ASSESSMENT OF COPPER RECOVERY FROM LEACHING OF MICROWAVE PRE-TREATED TAILINGS FROM THE OTJIHASE MINE

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ABSTRACT

Copper forms one of the world's most important metals, with vital properties such as high malleability, toughness, and is an excellent conductor of heat and electricity. These properties make copper suitable for a vast range of industrial applications, and predominantly electrical applications. Currently, Namibia has a limited number of active copper mines, and hence a means to recover copper from secondary sources would positively impact Namibia's copper production and would also be beneficial to the Namibian economy. In this study, the assessment of copper dissolution efficiency by microwave-assisted leaching is considered. XRD analysis of the as-received mine tailings revealed that copper is present in the tailings material in the form of sulphide minerals only, covellite (CuS) and chalcopyrite ($CuFeS_2$). Dry mine tailings of particle size -75μm were subjected to microwave pre-heating for 6 minutes in a domestic microwave oven for varying microwave intensities. This was followed by leaching with 0.5M Sulphuric Acid at varying temperatures and leaching times, in a water bath at atmospheric pressure. Results of the effect of leaching time, leaching temperature and microwave irradiation intensity are provided in this work. The results suggest that increasing leaching time and leaching temperature has a slight positive impact on copper leaching efficiency, with the highest recovery of 36.13% obtained at a leaching time of 50 minutes, leaching temperature of 80°C and microwave pre-treatment power of 700W. It was also observed that increasing microwave power from 100 to 700W had no significant impact on the efficiency of copper dissolution. Shrinking core models revealed that diffusion through the product layer, as governed by the equation $k_d t = 1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$ was found to be the rate-determining step, and hence the dissolution reaction mechanism. Arrhenius plots were used to determine the activation energy, which was calculated to be in the range of 7.7-22.69kJ/mol. Multiple linear regression revealed that microwave power, leaching time and leaching temperature were related to percentage copper recovery by the following equation: $R_{Cu} = 4.8525 * 10^{-4} i + 4.8325 * 10^{-2} t + 1.11565 * 10^{-1} T + 23.92999$

LIST OF PUBLICATIONS/CONFERENCE PROCEEDINGS

Conferences:

I. Amuthenu, V.L., Johnson, O.T., Alaneme, K.K. & Kavishe, F.P.L., 2015. 'Impact of microwave irradiation on leaching of copper from sulphide sources: A review', *3rd Annual Science Research Conference,* University of Namibia, 18-19 November.

II. Amuthenu, V.L., Kavishe, F.P.L., Johnson, O.T. & Alaneme, K.K., 2015. 'A study on optimisation of copper recovery from a Namibian mine tailings using microwave-assisted leaching' *3rd Annual Science Research Conference*, University of Namibia, 18-19 November.

Journals:

I. Amuthenu, V.L., Kavishe, F.P.L., Johnson, O.T. & Alaneme, K.K., 2020. Kinetics of copper dissolution from low-grade mine tailings subjected to microwave pre-treatment. *Journal of Chemical Technology and Metallurgy*, 55(1), pp.119-128.

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ICDD = International Centre for Diffraction Data

ICP-OES = Inductively Coupled Plasma Optical Emission Spectrometer

kV = kilovolts

M = Molar

$MgFe_2O_4$ = Magnesioferrite

min = minute

Mn_7SiO_{12} = Braunite

$Na_{1.72}Cr_{1.71}Ti_{6.29}O_{16}$ = Priderite

SEM = Scanning Electron Microscopy

$Si_{192}O_{384}$ = Zeolite

SiO_2 = Silica

SO_2 = Sulphur dioxide

W = Watts

XRD = X-Ray diffraction

XRF = X-Ray Fluorescence

µm = micrometre

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DECLARATION

I, Victoria Ligola Amuthenu, hereby declare that this study is my own work and is a true reflection of my research, and that this work, or any part thereof has not been submitted for a degree at any other institution.

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VICTORIA L. AMUTHENU		11/12/2019
Name of Student	Signature	Date

CHAPTER ONE

1. INTRODUCTION

1.1 Orientation of the proposed study

Copper is one of the world's most important metals which is highly malleable, tough and conductive (Elsentriecy, et al., 2015). These properties make it suitable for a vast range of applications which include architectural, industrial, and in most cases, electrical applications such as in electrical motors, generators and wiring (Davis, 2001). Copper is an excellent conductor of electricity, and can work within a wide range of power networks, making copper the ideal metal for electrical wiring operations. In addition, copper also has excellent thermal and corrosion resistance properties (Prashanth, et al., 2018). Copper is also used in transformers, motor windings, and electronic components of televisions and mobile phones (Bell, 2018). Furthermore, copper can be blended with metals such as zinc and tin to form alloys that are used in the production of coins, pipe fittings, musical instruments (trumpets, trombones, saxophones), and motor vehicle wheel rims, door knobs, locks, faucets, and hinges, amongst others (Bell, 2018). Other copper alloys are corrosion resistant, a property which makes these alloys suitable for use in salt water and industrial environments, as well as in the transportation of potable water (Tuthill, 1987).

Copper is common in many minerals and occasionally may occur in native form. However, most of the world's copper comes from the minerals chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S) with about 70% of world copper contained in the mineral chalcopyrite (Córdoba, et al., 2008; Zhao, et al., 2019). Copper can also be mined from other sources such as Chrysocolla ($Cu_2H_2Si_2O_5(OH)_4$) and Malachite ($Cu_2CO_3(OH)_2$) (Smith, 2015).

Traditionally, the extraction of copper has been based on pyrometallurgical processes, including mineral processing, smelting, followed by electrorefining. However, recently, the pyrometallurgical route of copper extraction has begun to receive less interest in the industry due to high energy cost and the release of sulphur dioxide (SO_2) into the atmosphere (Dimitrijevic, et al., 2009), thereby causing environmental pollution, while also exposing employees to harmful arsenic (Qingshan, et al., 2015). Conversely, the hydrometallurgy route is increasingly being favoured for copper extraction, due to the environmentally friendly nature (Oraby & Eksteen, 2014), by favouring the formation of elemental sulphur instead of gaseous SO_2 and lower capital and operational costs. However, the conventional leaching of chalcopyrite has been reported to have very low leaching efficiencies (Leonard, 2013), and slow kinetics (Abraitis, et al., 2004) due to the passivation of the chalcopyrite (De Lourdes Velasquez Yevenes, 2009). In order to counteract passivation and its effects, researchers have ventured into the application of microwave radiation to the ores to accelerate the leaching reaction rate using microwave energy (Al-Harahsheh, et al., n.d).

Namibia has copper deposits, some of which are currently being mined (Tschudi mine) whereas others have halted their operations (Tsumeb, Matchless and Otjihase copper mines). The Otjihase copper mine has a concentrating plant, which utilises froth flotation to obtain a 28% Cu concentrate, and tailings. However, production at the Otjihase mine stopped in September 2015 and both the mine and plant are currently on care and maintenance. During the many years of operation, the concentrating plant produced tailings amounting to approximately 700 000 tons averaging 0.18% Cu. Previous research has shown that Cu is available mainly in the form of chalcopyrite ($CuFeS_2$) (Leonard, 2013).

The low number of operational copper mines in Namibia signifies a limited number of primary copper sources in the country. Therefore, environmentally friendly means to recover copper from low-grade secondary sources such as tailings would contribute to achieving the national and global copper requirements.

Studies have been conducted on copper recovery from the Otjihase tailings using oxidative leaching; yielding low copper recoveries at lower leaching times (Leonard, 2013). However, other researchers (Chunpeng, et al., 1990; Hwang, et al., 2002; Schmuhl, et al., 2011; Koleini & Barani, 2012; Wen, et al., 2017) have used microwave-assisted leaching to recover copper from various sources such as concentrates as well as low-grade ores. There are discrepancies in the results reported on microwave-assisted leaching in literature, which could be attributed to the various leaching conditions used, as well as to the ore mineralogy. Therefore, there is a need to study the response of the Otjihase tailings to microwave-assisted leaching.

1.2 Problem statement

Namibia has limited primary copper sources, and a means to recover copper from secondary sources which would otherwise be considered uneconomical to exploit has major benefits for the local and global copper market. Previous studies have been carried out on copper recovery from the Otjihase tailings using the oxidative leaching process (Leonard, 2013). In his study, Leonard (2013) utilised conventional heating, which resulted in a low copper recovery of 8% when 0.5M sulphuric acid was used as the leaching medium for 150 minutes in the presence of oxidising agents. Cu could therefore not be efficiently recovered from this mine's tailings using the oxidative leaching process. There are other methods such as microwave-assisted leaching, which have been conducted by various researchers such as Schmuhl, et al., (2011); Zhai, et al., (2009); Havlik, (2008); and Al-Harahsheh, et al., (2005), in an attempt to recover valuable metals from ores, concentrates and tailings. There are disparities in the results reported, with some studies reporting high copper recoveries, and others reporting low copper recoveries. Furthermore, it is imperative to note that ores from different geological locations have different ore mineralogy, which would make their response to leaching under similar conditions different. Therefore, there exists a need to investigate the response of Otjihase tailings to microwave-assisted leaching, which is believed to have more benefits than conventional leaching methods as established by various researchers (Chunpeng, et al., 1990; Hwang, et al., 2002; Koleini & Barani, 2012). In this work, the microwave-assisted leaching behaviour of the Otjihase tailings will be studied, with a view to enhance copper recovery.

1.3 Aim and objectives of the study

The main aim of this study is to investigate the response of the Otjihase tailings to leaching under varying microwave conditions, in order to determine conditions that would yield enhanced copper recovery. The specific objectives of the study are therefore to:

a) evaluate the effect of microwave intensity on the efficiency of copper dissolution from the Otjihase Mine tailings, at varying leaching time and temperature;
b) establish the effect of leaching time and temperature on copper recovery, after microwave pre-treatment;
c) determine the kinetics (rate equation, activation energy) of chalcopyrite dissolution in sulphuric acid; and
d) develop a mathematical model that relates copper recovery to microwave irradiation intensity as well as leaching time and temperature

1.4 Hypotheses

H_0: Increasing microwave pre-treatment intensity does not enhance percentage copper recovery from leaching of Otjihase Mine tailings at 95% confidence interval.

H_1: Increasing microwave pre-treatment intensity enhances percentage copper recovery from leaching of Otjihase Mine tailings.

1.5 Significance of the study

This study is expected to extend the frontiers of knowledge in the recovery of copper from sulphide ores using hydrometallurgical processes; more specifically leaching after microwave pre-treatment. More specifically, the study will reveal how the Otjihase tailings respond to leaching after being subjected to microwave pre-treatment, a finding which will majorly be considered for further copper recovery studies on these tailings material. In addition, the findings of the study may aid process and metallurgical engineers in designing a large scale operation for the recovery of copper from the Otjihase tailings and similar ore deposits. Furthermore, findings of the study may lead to reduced tailings metal content, thereby reducing possibility for underground water pollution. Also, it would promote Cu recovery from secondary sources that would otherwise be considered uneconomical to exploit. Moreover, the study may also provide knowledge on conditions required for optimum copper recovery from the tailings.

1.6 Scope and limitations of the study

This study is delimited to tailings from the Otjihase copper concentrating plant in Namibia, in which the extraction of copper from these tailings will be limited to the hydrometallurgy route. Samples will be subjected to microwave irradiation prior to leaching (with an exception to the control experiments). The parameters to be investigated are microwave irradiation intensity (0, 100, 300, 500, 700W), leaching time (20, 30, 40, 50 minutes) as well as leaching temperature (50, 60, 70, 80°C).

Due to the unavailability of some analytical instruments such as Atomic Absorption Spectrometer (AAS), X-ray Diffractometer (XRD) as well as Scanning Electron Microscope (SEM) in the University of Namibia premises, samples will be sent to external laboratories for analyses.

1.7 Structural organisation

The rest of the thesis is structured as follows:

Chapter 2 gives an extensive literature review on copper, its occurrence in the earth's crust, extraction techniques; and highlights the uses and importance of copper in everyday life. It also gives a review of published work on microwave radiation and its use in leaching of sulphide minerals, while focusing on the various breakthroughs of this technique, and existing gaps that need to be filled. Furthermore, this chapter presents results obtained by other researchers on microwave-assisted leaching, providing specific conditions used.

Chapter 3 establishes the methods used in this work, with a comprehensive outline of the experiments conducted and the tools used in these experiments.

Chapter 4 presents the results obtained from the leaching tests conducted and provides a detailed discussion of these results

Chapter 5 concludes this work and lays out recommendations for future work.

CHAPTER TWO

2. LITERATURE REVIEW

This chapter provides contextual information on copper; its occurrence in the earth's crust, its properties as well as uses in everyday life. It also gives a summary of the various copper alloys and their uses. Furthermore, this chapter outlines in details the various methods employed for copper processing and extraction from its sources. It then gives a detailed review on microwave-assisted leaching, outlining its benefits and shortcomings, while focusing on various conditions used, results obtained thereof, and identifies a research gap that necessitated this study and led to the formulation of the research topic.

2.1 Copper occurrence and ores

According to (Ghosh & Ray, 1991) as cited in Adebayo, (Adebayo, et al., 2003), copper is the third most produced metal globally, after iron and aluminium, although it has a very low mass fraction in the earth's crust (about 0.01%). Metallic copper is soft, malleable, and ductile and has excellent thermal and electrical conductivity. These properties make copper suitable for use in electrical wiring, electronic applications as well as heating systems (Davis, 2001). Copper can also be alloyed with metals such as zinc (Zn) and tin (Sn) to produce alloys used for the production of coins, musical instruments etc. (Naboka & Giordano, 2011). Although global copper prices are currently not at an all-time high, devising ways to recover copper from especially secondary sources can help contribute to the global copper requirements, especially when the prices pick up. Figure 2-1 shows a chart displaying a trend of the global copper prices over a period of 5 years.

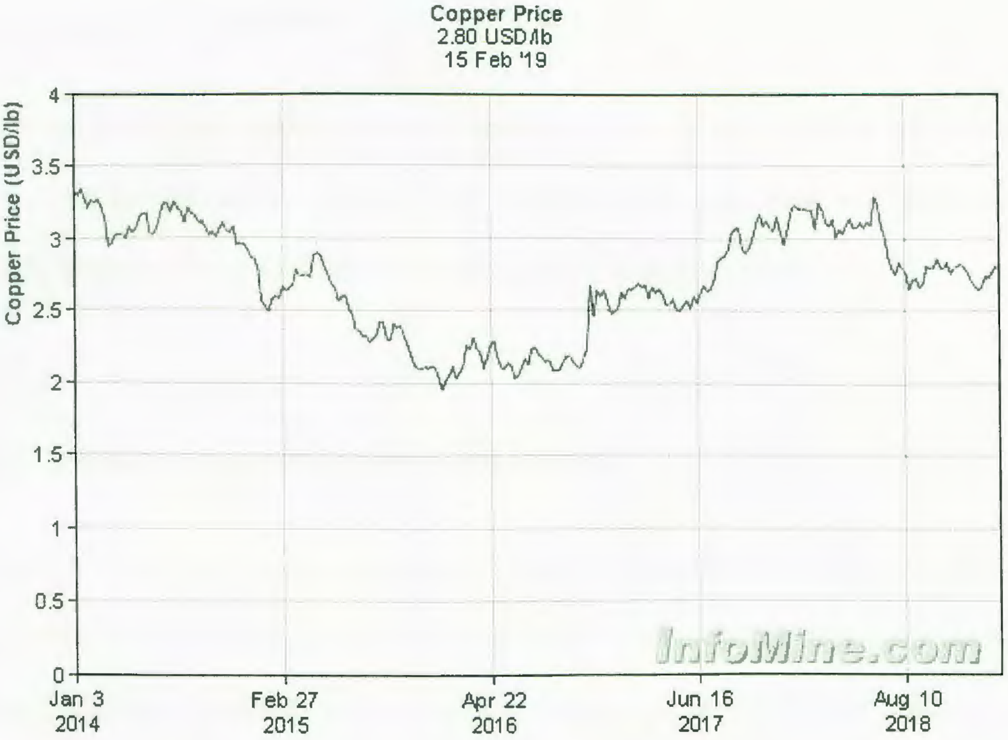


Figure 2-1: *Trend of the global copper prices over a 5-year span* (InfoMine, 2019)

Copper is found present in various forms, usually combined with elements such as oxygen, iron, sulphur and carbon, although in rare occurrences, it can also be found as native copper (Bornhorst & Mathur, 2017; Cooper, 2011). Some of the copper-bearing minerals are: chalcopyrite, chalcocite, covellite, bornite, tetrahedrite, malachite, azurite, cuprite, chrysocolla, and tennantite (British Geological Survey, 2007). The most abundant copper-bearing mineral however is chalcopyrite ($CuFeS_2$), with about 70% of the world copper contained in this mineral (Córdoba, et al., 2009). The mineral chalcopyrite has a brassy yellow colour, metallic lustre, and high specific gravity. It is similar in appearance to pyrite and gold. However, the major differences in the three minerals are as follows: Gold is soft; with a yellow streak and has a specific gravity much higher than chalcopyrite. Chalcopyrite is brittle with a greenish grey streak. On the other hand, pyrite is harder than chalcopyrite, such that it cannot be scratched by a nail, which easily scratches chalcopyrite (King, 2018).

2.2 Copper extraction

The route chosen for copper extraction depends on the nature of the ore. Sulphide ores go through the concentration process of froth flotation, while oxide ores undergo leaching prior to subsequent processes that lead to attaining copper in its pure form.

2.2.1 Mineral processing of copper sulphide ores

Mineral processing of copper sulphide ores involves comminution, sizing, and froth flotation to produce a concentrate, usually with a copper grade of 20-30%. Comminution is the reduction in particle size of solid material by fracture, achieved through crushing, grinding, milling, or other related processes (Yang, 2015). The comminution process is vital for the liberation of especially low-grade ores, which have the valuable mineral finely disseminated within the gangue minerals (Wills & Finch, 2015). Comminution reduces the particle size of the ore, thereby increasing the surface area available for chemical reactions. Various types of crushers such as jaw crushers, gyratory crushers and cone crushers are used for the first stage of comminution, while grinding mills such as rod mills and ball mills are used for the second stage of comminution. Comminution is followed by the classification stage; in which various types of classifiers are used to separate fine (liberated) from coarse (unliberated) solid particles. The coarse particles undergo further grinding, until they reach the size required for the next stage of the process, which is froth flotation. The froth flotation process separates gangue from valuable minerals and increases the ore grade prior to further processing downstream, and in order to render low-grade ores economical to process (Hocking, 2005). A schematic representation of the froth flotation process is given in Figure 2-2.

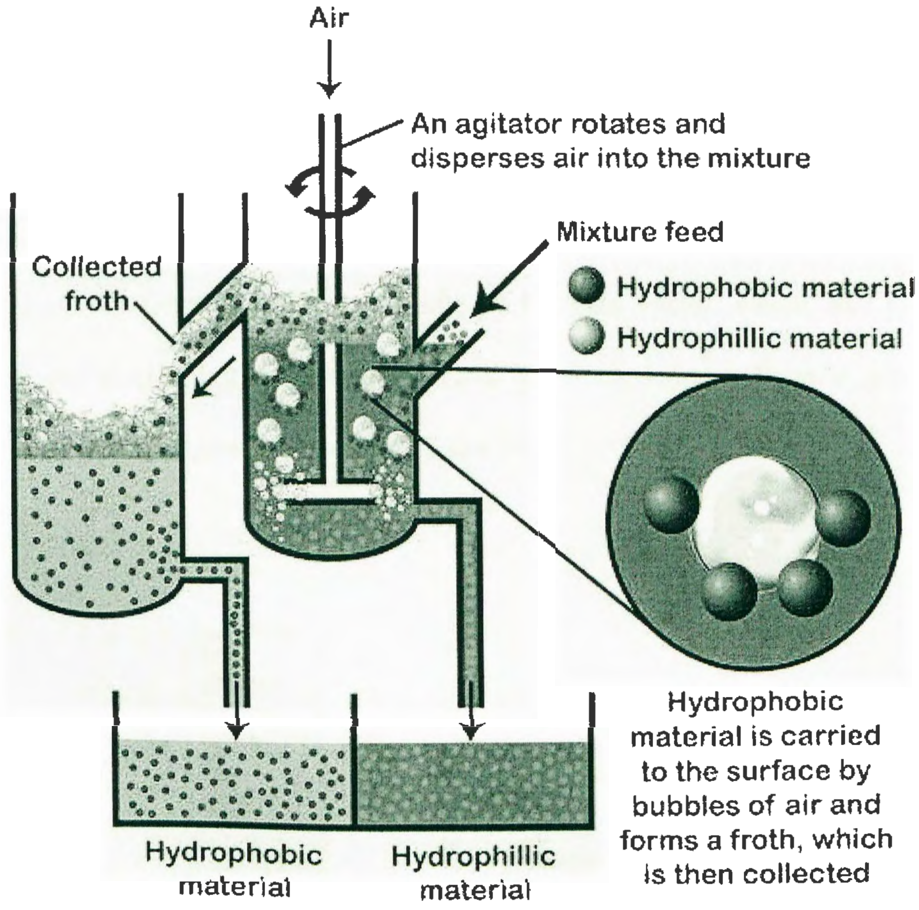


Figure 2-2: *Schematic representation of the froth flotation process* (Schlesinger, et al., 2011)

The froth flotation process makes use of the surface properties of liberated minerals to separate hydrophobic minerals from hydrophilic minerals (Quinn & Crawford, 2017). A flotation cell is fed with slurry made up of ore and water, as well as flotation reagents. Air is bubbled into the flotation cell while the slurry is stirred to create a homogeneous mixture. The hydrophobic particles attach to air bubbles and are carried to the surface, from which they are scrapped as froth (Quinn & Crawford, 2017), and are subsequently filtered to produce a concentrate. Special reagents are used to aid in the froth flotation process, particularly in changing the surface properties of mineral particles, to render them hydrophobic or hydrophilic. Surfactants such as collectors modify the surface properties of the minerals, rendering them hydrophobic, whereas depressants modify the surface properties of minerals, rendering them hydrophilic. Frothers help to stabilise the air bubbles, so that they do not breakdown within the slurry, before reaching the surface. Sulfide minerals are hydrophilic in nature; however when conditioned with collectors, they become hydrophobic and are easily floated (Schlesinger, et al., 2011). Hydrophilic minerals remain wetted and are hence not floated, and after a series of flotation cycles, which take place in the stages of roughing, cleaning and scavenging, and are discarded as tailings. A generic flowsheet of the froth flotation circuit is given in Figure 2-3.

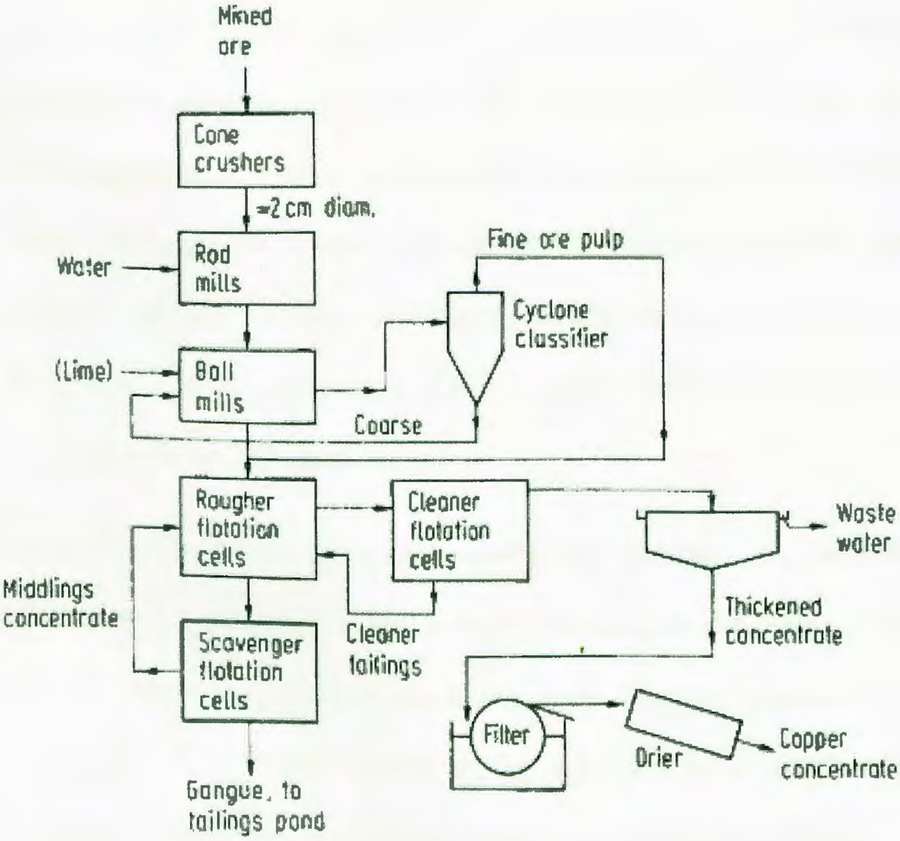


Figure 2-3: *Generic flowsheet of a mineral processing (froth flotation) circuit* (Schlesinger, et al., 2011)

2.2.2 Hydrometallurgical copper extraction

The hydrometallurgical processing route has been used for many decades for processing of various ore minerals, particularly low-grade oxide ores (Petersen, 2016; Yin, et al., 2018). However, conventionally, sulphide copper ores have been processed through the pyrometallurgical route. Furthermore, over the recent years, as opposed to pyrometallurgical processing of copper, researchers have ventured into hydrometallurgical processing of even sulphide ores, due to its environmentally friendly nature (Oraby & Eksteen, 2014; Olubambi & Potgieter, 2009; Zhao, et al., 2019). With the gradual depletion of rich ore deposits, and the stringent requirement to prevent the emission of SO_2 into the atmosphere, the hydrometallurgical route is being considered for copper production (Pradhan, et al., 2008). Other environmental issues associated with pyrometallurgical copper processing are emissions of toxic compounds of heavy metals such as arsenic, antimony amongst others (Qiu, et al., 2003). A representation of a hydrometallurgical technique that makes use of heap leaching is shown in Figure 2-4.

However, various researchers have reported that sulphide ores, particularly those containing chalcopyrite, do not respond well to hydrometallurgical processing especially in sulfuric acid (H_2SO_4) media due to slow dissolution rates which is triggered by the formation of a passivating layer on the surface of the mineral (Havlik, 2010; Córdoba, et al., 2008; Tshilombo, 2004; Stott, et al., 2000; Hackl, et al., 1995; Nikol, 2017).

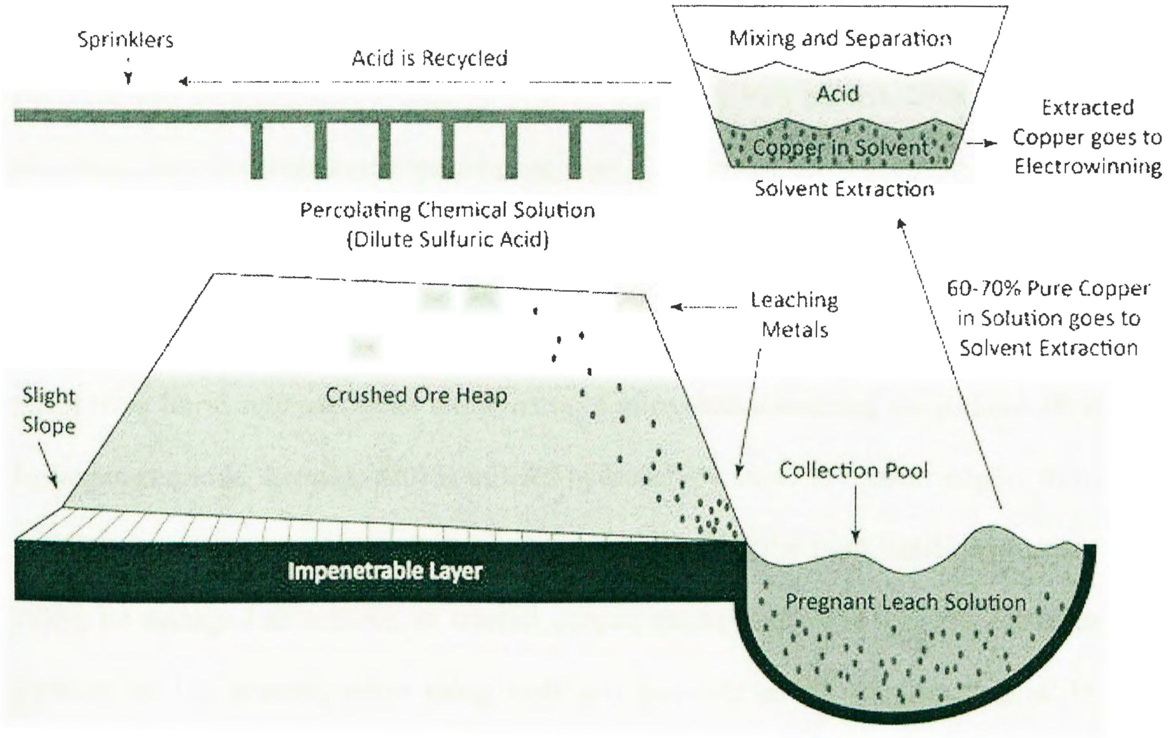


Figure 2-4: *Hydrometallurgical copper extraction* (Superfund Research Program, 2018)

2.2.3.1 Oxidative leaching of chalcopyrite

Oxidative leaching of chalcopyrite has been conducted, particularly on chalcopyrite concentrates. According to Lu (2010) as reported in Schaming (2011), the dominant chalcopyrite leaching reactions are reactions (1) and (2).

$$CuFeS_2 + 5H^+ + O_2 \rightarrow Cu^{2+} + 2Fe^{2+} + 2S^0 + 2H_2O \quad \text{..........(1)}$$

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \quad \text{..........(2)}$$

These reactions both represent oxidative leaching of chalcopyrite. However, (Schaming, 2011) reported that the major setback in chalcopyrite leaching in an oxidative environment (with ferric sulphate) at temperatures below 110°C is chalcopyrite passivation which occurs once about 30% of Cu in the concentrate is leached.

Some researchers considered using oxidative leaching to aid in the dissolution of copper sulphide ores on a laboratory scale (Hollitt, et al., 2008; Van Staden, 2008; Muller, 2007), also using ferric sulphate as the leaching lixiviant. On average, a copper recovery of 75% was achieved when ferric sulphate was used as the lixiviant, for at least 3360 hours (Hollitt, et al., 2008; Van Staden, 2008; Muller, 2007).

Apart from ferric sulphate, other oxidisers used in oxidative leaching are sodium nitrate and hydrogen peroxide. Leonard (2013) utilised hydrogen peroxide to recover copper from mine tailings that originally concentrated a chalcopyrite ore using the froth flotation process. In his study, he managed to achieve an overall copper recovery of 95% at 70°C for a leaching duration of 150 minutes when using hydrogen peroxide as the oxidising agent. He also reported chalcopyrite passivation at temperatures above 70°C, an observation which agrees with Schaming (2011). Generally, the purpose of oxidative leaching is to convert the sulphide minerals to sulphates, which easily dissolve in acid. However, even with oxidative leaching, chalcopyrite passivation was still observed as reported by the authors above. There is therefore a need for an environmentally friendly method of recovering copper from sulphide sources, while minimising chalcopyrite passivation and its effects. This is the gap that necessitated this study.

2.2.3.2 Chalcopyrite passivation

According to Turan, et al. (2015), passivation is the formation of elemental sulphur due to oxidation of sulphide. However, BioMineWiki (2008) defines passivation as the formation of a hard, non-reactive surface/film on the mineral surface. The non-reactive film/layer formed inhibits further leaching and decreases leaching rate of the mineral by creating a diffusion barrier. This leads to reduced leaching efficiency. Studies on chalcopyrite passivation have been conducted (Watling, 2006; Klauber, 2008; Debernardi & Carlesi, 2013) but could not all reach consensus on its causes. Based on studies conducted by various researchers, three possible causes of passivation were identified as:

- formation of an iron precipitate layer that prevents contact between chalcopyrite and the leaching solution (Stott, et al., 2000; Córdoba, et al., 2009).
- formation of elemental sulphur which creates a diffusion barrier (Carneiro & Leão, 2007; Munoz, et al., 1979).
- formation of an intermediate layer of sulphides, disulfides or polysulfide compounds which have slow reaction kinetics and therefore control the overall rate of dissolution (Debernardi, et al., 2013; Klauber, 2008; Parker & Hope, 2008; Harmer, et al., 2006).

However, in their study which looked at two methods of avoiding chalcopyrite concentrate passivation in an oxidative leaching environment, Debernardi, et al. (2013) concluded that the formation of iron precipitates on chalcopyrite is not the cause of chalcopyrite passivation, since passivation still occurred even in the absence of iron precipitates. Debernardi, et al. (2013) further concluded that chalcopyrite passivation still occurred when sulphur oxidising bacteria (thiooxidants) were present. Figure 2-5 is a representation of one form of chalcopyrite passivation during the leaching process.

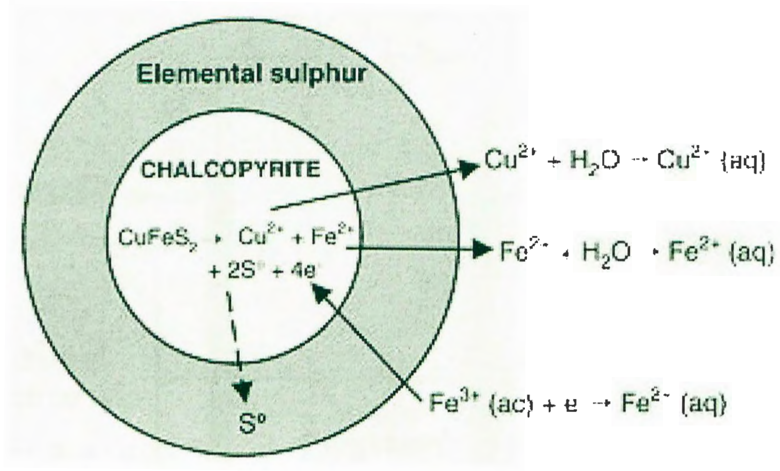


Figure 2-5: *Schematic illustration of chalcopyrite oxidation by ferric ions, with a formation of a layer of elemental sulphur* (Córdoba, et al., 2008)

2.2.3 Electrometallurgy & electro-refining

Apart from pyrometallurgical processing, the copper concentrate obtained from sulphide sources via froth flotation may be leached in order to obtain a copper-rich solution which undergoes solvent extraction to make it suitable for electro-winning (Young, et al., 2003), and if required, electrorefining.

Electro-winning of copper involves the use of direct current which passes from anodes to cathodes in a cell containing an electrolyte. The electrolyte is a concentrated copper sulphate solution (45-55g/L Cu), with high conductivity, (Schlesinger, et al., 2011), while the anode is made of materials such as carbon or lead which do not dissolve in the electrolyte (Michaud, 2016). The cathode can be stainless steel or can be made of the metal that is to be recovered (copper) and onto which pure copper electroplates, from the solution (Schlesinger, et al., 2011). Figure 2-6 shows a general schematic representation of an electro-winning cell, whereas Figure 2-7 shows the copper electro-winning cell setup.

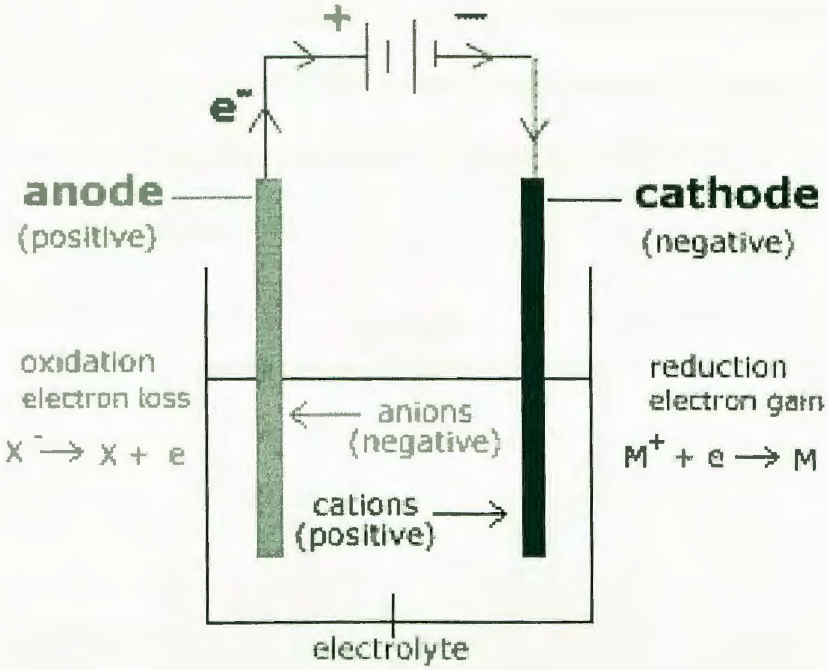


Figure 2-6: Schematic representation of an electrolytic (electrowinning) cell (Lok, 2011)

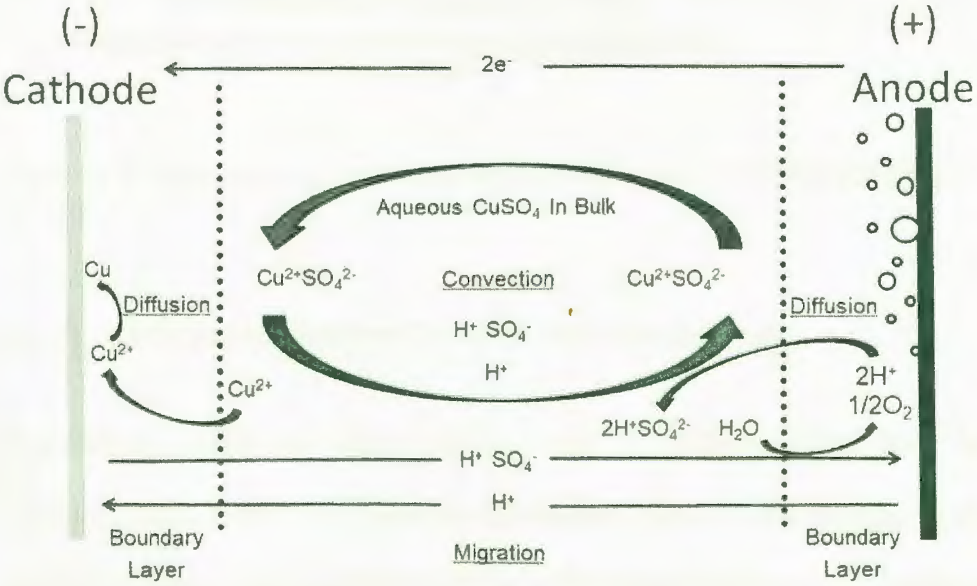


Figure 2-7: Representation of a copper electrowinning cell (Werner, et al., 2018)

Electrorefining of copper is similar to electro-winning in that they both make use of electrolysis. However, the difference is in the anode and cathode composition. For electrorefining of copper, the anode is made up of impure copper that needs to be purified, whereas the cathode is made of thin copper starter sheets or stainless steel. The cathode is the electrode where the pure metal is deposited (Lok, 2011). The electro-refining cell is illustrated in Figure 2-8.

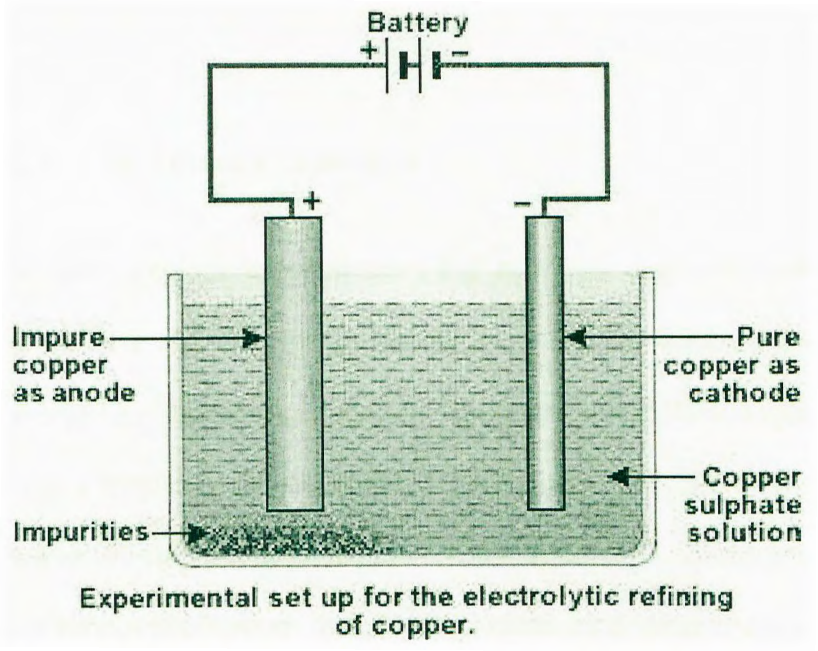


Figure 2-8: *Schematic representation of the copper electrorefining cell* (TutorVista, 2019)

2.3 Attempts to recover Cu from Otjihase tailings

Unpublished studies on copper recovery from the Otjihase tailings have been conducted. Leonard (2013) carried out oxidative leaching of otjihase mine tailings. In the study, it was established that it was possible to achieve 95% copper recovery by using hydrogen peroxide as the oxidising agent, and using H_2SO_4 as the lixiviant. The concentration of H_2SO_4 used was 2M, while the H_2O_2 concentration was 1M. Leaching was conducted at 70°C for 240 minutes. It is imperative to note that although a high copper recovery was achieved at these conditions, it was mostly attributed to the high concentrations of reagents used, and to the oxidising agent used. The use of reagents of high concentration leads to high operational costs, which can affect the profitability of the operation, due to the high cost of reagents. This study aims to consider the use of microwave radiation to preheat the tailings sample prior to leaching, and carry out leaching using reagents of lower concentrations, as well as reduced leaching time.

2.4 Microwave radiation

In order to counteract passivation and its effects, researchers ventured into the application of microwave radiation to the ores to accelerate the leaching reaction rate using microwave energy (Al-Harahsheh, et al., n.d). Microwave radiation is a type of electromagnetic radiation with a frequency ranging between 300MHz and 300 GHz or a wavelength ranging from 0.1 cm to 100 cm (Helmenstine, 2017; Talebnejad, et al., 2018). Generally, microwaves are used for various applications including communication, radar and cooking. The use of microwaves in cooking is possible because microwaves can be used to transmit thermal energy (Lucas, 2018). Microwave radiation can be reflected, transmitted, and absorbed, leading to heat production in the absorbing material. Additionally, microwaves give and enhance the resonance of molecules and ions (Pozar, 2012; Onol & Saridede, 2012; Sanghi, 2000). Figure 2-9 compares heat induction as well as temperature distribution between conventional heating and microwave heating.

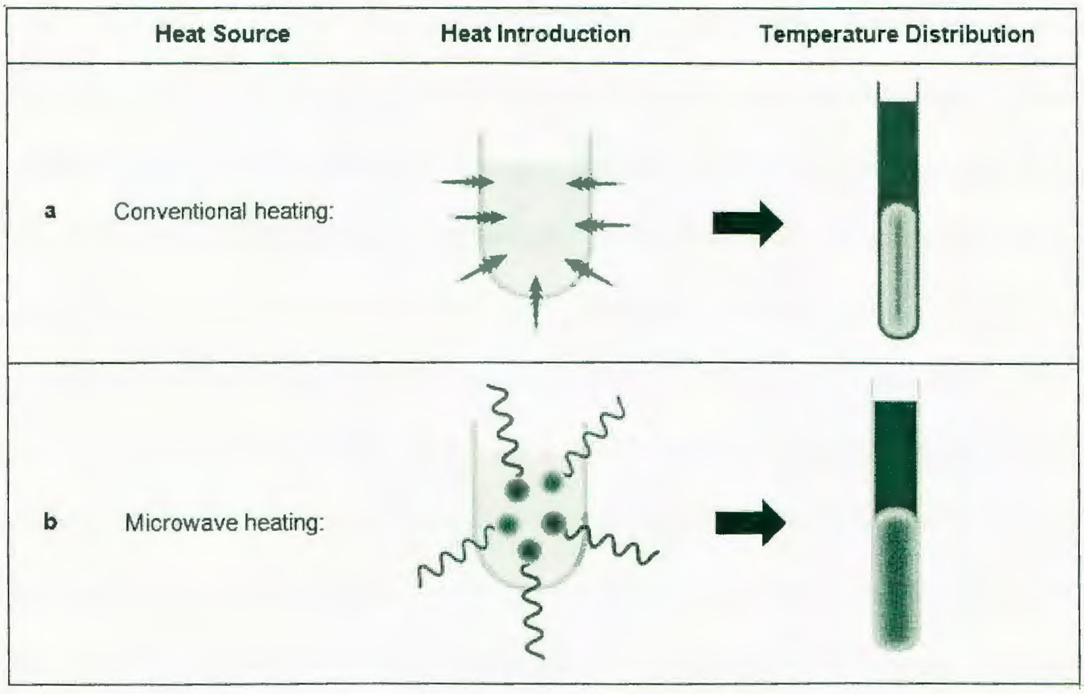


Figure 2-9: *Illustration of conventional vs microwave heating* (Paar, 2018)

2.5 Microwave-assisted leaching

In earlier years, researchers have used microwave radiation to aid dissolution of metals, minerals and other chemical products (Matthes, et al., 1983; Kingston & Jassie, 1988). Microwave irradiation is believed to have various advantages when compared to conventional heating methods. Amongst the many advantages, some of them are: lower energy usage and higher chemical yield, reduced processing time, direct heating throughout the entire volume of the sample, as well as a heating process that can easily be controlled (Chunpeng, et al., 1990; Hwang, et al., 2002; Koleini & Barani, 2012; Kucinska-Lipka, et al., 2017). Wang and Mujumdar (2007), reviewed various reports on studies conducted on the use of microwave irradiation for leaching. The report highlighted that due to economic, environmental and technical reasons, hydrometallurgical extraction of metals from their ores is advantageous when compared to pyrometallurgical extraction. These advantages are especially true for minerals that readily dissolve in leach solutions, but not for most sulphide minerals which undergo passivation, a phenomenon that poses a challenge to leaching of sulphide minerals. In their review, Wang and Mujumdar (2007) hence established that the use of microwaves can be applied to mineral processing as well as extraction of various metals including copper. Old studies have been conducted to explain the microwave heating mechanism on minerals, and on mineral processing. According to Walkiewicz, et al., (1988), the microwave heating mechanism is such that the mineral undergoing microwave irradiation absorbs microwave energy, which causes thermal stress within the material. Thermal stress then causes micro-fracturing along the grain boundaries, making the mineral sample more amenable to grinding. Other researchers have utilised microwave heating to improve the grindability of ores (Tavares & King, 1996; Marland, et al., 2000; Vorster, et al., 2001; Koleini, et al., 2012).

Microwave heating is believed to be material specific, with advantages such as increased heating rate and faster dissolution rate when compared to conventional heating methods (Koleini & Barani, 2012). In another study by Hwang, et al., (2002), it was established that fast leaching kinetics were achieved as a result of microwave treatment. In addition, Al-Harahsheh, et al., (n.d) in a comprehensive study investigated the influence of microwaves on the dissolution kinetics of chalcopyrite and sphalerite in ferric ion media. The study reports that chalcopyrite is a good microwave absorber. Also, the reaction rate of chalcopyrite leaching was found to be slightly higher when microwave radiation was used as the heat source, when compared to conventional heating methods.

Other researchers, Onol and Saridede (2012) have considered using microwave-assisted leaching in order to improve the leaching recoveries. They investigated conventional versus microwave-assisted leaching. A similar study was also carried out by Al-Harahsheh, et al., (2005). Both studies concluded that microwave-assisted leaching yields higher Cu recoveries.

The leaching was conducted in a microwave digestion device, and the optimum conditions obtained were leaching time of 1 hour, leaching temperature of 140°C, and a leaching solution consisting of a mixture of 0.5 M H_2SO_4 and 0.05 M $Fe_2(SO_4)_3$.

On the other hand, the study by Al-Harahsheh, et al., (2005) concluded that although microwave-assisted leaching yielded recoveries higher than those obtained in conventional leaching, the difference was minimal, with the highest difference in copper recovery (for conventional and microwave-assisted leaching) less than 5%. Leaching of chalcopyrite natural crystals was conducted in a microwave accelerated reaction systems apparatus that delivers three levels of power: 300, 600 and 1200 W. The leaching solution was made up of 0.5M sulphuric acid and 0.25M ferric sulphate. Similar results were obtained by Onol and Saridede, (2012), with only one of the four materials used in the study showing a difference in conventional and microwave-assisted leaching copper recovery of about 13%. The other three materials used in the study all showed a difference of about 5%. Microwave-assisted leaching of nickel laterite ores conducted by Zhai, et al., (2009), reporting a high copper recovery of 92%. The optimum microwave intensity was found to be 800W, whereas the optimum microwave irradiation time was found to be 6 minutes at a temperature of 90°C and leaching time of 90 minutes. In this study, conditions similar to these were applied to the mine tailings, in an attempt to recover copper. Additionally, the difference in leaching recoveries obtained by various researchers warrants a need to thoroughly study the response of various minerals to microwave-assisted leaching, in order to understand the difference in conclusions by different researchers.

Figures 2-10 to 2-13 show results obtained by some researchers on microwave-assisted leaching. It can be seen that the copper yield was as high as 60% in some studies, while other studies could only achieve a yield of about 17% as the highest for the set of conditions investigated in such studies.

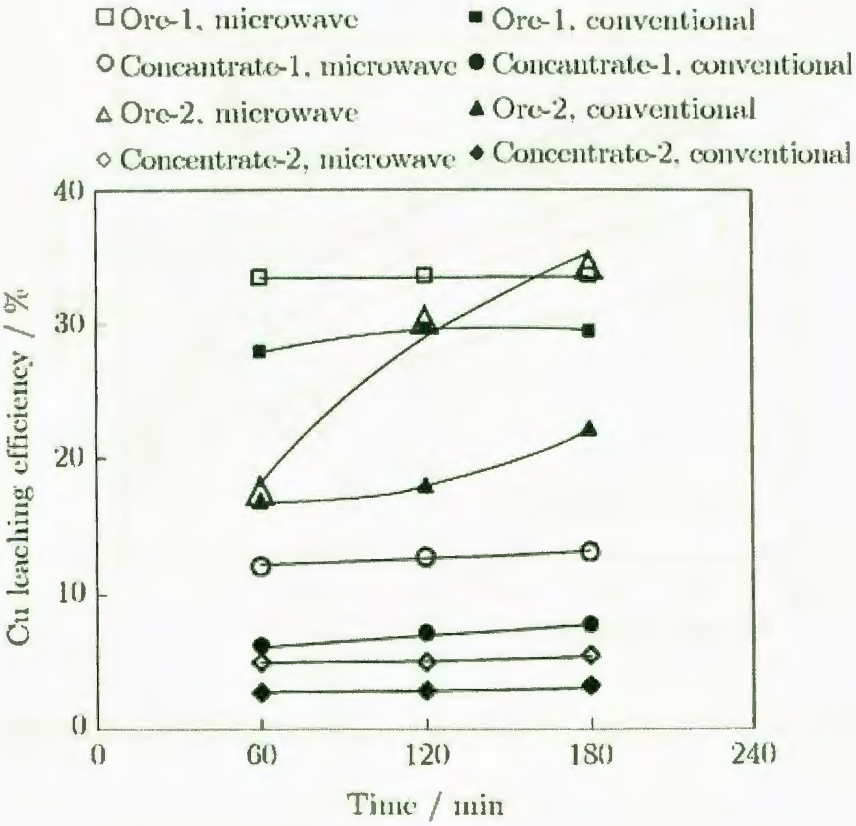


Figure 2-10: *Conventional vs microwave-assisted leaching of copper and iron* (Onol & Saridede, 2012)

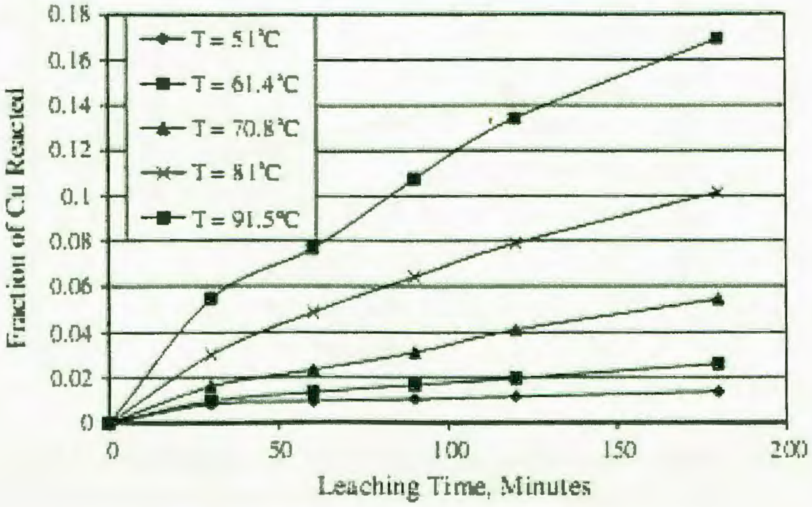


Figure 2-11: *Effect of temperature and leaching time on microwave-assisted leaching at 300W microwave power* (Al-Harahsheh, et al., 2005)

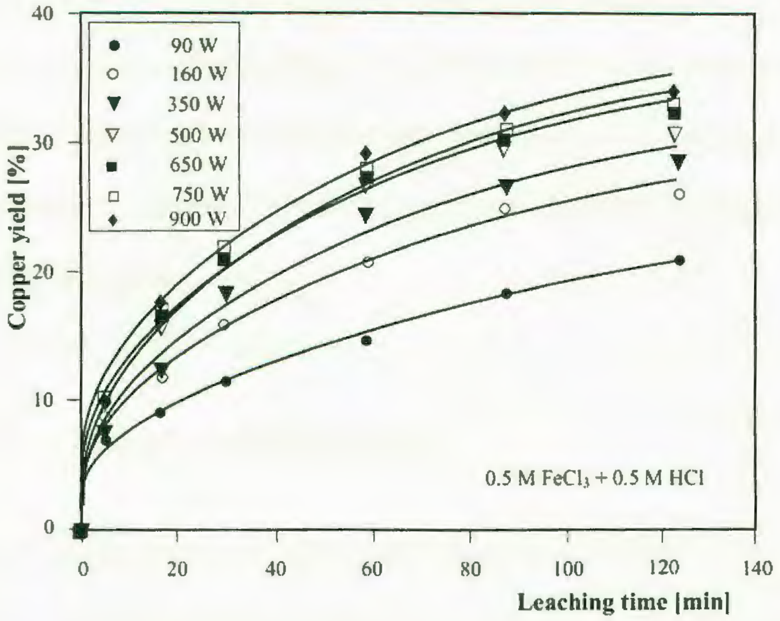


Figure 2-12: Effect of microwave power and leaching time on copper yield (Havlik, 2008)

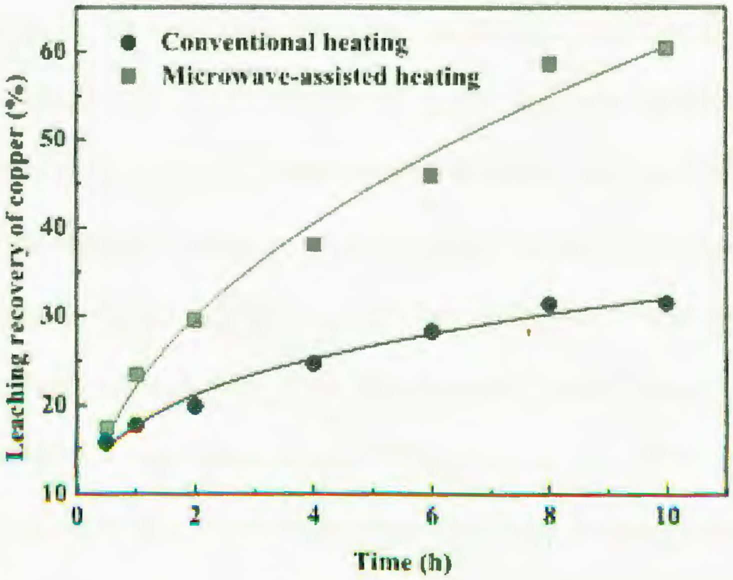


Figure 2-13: *Leaching recovery of copper in microwave-assisted and conventional leaching in boiling solution at microwave power of 300W* (Wen, et al., 2017)

Different results have been obtained by various researchers, as is shown in Figures 2-10 to 2-13. However, it is noteworthy to emphasize that the available studies have placed minimal emphasis on the Namibian copper-bearing sulphide minerals, particularly from secondary sources such as mine tailings. It is imperative to study and establish the response of the Otjihase tailings to microwave-assisted leaching over a wide range of conditions to determine whether it is technically viable to recover copper from these tailings using microwave-assisted leaching.

2.6 Copper leaching kinetics

The leaching kinetics of chalcopyrite have been studied by various researchers (Li, et al., 2013; Gok, et al., 2013; Tanda, et al., 2019). The experimental conditions studied were different, while at the same time, different leaching media were used. As a result, varying conclusions on the chalcopyrite dissolution mechanism have been reported. Various rate equations are reported in literature for different leaching conditions. For leaching conducted in sulfuric acid media, the kinetic model has been reported as either as diffusion, surface reaction as well as a mixed model (diffusion and surface reaction) (Khoshkhoo, 2014). Additionally, Antonijevic, et al., (2004) concluded that chalcopyrite dissolution mechanism (using hydrogen peroxide as oxidising agent) conformed to the surface reaction controlled shrinking core model, with an activation energy value of 60 kJ/mol. However, other researchers (Aydogan, et al., 2006; Ikiz, et al., 2006) concluded in their studies that chalcopyrite dissolution conformed to the ash or product layer diffusion controlled model, with activation energies of 19.88 kJ/mol and 24 kJ/mol, respectively. On the other hand, Sokic, et al., (2009), in their study on kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid, concluded that the experimental data were best fitted by a mixed control kinetic model, with an activation energy of 83 kJ/. According to Li, et al., (2013), due to reduced control of the leaching parameters in studies conducted by various authors, as well as the different experimental conditions used, the activation energies reported from various studies cannot be compared. Generally, temperature has been reported to have the most notable impact on chalcopyrite leaching rate. Other factors considered to have an effect on chalcopyrite leaching rate are acid concentration (although various researchers have different conclusions on how acid concentration affects chalcopyrite leaching rate (Kimball, et al., 2010; Li, et al., 2010; Dutrizac, 1979), particle size and stirring speed (Li, et al., 2013). There is therefore no general consensus on the kinetics of chalcopyrite leaching, as the models developed by various researchers are diverse.

The following generally accepted shrinking core models are used for reaction mechanism studies as reported in (Onyedika, et al., 2013).

Film diffusion: $k_f t = X_B$ ....(3)

Surface reaction: $k_r t = 1 - (1 - X_B)^{1/3}$ ....(4)

Ash layer/product diffusion: $k_d t = 1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$ ....(5)

Where k_f, k_r and k_d are rate constants for film dissusion, surface chemical reaction and ash layer diffusion, respectively, t is contact (leaching) time and X_B is the fraction reacted (Onyedika, et al., 2013). According to the shrinking core models, three key stages transpire during the leaching process as described by equations (3) – (5). The slowest of these steps is taken as the rate-determining step, and therefore determines the dissolution mechanism.

2.7 Research problem formulation

Namibia currently has only one copper mine in operation, the Tschudi copper mine. The rest of the copper mines that were once operational have either closed down (the Tsumeb copper mine) or entered into a care and maintenance phase (the Otjihase mine and the Matchless mine). Feasibility studies are currently being conducted to determine the technical and financial viability of mining copper from the Haib copper deposit in Southern Namibia (Deep South Resources, 2019). This symbolises a deficit in the primary copper sources in Namibia. Devising a means to recover copper from secondary sources such as mine tailings will help not only contribute to the national but also global copper requirements. Also, it would aid in reducing the metal content of the mine tailings, thereby reducing possibility for underground water contamination. With the known slow dissolution of chalcopyrite in conventional leaching methods, this study attempts to determine whether it is technically feasible to recover copper from low-grade mine tailings using microwave-assisted leaching.

2.8 Chapter summary

In this chapter, an overview of copper occurrence and extraction methods was given. The uses of copper were also outlined, as well as the kinetics of the copper leaching process. Two extraction methods were looked at, pyrometallurgy and hydrometallurgy. The pyrometallurgical route for copper extraction was reported to have high energy requirements, particularly when treating low-grade ores (Dimitrijevic, et al., 2009). Also, pyrometallurgy has the disadvantage of possible emission of SO_2 into the atmosphere. Hydrometallurgy was reported to have low energy requirements (Petersen, 2016; Yin, et al., 2018). However, copper sulphide ores do not respond well to the leaching process, due to the passivation of chalcopyrite in the ore. Microwave-assisted leaching was conducted by various researchers in an attempt to counteract passivation, and they reported differing conclusions from their findings. The studies conducted were however not based on a Namibian copper deposit. The next chapter will outline the methods used in conducting this study. It will also illustrate how conditions similar to those used by various researchers were incorporated into this work, while focusing on a Namibian mine's copper tailings.

CHAPTER THREE

3. METHODOLOGY

This chapter illustrates the research methods employed in this work. It provides a detailed description of the characterisation of the mine tailings used as well as the microwave and leaching conditions used in this study. It also outlines in details the equipment used in the study, and the analytical techniques used to characterise the filtrate and residues from the leaching experiments. As stated before, this study investigated the use of microwave-assisted leaching for recovery of copper from mine tailings.

3.1 Research Materials and Preparation

3.1.1 Mine tailings sample collection

The sampling technique used was simple random sampling across the tailings dam. This is because the tailings dam is extremely large for systematic sampling, hence random sampling was utilised. The Otjihase tailings dam has varying levels (height above ground). The samples were collected from each of the levels of the tailings dam. At each level, a sampling probe was hammered about 1m deep into the tailings dam, and collected tailings samples in the process, which were then placed in large plastic sacks. Apart from the sampling probe, a shovel was also used to randomly collect samples of the tailings dam by digging by hand. This ensured that the sample collected was from various locations of the tailings dam, and that it was a true representative of the tailings dam.

3.1.2 Research instruments

Various instruments were used for different purposes in this study, and a detailed description of these is given in this section.

- Laboratory sieves

Laboratory sieves were used for particle size analysis experiments, in order to obtain the particle size distribution of the as-received sample, as well as to obtain the particle size required for the leaching experiments.

- Laboratory oven

A laboratory oven (Memmer 100) was used to dry the raw tailings sample by heating the samples at 110°C for 4 hours.

- Microwave oven

A domestic microwave oven of a Samsung make and with a maximum output of 1000W was used to exposure the tailings samples to microwave radiation prior to leaching. The samples were all pre-heated for 6 minutes, and the microwave power was varied at 0, 100, 300, 500 and 700W respectively.

- Leaching bath

A leaching bath (Labotec Eco Bath shaking water bath) as shown in Figure 3-1 was used for leaching experiments. The leaching time was varied at 20, 30, 40 and 50 minutes, while the leaching temperature was varied at 50, 60, 70 and 80 °C, respectively.

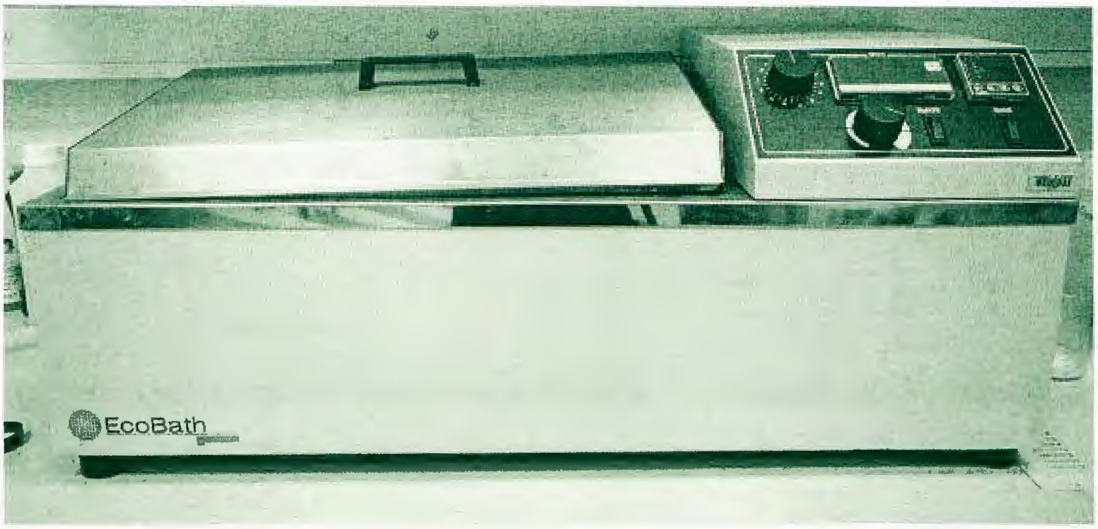


Figure 3-1: Leaching bath (Labotec Eco Bath)

- Grinding mill

Milling of the tailings samples was conducted using a laboratory ball mill. Grinding of the tailings samples was done in order to reduce the particle size of the material, and obtain the size required for leaching experiments (-75 µm).

- X-Ray Diffraction (XRD) analyser

An XRD analyser of the make Philips PW1710 X-Ray Diffraction Spectrometer X-Ray Diffractometer was used for mineralogical characterisation of the tailings sample, in order to determine the mineral phases present in the sample. The Philips PW1710 uses Cu K-α radiation produced at 40kV and 30mA. The sample was scanned between 5 to 90° 2θ, in step sizes of 0.01°, and a scan speed of 0.5°/minute. When the XRD scans were completed, the mineral phases present were identified using the International Centre for Diffraction Data (ICDD) (PDF 2010) data cards.

- XRF analyser

An X-Ray Fluorescence analyser (Niton Xl3t) was used for elemental analysis of the raw tailings sample.

- ICP-OES analyser

An Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) of the make PerkinElmer Optima 7300 DV was used for elemental constituents' analysis of the filtrate as well as the leaching residue after digestion.

- Scanning Electron Microscopy

Tailings samples and leaching residue morphology was assessed using a Philips (XL30 SERIES) Scanning Electron Microscope (SEM) equipped with a field emission gun operating between 5 and 30kV.

3.2 Research design

A quantitative randomised factorial design was used for the study. The experiments entailed leaching of the mine tailings, first without microwave pre-treatment at varying leaching temperatures and leaching times, followed by leaching at the same conditions after microwave pre-heating for 6 minutes at varying microwave intensities. All leaching experiments were conducted in triplicate, to ensure results repeatability. The conditions used for the leaching experiments are as displayed in Table 3-1.

Table 3-1: *Experimental plan for leaching conducted outside microwave oven*

Factor	**No. of levels**	**Levels**
Irradiation intensity (W)	5	0, 100, 300, 500, 700
Leaching temperature (°C)	4	50, 60, 70, 80
Leaching time (min)	4	20, 30, 40, 50
Replications: 3 Number of experiments: $5*4^2*3 = 240$ **Additional 80 experiments** for Model Validation, Total number of experiments conducted = 320		

3.3 Experimental Procedure

This section provides a detailed description of all experiments conducted during this study.

3.3.1 Tailings sample preparation

The tailings samples collected were moist, and were therefore placed in an oven at 110°C for 4 hours, to dry. After drying, a hand-held pestle was used to break the large agglomerates in the samples. A large polythene bag was laid on a clean floor, and the dried samples were then put on it and blended using a shovel. After blending, the samples were subjected to sieving using laboratory sieves on a sieve shaker in order to determine the particle size distribution of the samples and to obtain the particle size (-75μm) required for the leaching experiments.

For sieving experiments, sieves were arranged in order from largest (425μm) to smallest (75μm) with a collecting pan placed below the 75μm sieve and a cover placed on the 425μm sieve, and placed on a laboratory sieve shaker. A known mass of sample was placed into the first (425µm) sieve, and the sieve shaker was run for 10 minutes, in order to allow all particles a chance to be presented onto the sieves surfaces. When sieving was complete, oversized particles collected on each of the sieves, as well as the -75µm particles collected in the pan were weighed. The oversized particles were collected in one bag, and the -75µm samples were also put together in another bag and sealed.

All +75µm particles were ground using a ball mill at the Global Materials Testing Services (GMTS), in Ondangwa. When grinding was completed, the samples were put together on a large polythene bag laid on the floor, and mixed well using a shovel, followed by sieving in order to collect the -75µm particles. Grinding and sieving were repeated until there was a sufficient mass of the -75µm particles.

The -75µm particles were further blended using a jones riffle splitter, to ensure homogeneity of the main sample. Thorough mixing of the samples was done by pouring the material into a riffle splitter, then hand mixing the samples in the 2 receiving chambers, followed by pouring the material into one bucket, then back into the splitter, repeating the exercise 5 times to ensure samples uniformity. The sample obtained after thorough blending of the -75µm particles was ready for use in leaching experiments, and was placed in a bucket with a lid. A flowsheet of the sample preparation procedure is given in Appendix A.

3.3.2 Sample characterisation

Two samples were randomly obtained from the sample storage bucket and characterised using the X-Ray Fluorescence (XRF) spectrometer in order to determine the elemental composition of the as-received tailings material. In addition, the as-received tailings material was characterised using Scanning Electron Microscopy (SEM), to determine its surface morphology. Furthermore, X-Ray Diffraction characterisation (XRD) was done to determine the mineralogical composition of the as-received sample.

3.3.3 Reagent preparation

Sulphuric acid (H_2SO_4) of 0.5M concentration was used for all leaching experiments. Analytical Reagents (AR) grade Sulphuric acid was used to prepare the leaching solution, and had an acid strength of 97%, and a density (ρ) of 1.84kg/L. The 0.5M acid was prepared as shown in Appendix B.

The acid used for leaching was prepared by measuring 500ml of distilled water into a 1 litre volumetric flask, then adding 27.5ml of acid using a measuring cylinder. This was followed by rinsing the cylinder 3 times with distilled water, and adding that to the volumetric flask. Finally, distilled water was added to the volumetric flask to top up the solution up to the 1 L mark. Fresh leaching solution was used for each leaching experiment.

3.3.4 Leaching experiments

Leaching experiments were conducted in a leaching bath outside the microwave oven. Some experiments were conducted without exposure to microwave radiation, while other experiments were exposed to microwave radiation prior to leaching in the leaching bath. This was done in order to establish the response of the Otjihase tailings to leaching under different conditions. Results obtained from these experiments would determine the effect of irradiation intensity, leaching time and leaching temperature on copper recovery, as well as determine the how the Otjihase tailings would respond to leaching under conditions similar to those that yielded promising results in literature.

3.3.4.1 Control experiments

Control experiments were conducted with no microwave irradiation involved. However, all leaching experiments were conducted using 20g of dry tailings material of particle size -75µm and 100ml of 0.5M H_2SO_4. This makes up a solid to liquid ratio (weight to volume) of 1:5. Water was poured into the leaching bath, and its temperature was set to the desired temperature. After the desired temperature was attained, 100ml of the 0.5M H_2SO_4 leaching solution was added to a conical flask, which was placed in the leaching bath until the acid temperature reached the water bath temperature. When the acid in the conical flask reached the desired temperature, 20g of the tailings material were added to the same flask. The flask was then covered with a plastic stopper and placed back in the leaching bath at the desired temperature, and for the desired leaching time. When the desired time had elapsed, the slurry was poured onto a funnel with filter paper, for filtration. The filtrate was collected and put into clean sample bottles, whereas the residue was air dried in an incubator (laboratory fume hood). The dry samples were then placed into sample storage bags, and later sent for analysis for Cu content. Leaching temperature and leaching times were then varied accordingly, until all control experiments were done.

3.3.4.2 Microwave-assisted leaching experiments

Leaching experiments that required the use of microwave pre-treated tailings samples were conducted when control leaching experiments were completed. The microwave treatment of the samples was carried out by weighing 20g of the tailings sample into a ceramic crucible and placing it in a domestic microwave oven. The microwave power was varied as described in Table 3.1, while microwave treatment time was kept constant at 6 minutes. For each microwave intensity (100, 300, 500, 700W), when the microwave pre-treatment was complete, the sample was poured into a conical flask containing 100 ml of leaching solution (which had been placed in the leaching bath to attain the desired leaching temperature). The flask was then placed into the leaching bath at the desired temperature, and leaching was carried out at varying times as described in Table 3-1. All experiments were conducted in triplicate.

When a specific leaching time was attained, the slurry was filtered. The filtrate was put into clean sample bottles, while the residue was allowed to air dry in a laboratory fume hood. The dry residue was then put into sealable sample bags, and sent to an external laboratory for elemental Cu analysis. Analysis of solution samples was done by using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique. Solid samples were digested using the Mixed Acid Digestion technique, and subsequently analysed using ICP-OES. Selected leach residue samples were then characterised in terms of phases present using XRD and morphology using SEM. The procedure followed for leaching of microwave pre-treated samples is shown as a flowsheet in Appendix C.

3.3.4.3 Model validation experiments

For each of the leaching conditions shown in Table 3-1, one additional experiment was conducted, after completion of the control experiments as well as microwave-assisted leaching experiments (main experiments). The results obtained from these leaching experiments would be used to validate the model developed using results obtained from the main leaching experiments.

3.4 Data analysis

3.4.1 Analysis of Variance (ANOVA)

Analysis of variance (ANOVA) was used to test the difference between average copper recoveries for the various factors studied.

3.4.2 Leaching kinetics analysis

Shrinking core models were used to determine the dissolution reaction mechanism, as well as to determine the other kinetic parameters of chalcopyrite dissolution in H_2SO_4.

3.4.3 Multiple regression analysis

Empirical models developed on basis of multiple regression analysis were used to determine the relationship between the independent factors studied (microwave irradiation intensity, leaching time and leaching temperature) and the dependent variable (copper recovery) from the tailings. A mathematical model was also developed to predict the recovery of copper from the tailings at specific leaching conditions.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

This chapter presents results obtained from characterisation of the as-received mine's tailings, particle size analysis, microwave-assisted leaching of these tailings as well as elemental and mineralogical analysis of the filtrate and residues from leaching experiments. It also provides a detailed discussion of all the results obtained in this work, with regards to microwave-assisted leaching of mine tailings. Finally, it generates a mathematical model that gives a relationship between percentage copper recovery and leaching time, leaching temperature as well as microwave irradiation intensity.

4.1 Results

4.1.1 Particle size analysis

Particle size analysis is conducted to determine the particle size distribution of a sample, as well as to obtain the specific particle size range required to conduct experiments. For this study, the required particle size for leaching experiments was -75 μm. Particle size analysis was conducted using sieves of aperture sizes 425, 180, 106 and 75 μm. The data displayed in Appendix D was used to generate a plot of cumulative percent passing vs aperture size. The generated plot is shown in Figure 4-1, and reveals that the tailings material has a P_{50} of 270 μm, and a P_{70} of 380 μm. This shows that the material is quite fine-grained, which is attributed to prior mineral processing steps of crushing, but more specifically grinding which were used in the concentrating plant's froth flotation circuit, to precede the froth flotation process.

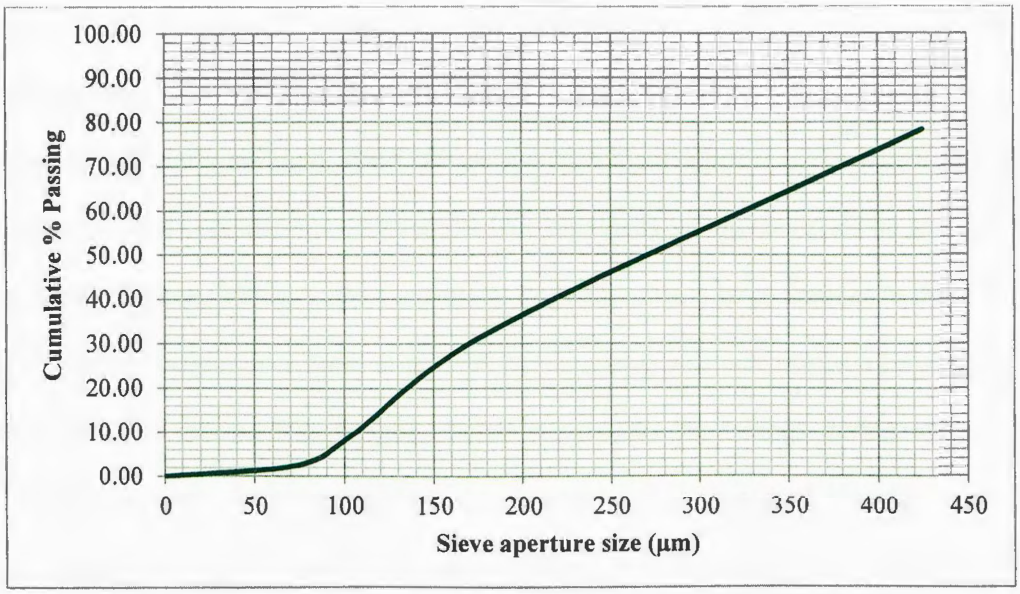


***Figure 4-1**: Plot of cumulative % passing vs sieve aperture size*

4.1.2 Characterisation of the as-received tailings sample

4.1.2.1 Elemental analysis of the raw tailings sample

The elemental composition of the as-received tailings was determined using an XRF analyser (Niton XL3t), and the results are presented in Table 4-1.

***Table 4-1:** Elemental composition of the as-received tailings sample*

Element	Ca (%)	Si (%)	Al (%)	P (%)	Mg (%)	Fe (%)	K (%)	S (%)	Ba (%)	Cu (%)	Mn (ppm)	Zn (ppm)	Ni (ppm)	Zr (ppm)	As (ppm)
Average composition	1.58	21.38	4.29	0.14	2.84	15.74	1.67	17.61	0.3	0.123	1000.25	78.73	86.44	303.35	12.66

The elemental composition results of the as-received tailings sample shown in Table 4-1 reveal the presence of various metallic and non-metallic constituents in the tailings material. The elements found to be in the highest concentration in the tailings sample were silicon (Si), Sulfur (S) and Iron (Fe) with average concentrations of 21.38%, 17.61% and 15.74% respectively. This can be attributed to the fact that Silica forms a large constituent of the ore (and subsequently tailings). The Otjihase and Matchless deposits (from which ores processed at the Otjihase copper concentration plant are obtained) are characterised by massive sulphide deposits (Killick, 2000), hence the presence of sulphur in a large amount in the tailings. This sulphur was originally present in the ore. Pyrite (FeS_2) also constituted a large portion of the ore, and was removed as gangue, which reported to the tailings during the copper froth flotation process. Previous research by Leonard (2013) reported that the Otjihase mine tailings had a copper concentration of 0.18%, and samples used for this study were found to have an average copper concentration of 0.123%.

4.1.2.2 XRD and SEM and EDS analysis of the as-received tailings sample

The SEM micrograph shown in Figure 4-2 is that of the raw (unleached) tailings. The surface morphology of the raw tailings material exhibits small crystalline grains which are porous in nature. Figure 4-3 shows the XRD pattern of the as-received tailings sample. XRD results showed that the tailings material is made up of various minerals such as priderite ($Na_{1.72}Cr_{1.71}Ti_{6.29}O_{16}$), covellite ($CuS$), magnesioferrite ($MgFe_2O_4$), zeolite ($Si_{192}O_{384}$), chalcopyrite ($CuFeS_2$), braunite ($Mn_7SiO_{12}$), pyrite ($FeS_2$) and silica ($SiO_2$). These minerals are all well represented in the main peaks. It is noteworthy to indicate that in this tailings material, copper is contained in sulphide minerals only, covellite (CuS) and chalcopyrite ($CuFeS_2$). The high pyrite content (as is visible on the Fe composition of the sample) confirms that these are tailings of a froth flotation process, which aimed to remove pyrite as gangue from the ore. Figure 4-4 shows the Backscattered Electron image (BSE) with EDS of the as-received sample, which revealed that the raw tailings material was porous, with Fe present in a high composition, as was reported by elemental analysis of the as-received tailings sample. Copper was not detected in the region shown by Figure 4-4, and this can be attributed to the very low percentage composition of copper in the as-received tailings material.

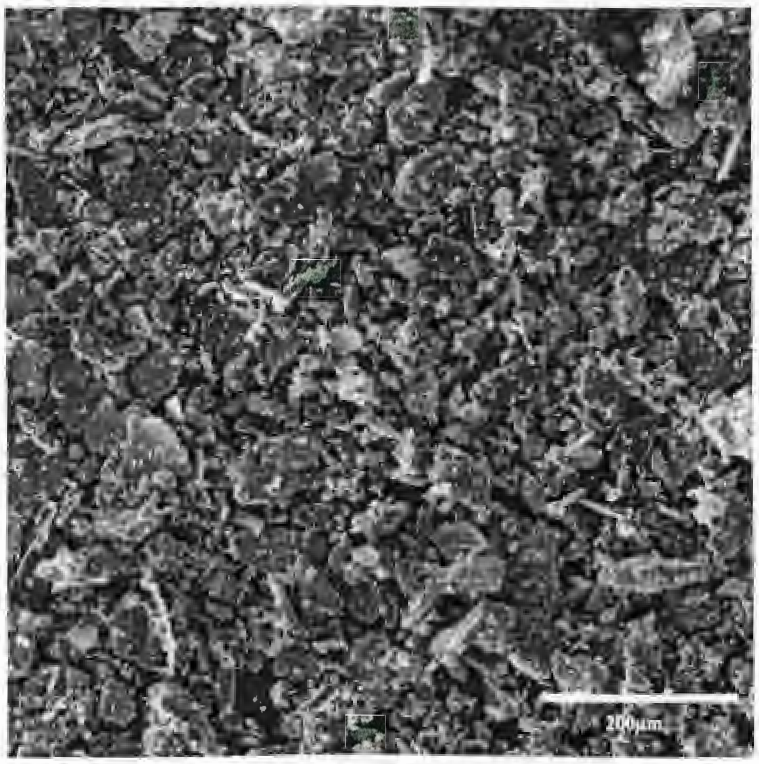
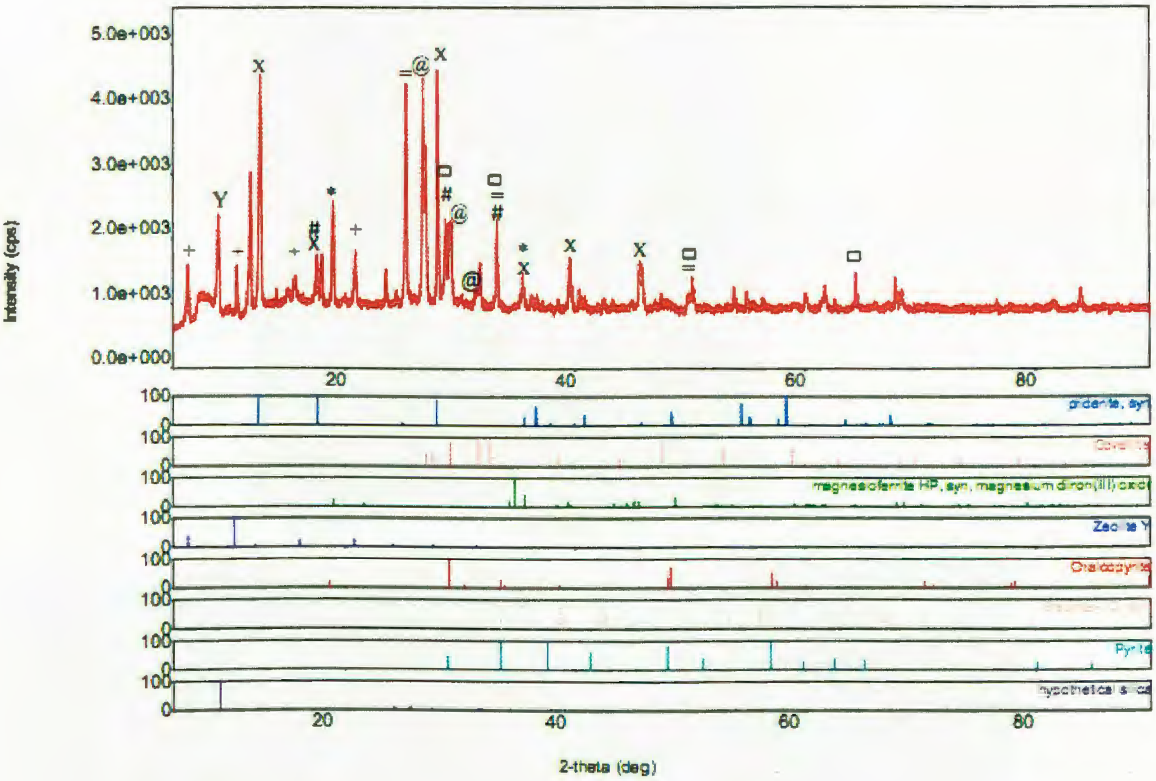


Figure 4-2: *SEM micrograph of raw tailings sample*



Key:

X – Priderite ($Na_{1.72}Cr_{1.71}Ti_{6.29}O_{16}$

@ - Covellite (CuS)

* - Magnesioferrite ($MgFe_2O_4$)

\+ - Zeolite ($Si_{192}O_{384}$)

\# - Chalcopyrite ($CuFeS_2$)

= - Braunite (Mn_7SiO_{12})

□ - Pyrite (FeS_2)

Y – Silica (SiO_2)

Figure 4-3: *Mineralogical analysis of the as-received tailings sample*

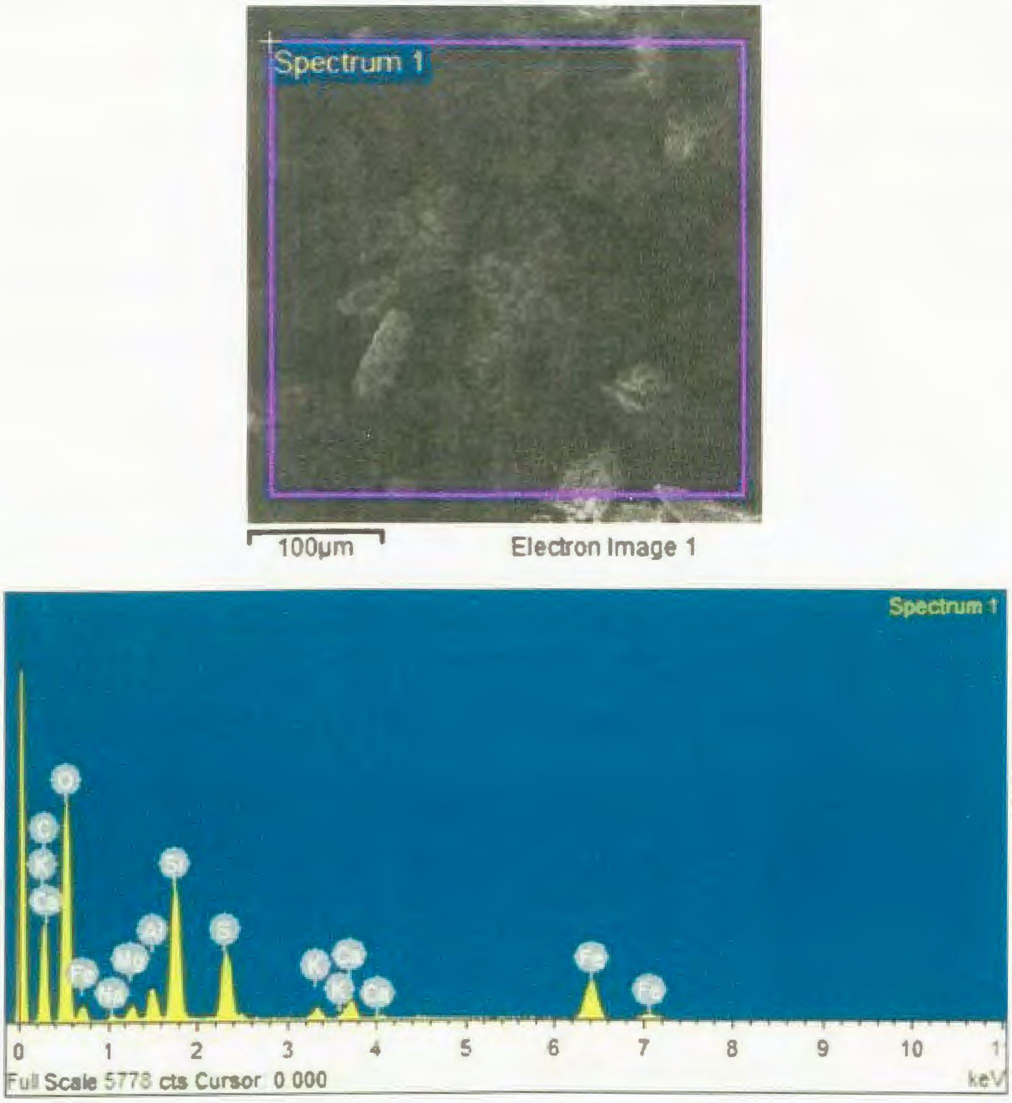


Figure 4-4: Backscattered electron image (up) with EDS (down) of the raw tailings sample

4.2 Discussion

This section discusses results obtained from leaching tests conducted. Leaching was conducted at varying temperatures of 50, 60, 70 and 80°C. The leaching time was varied at 20, 30, 40 and 50 minutes, while the microwave irradiation intensity was varied at 0, 100, 300, 500 and 700 W. The data presented in Appendix E shows the conditions used for leaching experiments as well as the copper grade obtained at each set of conditions. This data was used to determine the effect of leaching time, leaching temperature and microwave intensity on copper recovery. Additionally, kinetic studies on chalcopyrite leaching using dilute sulphuric acid will be discussed in detail in this section. Finally, a mathematical model was developed, to provide the relationship between leaching time, leaching temperature, microwave intensity and copper recovery.

4.2.1 Effect of leaching time and leaching temperature on copper recovery

The range of time used for leaching experiments was 20 minutes to 50 minutes, with 10 minutes intervals; while the leaching temperatures studied were 50 to 80°C, with 10°C temperature intervals. Figures 4-5 to 4-8 illustrate results obtained from experiments conducted at various times and temperatures. The results obtained show that there was no large change in Cu recovery with the time range used in this study. However generally, increasing leaching time resulted in higher copper recovery. The longest leaching time of 50 minutes yielded the highest copper recovery of 36.13% at 700W microwave intensity. The slight change in percentage copper recovery observed over the time range used in this study could be attributed to the time interval used for leaching experiments. Although the study aimed to utilise reduced time and investigate how this affects the efficiency of copper dissolution from the tailings, the time and time intervals used proved to not be sufficient enough to yield a notable difference in copper recovery. Leaching time range may therefore need to be widened, in order to investigate the possibility of obtaining a significant effect of leaching time on Cu recovery of the Otjihase tailings. Another possibility is the slow kinetics of chalcopyrite dissolution in sulphuric acid as reported by Li, et al., (2013), due to chalcopyrite passivation. The microwave pre-treatment step was conducted with an aim to counteract passivation and its effects; however, the results obtained suggest slow leaching kinetics, which could also be due to the extremely low-grade of copper in the tailings material.

From the same set of Figures 4-5 to 4-8, the effect of leaching temperature on copper recovery can be observed. It can be seen across all leaching times that the highest temperature of 80°C is associated with a copper recovery higher than all other temperatures studied. The high temperature-high recovery phenomenon is in agreement with literature which suggests that increasing reaction temperature helps increase reaction kinetics, thereby resulting in increased metal recovery, as reported by Wen, et al., (2017). Although the overall difference in copper recovery at various temperatures was slight, it can be seen clearly that increasing temperature increases the efficiency of copper dissolution from the Otjihase tailings. The highest copper recovery of 36.13% was obtained at 700W and 80°C, for leaching conducted for 50 minutes. The results obtained on leaching time temperature suggest a possibility for higher copper recoveries if the leaching time and temperature are increased.

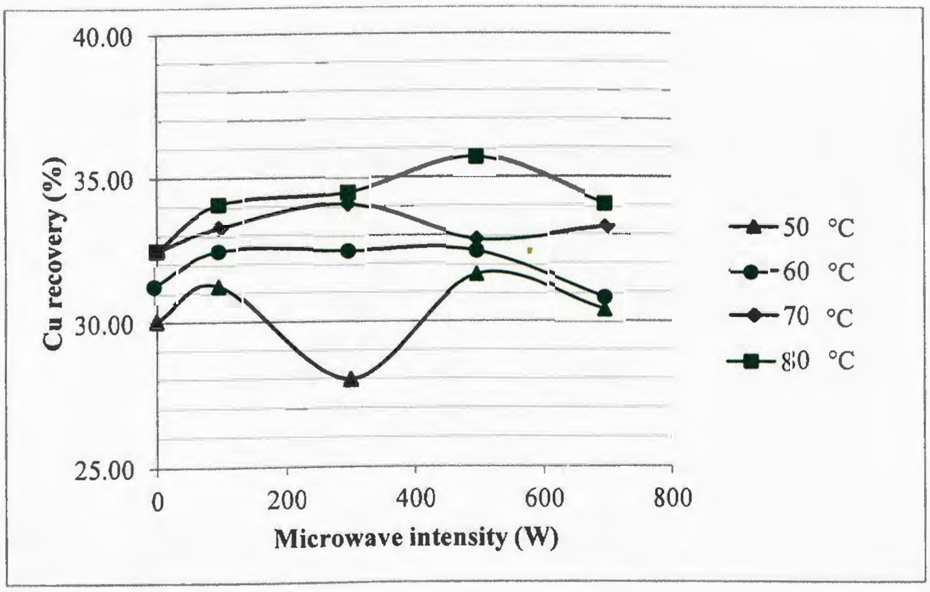


Figure 4-5: Effect of microwave intensity on efficiency of copper dissolution at 20 minutes leaching time

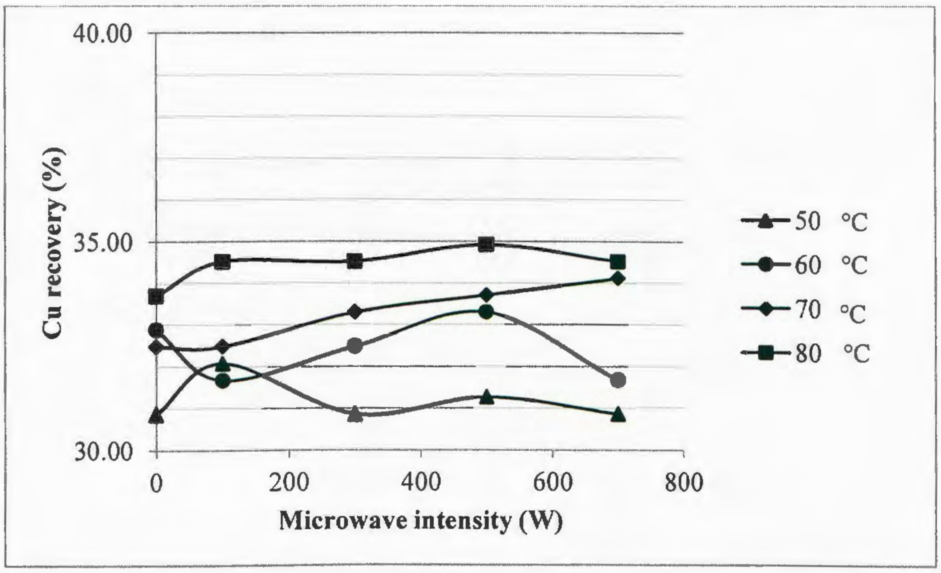


Figure 4-6: *Effect of microwave intensity on efficiency of copper dissolution for 30 minutes leaching time*

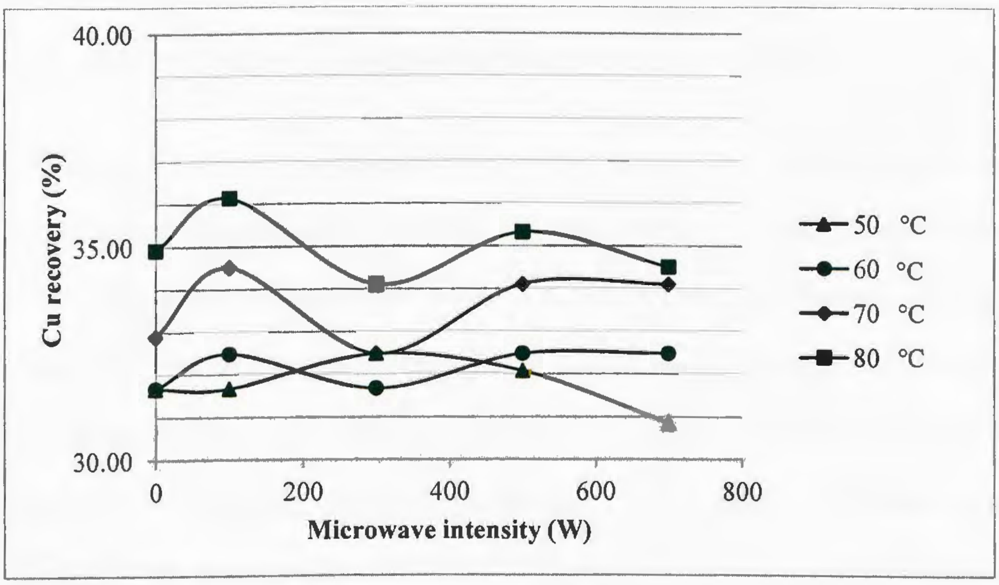


Figure 4-7: *Effect of microwave intensity on efficiency of copper dissolution for 40 minutes leaching time*

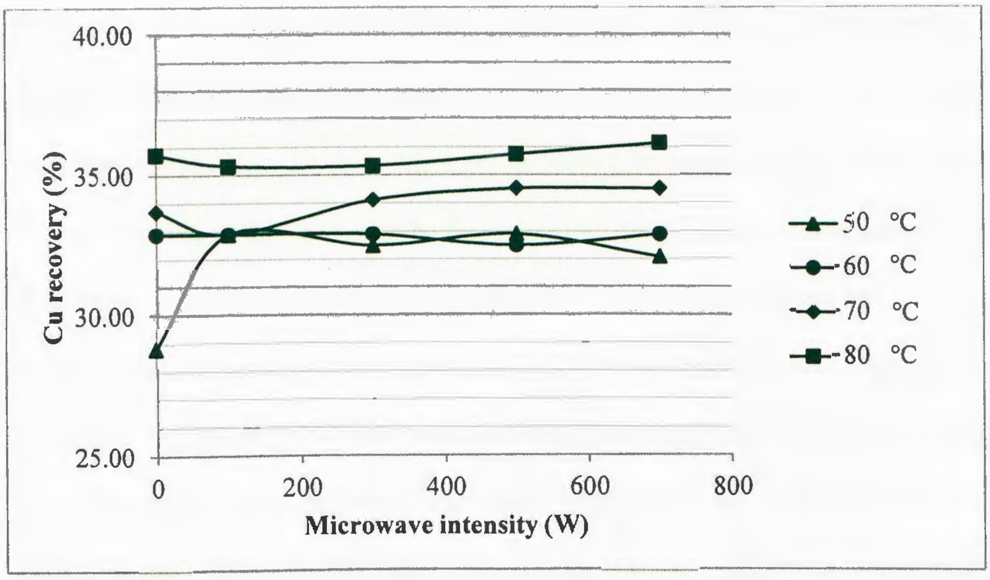


Figure 4-8: *Effect of microwave intensity on efficiency of copper dissolution for 50 minutes leaching time*

4.2.2 Effect of microwave irradiation intensity on copper recovery

In this study, microwave-assisted leaching was conducted by heating a known mass of dry tailings inside a domestic microwave oven at varying microwave intensities and a fixed time of 6 minutes. The preheating time used is the same as that used by Zhai, et al., (2009), in which they were able to achieve up to 92.76% recovery for leaching of a Nickel laterite ore leached for 90 minutes. In this study, microwave power was varied at 0, 100, 300, 500 and 700 Watts, whereby dry tailings samples (and not the leach slurry) were subjected to microwave pre-treatment. Results shown in Figures 4-9 to 4-13 reveal that microwave pre-treatment had no significant impact on the efficiency of copper dissolution from the mine tailings. This opposes results obtained by some researchers (Schmuhl, et al., 2011; Wen, et al., 2017) who reported increased metal recoveries on account of microwave-assisted leaching. In addition, Onol & Saridede, (2012) for instance, reported an increase in copper recovery from 29.4% to 33.54% for conventional and microwave leaching, respectively, conducted for a period of 180 minutes. However, the copper recovery obtained by Onol & Saridede, (2012) is lower than this study achieved, in less leaching time of 50 minutes. The results obtained in this study can be due to various factors: The microwave irradiation time of 6 minutes, although worked for some ores (Nickel laterite ores), may not be sufficient for Cu tailings pre-treatment, hence the lack of a significant increase in copper recovery between conventional leaching and microwave-assisted leaching. Additionally, the tailings material was ground to -75µm, the results obtained therefore support a finding by Schmuhl, et al., (2011) which suggested that larger particle size fractions respond better to microwave pre-treatment than fine particle size fractions, due to the high volume percentage of microwave absorbing phases in larger sized particles.

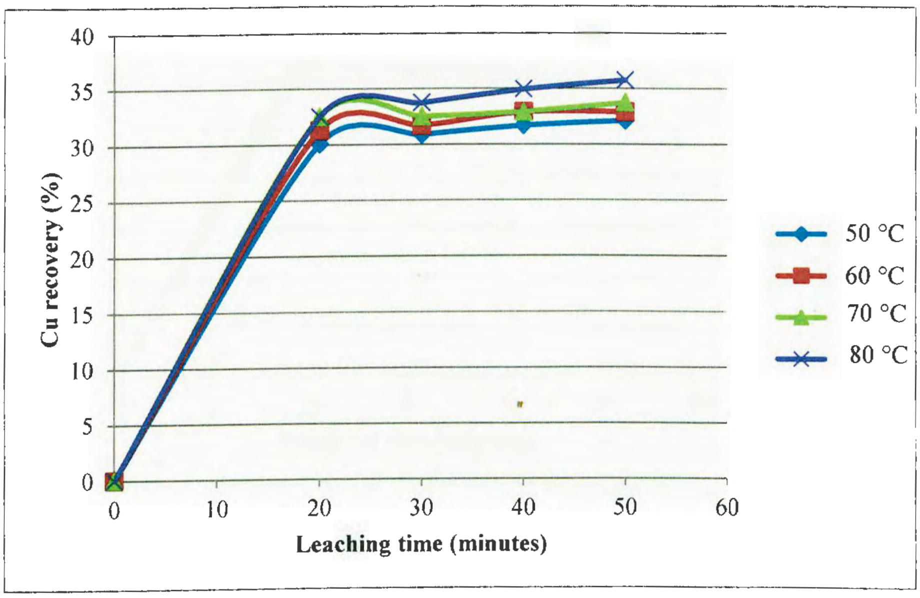


Figure 4-9: *Effect of leaching time on efficiency of copper dissolution at 0W microwave intensity*

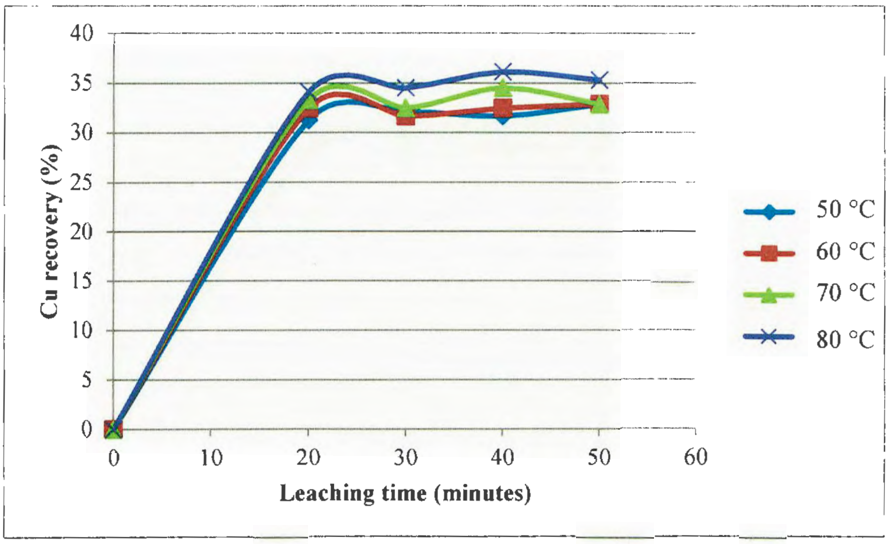


Figure 4-10: *Effect of leaching time on efficiency of copper dissolution at 100W microwave intensity*

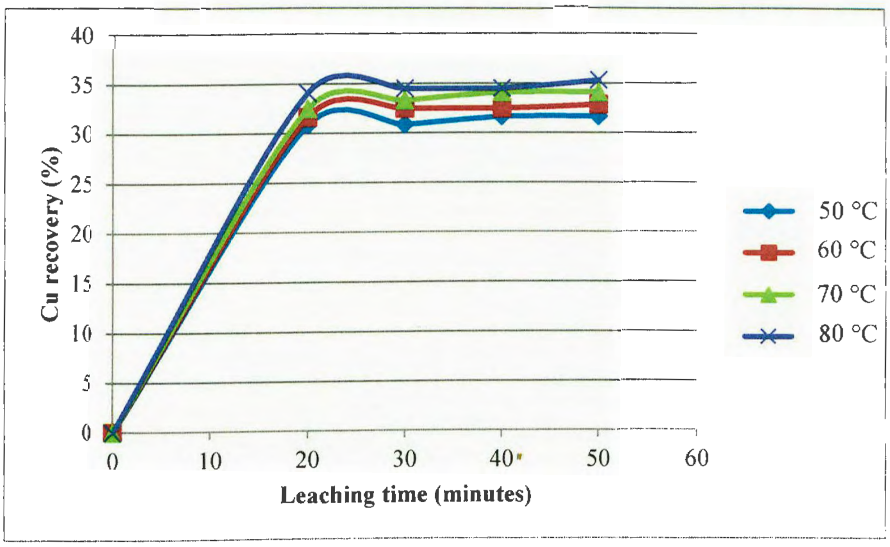


Figure 4-11: *Effect of leaching time on efficiency of copper dissolution at 300W microwave intensity*

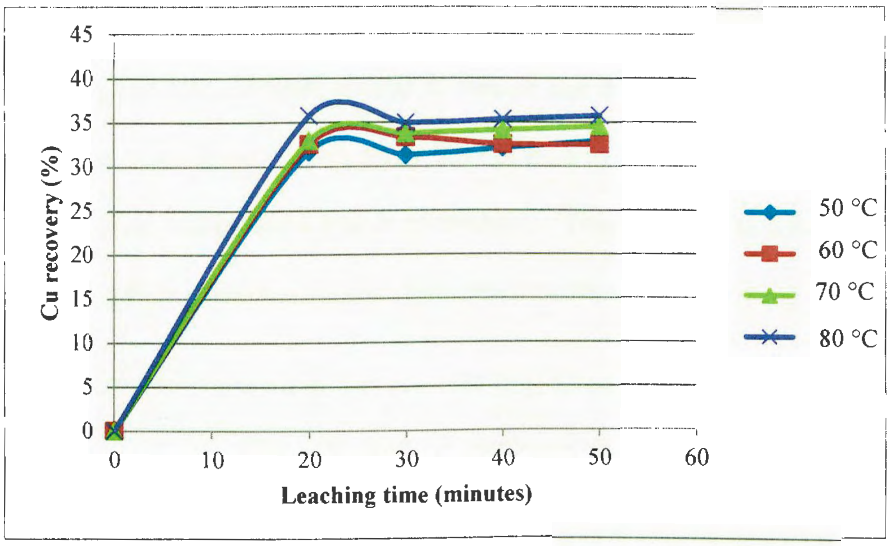


Figure 4-12: *Effect of leaching time on efficiency of copper dissolution at 500W microwave intensity*

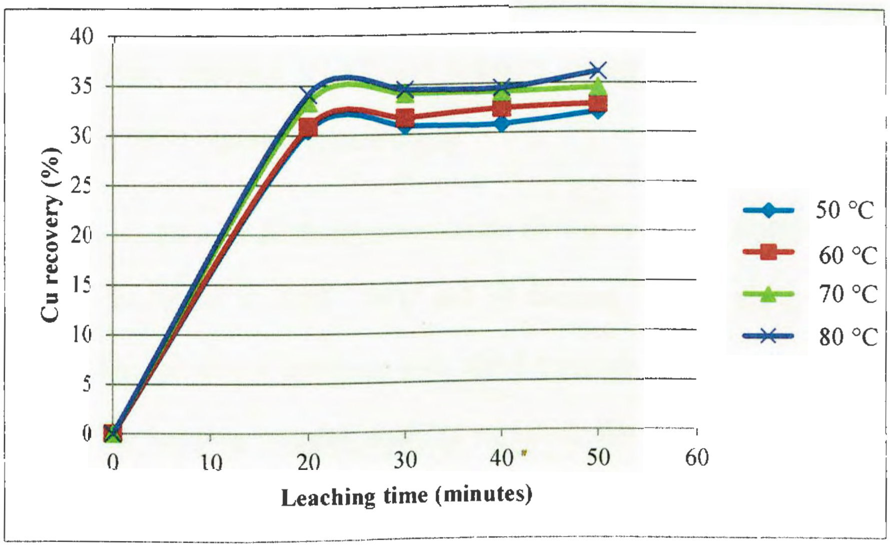


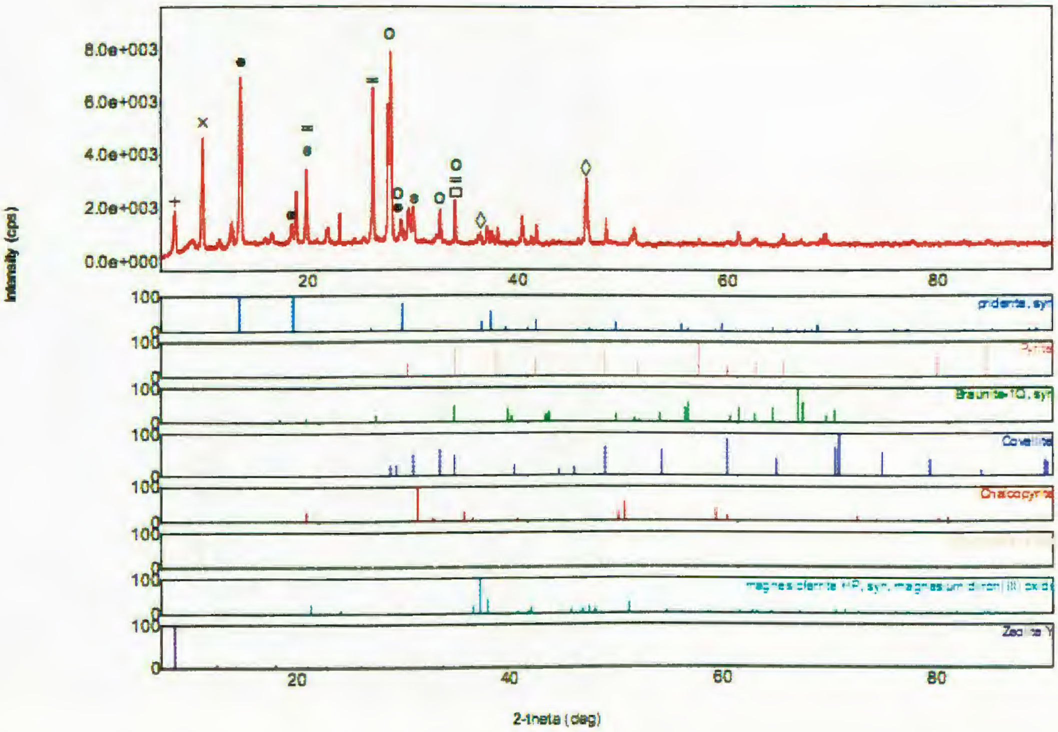
Figure 4-13: *Effect of leaching time on efficiency of copper dissolution at 700W microwave intensity*

4.2.3 XRD, SEM and EDS characterisation of leach residue

XRD analysis of the leach residue revealed mineralogical composition very similar to the raw tailings sample, which shows that no new compounds were formed as residues in the leaching process. Figure 4-14 shows an XRD plot of the residue obtained after leaching at 700W, 70°C and 50 minutes leaching time. Plots obtained for other leaching conditions revealed mineralogical compositions similar to this. It can therefore be assumed that leaching under conditions investigated in this study did not lead to formation of new mineral phases, as the mineralogical composition remained unaltered. This also agrees with leaching recovery data obtained, which exhibited similar characteristics for various leaching conditions studied.

SEM micrographs shown in Figures 4-15 to 4-17 also reveal similar morphologies, although they represent residues obtained at different leaching conditions. The leach residue morphologies reveal crystalline grains which are generally evenly distributed within the tailings material. Additionally, the grains appear more porous when compared to the raw sample micrograph shown in Figure 4-2, a characteristic which could be attributed to acid attack during the leaching process. The observation made on similar surface morphologies for leach residues obtained at different leaching conditions is similar to what Olubambi & Potgieter, (2009) reported in their study.

The BSE image with EDS characterisation shown in Figure 4-18 is for a leach residue for leaching conducted at 300W, 70°C and 30 minutes. It is similar to that of the as-received tailings material shown in Figure 4-4, which suggests that no new phases were formed as a result of the leaching process. Also, as expected, elemental copper was not detected by the EDS analysis, which is attributed to the very low copper composition of the leach residue.



Key:

● - Priderite ($Na_{1.72}Cr_{1.71}Ti_{6.29}O_{16}$)

o - Covellite (CuS)

◊- Magnesioferrite ($MgFe_2O_4$)

+ - Zeolite ($Si_{192}O_{384}$)

• - Chalcopyrite ($CuFeS_2$)

= - Braunite (Mn_7SiO_{12}) ,

□ -Pyrite (FeS_2)

× - Silica (SiO_2)

Figure 4-14: *XRD plot of residue for leaching conducted at 700W, 70°C and 50 minutes*

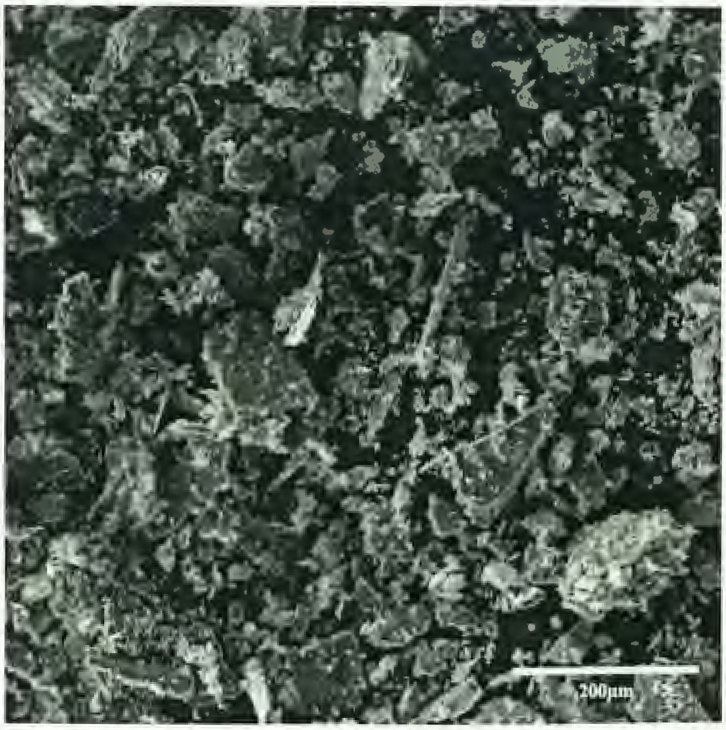


Figure 4-15: *SEM micrograph of residue for leaching conducted at 300W, 70°C and 30 minutes*

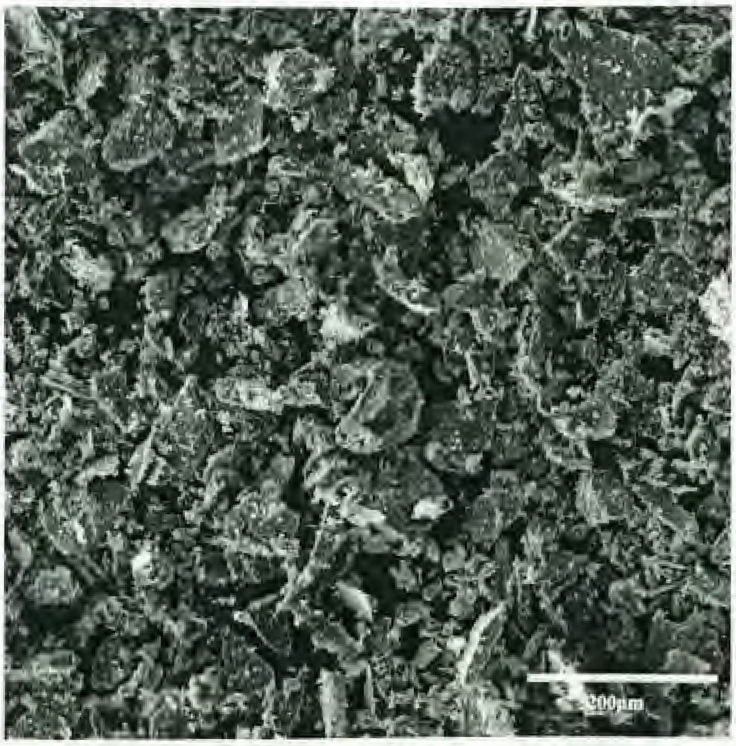


Figure 4-16: *SEM micrograph of residue for leaching conducted at 0W, 60°C and 20 minutes*

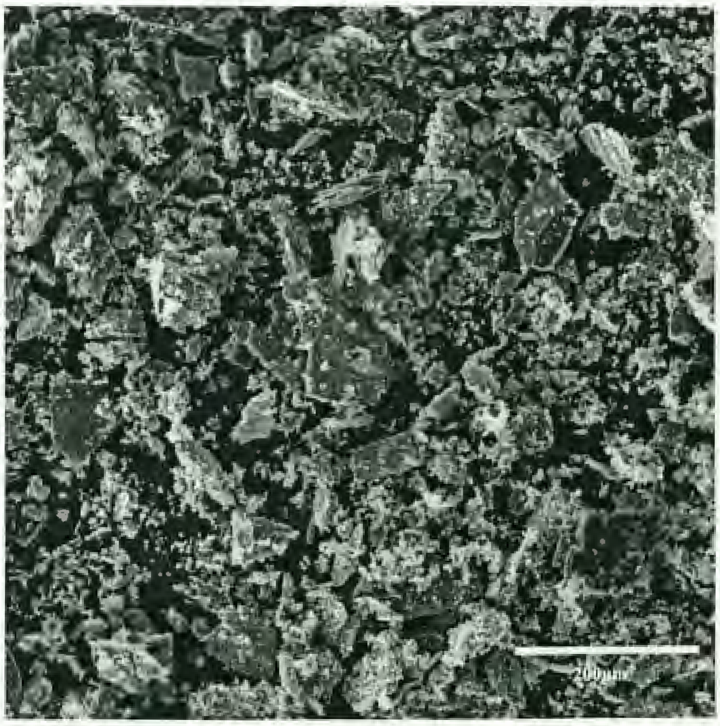


Figure 4-17: *SEM micrograph of residue for leaching conducted at 700W, 70°C and 50 minutes*

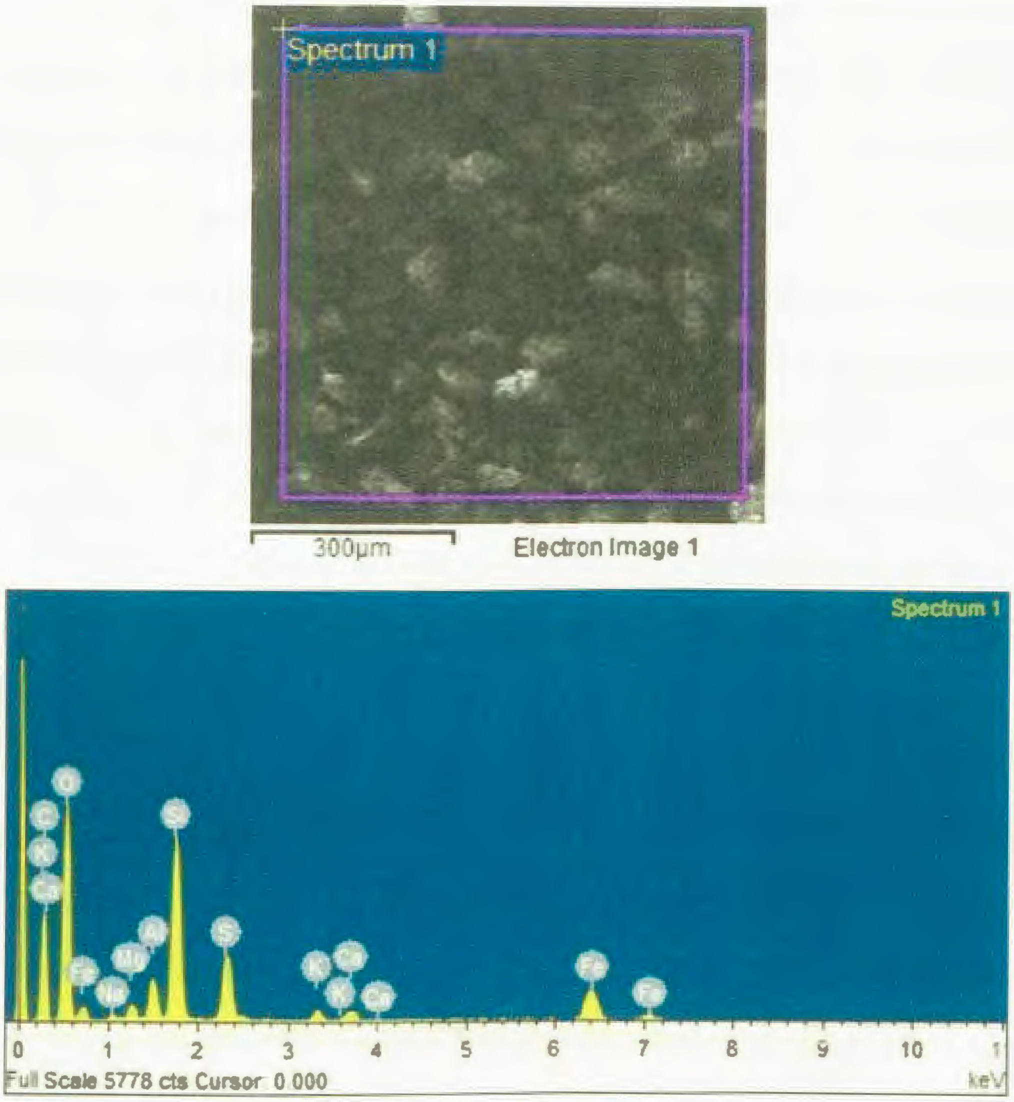


Figure 4-18: Backscattered Electron image (up) with EDS (down) of the leach residue

4.2.4 Kinetic analysis

4.2.4.1 Reaction mechanism determination

The plots of copper dissolved at various leaching times and temperatures were linearised using the three shrinking core models which are described in section 2.6. A summary of the apparent rate constants as well as coefficients of determination is given in Table 4-2. Careful analysis of the apparent rate constants, which are obtained from the slopes of the linearised curves as reported by Onyedika, et al., (2013) and Antonijevic, et al., (2004); and coefficients of determination (R^2) which can be used to identify reaction mechanism (Cadenato, et al., 2007) revealed that the slowest step in leaching was the Ash layer diffusion, which is governed by the equation $k_d t = 1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$ (Equation 5). Results displayed in Figures 4-19 to 4-23 show plots on copper recovery vs leaching time linearised using the ash layer diffusion shrinking core model. Ash layer diffusion was associated with the lowest rate constants; and additionally, the coefficients of determination reveal that the copper dissolution data best fit the ash layer diffusion equation more, when compared to other reaction mechanisms. The slow diffusion through the ash layer could be attributed to the formation of a passivating sulphur layer on the chalcopyrite surface (Sokic, et al., 2009), which then acts as a diffusion barrier for the reactants, through the reaction products on the particle (Antonijevic, et al., 1994), and hence prevents further leaching from taking place. Furthermore, slow dissolution rate may also be as a result of low concentration of reactants (0.123% Cu in the tailings material) and 0.5M H_2SO_4 used for the leaching experiments, which is in agreement with an observation made by Shamsuddin (2016) on how low reactant concentration is associated with ash layer diffusion mechanism.

Table 4-2: *Kinetic parameters for determining rate-determining step*

		Apparent rate constant (min-1)			Coefficient of determination (R^2)		
	Temp. (K)	k_f	k_d	k_r	**Film diffusion**	**Product layer diffusion**	**Chemical reaction**
0W	323	0.0006	0.00005	0.0003	0.985	0.985	0.985
	333	0.0006	0.00006	0.0003	0.883	0.881	0.882
	343	0.0004	0.00004	0.0002	0.835	0.832	0.834
	353	0.0011	0.0001	0.0005	0.992	0.994	0.992
100W	323	0.005	0.00005	0.0002	0.964	0.964	0.964
	333	0.00004	0.000004	0.00002	0.011	0.012	0.011
	343	0.0004	0.00004	0.0002	0.356	0.344	0.354
	353	0.0005	0.00005	0.0002	0.573	0.563	0.570
300W	323	0.0003	0.00003	0.0006	0.798	0.799	0.850
	333	0.0004	0.00003	0.0002	0.853	0.856	0.853
	343	0.0006	0.00005	0.0002	0.891	0.892	0.891
	353	0.0004	0.00004	0.0002	0.853	0.850	0.852
500W	323	0.0005	0.00005	0.0002	0.966	0.963	0.965
	333	0.0002	0.00002	0.0001	0.600	0.600	0.600
	343	0.0005	0.00005	0.0002	0.966	0.969	0.967
	353	0.0003	0.00003	0.0001	0.891	0.892	0.891
700W	323	0.0005	0.00004	0.0002	0.800	0.796	0.799
	333	0.0007	0.00006	0.0003	0.980	0.982	0.980
	343	0.0004	0.00004	0.0002	0.853	0.856	0.853
	353	0.0006	0.00006	0.0003	0.763	0.758	0.761

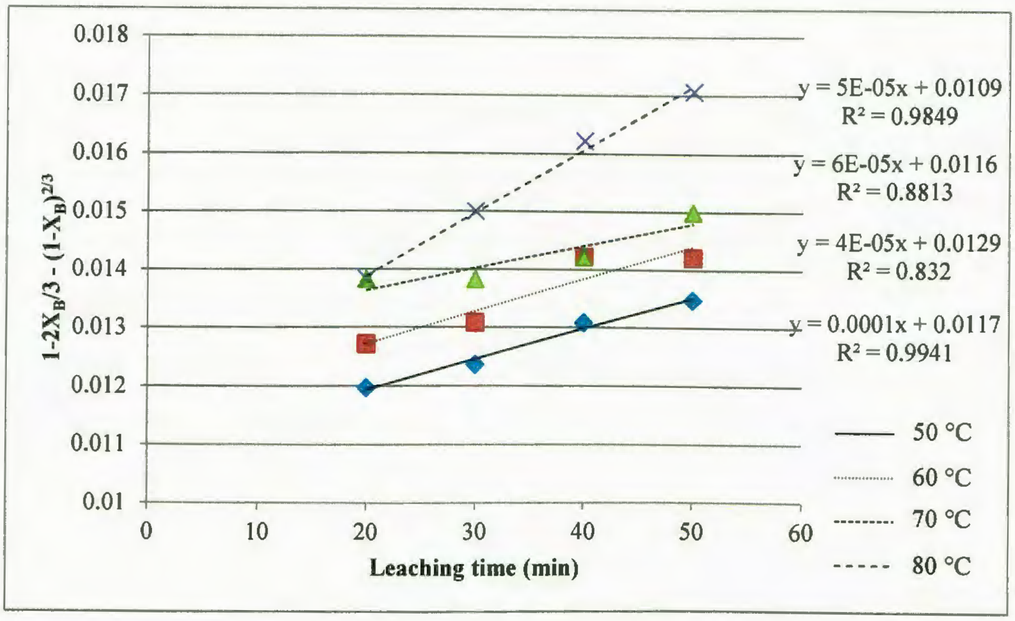


Figure 4-19: *Plot of Equation 5 vs leaching time at 0W microwave intensity*

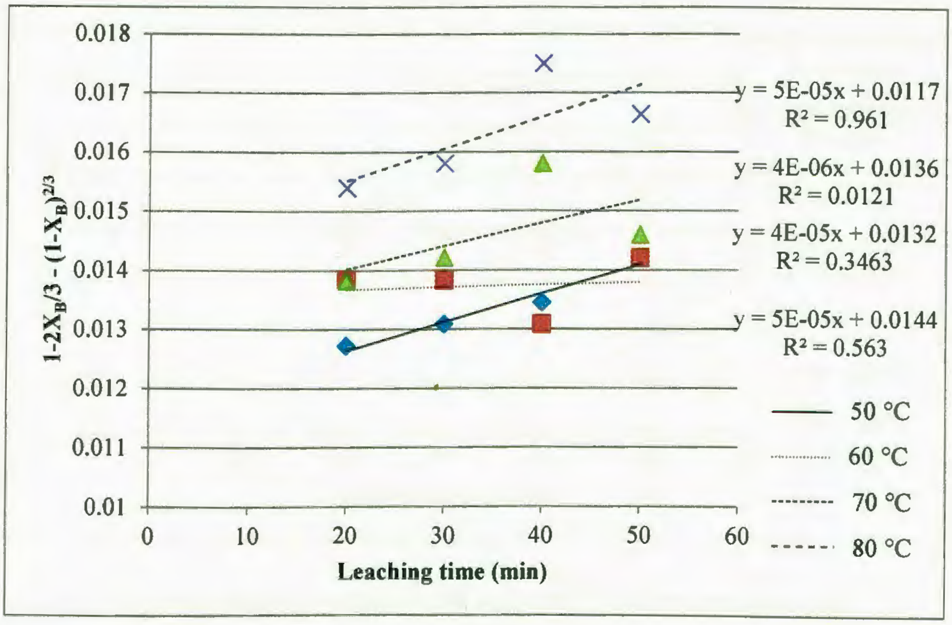


Figure 4-20: *Plot of Equation 5 vs leaching time at 100W microwave intensity*

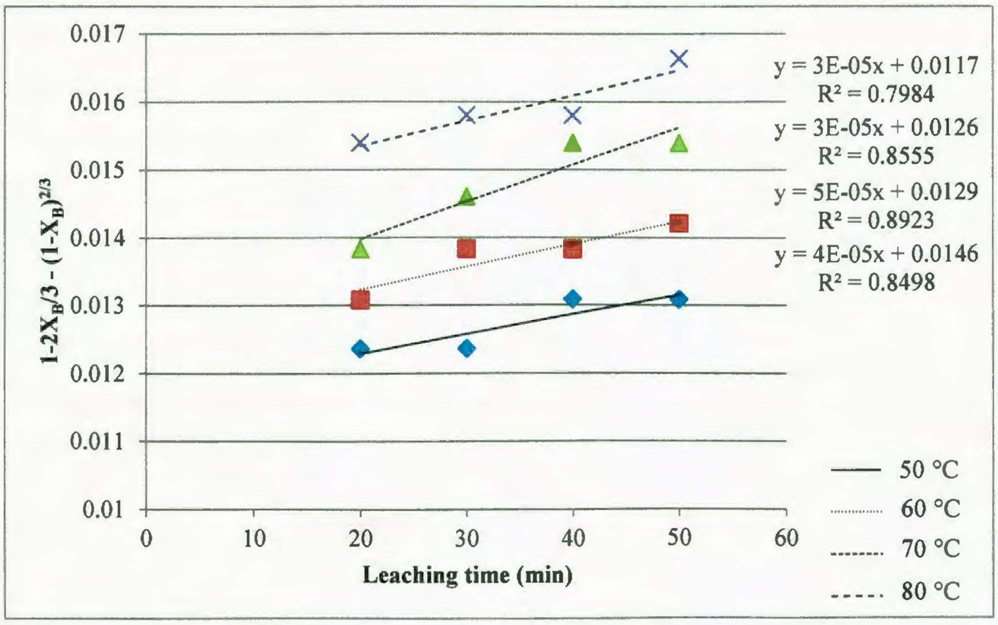


Figure 4-21: *Plot of Equation 5 vs leaching time at 300W microwave intensity*

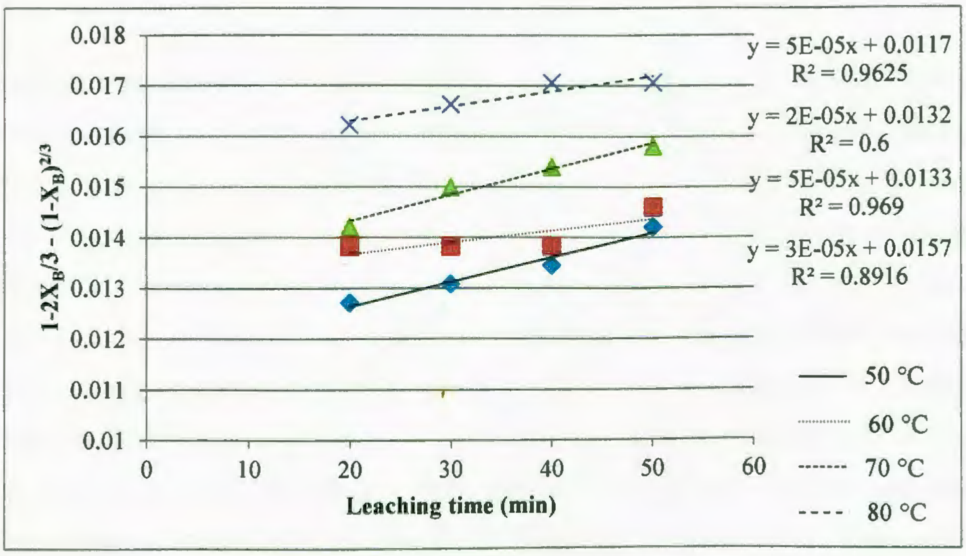


Figure 4-22: *Plot of Equation 5 vs leaching time at 500W microwave intensity*

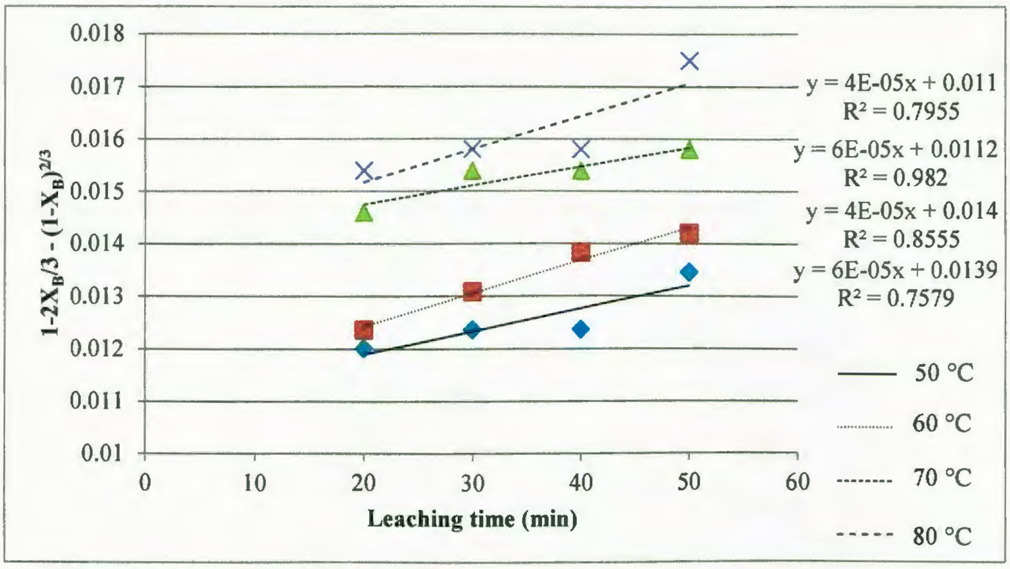


Figure 4-23: *Plot of Equation 5 vs leaching time at 700W microwave intensity*

4.2.4.2 Activation energy determination

Activation energy (Ea) was calculated from the rate constants of the rate-limiting step. The rate constant values were obtained from Figures 4-19 to 4-23. Table 4-3 shows rate constant values (k_d) at respective temperatures for the dissolution of $CuFeS_2$ in H_2SO_4 based on Equation (5). It can be seen that the rate constant is generally similar for all microwave powers studied, which suggests that increasing microwave power did not have a significant effect on the rate of copper dissolution from the tailings material, which was also the observation made in section 4.2.2. The natural logarithm and the inverse of the temperature were used to generate the Arrhenius plots which are shown in Figures 4-24 to 4-28 for various microwave intensities studied. The Arrhenius plots were used to determine the apparent activation energy (Ea) of the copper dissolution reaction. It has been empirically determined that activation energy can be given as the slope of the Arrhenius plot times the universal gas constant, R, that is: *Ea = slope x R* (Onyedika, et al., 2013). From the Arrhenius plots in Figures 4-24 to 4-28, the activation energies were then calculated as 15.46, 20.24, 13.14, 22.69 and 7.7kJ/mol, respectively. This study established that there is no significant effect of microwave intensity on copper recovery, hence the Ea can be assumed to generally be in the range of 7.7-22.69 kJ/mol. This Ea range and the average activation energy value is well within what literature suggests as Ea magnitude for ash or product layer diffusion controlled mechanism (Youcai, et al., 2014; Yuliusman, et al., 2018; Souza, et al., 2007).

Table 4-3: *Rate constant values (k_d) at respective temperatures for the dissolution of $CuFeS_2$ in H_2SO_4 based on Equation 5*

	k_d	$\ln k_d$	T	1/T
0W	0.00005	-9.90349	323	0.003096
	0.00006	-9.72117	333	0.003003
	0.00004	-10.1266	343	0.002915
	0.0001	-9.21034	353	0.002833
100W	0.00005	-9.90349	323	0.003096
	0.000004	-12.4292	333	0.003003
	0.00004	-10.1266	343	0.002915
	0.00005	-9.90349	353	0.002833
300W	0.00003	-10.4143	323	0.003096
	0.00003	-10.4143	333	0.003003
	0.00005	-9.90349	343	0.002915
	0.00004	-10.1266	353	0.002833
500W	0.00005	-9.90349	323	0.003096
	0.0003	-8.11173	333	0.003003
	0.00005	-9.90349	343	0.002915
	0.0002	-8.51719	353	0.002833
700W	0.00004	-10.1266	323	0.003096
	0.00006	-9.72117	333	0.003003
	0.00004	-10.1266	343	0.002915
	0.00006	-9.72117	353	0.002833

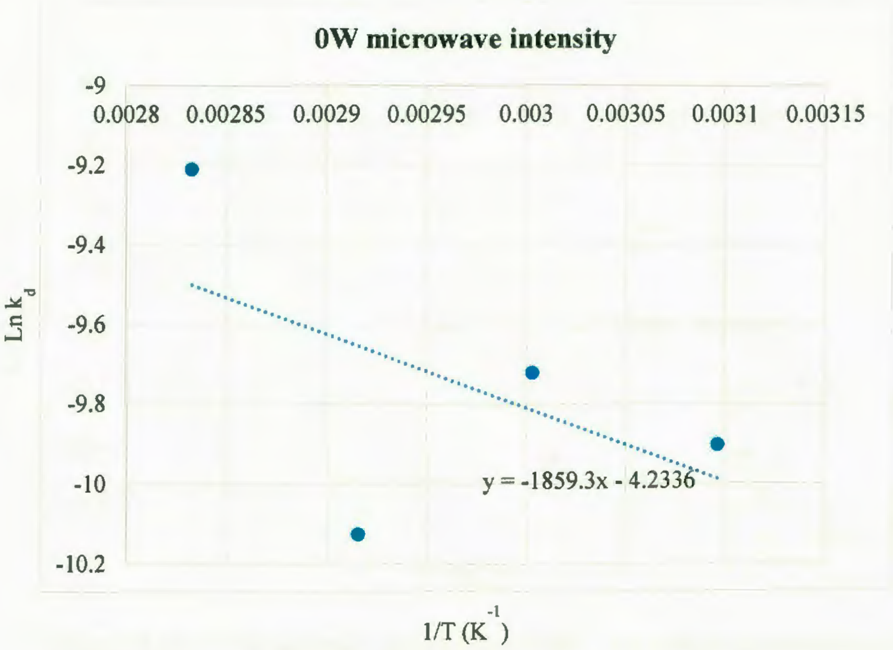


Figure 4-24: *Arrhenius plot of lnkd vs 1/T (K^{-1}) for ash/product layer diffusion mechanism at 0W microwave intensity*

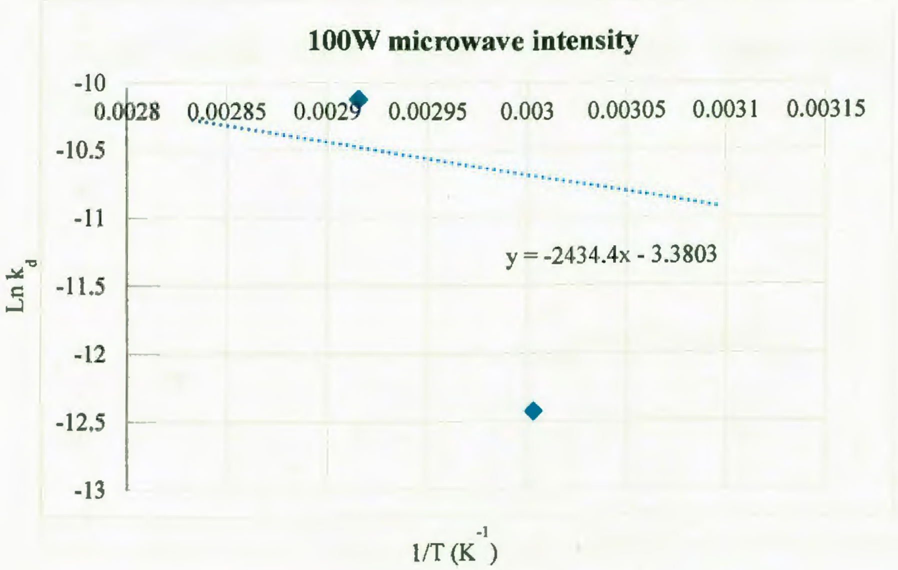


Figure 4-25: *Arrhenius plot of lnkd vs 1/T (K^{-1}) for ash/product layer diffusion mechanism at 100W microwave intensity*

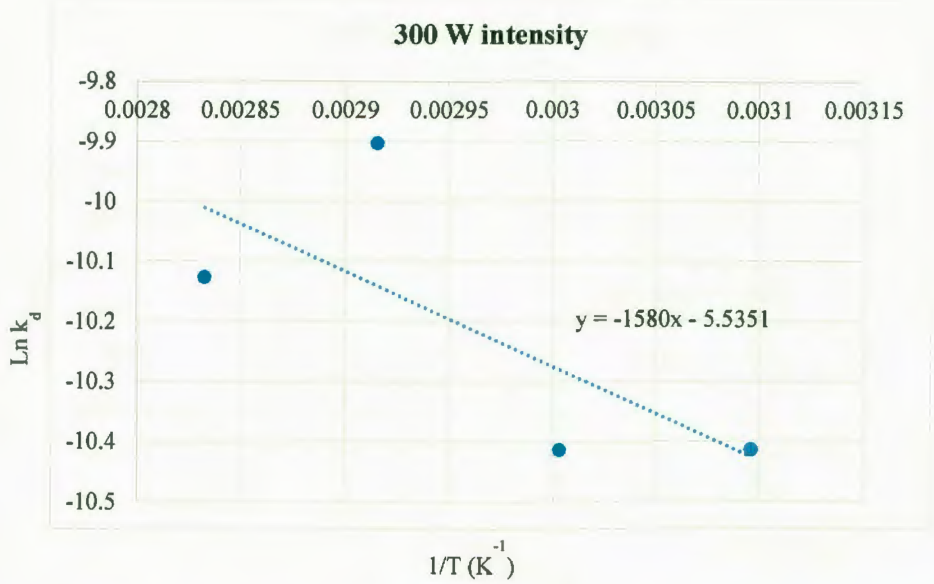


Figure 4-26: *Arrhenius plot of lnkd vs 1/T (K^{-1}) for ash/product layer diffusion mechanism at 300W microwave intensity*

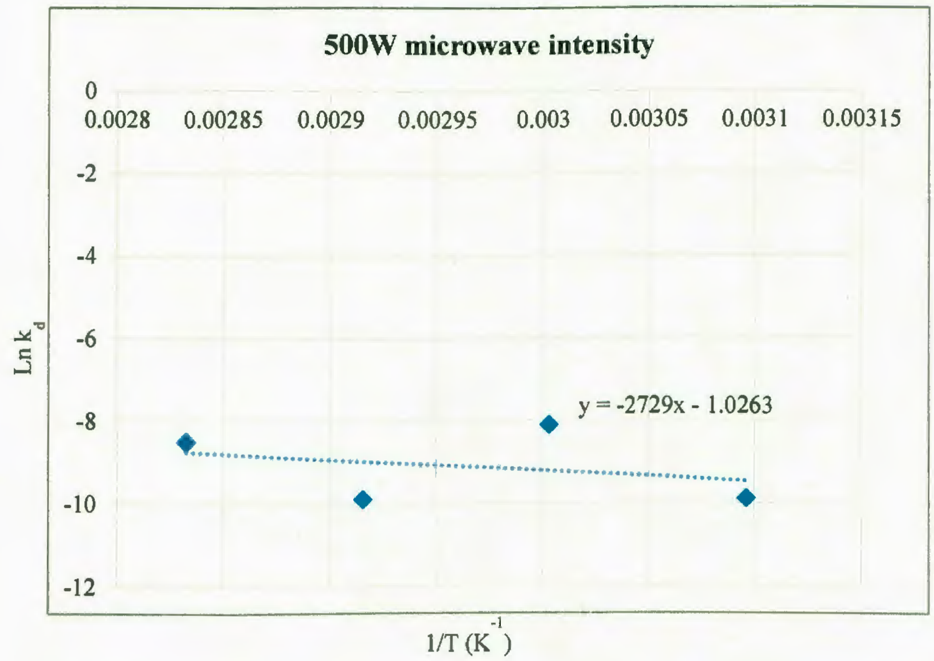


Figure 4-27: *Arrhenius plot of lnkd vs 1/T (K^{-1}) for ash/product layer diffusion mechanism at 500W microwave intensity*

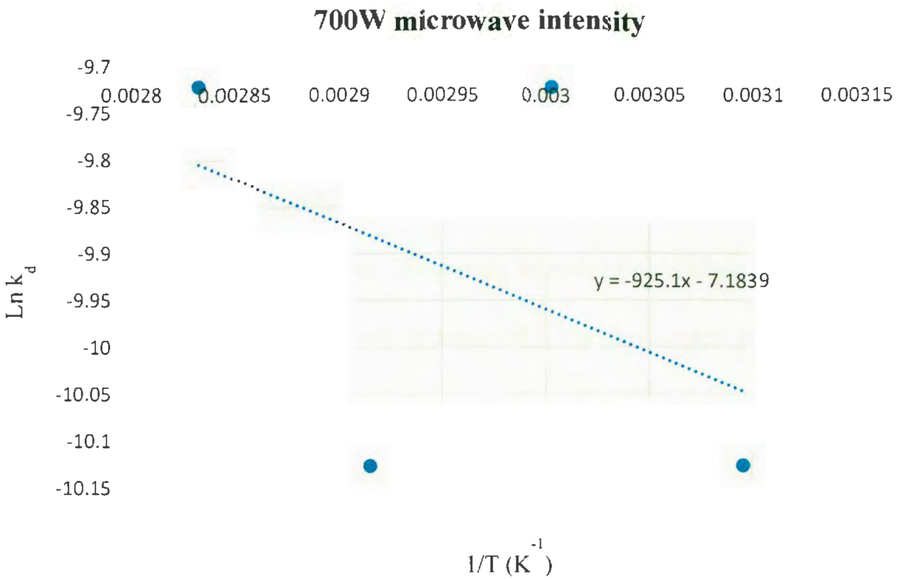


Figure 4-28: *Arrhenius plot of lnkd vs 1/T (K^{-1}) for ash/product layer diffusion mechanism at 700W microwave intensity*

4.2.5 Multiple linear regression analysis for prediction of copper recovery

4.2.5.1 Model development

The data shown in Appendix E was used to develop a mathematical model using the method of multiple linear regressions. However, in order to validate the model developed, additional independent experiments were conducted. The developed model would then be utilised to predict copper recovery for leaching conducted at known conditions, and the results obtained would be compared to the actual experimental results. The data shown in Appendix F are the leaching conditions as well as copper grade of the filtrate from the "model validation" experiments.

Table 4-4 shows results obtained from multiple linear regression analysis of copper dissolution data which is displayed in Appendix E, for all conditions used in this study. In Table 4-4:

i represents microwave intensity in Watts;

t represents leaching time in minutes; and

T represents leaching temperature in °C

Based on the coefficients obtained in Table 4-3, for each of the factors studied, a mathematical model relating copper recovery to microwave intensity, leaching time and leaching temperature can be written as:

$$R_{Cu} = 4.8525 * 10^{-4}i + 4.8325 * 10^{-2}t + 1.11565 * 10^{-1}T + 23.92999 \qquad (4)$$

In the above equation, R_{Cu} is percentage copper recovery.

The model developed as a whole can be said to be statistically significant at 95% confidence interval, as all p values obtained for all factors studied are less than 0.05. The contributions of the individual parameters to the model are as follows:

Intercept: $p\ (7.76E\text{-}66) < \alpha\ (0.05)$

Intensity, i: $p\ (0.037) < \alpha\ (0.05)$

Time, t: $p\ (5.03E\text{-}14) < \alpha\ (0.05)$

Temperature, T: $p\ (9.24E\text{-}34) < \alpha\ (0.05)$

Additionally, the *Significance F* of the model is 1.63E-34 (it is less than 0.05) which shows that the model developed is statistically significant, since the *Significance F value* is less than the *F statistic* value (Morris, et al., 2011). Furthermore, the coefficient of determination (R^2) obtained is 0.877, which means the data is 87.7% close to the fitted regression model developed (Morris, et al., 2011). The coefficients obtained for microwave intensity, leaching time and leaching temperature reveal that for this study, microwave intensity has the least effect on copper recovery, since it had the least coefficient (Morris, et al., 2011).

Table 4-4: *Regression analysis relating microwave intensity, leaching time and leaching temperature to copper recovery*

Regression Statistics	
Multiple R	0.936574
R Square	0.877172
Adjusted R Square	0.872323
Standard Error	0.524053
Observations	80

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	149.0563	49.68543	180.9167	1.63E-34
Residual	76	20.872	0.274632		
Total	79	169.9283			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	23.92999	0.398078	60.1139	7.76E-66	23.13715	24.72283
i	0.000485	0.000229	2.121234	0.037163	2.96E-05	0.000941
t	0.048325	0.005241	9.221395	5.03E-14	0.037888	0.058762
T	0.111565	0.005241	21.28888	9.24E-34	0.101128	0.122002

4.2.5.2 Model validation

Table 4-5 shows experimental conditions and corresponding percentage Cu recovery obtained for each set of conditions, based on results from additional (model validation) experiments conducted, as well as based on prediction using the developed mathematical model.

Recovery based on the additional (model validation) experiments was compared to the model predicted percentage copper recovery in Table 4-5, and average error was computed. From the results obtained, it can be observed that the model prediction results are close to the experimental results. Only one set of experimental conditions was found to have a result with a difference between predicted and experimental percentage Cu recovery above 10%. However, the average absolute percentage difference between the model predicted and the experimental percentage Cu recovery was found to be 3.55%. The model developed can therefore be said to be reliable in predicting copper recovery for leaching conducted within the range of conditions used in this study.

Table 4-5: *Comparison of experimental and model predicted percentage copper recovery*

Leaching Temp (°C)	Leaching time (min)	Irradiation intensity (Watts)	Experimental % Recovery	Model predicted % Recovery	Absolute % difference between experimental and model predicted Recovery
50	20	0	32.89	30.47474	7.33
60	20	0	32.48	31.59039	2.74
70	20	0	32.89	32.70604	0.55
80	20	0	33.70	33.82169	0.36
50	30	0	33.29	30.95799	7.01
60	30	0	32.89	32.07364	2.47
70	30	0	33.29	33.18929	0.31
80	30	0	33.70	34.30494	1.8
50	40	0	34.10	31.44124	7.81
60	40	0	33.29	32.55689	2.21

70	40	0	34.92	33.67254	3.56
80	40	0	35.73	34.78819	2.63
50	50	0	34.51	31.92449	7.49
60	50	0	36.13	33.04014	8.56
70	50	0	36.13	34.15579	5.48
80	50	0	36.95	35.27144	4.53
50	20	100	31.67	30.52327	3.62
60	20	100	32.07	31.63892	1.36
70	20	100	31.67	32.75457	3.43
80	20	100	32.07	33.87022	5.6
50	30	100	33.29	31.00652	6.87
60	30	100	32.48	32.12217	1.1
70	30	100	32.48	33.23782	2.33
80	30	100	34.10	34.35347	0.73
50	40	100	34.51	31.48977	8.75
60	40	100	34.10	32.60542	4.4
70	40	100	34.10	33.72107	1.13
80	40	100	34.51	34.83672	0.94
50	50	100	34.51	31.97302	7.35
60	50	100	36.95	33.08867	10.44
70	50	100	35.73	34.20432	4.27
80	50	100	36.54	35.31997	3.34
50	20	300	31.26	30.62032	2.05
60	20	300	32.48	31.73597	2.29
70	20	300	32.48	32.85162	1.14
80	20	300	32.89	33.96727	3.29
50	30	300	33.29	31.10357	6.58
60	30	300	33.29	32.21922	3.22
70	30	300	32.48	33.33487	2.63
80	30	300	33.29	34.45052	3.48
50	40	300	30.86	31.58682	2.37
60	40	300	34.10	32.70247	4.11
70	40	300	34.10	33.81812	0.84
80	40	300	34.51	34.93377	1.23
50	50	300	34.10	32.07007	5.97
60	50	300	34.51	33.18572	3.84
70	50	300	36.54	34.30137	6.13
80	50	300	35.73	35.41702	0.87
50	20	500	30.86	30.71737	0.45
60	20	500	31.67	31.83302	0.52
70	20	500	32.07	32.94867	2.72
80	20	500	32.48	34.06432	4.88
50	30	500	32.07	31.20062	2.73

60	30	500	32.48	32.31627	0.51
70	30	500	33.70	33.43192	0.79
80	30	500	32.89	34.54757	5.05
50	40	500	33.29	31.68387	4.83
60	40	500	33.29	32.79952	1.48
70	40	500	34.92	33.91517	2.87
80	40	500	34.10	35.03082	2.72
50	50	500	35.32	32.16712	8.93
60	50	500	34.92	33.28277	4.68
70	50	500	34.92	34.39842	1.48
80	50	500	35.73	35.51407	0.6
50	20	700	31.26	30.81442	1.43
60	20	700	30.86	31.93007	3.48
70	20	700	32.89	33.04572	0.48
80	20	700	32.48	34.16137	5.17
50	30	700	32.07	31.29767	2.42
60	30	700	33.29	32.41332	2.64
70	30	700	32.89	33.52897	1.95
80	30	700	32.89	34.64462	5.35
50	40	700	34.10	31.78092	6.81
60	40	700	34.92	32.89657	5.79
70	40	700	35.32	34.01222	3.71
80	40	700	34.51	35.12787	1.79
50	50	700	34.92	32.26417	7.6
60	50	700	34.51	33.37982	3.28
70	50	700	36.13	34.49547	4.54
80	50	700	36.13	35.61112	1.45

4.2.6 Statistical data analysis of the results obtained

Statistical analysis of the data was conducted to determine the overall statistical effect of microwave pre-treatment on copper recovery and hence test the hypothesis of the study. Tables 4-6 to 4-9 show results obtained from Analysis of Variance (ANOVA) of copper dissolution results for leaching with no microwave pre-treatment, and leaching at various microwave pre-treatment intensities of 100, 300, 500 and 700W. All results revealed that at 95% confidence level, the *F Calculated* value was less than *F Critical*, and the *p-value* was greater than 0.05. Based on these results, we then fail to reject the null hypothesis (Morris, et al., 2011), which means based on this study, the null hypothesis, which is "Increasing microwave pre-treatment intensity does not enhance percentage copper recovery from leaching of mine tailings at 95% confidence interval" stands true. Results of ANOVA agree with what the study already established on the effect of microwave power on copper dissolution efficiency, that microwave pre-treatment had no significant impact on the efficiency of copper dissolution from the mine tailings.

Table 4-6: *ANOVA summary for leaching with no microwave pre-treatment vs leaching after microwave pre-treatment of 100W*

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0W	16	518.4734	32.40459	2.971986
100W	16	530.6537	33.16585	1.927979

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.636216	1	4.636216	1.892347	0.179122	4.170877
Within Groups	73.49949	30	2.449983			
Total	78.1357	31				

Table 4-7: *ANOVA summary for leaching with no microwave pre-treatment vs leaching after microwave pre-treatment of 300W*

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0W	16	518.4734	32.40459	2.971986
300W	16	525.7816	32.86135	3.065398

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.669038	1	1.669038	0.552901	0.462919	4.170877
Within Groups	90.56076	30	3.018692			
Total	92.2298	31				

Table 4-8: *ANOVA summary for leaching with no microwave pre-treatment vs leaching after microwave pre-treatment of 500W*

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0W	16	518.4734	32.40459	2.971986
500W	16	535.5258	33.47036	2.065349

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9.086984	1	9.086984	3.607854	0.06716	4.170877
Within Groups	75.56003	30	2.518668			
Total	84.64701	31				

Table 4-9: *ANOVA summary for leaching with no microwave pre-treatment vs leaching after microwave pre-treatment of 700W*

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
0W	16	518.4734	32.40459	2.971986
700W	16	527.4056	32.96285	2.906049

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.493254	1	2.493254	0.848329	0.364373	4.170877
Within Groups	88.17053	30	2.939018			
Total	90.66379	31				

CHAPTER FIVE

5. CONCLUSIONS and RECOMMENDATIONS

5.1 Conclusions

In this study, assessment of copper recovery from low-grade mine tailings was conducted. Dry tailings material ground to -75µm were leached in 0.5M H_2SO_4 with and without microwave pre-treatment. The various conditions used for leaching were pre-treatment with microwave intensities of 0, 100, 300, 500 and 700W; leaching time of 20, 30, 40 and 50 minutes; as well as leaching temperature of 50, 60, 70 and 80°C. The effect of microwave intensity, leaching time and leaching temperature on copper recovery were investigated. Furthermore, kinetic studies of chalcopyrite dissolution on dilute H_2SO_4 were carried out. Finally, a mathematical model was developed, that relates all the parameters studied to copper recovery.

All objectives of the study were achieved and the following conclusions were drawn from the study:

- Microwave pre-treatment had no significant impact at 95% confidence interval on copper recovery.
- Copper recovery increased slightly with an increase in leaching temperature and leaching time
- Diffusion through the ash/product layer governed by the equation $k_d t = 1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$ was found to be the rate-determining-step, and hence the copper dissolution mechanism.
- Activation energy determined was found to be in the range of 7.7-22.69kJ/mol.

- Multiple linear regression revealed that microwave power, leaching time and leaching temperature were related to percentage copper recovery by the following equation: $R_{Cu} = 4.8525 * 10^{-4}i + 4.8325 * 10^{-2}t + 1.11565 * 10^{-1}T + 23.92999$
- The model as a whole and the model parameters are all statistically significant at 95% confidence interval.

5.2 Recommendations

- Increase the microwave pre-heating time for further microwave assisted leaching studies, to determine if at the same set of microwave intensities, increased copper dissolution can be obtained.
- Consideration to conduct leaching tests by pre-heating slurry (a mixture of tailings samples and sulfuric acid) in the microwave oven and compare results to leaching conducted after pre-heating dry tailings material.
- Leaching time should be extended in further studies to test for the possibility of higher copper dissolution.
- Larger particle size fractions should be used in further studies, to determine whether they would respond better to microwave pre-treatment than fine particle size fractions, as reported by some researchers.

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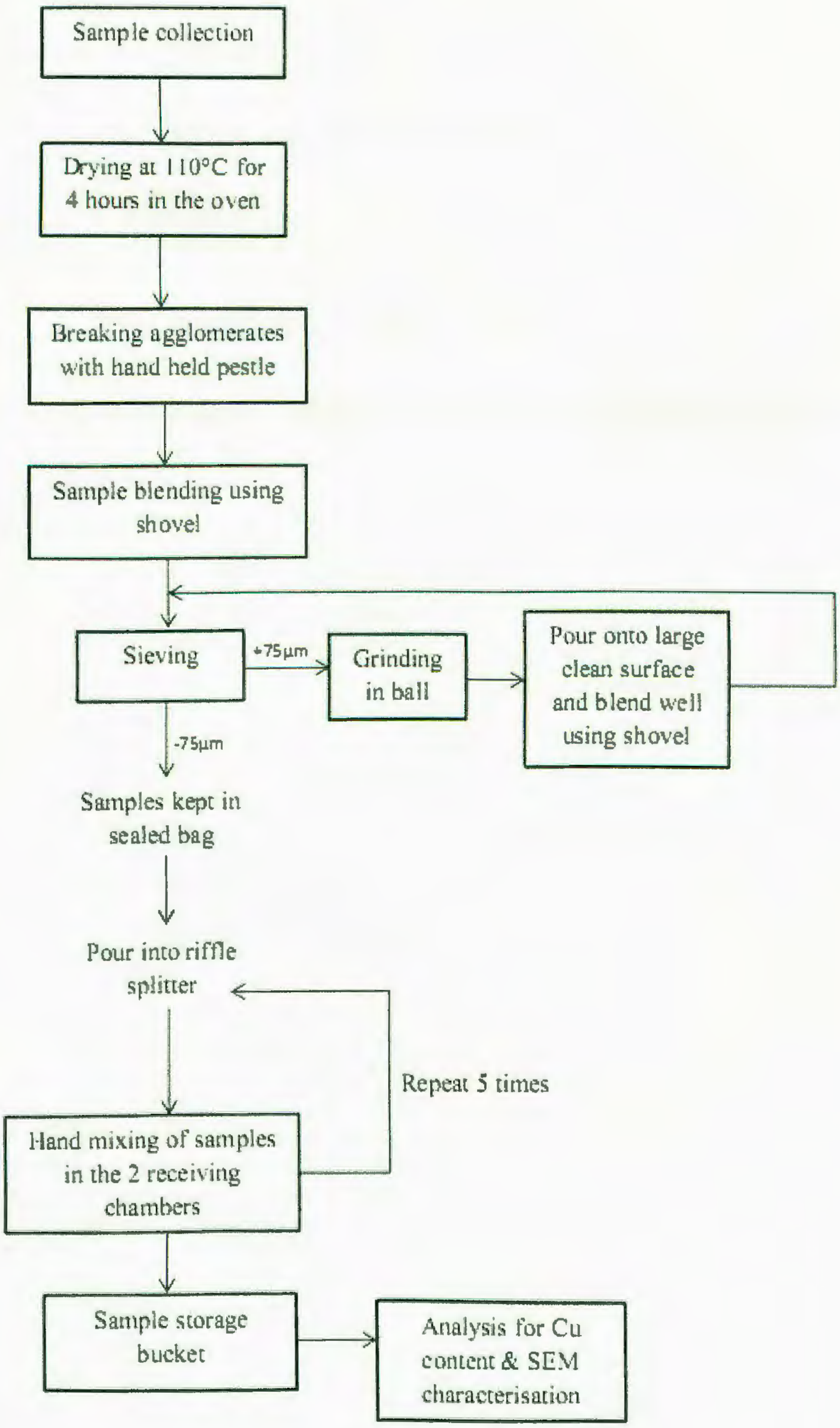
APPENDICES

Appendix A: Sample preparation flowsheet



Appendix B: Reagent Preparation

$\rho = 1840\text{g/L}$

$$Mass\ (g) of\ acid\ per\ L = \rho * \text{Acid strength}$$

$$= (1840 g/L) * 97\% = (1784.8\ g)/L$$

$$Moles\ of\ acid\ per\ L = \frac{Mass\ (g) of\ acid\ per\ L}{Acid\ molar\ mass}$$

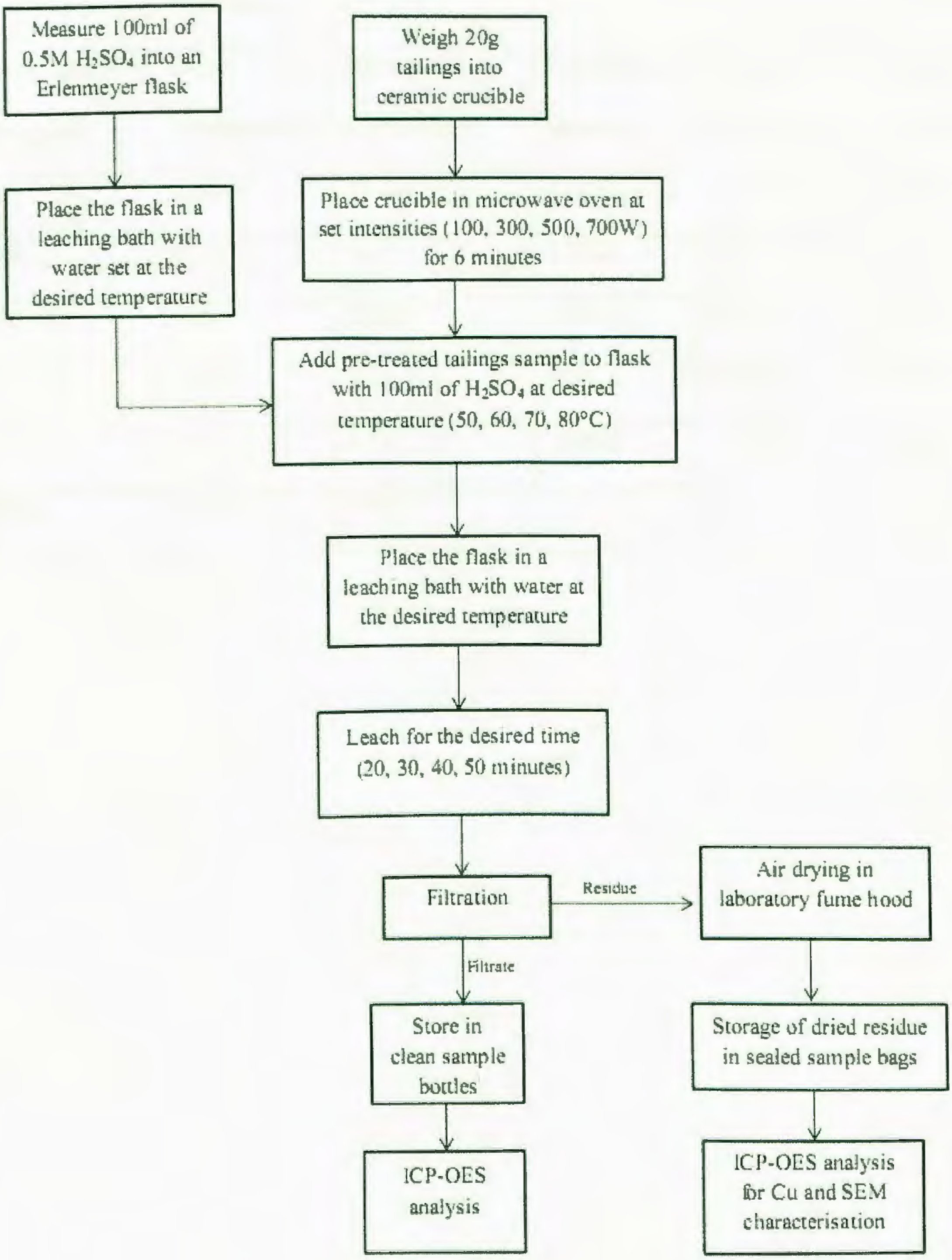
$$= (1784.8\ g/L)/(98.08\ g/mol) = 18.21M$$

$$Volume\ of\ acid\ required\ to\ make\ 1L\ of\ 0.5M\ acid\ solution = \frac{(Required\ molarity) * (1000ml)}{Molarity\ of\ fresh\ acid}$$

$$= (0.5M) * \frac{1000ml}{18.21M}$$

$$= 27.5ml$$

Appendix C: Flowsheet for leaching of microwave pre-treated samples



Appendix D: Particle size analysis of the tailings material

	Retained				**% passing**
Sieve aperture size (µm)	**Mass retained (g)**	**Retained percentage**	**Cumulative mass (g)**	**Cumulative percentage**	**Cumulative % passing**
425	434.5	21.74	434.5	21.74	78.26
180	921.3	46.11	1355.8	67.85	32.15
106	445.7	22.30	1801.5	90.15	9.85
75	145.1	7.26	1946.6	97.41	2.59
0	51.8	2.59	1998.3	100.00	0.00
Total	1998.3	100.0			

Appendix E: Copper grade obtained at various leaching conditions

Leaching temp (°C)	**leaching time (min)**	**Irradiation intensity (Watts)**	**Cu content (ppm)**
50	20	0	**74**
60	20	0	**77**
70	20	0	**80**
80	20	0	**80**
50	30	0	**76**
60	30	0	**81**
70	30	0	**80**
80	30	0	**83**
50	40	0	**78**
60	40	0	**78**
70	40	0	**81**
80	40	0	**86**
50	50	0	**71**
60	50	0	**81**
70	50	0	**83**
80	50	0	**88**
50	20	100	**77**
60	20	100	**80**
70	20	100	**82**
80	20	100	**84**
50	30	100	**79**
60	30	100	**78**
70	30	100	**80**
80	30	100	**85**
50	40	100	**78**
60	40	100	**80**
70	40	100	**85**
80	40	100	**89**
50	50	100	**81**
60	50	100	**81**
70	50	100	**81**
80	50	100	**87**
50	20	300	**69**
60	20	300	**80**
70	20	300	**84**
80	20	300	**85**
50	30	300	**76**
60	30	300	**80**

70	30	300	**82**
80	30	300	**85**
50	40	300	**80**
60	40	300	**78**
70	40	300	**80**
80	40	300	**84**
50	50	300	**80**
60	50	300	**81**
70	50	300	**84**
80	50	300	**87**
50	20	500	**78**
60	20	500	**80**
70	20	500	**81**
80	20	500	**88**
50	30	500	**77**
60	30	500	**82**
70	30	500	**83**
80	30	500	**86**
50	40	500	**79**
60	40	500	**80**
70	40	500	**84**
80	40	500	**87**
50	50	500	**81**
60	50	500	**80**
70	50	500	**85**
80	50	500	**88**
50	20	700	**75**
60	20	700	**76**
70	20	700	**82**
80	20	700	**84**
50	30	700	**76**
60	30	700	**78**
70	30	700	**84**
80	30	700	**85**
50	40	700	**76**
60	40	700	**80**
70	40	700	**84**
80	40	700	**85**
50	50	700	**79**
60	50	700	**81**
70	50	700	**85**
80	50	700	**89**

Appendix F: Model validation experiments

Leaching temp (°C)	leaching time (min)	Irradiation intensity (Watts)	Copper content of filtrate (ppm)
50	20	0	81
60	20	0	80
70	20	0	81
80	20	0	83
50	30	0	82
60	30	0	81
70	30	0	82
80	30	0	83
50	40	0	84
60	40	0	82
70	40	0	86
80	40	0	88
50	50	0	85
60	50	0	89
70	50	0	89
80	50	0	91
50	20	100	78
60	20	100	79
70	20	100	78
80	20	100	79

50	30	100	82
60	30	100	80
70	30	100	80
80	30	100	84
50	40	100	85
60	40	100	84
70	40	100	84
80	40	100	85
50	50	100	85
60	50	100	91
70	50	100	88
80	50	100	90
50	20	300	77
60	20	300	80
70	20	300	80
80	20	300	81
50	30	300	82
60	30	300	82
70	30	300	80
80	30	300	82
50	40	300	76
60	40	300	84
70	40	300	84
80	40	300	85

50	50	300	44
60	50	300	85
70	50	300	90
80	50	300	88
50	20	500	76
60	20	500	78
70	20	500	79
80	20	500	80
50	30	500	79
60	30	500	80
70	30	500	83
80	30	500	81
50	40	500	82
60	40	500	82
70	40	500	86
80	40	500	84
50	50	500	87
60	50	500	86
70	50	500	86
80	50	500	88
50	20	700	77
60	20	700	76
70	20	700	81
80	20	700	80

50	30	700	79
60	30	700	82
70	30	700	81
80	30	700	81
50	40	700	84
60	40	700	86
70	40	700	87
80	40	700	85
50	50	700	86
60	50	700	85
70	50	700	89
80	50	700	89