SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

THE EXTRACTION OF TIN AND COPPER FROM ROASTED COPPER DROSS (RCD) AND COPPER DROSS (CD)

by

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of the requirements for degree of Bachelor of Engineering with Honours
(Mineral Resources Engineering)

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "The Extraction of Tin and Copper from Roasted Copper Dross (RCD) and Copper Dross (CD)". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any other examining body, Institution or University.

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SYMBOLS AND ABBREVIATION

SYMBOLS

℃	Degree celsius
%	Percentage
µm	Micrometer
g	Gram
kg	Kilogram
ml	Millilitre
min	Minute
M	Molarity/Concentration

ABBREVIATION

XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
PSD	Particle size distribution
LOI	Loss on Ignition

CHEMICAL FORMULA

H_2SO_4	Sulfuric Acid
HCL	Hydrochloric Acid

PENGEKSTRAKAN BIJIH TIMAH DAN KUPRUM DARIPADA DROS KUPRUM PANGGANG (RCD) DAN DROS KUPRUM (CD)

ABSTRAK

Dros tembaga (CD) adalah produk sampingan daripada proses peleburan timah di Malaysia sebagai hasil daripada pengekstrakan tembaga atau pendopan. Semasa proses peleburan, benda asing tembaga menjadi sanga yang terapung pada bahagian atas logam lebur selepas penambahan sulfur. Debu tembaga panggang (RCD) adalah produk terhasil selepas pemanggangan CD. Pengekstrakan bijih timah dan tembaga dari dros tembaga (CD) dan dros tembaga panggang (RCD) oleh proses pelarutan telah dilakukan dengan menggunakan asid sulfurik dan hidroklorik sebagai agen larut. Sampel CD dan RCD dicirikan dengan menggunakan XRF, SEM, EDX dan XRD. Dari analisis XRD, kerana sifat CD dan RCD sebagai produk sampingan, ia terdiri daripada gabungan kompleks fasa yang berlainan, di mana puncak kuarza, kasiterit dan puncak kalkopirit telah dikenalpasti. Bagi keputusan XRF, sampel RCD mengandungi beberapa unsur utama seperti timah, tembaga, sulfur dan alumina. Dalam merancang proses larutan, model statistik menggunakan Fractional Factorial Design (FFD) dilakukan dalam kajian ini. Parameter pelarutan seperti kepekatan asid, suhu, jenis asid, jenis dross (CD dan RCD) dan kadar kacau di identifikasikan. Dari analisis FFD, didapati bahawa jenis asid dan jenis asid adalah faktor yang paling penting dalam mempengaruhi pengekstrakan timah. Bagi pemulihan tembaga, tiada faktor penting dikenalpasti. Walau bagaimanapun, masa larutan memainkan peranan utama dalam mempengaruhi pemulihan tembaga berbanding dengan faktor lain. Pengekstrakan larutan optimum dicapai apabila keadaan pelupusan adalah pada 70 ℃ dalam 1.0 M HCL menggunakan RCD sebagai suapan, kadar penggantian 450 rpm dan waktu larut 6 jam untuk tembaga (28.42% Cu pemulihan) dan pada 80 ℃ dalam 1.2 M HCL, menggunakan CD sebagai suapan, kadar pengadukan 350 rpm dan 4.5 jam (pemulihan timah pada 31.91%). Sebagai kesimpulan, pemulihan Cu dan Sn dari dros tembaga dengan

kaedah pelarut telah berjaya dilaksanakan dan ini akan dapat meningkatkan nilai pasaran produk yang bakal dihasilkan dan sisa daripada peleburan timah dan kajian lanjut harus dilakukan dengan lebih teliti untuk meningkatkan peratus pengekstrakan Sn dan Cu.

THE EXTRACTION OF TIN AND COPPER FROM ROASTED COPPER DROSS (RCD) AND COPPER DROSS (CD) IN ACID SOLUTIONS

ABSTRACT

Copper dross (CD) is a by-product from tin smelting process in Malaysia as the result of copper extraction or doping. During smelting processes, the impurities of copper become slag which floats on the molten metal after the addition of sulfur. Roasted Copper Dross (RCD) is the product of roasting of CD. The extraction of tin and copper from copper dross (CD) and roasted copper dross (RCD) by leaching process was carried out by using sulfuric and hydrochloric acid as a leaching agent. The CD and RCD samples was characterized by using XRF, SEM, EDX and XRD. From XRD analysis, due to the nature of CD and RCD as by-product of roasting, it is consist of complex mixture of different phases, where quartz, cassiterite and chalcopyrite peak have been identified. As for XRF results has shown that the RCD sample contain a few major constituents such as tin, copper, sulfur and alumina. In designing leaching process, statistical model using Fractional Factorial Design (FFD) was performed in this study. The leaching parameters such as acid concentration, temperature, type of acids, type of dross (CD and RCD) and stirring rate were investigated. From FFD analysis, it was found that the type of dross and the type of acid are the most significant factor in affecting the recovery of tin. As for the recovery of copper, there is no significant factor was identified. However, leaching time play the major role in affecting the recovery of copper compared to the other factors. The optimum leaching extraction achieved when leaching condition is at 70 ℃ in 1.0 M of HCL using RCD as feed, 450 rpm stirring rate and 6 hours leaching time for copper (28.42 % Cu recovery) and at 80 ℃ in 1.2 M of HCL, using CD as feed, 350 rpm stirring rate and 4.5 hours (tin recovery at 31.91 %). As a conclusion, the recovery of Cu and Sn from copper dross by leaching method is viable and this will increase the economic values of waste from tin smelting and further study should be more focus on increasing the recovery of Sn and Cu.

CHAPTER 1

INTRODUCTION

1.1 Background

Since 3500 BC, tin has become one of the oldest metals discovered by humans and its use is particularly in bronze (a tin-copper alloy). Pure tin is produced from ores, concentrates and used materials. In Egypt, the Bronze Age started and followed by Britain by about 1800 BC. Cornwall has become the place to mine the tin used in the western world until the nineteenth century but tin mining there stopped in 1998. Annual world mine production is typically about 205000–225000 tonnes. Southeast American and Southeast Asia were the major tin producers, but now China is the dominant source. Secondary tin is an important source at about 25% of American supply, and globally accounts for near 10% of production.

Tin is a malleable, soft, ductile and highly crystalline silvery-white metal. When a bar of tin is bent, a crackling sound known as the "tin cry" can be heard from the twinning of the crystals (Holleman et al., 1985). It has a density of 7.29 g/cm, a low melting point of 231.88 °C (449.38 °F), and a high boiling point of 2,625 °C (4,757 °F) (Age., 1998). Tin melts at the lowest temperature in group 14. The melting point is further lowered to 177.3 °C (351.1 °F) for 11 nm particles (Lee Hyuck Mo, 2011).

Cassiterite has become the only important profitable source of tin, although tin are also recovered in small amount from complex sulphides such as stannite, cylindrite, franckeite, canfieldite and teallite. Granite rock almost always associated with minerals that has tin content usually at level of 1% tin oxide content.

Over the years, intensive studies are being done so that the production of tin can meet the demand of industries (Nayl et al., 2012). The ore are usually associated with other elements such as iron (Fe), copper (Cu), zinc (Zn), aluminium (Al), silica (Si), calcium (Ca) (Nayl et al., 2012) antimony (Sb), sulfur (S) and arsenic (As).

In Malaysia Smelting Corporation Bhd. (MSC), each of the elements has their own way of processing and for Cu impurities, it will be doped with sulfur and react with it to produce CuS and cause it to float on the upper part of the layer of molten metals as it has lower specific gravity. From this process, copper dross (CuCD) was driven out. The problem occur when the CuCD is being separated together with about 60 % of Sn and it cause the CuCD to contain higher Sn compared to Cu. CuCD was produced in a large amount as copper doping process is a compulsory stage of processing. Increasing amount of CuCD means an increase in amount of waste and the concentration of Sn in CuCD need to be recovered in order to prevent profit loss of the company. In order to overcome this problem, several test of experiment is being done with the main objective is to recover the Sn content in CuCD. However, the results of experiment were not as desired.

Copper dross is a by-product from smelting as the result of copper extraction or doping. During smelting processes, the impurities of copper become slag which floats on the molten metal after the addition of sulfur. It produces angular granules which are dumped as waste or can be utilized.

1.2 Problem Statement

In order to produce a pure metal, industries are usually needs to focus on one type of element in which the processing circuit are only made up of that particular element. For that case, many of the industry are producing waste more than the production of desired metal. The significant increase in the amount of waste or by-products can cause many adverse effects on

the industry of mineral either in term of economics or social effects. This is due to the reason that the product can be utilized to produce more profit. However, limited knowledge of treating the by-product cause it very hard to process the minerals and exploit it metal contents. In tin processing industry in Malaysia, tin ore are usually associated with a lot of other valuable metals such as iron (Fe), copper (Cu), Arsenic (As), Antimony (Sb) and other metals that can be further utilized in order to manage the demand in these metals. A pyrometallurgical process can be done to separate those minerals present in the ore by studying the physical properties of each elements such as specific gravity and also their chemical properties such as melting point, boiling point, etc. During the process of separating metals in a form of molten metals, the physical tools that are using to separate the minerals layer of different minerals can cause a major loss of desired metals to the by-product.

In this case, copper dross is the example of by-products of tin processing that is underutilize as when the copper dross were produced from the copper doping in refining process, it became the final form that a company can produce. For that reason, company tries to utilize the presence of copper dross but could not made a clear methodology in searching for the suitable parameters to extract the copper and also tin content from the copper dross.

In this study, the CuCD will be treated by using common acid. The main issue of treating the CuCD is because of the sulphur content in the dross will make it harder to react with acid. These CuCD is supposed to react and produce any form of copper salt. Otherwise, the dross need to be processed again in the roaster to reduce the amount of sulphur to make sure that copper dissolve in sulfuric acid.

From this study, the high amount of tin can also be recovered so that the copper dross will be fully utilized and enhanced its economical values. By designing the experiment, the

suitable parameters can be constructed and used so that the experiment will produce a desired result.

1.3 Objective

In investigating the suitable parameters that can be used in the experiment, the objective specifically targeting as below:

1. To perform characterization study on Roasted Copper Dross and Copper Dross products that gives information on mineral phases, composition and particle shapes.
2. To study the suitable method for the recovery of tin and copper from copper dross products.
3. To study significant leaching parameters for extraction of copper from RCD and CD using fractional factorial design.

1.4 Scope of study

The parameters that were chosen in the project are temperature, acid concentration, types of acid, type of dross, stirring rate and leaching time. There are three different temperatures used in the experiment which are 70℃, 80℃ and 90℃. The types of acid used in this experiment are hydrochloric acid (HCL) and sulfuric acid (H_2SO_4). The acids are experimented with 1.0 M, 1.2 M and 1.4 M of acid concentration. The types of dross that are used in this study are RCD and CD. Stirring rate are also manipulated with the value of 250 rpm, 350 rpm and 450 rpm. The leaching time are also taken into consideration in which time for experiment are 3 hours, 4.5 hours and 6 hours.

All the parameters are tested simultaneously for leaching process. It is being conducted for 0 min, 15 min, 30 min, 45 min, 1 hour, 2 hours, 3 hours, 4 hours, 5 hours and 6 hours. About 10 g of RCD and CD are used as leaching feed for each leaching time. The residue was dried

and sent to X-Ray Fluorescent (XRF) and Scanning Electron Microscope (SEM). The fraction of tin dissolved was calculated from the initial difference in weight and iron residue after leaching. The residue is dried at 80℃ for 3 hours to ensure the residue is completely dry since HCL and H_2SO_4 will start to vaporize at 80℃.

1.5 Flow of dissertation

This dissertation start with chapter 1, where all Background**,** Problem Statement, Objective, Scope of study and Flow of dissertation are cited. Then, followed by chapter 2, where literature review on Tin ore background, Industry demand of Tin, Uses of Tin Ore, Copper dross as a by-product in tin smelting, Beneficiation of Tin Ore, Beneficiation of Tin Ore Using Pyrometallurgy and Hydrometallurgy. Chapter 3 represented all of the procedure and methodology of Sample Preparation, List of chemicals and equipment, Chemical, Sample Preparation, Comminution and sizing, Crushing, Grinding, Sieving, Sample characterization, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Loss on Ignition (LOI), Scanning Electron Microscope (SEM), Design of Experiments, Leaching, Solution preparation and Leaching process. Next, chapter 4 show all kinds of results on Introduction, Ore Characterization, X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX), EDX, Analysis of Roasted Copper Dross (RCD), EDX Analysis of Copper Dross (CD), Design of Experiment (DOE) and Acid Leaching of Tin and Copper. Lastly, conclusion and recommendation are stated in chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Tin ore background

Tin is a relatively soft and ductile metal with a silvery white color. It has a density of 7.29 g/cm, a low melting point of 231.88 °C (449.38 °F), and a high boiling point of 2,625 °C (4,757 °F) (Age., 1998). Tin has huge number of applications in the world. In order to get a high-grade tin, the tin ore must be mined first from the mining industry that is specifically built just to produce tin ores.

After mining, the mineral processing play a major role in extracting ores and producing a pure tin metals, alloys or impure form consist of tin solders that are required by industries. As for the tin production, number of methods were developed to extract tin from its ore. The processing of tin oxide concentrate is by using screening, wet and dry gravity method and magnetic and electrostatic separation and reduced into tin metal most commonly conducted in reverberatory furnaces by reduction of tin oxide with charcoal (Henao et al., 2015).

Since the 19^{th} century, more initiatives to produce tin is being done resulting from the increasing of electronic industry and from that the demand of tin increases (Soewarno et al., 2014).

Cassiterite (SnO_2) has become the only important profitable source of tin, although tin are also recovered in small amount from complex sulphides such as stannite, cylindrite, franckeite, canfieldite and teallite. Granite rock almost always associated with minerals that has tin content usually at level of 1% tin oxide content.

Table 2.1 General properties of cassiterite (Mineral Data Publishing, (2005), (2006))

Chemical Formula	SnO_2
Molecular Weight	150.71 g/mol
Empirical Formula	SnO_2

Based on the occurrence it can be seen that most sources of cassiterite today are found in alluvial or placer deposits containing the resistant weathered grains. The best sources of primary cassiterite are found in the tin mines of Bolivia, where it is found in hydrothermal veins. Rwanda has a nascent cassiterite mining industry. Fighting over cassiterite deposits (particularly in Walikale) is a major cause of the conflict waged in eastern parts of the Democratic Republic of the Congo. This has led to cassiterite being considered a conflict mineral.

Cassiterite is a widespread minor constituent of igneous rocks. The Bolivian veins and the old exhausted workings of Cornwall, England, are concentrated in high temperature quartz veins and pegmatites associated with granitic intrusives. The veins commonly contain tourmaline, topaz, fluorite, apatite, wolframite, molybdenite, and arsenopyrite. The mineral occurs extensively in Cornwall as surface deposits on Bodmin Moor, for example, where there are extensive traces of an hydraulic mining method known as streaming. The current major tin production comes from placer or alluvial deposits in Malaysia, Thailand, Indonesia, the Maakhir region of Somalia, and Russia. Hydraulic mining methods are used to concentrate mined ore, a process which relies on the high specific gravity of the SnO2 ore, of about 7.0.

Table 2.2 General properties of cassiterite (2001-2005 Mineral Data Publishing, Version 1)

Color	Black, brownish black, reddish brown, red, yellow, grey, white, rarely colourless.
Luster	Adamantine to adamantine metallic, splendent; may be greasy on fractures.
Hardness	6–7
Specific Gravity	6.98 - 7.1
Streak	White to brownish
Tenacity	Brittle
Transparency	Transparent when light coloured, dark material nearly opaque; commonly zoned
Crystal System	Tetragonal
Fracture	Sub-conchoidal to uneven

2.2 Industry demand of Tin

Well and great demand expected for 2017. As for 2016, the world tin consumption is estimated to have grown 3.5%, primarily driven by the growth of tin-consuming industries such as the electronics industry. On-year in 2016, global semiconductor shipments, which are a ambassador for the electronics manufacturing industry and demand for solder alloy products, grew 1.1%. Global semiconductor shipments will grow 3.3% in 2017 and 2.3% in 2018, and the steady global demand for consumer electronics will continue to support demand for tin solder, which contributes to about half of refined tin consumption. This statement is according to World Semiconductor Trade Statistics (WSTS). Tin demand is expected to see stable growth from 1.6% in 2017 to 2.0% in 2018.

Also, there will be increasing demand for its use in automotive electronic components and in new electronics applications, namely power semiconductors, photovoltaic (PV) cells and LED lighting. China accounted for 43.4% of total refined tin consumption in 2015, and will continue to be the largest tin consumer, with its demand forecast to grow 1.5% in 2017

on the back of rising output of electronic goods encouraged by government policies to promote consumer spending. Meanwhile, global demand for tin ex-China is expected to remain flat in 2017 (Disclosure and Barring Service (DBS) Group Research, 2017).

Figure 2.1 : Pie Chart of Tin Ore Reserves

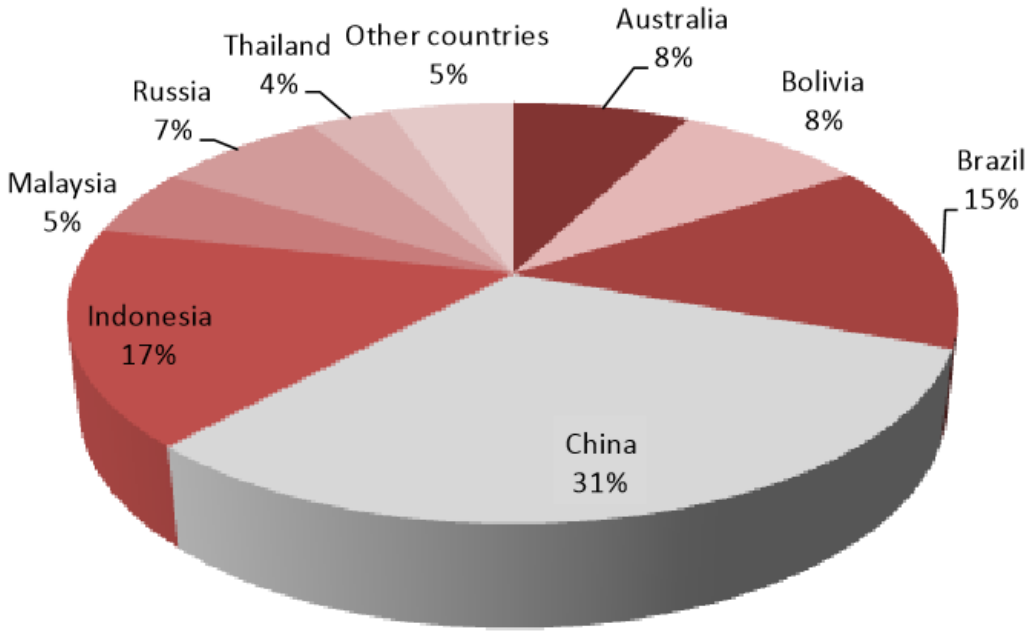


Figure 2.2 : Pie Chart of Tin Usage Breakdown For 2015

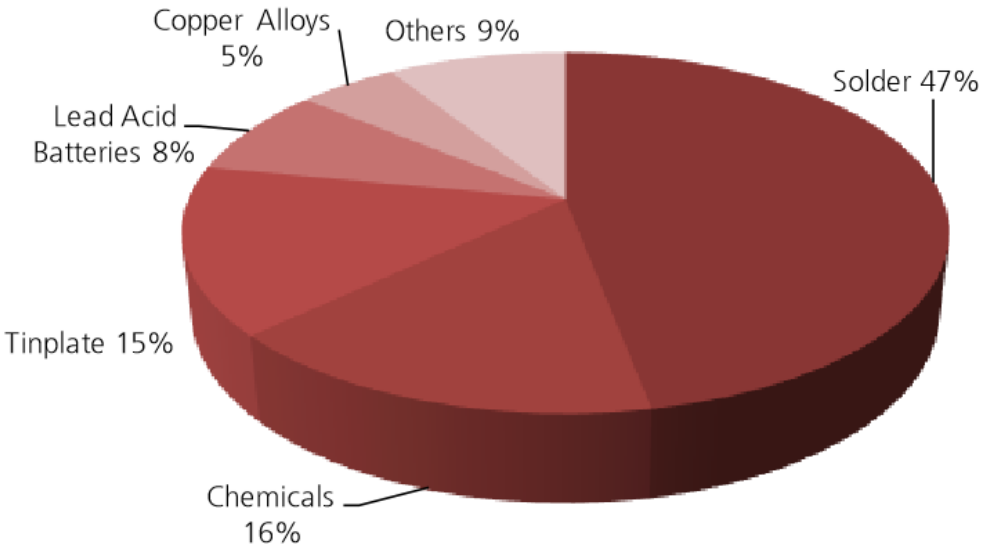


Figure 2.3 : Tin global consumption (‘000 ton) and China’s share (%)

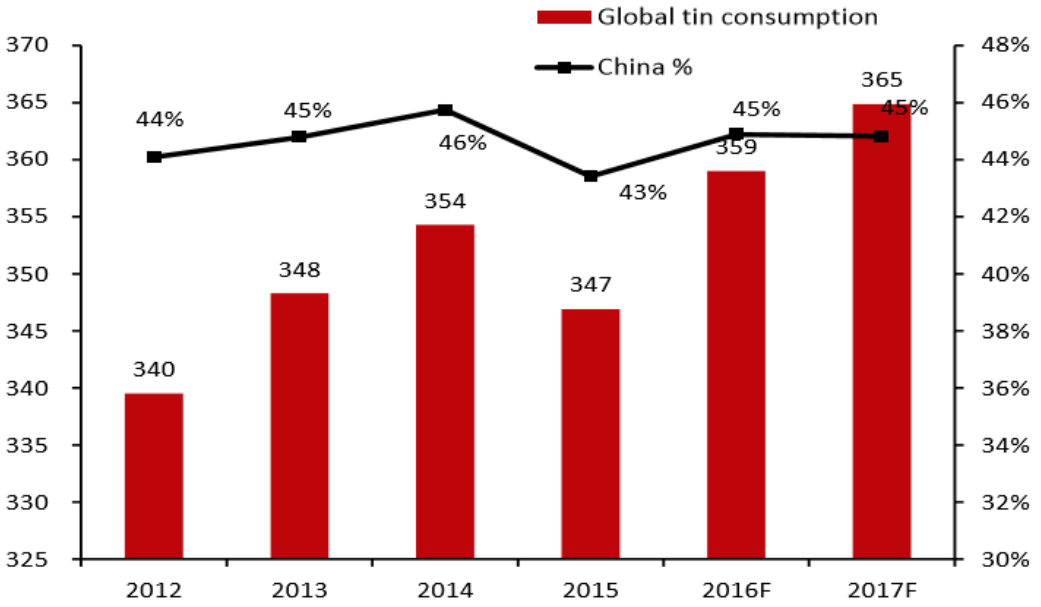


Figure 2.4 : London Metal Exchange (LME) tin price and warehouse stock

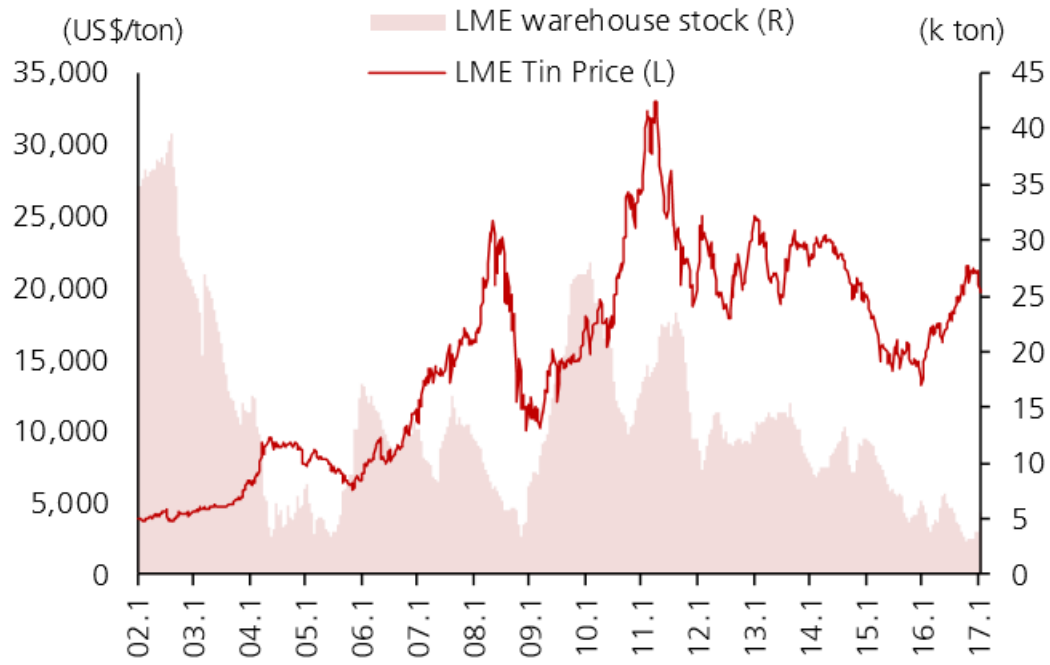
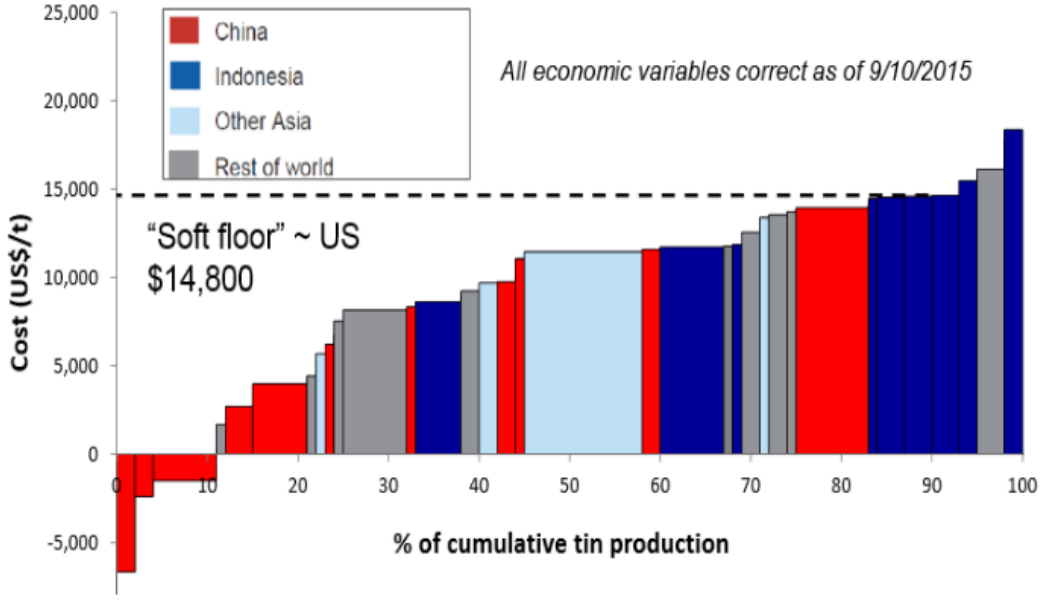


Figure 2.5 : Global tin production cost curve



2.2.2 Uses of Tin Ore

Tin has been used in wide areas of industries. Since tin is a very stable elements from being oxidised, it has been used in coating of metals to prevent the metals from corrosion or rusting. The main example of the application are such as in tin cans, which are made of tin-coated steel. Alloys of tin play a very important role in industry such as soft solder, pewter, bronze and phosphor bronze. A niobium-tin alloy is used for superconducting magnets. Floating molten glass on molten tin is being used to make most window glass and it is used to produce a flat surface. Electrically conductive coatings are produced from tin salts sprayed onto glass.

Tin(II) chloride, which is used as a reducing agent and as a mordant for dyeing calico and silk are the most important tin salt. Tin(IV) oxide is used for ceramics and gas sensors. Zinc stannate (Zn2SnO4) is a fire-retardant used in plastics. In order to prevent the barnacles from fading, some of the tin compounds have been used as anti-fouling paint for chips and boats. Although, these compounds are deadly to marine life even at low levels especially oysters. Its use has now been banned in most countries.

2.3 Copper dross as a by-product in tin smelting

The process of tin smelting process will start with the processing of ore using a Roaster. Roaster is a section that been used for removal of arsenic from the furnace feed materials or the acceptable ores based on the laboratory test result, before being smelted in the furnace. Besides, the purpose of roasting section is to reduce the workload on refinery section in arsenic removal from the crude metal in order to meet the market specifications.

Copper dross is a by-product from smelting as the result of copper extraction or doping. During smelting processes, the impurities of copper become slag which floats on the molten metal after the addition of sulfur. It produces angular granules which are dumped as waste or can be utilized.

Copper doping is the addition of a second material in small quantity to a large quantity of a first material. The addition may or may not result in a crystal structure change of the first material and the effect will be a change in the properties of the doped material superficial only. As for copper doping, it is the process of removal of copper from the kettle after being heated in furnaces. The metal needed to be doped for copper is firstly maintained at about 260ºC to 290ºC with minimal dross floating on top of the metal. The metal level must be about 35 to 40 metre level in the 50 meter kettle. A 50 horsepower (hp) stirrer is used for the process. The chemical reaction involved in the doping reaction is as follows:

$$Cu_{(Sn)} + S \longrightarrow CuS_{(dross)} \quad (1)$$

The amount of sulphur required to produce successful copper doping is obtained by using the formula in equation number 2:

$$\text{Sulfur required} = \frac{\%\ \text{Cu in metal}}{100} \times \frac{\text{wt. of metal (kg)}}{2} \quad (2)$$

In order to allow some burning off in the hot metal, a slight excess of sulfur is added. The weight of sulfur required is estimated to the nearest 10 kg from a standard 50kg bag of sulfur and from analysis of Cu in the metal during doping. From the process of copper doping, copper dross is produced. However, the mass of production of copper dross has certain effect on several aspects such as economics and environments. Due to the huge amount of dross compared with those of the target metal, it is compulsory to use the dross as a product (Lee,2014). The alloy dross still contains copper and other valuable metals like nickel, cobalt or tin even after matte smelting and standard dross cleaning in submerged arc furnaces (Lee,2014). Therefore, sustainable dross management is mandatory from the economic and environmental perspective (Lee,2014).

2.4 Beneficiation of Tin Ore

Since the tin ore consists of many minerals such as cassiterite (major constituent), stannite, cylindrite, franckeite, canfieldite and teallite, the minerals need to be liberated and extracted in order to get the desired percentage of tin. Thus, the tin ore can be processed using the pyrometallurgical method that are using heat and fire to extract the minerals and separated it based on the melting and boiling point of the elements. Meanwhile, the hydrometallurgical method is using liquid as the reagents that will help the elements to react and associate with the reagents and after that, precipitation of elements occur and the specific element will be acquired.

2.4.1 Beneficiation of Tin Ore Using Pyrometallurgy

Over the years, intensive studies are being done so that the production of tin can meet the demand of industries (Nayl et al., 2012). The ore are usually associated with other elements such as Fe, Cu, Zn, Al, Si, Ca (Nayl et al., 2012), Sb, S and As. Before being smelted, low-

grade concentrates from complex ores are first roasted in a roaster between 550 to 650 °C to drive off the sulfur (Age,1998) and arsenic content in the ore.

Roaster is a section that been used for removal of arsenic from the furnace feed materials or the acceptable ores based on the laboratory test result, before being smelted in the furnace. Besides, the purpose of roasting section is to reduce the workload on refinery section in arsenic removal from the crude metal in order to meet the market specifications. At temperature of 500℃ to 650℃ under oxidizing atmosphere, arsenic content can be easily volatilized as trioxide in the roasting process. The percentage of arsenic in the feed and roasted product varies from 0.3 % to 45 % and 0.03 % to 2 % respectively. The arsenic in the ores is mainly in form of arsenopyrites (Fe As S). The chemical reaction take place during the roasting process as shown below :

$$\underset{(Arsenopyrites)}{Fe\ As\ S} \xrightarrow{heating} FeS + As$$

$$4\ As + 3\ O_2 \xrightarrow{yields} \underset{(Arsenic\ Trioxide)}{2(As_2O_3)}$$

$$2\ FeS\ + \frac{7}{2} O_2 \xrightarrow{yields} Fe_2O_3 + 2SO_2$$

$$4\ As\ + 3\ SO_2 \xrightarrow{yields} 2(As_2O_3) + \frac{3}{2} S_2$$

The higher percentage of iron in the roasting materials might cause the formation of iron arsenate which is not volatile and remains in the roasted material. In order to prevent the formation of iron arsenate, anthracites (2% to 5%) is added into the process. The formation of iron arsenate as follows:

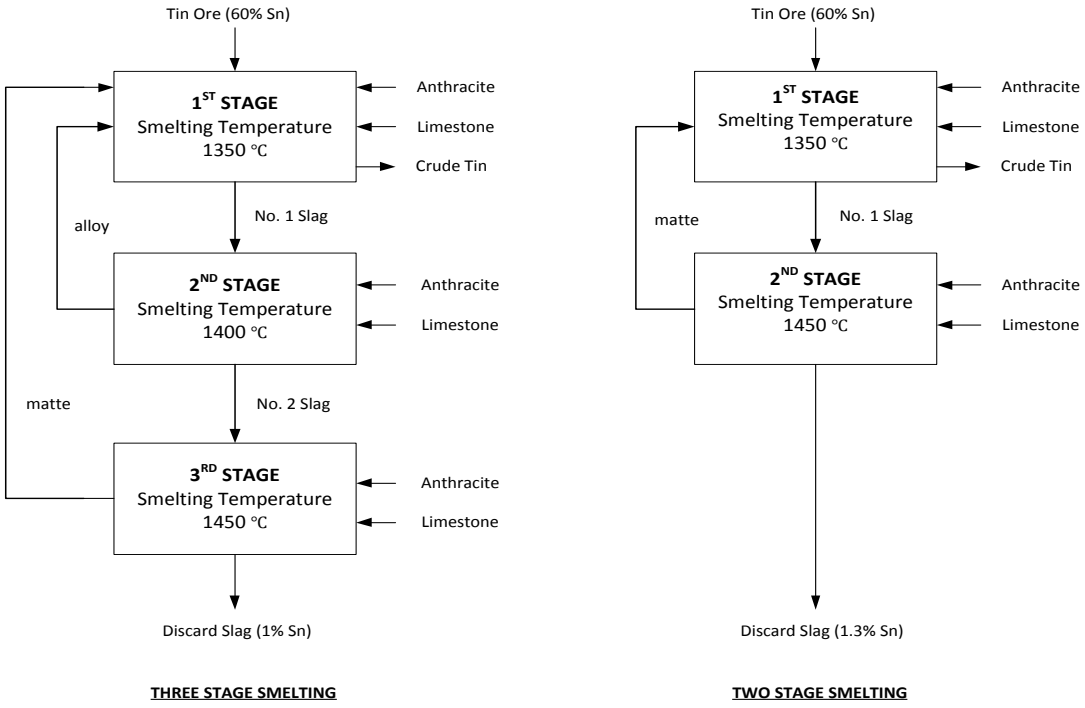
$$2(As_2O_3) + 2Fe_2O_3 + 2SO_2 \xrightarrow{yields} \underset{(Iron\ arsenate)}{4\ FeAsO_4}$$

After roasting, the ore will be treated in the reverberatory furnaces either using 3 stages or 2 stages smelting processes. The reducing agent that is used in smelting is commonly a

source of carbon such as coke, or in earlier times charcoal. As most ores are impure, it is often necessary to use flux, such as limestone, to remove the accompanying rock gangues slag. For the 3 stages process, the 3 furnaces will be used and it increases in temperature starting from 1350 ℃ for the 1st Stage that will produce the crude tin that will be further treated in a kettle and the No. 1 slag that will be further treated in the 2nd Stage Furnace. As for the 2nd Stage which has a temperature of 1400 ℃, the No. 1 slag which still has a significant amount of tin is being treated by using the same reducing agent which are limestone and anthracite until it produces an alloy which has some amount of tin to be processed back to produce a crude tin and No.2 Slag which will be processed in the 3rd stage processing furnace. Then, for the 3rd Stage which has a 1450℃ temperature, same reducing agent and same process is being done, the only difference is in term of temperature, the final slag will be produced to be discarded as the amount of tin in the slag are very limited. As for the 2 stages process, 2 furnaces will be used and the same process as in the 3 stage process are done and it will increase from 1350 ℃ for the 1st Stage to 1450 ℃ for the 2nd Stage.

After all of the elements and minerals were melted, the elements which in liquid state will form several layer of different minerals and this was affected by the specific gravity of the elements. Therefore, the denser elements will tend to settle at the bottom part of reverberatory furnaces meanwhile the less dense elements will be on the top of the furnaces. The separation is being done by the opening of the bottom hole of the furnaces and the denser elements will be separated first. After smelting processes were done, the product from smelting will be crude tin and final slag. The Figure 2.6 shows the overview of the process that has been simplified in term of flow process diagram.

Figure 2.6 : Schematic Diagram on Tin Processing in Furnace (Standard Operating Procedure Report, Malaysia Smelting Corporation Sdn. Bhd., 2004)



After the smelting process, the melted metals from furnaces is sent for the next stage of processing which are refining. In refining stage, the metals which the content in ore are significant such as iron, copper and arsenic is being extracted by a process called doping. The first doping start with the separation of iron from the melted metals. The separation procedure of iron only need an action of centrifugal force and specific gravity in which a worker is needed to stir the melted metals in a kettle so that the iron will float at the surface of the melted metals. The floated iron metals were then being scooped and the product produced from the process are called Iron Dross (FeCD). After the iron being separated from the crude tin, the next process will be copper doping.

Copper doping are done at the same kettle but the difference is only the addition of sulfur into the ingredients. The addition of sulfur cause the copper to react with sulfur and produce copper sulphide which is lower in term of specific gravity if compared to the other metals in the melted

metals. The floated copper sulfide are scooped and the product that are produced were named Copper Dross (CuCD). There were several types of dross produced by industries such as iron dross, copper dross (Lee,2014), zinc dross (Zheng,2007), solder dross (M.Henao,2015), aluminium dross (Jung,2017), antimony dross (L.N. Singh,2009) and etc.

Both of the process are then producing three types of tin metal concentrate which are tin metal (high content of As), tin metal (high content Sb) and standard tin metal. High arsenic tin metal will be doped for its arsenic content then. The high Sb tin metal were then being further processed in electrorefining process to produce 4N tin metals. 4N metals is the tin bullions that has purity of tin at 99.99 %. The standard tin metals is being processed in the next stage using the process called crystallizing to be further processed to produce solder, market metal (3N) and slime. Market metals or 3N metals in other words is the tin bullion that has 99.90 to 99.98 % of tin purity. Solder is a fusible tin metal alloy used to create a permanent bond between metal workpieces.

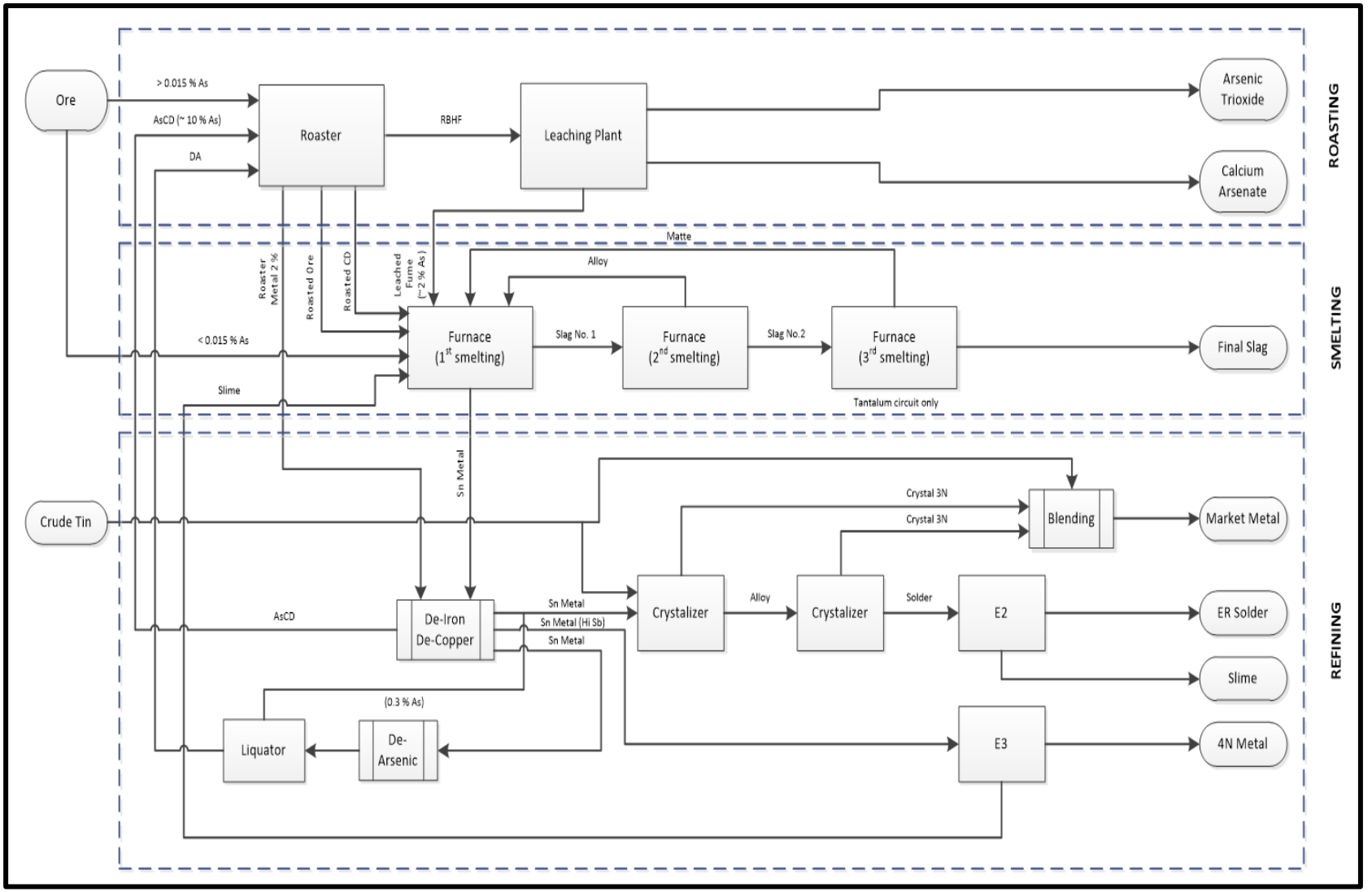


Figure 2.7 Overall Flow Chart of Tin Ore Processing (Standard Operating Procedure Report, Malaysia Smelting Corporation Sdn. Bhd., 2004)

2.4.2 Beneficiation of Tin Ore Using Hydrometallurgy

As secondary raw materials often are, hydrometallurgical processing method are most likely favorable for the treatment of complex and low grade materials. In most cases, the solid or liquid raw for materials usually contain dominant amounts of base metal elements. Thus, hydrometallurgical process are needed in order to extract valuable metals with only small concentrations and need a highly selective separation methods. Thus, if being compared to pyrometallurgical processes, hydrometallurgical processing method are also seen as more environmental friendly with lower energy consumption.

Leaching is a solid-liquid mass transfer process. Leaching is the process of dissolving the valuable minerals largely unaffected by aqueous solution or leaching solution. Leaching may be carried out at ambient condition (where we are considering the worst cases for the reaction to occur) or at elevated temperatures and under pressure. The objective is to produce metal ions or complexes which can then be extracted selectively from the leached solutions and the process condition will dependon chemical reaction taking place.

Leaching should yield metal rich pregnant solution from which the metal can be separated and recovered in higher state of purity and also a gangue or residue which is sufficiently free of valuable minerals for it to be dumped. Leaching is a heterogenous process involving three reaction steps which are diffusion, transport and chemical process (Gupta, 1990).

There are a variety of leaching processes, usually classified by the types of reagents used in the operation. The reagents required depend on the ores or pretreated material to be processed. A typical feed for leaching is either sulfide or oxide (Wikimedia Foundation Inc).

In general, there are three types of ore leaching which are heap leaching, agitation leaching and percolation leaching. Heap leaching is applied to low-grade ores and waste

materials. The ore is stacked in heaps and sprayed with acidified soluion. The solution that drains out of the bottom of the pile contains the dissolved metal. Percolation leaching is generally used for higher grade ores than those suitable for heap leaching. The ore is crushed and and placed in vats with filter bottoms so that the solution can be pumped in under the charge. Percolation can be upward or downward, although the former is usually preferred. Agitation leacing is used for high-grade ores or concentrates. The ore crushed, ground and leached agitation. This is frequently accomplished in pressure vessels involving oxygen atmospheres at elevated temperatures to oxidize metal sulphides, etc, to more soluble oxides (Webster 1984).

CHAPTER 3

METHODOLOGY

3.1 Sample Preparation Introduction

The sample is in the form of accumulated powder that form a stone shape. The sample was known as RCD and CD. The range size of the sample is from -75 µm to +4.75 mm for RCD and -75 µm to +5.00 mm for CD. The sample was crushed using a cone crusher as it is already in a form of rock pieces and do not need a jaw crusher. The open side setting for the cone crusher is 4mm. Then, the last stage of liberation process is via grinding. Planetary Ball Mill is used to grind the sample instead of using ring mill as prevention for the sample from being contaminated with iron. The grinding stage is used to produce fine particles and to obtain desired range of size fraction. Both sample of RCD and CD are sent for mineral characterization analysis such as X-Ray Diffraction (XRD), X-Ray Fluorescent (XRF), Loss of Ignition (LOI), Particle Size Distribution (Sieving), Particle Size Analysis (PSA) and Scanning Electron Microscope (SEM).

Samples are being weighed before undergoes into leaching process. The leaching process is started based on the determined runs that were constructed by the Design of Experiment (DOE). Each leaching process is done for 3, 4.5 and 6 hours. For 3 hours experiment run, the leachate are taken for every 0, 15, 30 minutes, 1, 2 and 3 hours. For 4.5 hours run, the leachate are taken for every 30 minutes, 1.5, 2.5, 3.5 and 4.5 hours. For 6 hours experiment run, the leachate are taken for every 30 minutes, 1, 2, 3, 4, 5 and 6 hours. The leaching residues were washed using 10 % of nitric acid (HNO_3) immediately after the experiment was done and filtered in order to stop the reaction from continue. The sample of leachate were then kept inside a refrigerator to secure the content of elements in it and to

prevent further reaction such as deposition of elements. The solid residue were dried, weighed and sent for SEM and XRF analysis. The leachate sample were then sent for ICP Analysis.

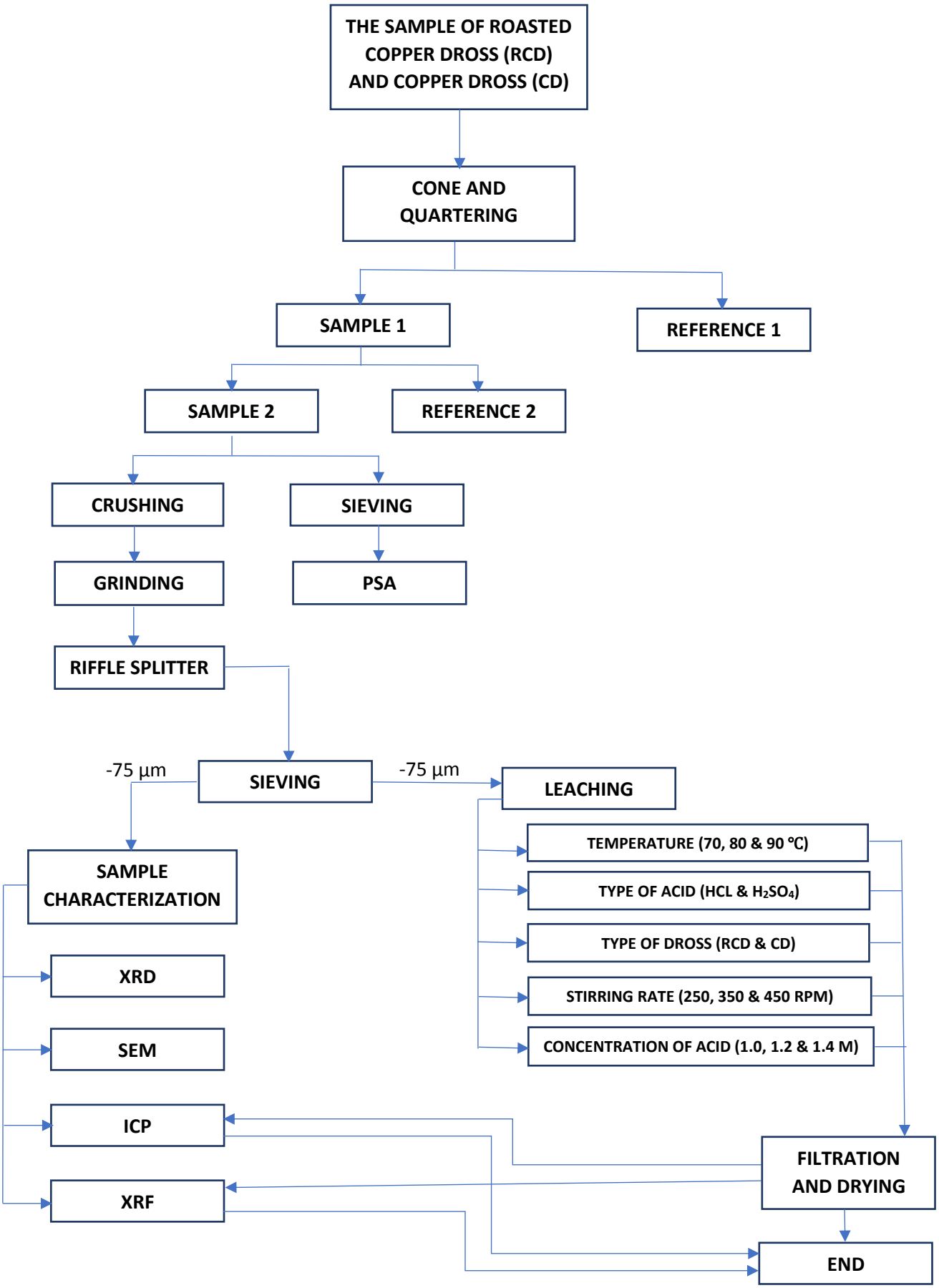


Figure 3.1 Flowchart of overall process of the project

3.2 List of chemicals and equipment

3.2.1 Chemicals

The chemicals used in this work is being listed in Table 3.1. The preparation, usage, storage, disposal were followed as regulated in the Material safety data sheet (MSDS). Chemicals can be obtained from the chemical laboratory. 1% nitric acid were used to wash all the glassware before start the experiment. It is also used while preparing the stock solution for leaching. 10 % of Nitric Acid are used to dilute the leaching solutions before sent for Inductively Coupled Plasma Mass Spectometry (ICP-MS).

Table 3.1 : List of chemicals used in the leaching process

Chemicals	Formula	Molarity (M)
Sulphuric Acid	H_2SO_4	18
Hydrochloric Acid	HCL	12

3.3 Sample Preparation

3.3.1. Crushing

The first basic stage in comminution is crushing where the contents inside the samples will be liberated by using this method. The samples that are being treated are Roasted Copper Dross (RCD) and Unroasted Copper Dross (CD). The average maximum particle size of the samples are 4.75 mm and 5 mm respectively. The first crusher used is Cone Crusher as the maximum size of the particles is about 5 mm. It crushed the sample in an average of 5:1 size reduction. The oversize product from cone crusher which is +4.00 mm will be further crushed again using cone crusher. The undersize ore which below 4.00 mm will be further liberated