercialized leaching techniques that uses higher temperatures and/or low temperatures that cannot completely dissolve copper in chalcopyrite.

Chapter 4 Conclusion

Recovery of copper from two resources were studied by applying flotation and high-pressure leaching process. This study has shown that the resource properties are very significant in determining the flowsheet design when recovering copper. Another consideration has been observed in parameters that has the most influence during flotation and high-pressure leaching. The following are the principle conclusion reached for each ore resource:

1) Mine tailing
   - The concentration of copper sulfide minerals during flotation was found to be dependent on slurry pH, particle size and type of collector parameters studied. At natural slurry pH of 4-6, recovery and grade were high. A moderate particle size of -100 µm was ideal to obtain high recoveries of <80% with grade of 6.72 wt%. The upgrading of copper and nickel was stifled at lower particle size because of fines reporting in the concentrate. The pressure leaching behavior of sulfide minerals was found to be dependent on temperature and acid concentration. The combined process indicated that an average 80% metal recovery of copper metal could be recovered which competitive to current metal in most processing plant.
2) Complex carbonaceous sulfide ore
   - The parameters observed in the concentration of copper in carbonaceous sulfide ore showed that recovery was mostly affected by

the presence of inorganic carbon. However, direct high-pressure leaching showed that over <90 % copper with maximum leachate concentration could be obtained at 180 ^{0}C for one-hour leaching when 1 mol dm^{-3} of sulfuric acid was used.

High pressure leaching of chalcopyrite from both resources indicated that maximum metal concentration in leachate was possible. Other studies have attributed low leaching kinetics due to passivation by elemental but this was not observed. Compared to other hydrometallurgical process, it is observed that high recoveries for chalcopyrite could be achieved at lower temperature (180 ^{0}C) for one hour compared to the existing Total Pressure leaching operated by Phelphs Dodger at more than 200 ^{0}C.

4.2 General Conclusion

This application of two advanced process for recovery of copper from different copper resources (mine tailing and complex carbonaceous sulfide ore) was developed by combination of flotation and high pressure leaching and direct leaching respectively.

4.3 Future Prospects

- According to the results obtained mine tailing and complex carbonaceous sulfide ores have a potential of being extended resources for copper.
- As such it is suggested that, to employ the proposed processes for recovering copper, mineralogical composition should be studied and be the same as those presented and applied to relevant studies.
- It is noted that copper in this study was left at the pregnant leached solution therefore it is recommended that further process such as solvent extraction and electrowinning be carried out to extract copper and make copper cathodes.

ACKNOWLEDGMENTS

First, I am indebted to my advisor Prof. Atsushi SHIBAYAMA. Since my first day in graduate school, Prof. Shibayama believed in me and offered endless support and motivation. It all started in April 2014, when he accepted me into his Resource Process engineering lab and under his supervision, I learnt a lot about research problems and solutions. On a personal level, Prof. Shibayama inspired me by his commitment and passionate attitude. To summarize I would like to give most of the credit to him for becoming the kind of engineering scientist I am today.

Beside my advisor, I would like to thank the rest of my dissertation committee members: Professors: Prof. Daizo ISHIYAMA and Prof. Yohei KAWAMURA, for their great support and invaluable advice. Their crucial remarks contributed and shaped my final dissertation. I am also thankful to Prof. Toyohisa FUJITA, for his insightful comments in making this dissertation a possibility.

I would also like to sincerely express my heartfelt appreciation to associate Prof. Dr. Yasushi TAKASAKI and Dr Kazutoshi HAGA for their mentorship and patience in helping with any technical problems related to laboratory equipment. My sincere thanks also go to Dr. Altansukhx BATANSAN for his patience and very stimulating ideas that helped me very much to improve my technical writing and thinking. And I would also like to thank other laboratory colleagues for helping me out with the Japanese language and showing me how to use most of the equipment.

In addition, this research was supported by the Program for Leading Graduate Schools, “New Frontier Leader Program for Rare metals and Resources” by Japan Society for the Promotion of Science (JSPS). I gratefully acknowledge their financial support. Without they precious support it would not be possible to conduct this research. Additionally, I would like to thank BCL mine company, Selebi Phikwe, Botswana and Nittetsu Mining Co. Ltd for providing me samples and allowing publication of results in this research.

More gratitude goes my industrial collaborators who I had the pleasure to work with. I spent a month at Botswana Institute for Technology Research and Innovation (BITRI) where I had the chance to collaborate with fantastic researches. More specifically, I would like to thank Dr Moepswa and Dr. Mapolelo for their continuous support and providing me the opportunity to work on non-academic field.

Nobody has been more important to me in the pursuit of this project than the members of my family and friends. I would like to thank my parents, (Magdeline, Miriam and German) and aunts who raised me with love and supported me in whatever I pursue. They are unlimited role models. My brothers who made it all fun and worth taking this journey. Most importantly, I wish to thank, my partner, Bolivia, who represented the epitome of nurture and teamwork during my PhD journey. Your love and support is highly appreciated and I am forever indebted to you.

Thanks for all your encouragement.

Refilwe S. Magwaneng

Akita University

March 2019

Publications in this PhD thesis

Peer-Reviews Journal Papers

(1) **Magwaneng, R.S**., Altansukh, B., Haga, K., Shibayama, A.;"Development of a Combined Flotation and High Pressure Leaching Process for Copper and Nickel Recovery from Mine Tailing", ***International Journal of Minerals and Materials Characterization and Engineering***. Vol.5, pp 118-131. (2017).

(2) **Magwaneng, R.S**., Altansukh, B., Haga, K., Shibayama, A., Kosugi M., Kawarabuki R., Mitsuhashi K., Kawata M.; "Investigation of Copper and Iron Recovery from Copper Ore by High Pressure Leaching" ***International Journal of Society of Materials Engineering for Resources.*** Vol.23, No.1, pp 80-83 (2018).

(3) **Magwaneng, R.S**., Altansukh, B., Haga, K., Shibayama, A.;"Extraction of Copper from Complex Carbonaceous Sulfide Ore by Direct High Pressure Leaching", ***Hydrometallurgy***.(Submitted for review).

International Conference Papers

(1) **Magwaneng, R.S.,** Altansukh, B., Haga, K., Shibayama, A., Kosugi M., Kawarabuki R., Mitsuhashi K., Kawata M.;"Pressure Leaching of Carbonaceous Sulfide Concentrates for Recovery of Copper and Iron", Proceedings of "XXIX International Mineral Processing Congress" (**IMPC-2018**) (Moscow, Russia) Ref. No: 545, (2018) (Reviewed).

(2) **Magwaneng, R.S**., Altansukh, B., Haga, K., Shibayama, A., Kosugi M., Kawarabuki R., Mitsuhashi K., Kawata M.; "Copper Recovery from Carbonaceous Sulphide Ore by Flotation" *Proceedings of Copper Cobalt Africa- 9th Base Metals Conference* (**Copper-Cobalt-201**8) (Livingstone, Zambia) pp 173-179 (2018) (Reviewed).

(3) **Magwaneng, R.S**., Altansukh, B., Haga, K., Shibayama, A., Kosugi M., Kawarabuki R., Mitsuhashi K., Kawata M.; "Investigation for Removal of Organic Carbon from Carbonaceous Copper Sulphide Ore and Improving the Recovery of Copper through Flotation", *Proceedings of "147th The Minerals,*
(4) *Metals & Materials Society"* (**TMS-2018**) (Phoenix, Arizona, USA) Ref. No: E118573, pp. 343-351 (2018) (Reviewed).

(5) **Magwaneng, R.S**., Altansukh, B., Haga, K., Shibayama, A., Kosugi M., Kawarabuki R., Mitsuhashi K., Kawata M.; "Investigation of Copper and Iron Recovery from Copper Ore by High Pressure Leaching", *Proceedings of "The 8th International Conference on Materials Engineering for Resources"* (**ICMR-2017**) (Akita, Japan) Ref. No: AP06, (2017) (Reviewed).

(6) **Magwaneng, R.S**., Haga, K., Shibayama. A.; "Recovery of Copper and Nickle from Multistage concentrates of Mine Tailings by High Pressure Leaching", *Proceedings of "Copper 2016"* (**Copper-2016**) (Akita, Japan) Ref. No: HY1-3, pp III-25 (2016) (Reviewed).

(7) **Magwaneng, R.S**., Haga, K., Shibayama. A.; "Multistage Flotation of Mine Tailings for Copper and Nickel Recovery and Upgrading", *Proceedings of "24th World Mining Congress"* (**WMC-2016**) (Rio de Janeiro, Brazil) pp 161-169 (2016) (Reviewed).