SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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THE EFFECT OF MILLING TIME, STIRRING SPEED AND BALL MILL TO POWDER RATIO OF MALAYSIAN TIN ORE

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "The Effect of Milling Time, Stirring Speed and Ball Mill to Powder Ratio of Malaysian Tin Ore". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABREVIATIONS

Al	Aluminium
Sn	Cassiterite
SnO_2	Tin Oxide
Fe_2O_3	Iron Oxide
Al_2O_3	Aluminum Oxide
Sb	Antimony
Fe	Iron
XRF	X-ray Fluorescence
XRD	X-ray Diffractiom
LOI	Loss on Ignition
SEM	Scanning Electron Microcope
EDX	Energy Dispersive X-ray Spectrocopy
DOE	Design of Experiment

SYMBOLS

g	Gram
µ	Micron
mm	Milimeter
%	Percentage
℃	Degree Celcius
Wt %	Weight percentage

KESAN PENGISARAN MASA, KELAJUAN PENGISARAN DAN NISBAH SERBUK KEPADA PENGISAR BEBOLA BAGI BIJIH TIMAH MALAYSIA

ABSTRAK

Dalam kajian ini, "Kesan Pengisaran Masa, Kelajuan Pengisaran dan Nisbah Serbuk Kepada Pengisar Bebola Bagi Bijih Timah Malaysia" telah dijalankan untuk mencirikan bahan mentah dan produk giling bijih timah menggunakan XRD, XRF dan SEM-EDX . Sebelum kerja eksperimen, bahan mentah dan produk giling dicirikan menggunakan XRD, XRF dan SEM-EDX. Kerja eksperimen direka berdasarkan reka bentuk faktorial 2^3 + 3 dengan tiga titik pusat. Tiga pembolehubah dalam proses penggilingan adalah masa penggilingan ($\boldsymbol{X_1}$), kelajuan kacau ($\boldsymbol{X_2}$), dan kilang bola hingga nisbah serbuk. Penyelidikan kesan utama dan kesan interaksi antara pembolehubah dianalisis dengan menggunakan ANOVA Minitab 18. Kesan pembolehubah penggilingan pada komposisi unsur dianggarkan oleh XRF. Berdasarkan model statistik yang dihasilkan dari ANOVA, didapati bahawa masa penggilingan ($\boldsymbol{X_1}$) mempunyai kesan yang paling ketara terhadap komposisi unsur diikuti dengan kelajuan kacau ($\boldsymbol{X_2}$). Hasil XRF menunjukkan kehadiran agregate mineral dan komposisi kimia yang berbeza iaitu Si, Al, Si, Fe, As, Mn, Mg, Na, Ti, P, Cu dan Zn. Corak fasa XRD menunjukkan bahawa mineral lain seperti cassiterite, hematite, magnetit, pyrite, arsenopyrite, rutile, stibnite dan ziron hadir dalam analisis XRD. SEM-EDX menunjukkan komposisi elemen seperti besi, kalsium, natrium, aluminium, arsenik dan silika, manakala SEM menunjukkan permukaan morfologi sampel.

THE EFFECT OF MILLING TIME, STIRRING SPEED AND BALL MILL TO POWDER RATIO OF MALAYSIAN TIN ORE

ABSTRACT

In this study, “The Effect of Milling Time, Stirring Speed and Ball Mill to Powder Ratio of Malaysian Tin Ore” has been carried out to characterize raw material and milled product of the tin ore sing XRD, XRF and SEM-EDX. Prior to experimental work, raw material and milled product was characterized using XRD, XRF and SEM-EDX. The experimental work is designed based on $2^3 + 3$ factorial design with three central point. The three variables in the milling process were milling time (X_1), stirring speed (X_2), and ball mill to powder ratio. The investigation of main significant effect and interaction effect between variables were analysed using ANOVA Minitab 18. The effect of milling variable on elemental composition was estimated by XRF. Based on the statistical model generate from the ANOVA, it was found that milling time (X_1) has the most significant effect on the elemental composition followed by the stirring speed (X_2).The XRF result showed the presence of different aggregates of minerals and chemical composition that are Si, Al, Si, Fe, As, Mn, Mg, Na, Ti, P, Cu and Zn. XRD phase pattern showed that the other minerals such as cassiterite, hematite, magnetite, pyrite, arsenopyrite, rutile, stibnite and zircon are present in the XRD analysis. SEM-EDX showed the elemental composition present such as iron, calcium, sodium, aluminium, arsenic and silica, while SEM showed the morphological surface.

CHAPTER 1

INTRODUCTION

1.1. SIGNIFICANT OF RESEARCH WORK

Peninsular Malaysia was one of the biggest and most vital tin makers in the world within the south Asian Tin Belt, before the collapse of the tin-value which lead to the closure of many tin mines in 1985. Gunung Paku near Klian Intan, Perak, is an essential tin store in Malaysia mined since 200 years back, contributing 3-5% of tin metal and over 70% of the Malaysian tin came from the hard rock mining activities (Ariffin, 2009)

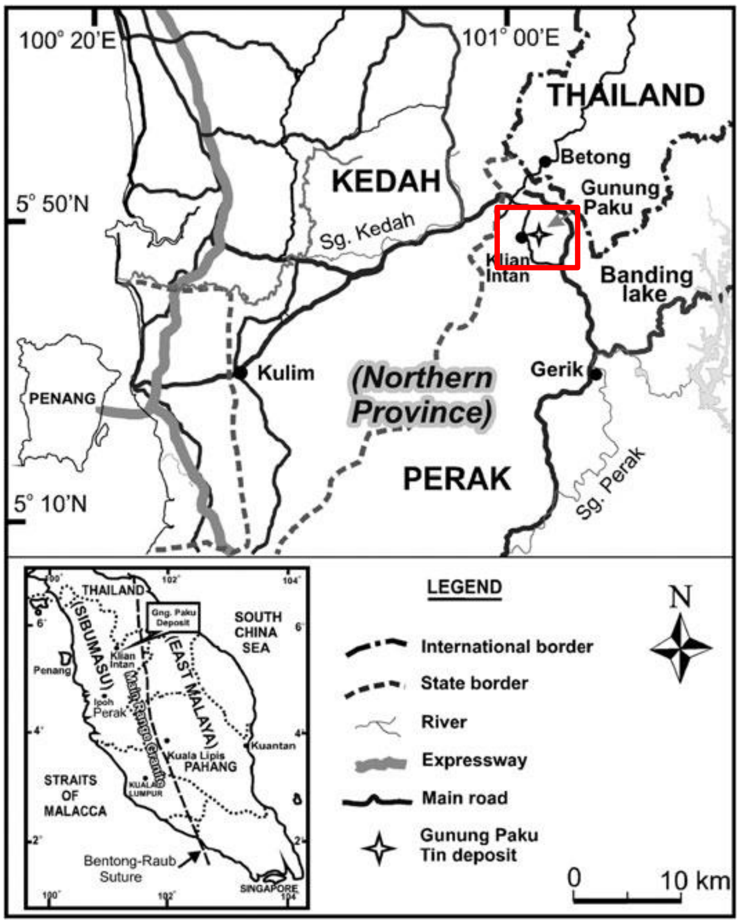

Figure 1.1: Map of Gunung Paku Tin Deposit (Ariffin, 2009)

Cassiterite (SnO_2), also known as a tinstone, has a commercial value which is only tin mineralthat is in sufficient abundance in earth’ s crust. Cassiterite contains 78.6% tin when chemically inert but the tin content varies between 73-75% when contaminated with impurities. The main commercial tinfields of the world are as follows: Burma, Siam, Malay states, and Indonesia; Weat of England, Britanny, and Erageburge; Bolivia; Nigeria; Autralasia; and Southern Africa (Falcon, 1982)

Tin is one of the main economic mineral in Klian Intan, Perak which is mainly mined from the oxide zone that comprises soft and hard rock overburden by open cut mining. The most common metallic minerals associated with tin mineralization is arsenopyrite, pyrite, and minor chalcopyrite, hematite, pyrrhotite, chalcocite and trippkeite, covellite, scorodite and other secondary ironoxyhydroxide. Otherwise, the other slightly occurences include trace amounts of complex lead-bismuth-antimony-molybdenum bearing minerals (Ariffin, 2009).

Perak and Selangor has been discovered in the mid- 19th century as a rich tin fields and high demand of tin was two main factors contributed to the rapid development of the Malayan tin industry. In October 1985 the world tin industry collapsed causing more than 50% price of tin fell (Yap, 2007).

Characterization of mineral phases is important in order to determine which processes are suitable to beneficiate the ore and what kind of technique should be use to extract the ore in mine. The information about the composition of an ore sample can be provided by X-Ray Diffraction techniques in terms of quantification of crystalline phases and also amorphous content. Modern quantification analysis by using a Rietveld Refinement are an attractive alternative as they do not require any standards and offer impressive accuracy and speed of analysis (Macchiarola *et al.*, 2007)

1.2. OBJECTIVES

The objectives of this research are:

i. To investigate the significant effect of the grinding variable on the tin milled product using ANOVA.
ii. To characterize raw material and milled product using XRF, XRD and SEM.

1.3. PROBLEM STATEMENT

The aim of this project is to characterize the received sample of tin ore in the form of cassiterite. Tin occurs in the form of cassiterite (SnO_2)and associated with other minerals either heavy metal or gangue mineral. Most of tin ores are concentrated within oxide, i.e. moderately to highly weathered profile of the area. Alluvial and placer deposits are the major sources of ore bearing cassiterite in Malaysia. This characterization covers the study of morphology features such as shape, size, growing patterns, as well as detailed in morphology analysis.

The detailed specification of mineral characteristics, both composition and texture, is most important for the optimisation of concentrator performance, but such information has been difficult to collect. Such information can been applied in studies of the fundamental mineral processing operations of liberation and separation. These include specific applications aimed at solving a particular plant problem, more general work aimed at defining the significance of mineralogical parameters to processing performance, and fundamental studies of the role of mineralogy in the mechanisms of different treatment processes (Sutherland and Gottlieb, 1991).

Tin oxide carrying a lot amount of impurities can affect its purity and it can cause decreasing in tin price. In order to produce higher grade of tin, suitable process to remove the impurities should be determine by the processing engineer. Therefore, it is important to study about quantitative analysis of tin ore in Malaysia to get information of the characterization phases of the tin ore.

1.4. SCOPE OF STUDY

The scope of this research will be performed using the sample of tin ore from the Rahman Hydraulic Tin Sdn. Bhd. The raw material and experimental product will be characterize and analyseby using loss of ignition (LOI), elemental composition using X-Ray Fluorescence (XRF), phase identification and quantification using X-Ray Diffraction (XRD), morphological study using optical microscope and Scanning Electron Microscope (SEM-EDX).

Sieve size analysis was conducted in this project to get the maximum efficiency by determine the optimum or suitable size of the feed to the process and also to reduce any losses that may occur by determine the size range (Wills and Napier-munn, 2006).

After sieve size analysis done, these samples were proceed to next step which is grinding process. Grinding process were design by design of experiment (DOE) using Minitab 18. Then the milled product were characterized in order to investigate the effect of grinding parameters,phase identification and quantificatiom by using X-Ray Diffraction (XRD) and elemental composition by using X-Ray Fluorescence (XRF).

1.5. THESIS ORGANIZATION

The main content in this thesis are five chapters which is include introduction, literature review, methodology, results and discussion and the last chapter is conclusion and recommendation.

Chapter one give some information about the research background, significant of the project, objectives, problem statement, and scope of study in this work. The next chapter is literature review on previous work and the information about works regarding the work project.

The following chapter is methodology that give details about the method and the arrangement of the project in a particular ways starting from the early stages until the last steps to accomplish the objectives research.

Result and discussion are the important part in this chapter which is recorded in Chapter Four. All the result of preparation work, experimental work and characterization of raw material and milled product were discuss in this chapter.

Last but not least, the conclusion is made based on the results and the discussion in this research. The recommendation for the future work also being discussed in this chapter.

CHAPTER 2

LITERITURE REVIEW

2.1. INTRODUCTION

In the history of world metallurgy, tin has been discovered as one of the preliminary known metals. Tin becomes more and more essential in human being and also in production that contributed to the fast development. In (Xu, Qin and Liu, 2012) state that most of the tin occur as cassiterite, meanwhile the other fraction may also occur as cassiteriteterite, stannite, mawsonite, and other tin sulphides. During the various steps of mineral processing, these tin sulphides have almost identical behaviour to pyrite (Rosenqvist *et al.*, 2009).

Floatation is widely used to beneficiate sulphide minerals and also known as a more productive mineral processing method. Other methods used to separate cassiterite from associated gangue minerals are gravity concentration and magnetic concentration (Xu, Qin and Liu, 2012). Even so, recovery and concentrate grade by these methods are distant from fulfilment (Chen *et al.*, 2005).

Due to low high grade ore in the world and lot of loses of mineral values during processing, it is crucial to develop efficient and more productive processing routes in order to recover valuable minerals from ore. However, to process the ore it is not quite straightforward, due to the fact that cassiterite as the main mineral of tin is fragile, and is easily overground (Mamontov *et al.*, 2007).

Fine cassiterite is hard to recover by the process mentioned up above. Occurrence of minerals, fine grain size and distribution in ore are other factors linked to the difficulties associated with this type of ore. Many earlier experiments have been attempt to develop techniques for concentration of very small particles of cassiterite was limited to laboratory tests, which were lack of pilot plant study and resulted to very little commercial success.

The difficulty lies in assuming the effectiveness or productiveness of a technique-irrespective of quality of ore and lack of pilot plant study (Fandrich *et al.*, 2007). Therefore, characterization of the ore was not systematically investigated prior to processing of the ore. On this point, the present work involves sufficient characterization of the ore, which is essential for process selection through laboratory and pilot plant tests.

2.2. HISTORY OF TIN MINING IN MALAYSIA

2.2.1. Discovery of Tin Ore

The main factors that contributed to the rapid development of the Malayan tin industry in the mid-19th Century are discovery of rich tin fields in Perak and Selangor and also due to high demand of tin because of the development of tin canning. By the end of the 19th Century, Malaya was already the world's largest tin producer. In Malaya, tin ore has been mined for centuries. In 1848, Long Ja'afar was the first man discovered massive deposits of tin ore in Larut, Perak, and he also begin the development of the mining industry in Malaya (Wilkinson, June 1934).

Chinese miners has been employed by Long Ja'afar to mine his land. The result of investment in the mine by Chinese merchants from the Straits Settlements caused to the increasing of Chinese immigrants. Meanwhile, discovery of tin ore deposit in Kinta Valley in Perak made it became the richest tin deposit in the world. Large deposits of tin were also found in Selangor.

2.2.2. Fall of the Tin Industry

Conflicts between Malay Chiefs and their respective Chinese partners in 1865 led to Larut War and resulted to decreasing of tin production. In Selangor, similar cases also happened. Disruption of tin supply because of the war led to the intervention of British in 1874(Yap, 2007).

The world of tin industry collapsed in October 1985 because of the price of tin fell by more than 50%. The other factor is there has been no new discovery of tin fields. Previously, most of the tin mining land was owned by the government. Furthermore, converting agriculture land for mining has become too expensive.

2.3. GEOLOGY OF TIN

2.3.1. Tin

Tin is named from the Anglo-Saxon tin from the metal and in periodic table the symbol used for tin is Sn for stanum comes from Latin. Meanwhile, cassiterite known as kassiteros in Greek (Christie and Brathwaite, 1989). Cassiterite (SnO_2) also known as tinstone can be considered as the only economically important tin mineral in the earth’s crust that has a commercial value.

Chemically pure cassiterite, which is rare, contains 78.6% while contaminated cassiterite with impurities contains varies tin content between 73% and 75% (Falcon, 1982). Other than cassiterite as a predominant ore mineral in tin, stannite (Cu_2FeSnS_4), tellite ($PbSnS_2$), cylindrite ($Pb_3Sn_3Sb_2S_{14}$), canfieldite (Ag_8SnS_6), and franckeite ($Pb_5Sn_3Sb_2S_{14}$) are small amount of mineral recovered from other tin-bearing minerals (Resources *et al.*, 1802). Common mineral associate in tin ore is tungsten; gold is generally absent, other mineral such as silver and molybdenum are also present in some deposit (Christie and Brathwaite, 1989).

Based on the research by (Ariffin, 2009), the common metallic minerals associate in tin mineralization are cassiterite, pyrite, chalcopyrite, arsenopyrite, rutile, trippkeite ($CuAsO_4$), covellite, scorodite and other secondary iron-hydroxide. Minor minerals occurrences are include complex lead-antimony-bismuth-molybdenum bearing minerals.

2.3.2. Chemistry of Tin

In a periodic table, tin is a metallic element belonging to group IVA (or 14). Atomic number of the element is 50 with an atomic mass of 119. The oxidation state of tin is -2, +2 and +4. Natural occurring isotopes of the elements are $Sn^{112}, Sn^{114}$to Sn^{120}, Sn^{122} and Sn^{124}. The mot abundance isotopes are Sn^{120}, Sn^{118} and $Sn^{116}$with respective mass 32.97%, 24.01% and 14.244% (Pb, 1997).

Table 2.1 Properties of Tin (Christie and Brathwaite, 1989)

Symbol	Sn
Atomic No.	50
Atomic Weight	118.69
Specific Gravity	5.77, 7.29
Valance	4.2
Melting Point	231.9℃
Boiling Point	2270℃
Crustal Abundance	2.5ppm
Preferred Analysis Method	X-ray Fluorescence Spectroscopy
Routine Detection Limit	4 ppm

Tin is relatively rare metal that is malleable, silvery and not simply oxidized in air. It has two allotropic forms, ordinary tin or white tin and grey (α) tin. Tin beta tin (ß-tin) also known as a white tin is silvery-white, has a tetragonal structure, malleable and stable at and above room temperature. It is somewhat ductile, soft and moderately heavy metal with a highly crystalline structure. This form of tin is easily melted at temperature 232˚C, non-toxic , extreme fluidity in the molten state, has excellent wetting characteristic and low coefficient of friction.

Grey tin is an amorphous formed at temperature below 13.2˚C by cooling of high purity white tin. It is brittle and has a crystal structure in a diamond cubic similar to silicon, germanium and diamond. The atoms of this tin form a covalent structure caused the electrons cannot move freely made it form a non-metallic element (Resources *et al.*, 1802; Christie and Brathwaite, 1989).

2.3.3. Mineralization of Tin in Malaysia

Eastern Province granitoid and the Late Triassic Main Range granitoid are the two major granitoid in the geology of Peninsular Malaysia (Gobett, 1973; Hutchinson, 1977; Cobbing, 1986). The Main Range appear in the west of Raub-Bentong suture which is in Peninsular Malaysia and spread out to the central Thailand and the granitoid appear typically S-type and made up biotite granite, which contain characteristics of ilmenite (Schwartz *et al.*, 1995).

The Eastern province consists of granitoid with extensive compositional that known as Permian Triassic. This province has equal levels of I-type monzogranite (metaluminous hornblende-biotite granites) possibly produced from an igneous precursor rock and S-type monzogranite (peraluminous biotite granite) with a metasedimentary.

Tin mineralization in Malaysia always partly associated with granite, that turn to be spinal bone of Peninsular Malaysia in a N-S direction. The other minerals that associated during mineralization of tin is highly concentration is Silicon Dioxide (SiO2), Thorium (Th), Cassiterite (Sn), Rubidium (Rb), Potassium Oxide (K2O) and Uranium (U) (Ariffin, 2009).

2.3.4. Current World Production of Tin

The Southeast Asian Tin Belt is usually the one of huge tin producer in the world. Since 1800 indicated of tin was 9.6 million tonnes, around 54% of world's production of tin majorities from the Southeast Asian countries including Malaysia, Thailand, Indonesia, and Myanmar. South China, Bolivia produce 10% of the tin in the world's production. and Cornwall (England). Rondonia tin in Brazil provide only 2% of the world's tin production may be the tin-producing giant the future. The biggest ore reserve and the production of tin increasing in certain recent years (Schwartz, 1995).

There are five tectonostratigraphic that recognized in Southeast Asia gradually gathering in the Mesozoic and Paleozoic ages. Sibumasu block (Sino-Burma, Malaya and Sumatera) and on the East Malaya block which are The Southeast Asian Tin Belt were located. Other a fault-bounded area or region with a characteristic stratigraphy are southwest Borneo, South China and Indochina. (Rajah, 1995).

2.3.5. Occurrences in Nature

Cassiterite is really a limited within nature. It basically related to granite during the formation of tin were intruded and molten into formation of sedimentary rocks. When granite was formed along the quartz vein and it from liquid state to solid state and finally become a vein which contain lots of metals ore. Cassiterite usually in the proper execution of sulphide and it associated with a few minerals (The International Tin Council, 1974).

80% the world production of tin reveals the effect were originate from the alluvial and eluvial deposits however not from the primary deposits. Cassiterite having a higher specific gravity, great resistance in mechanical and chemical weathering. The concentration of the tin minerals from the primary deposit may be the be a consequence of the tin-bearing vein and erosion of the host rock (Barry, 1983).

The minerals are going to be shifted by weathering processes and water to the stream or river. Collection of valuable minerals formed by process during sedimentary process to be collected in a place, the minerals particle must be dense than other minerals such as quartz. The cassiterite move in short distance from its sources since there are not as advanced in the weathering of granite as the crystal structure of cassiterite are rounded and smooth by the action of water. 0.015% of tin that produced from the alluvial deposits, elluvial deposits indicate a nearby supply of primary ore (The International Tin Council, 1974).

2.4. USES OF TIN

2.4.1. Industrial Uses

Almost without exception, tin is used in alloys. Tin is a metallic mineral, however it is rarely used in the elemental form because at temperature below 13.2 °C it is decomposed (Sainsbury, 1973). Tin can be incorporate with copper more than 28 percent, but only 10% yield an optimum-strength alloy and only 2% tin can harden copper (Resources *et al.*, 1802).

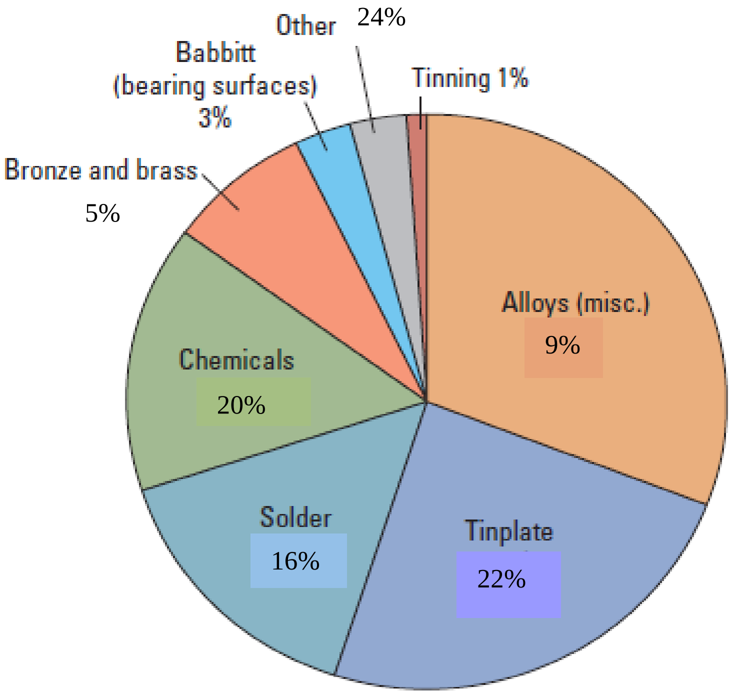

Figure 2.1.1: Total consumption of Tin in the United States in 2016 (US Geological Survey, 2017)

Figure 2.1 show the pie chart of major and uses of tin as a percentage of total consumption in the united states in 2016. US consumption of tin by end-use category was in cans and containers, 23%; construction, 18%; transportation, 17%; electrical, 12%; and other, 30% (US Geological Survey, 2017)

2.5. INTRODUCTION ON APPLIED MINERALOGY

2.5.1. Particle Size Analysis

Particle measurement influences several qualities of particulate components and is a valuable sign of quality and performance. Especially for powders, suspensions, emulsions, and aerosols. The measurement and model of powders influences flow and compaction properties. Greater, more round particles may usually flow quicker than smaller or high part ratio particles. Smaller particles reduce more quickly and lead to raised suspension viscosities than larger ones. Smaller droplet shapes and higher surface charge (zeta potential) may usually increase suspension and emulsion stability. Powder or drops in the product range of 2-5µm aerosolize better and may enter in to lungs greater than larger sizes. For these and a great many other reasons it is important to evaluate and get a grip on the compound measurement distribution of many products.

Measurements in the lab in many cases are built to aid unit operations taking devote a process environment. The most apparent case is milling (or measurement reduction by another technology) where in fact the purpose of the function is to reduce particle size to an ideal specification. Many other size reduction operations and technologies also involve lab measurements to track improvements in particle size including crushing, homogenization, emulsification, microfluidization, and others. Separation steps such as screening, filtering, cyclones, etc. may be monitored by calculating particle size before and following the process.

Particle size growth may be monitored all through operations such as granulation or crystallization

2.5.2. Elemental Analysis of X-ray Fluorescence

XRF is an analytical method that is precise, quickly and non-destructive to ascertain the substance arrangement of all kinds of materials. Often it needs just a minimum of sample preparation. The detail and reproductivity of XRF analysis is quite high. Very precise results are possible when good standard specimens are available, but also in applications where no specific standards can be found. The measurement time is dependent upon the amount of aspects to be determined and the required accuracy and varies between seconds and 30 minutes. The analysis time after the measurement is just a few seconds.

Brief details will be made on the concepts of X-ray fluorescence emission from the sample and on the XRF technique. Every time a material is irradiated with X-rays, inner-shell electrons of the constituent atoms are thrilled and removed. The atoms become ionized by losing their internal electrons, therefore electrons from outer shells decline to the vacancies left by the departed electrons. There's surplus power occurring with this event, i.e. a quality X-ray, named a fluorescent X-ray, and it's inherent to each type of element. Since their wavelength is constant with regards to the element type, fluorescent X-rays could be effectively useful for identification of elements and like work (Takahashi, 1996).

X-ray can be seen as beams of photons with associated energies or as electromagnetic waves with their associated wavelengths. Radio waves, light and gamma rays are another electromagnetic wave. Figure 2.2 shows the X-rays have wavelengths and energies between gamma rays and ultra violet light. The range of wavelength X-rays are in between 0.01 to 10 nm, which the range are equivalent to energies from 0.125 to 125 keV.

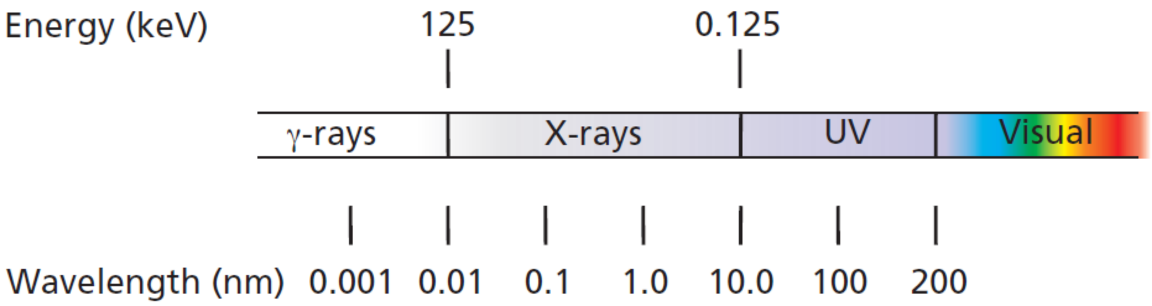

Figure 2.2: X-ray and other electromagnetic waves

X-rays photons may interact with the electrons in matter by three different mechanism as shown in Figure 2.3 and 2.4. First, when matter absorb the incident x-ray photon and then produces electron on X-ray photons it'll influence the photo-electric. 2nd, Compton spreading, where in fact the spreading of the incident X-ray photon is followed closely by some power transfer to the electron (inelastic scattering). Last but most certainly not least, Thomson (elastic) spreading where in fact the dispersed X-ray photons have the exact same power as in the incident beam. The photoelectric influence is more crucial than Compton spreading at a low energy (Rouzière, Bazin and Daudon, 2016).

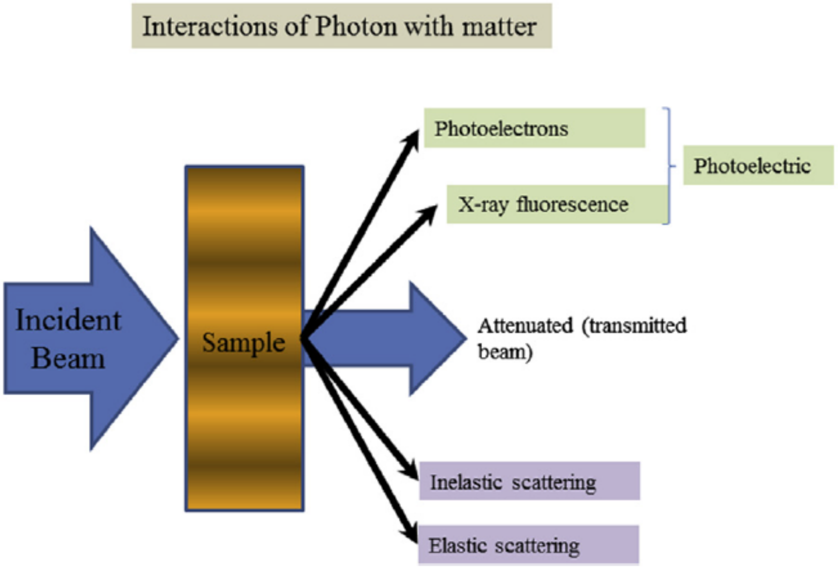

Figure 2.3: Schematic representation of the different interactions between X-rays and matter

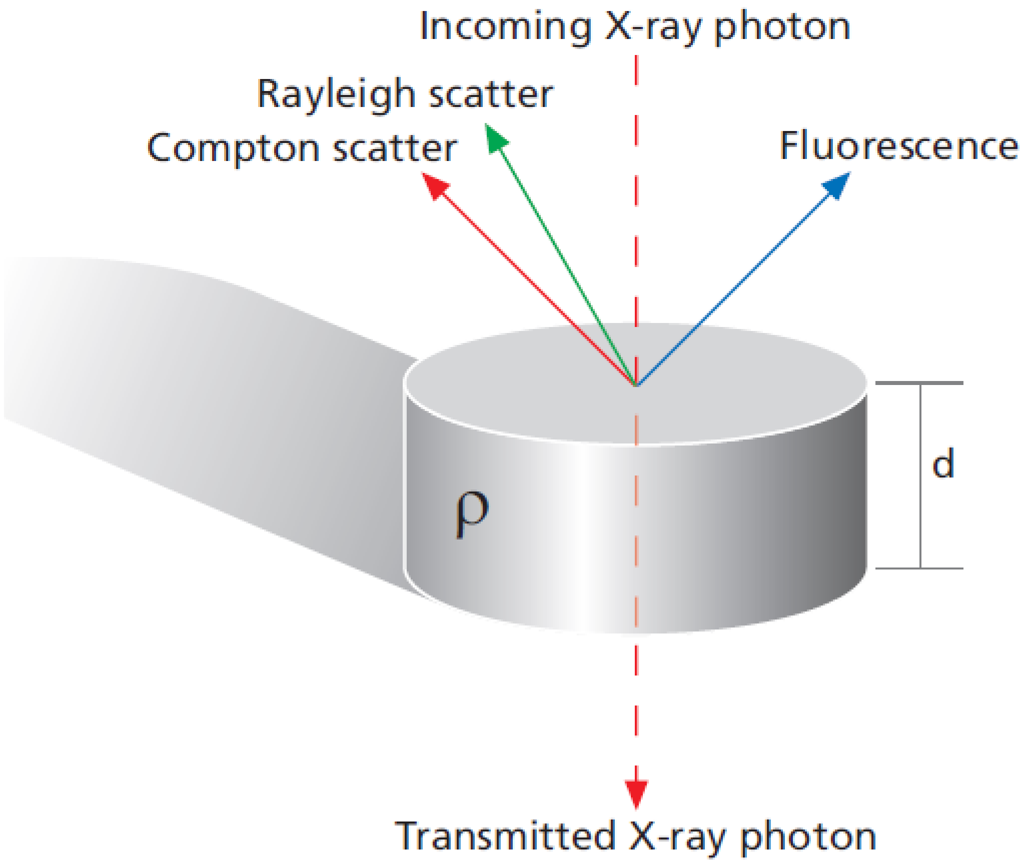

Figure 2.4: Three main interactions of X-ray and matter

In the XRF process, the qualitative and quantitative analyses of components found in a material are performed by doing spectral examination of fluorescent X-rays produced from the substance. A crystal spectroscope is principally employed for this spectral analysis. In quantitative examination, however, because a number of factors be determined by the X-ray wavelength such as absorbtion as a result of air, crystal reflecting power, fluorescence excitation effectiveness and counter effectiveness, these factors entail a lot of modifications to be made. Typically, the qualitative and quantitative analyses of heavy elements existing among light eleemnts may be easily carried out. Automatic rating can be easy, so their analytical techniques are helpful for managing large quantities of oxides, etc.

2.5.3. Identification and Quantification Using X-ray Diffraction

2.5.3.1. X-ray Diffraction

In 1913, Von Laue and Bragg father and son were discovered X-ray diffraction and also establish the popular Bragg formula,

$$2d \sin \Theta = n\gamma \text{ ………………………………. Equation 1}$$

Where,

n is a positive integer,

γ is a wavelength of the incident X-rays,

d is the atomic lattice interplanar distance,

Θ is angle corresponding to the constructive interferences of scattered wave.

The X-ray diffraction pattern is measured through a collection of diffraction peaks at different Bragg angles 2Θ, their angular positions and intensities being intimately related to the spatial arrangement of atoms. Figure 2.5 show to illustrate the corresponding diffraction patterns (Rouzière, Bazin and Daudon, 2016)

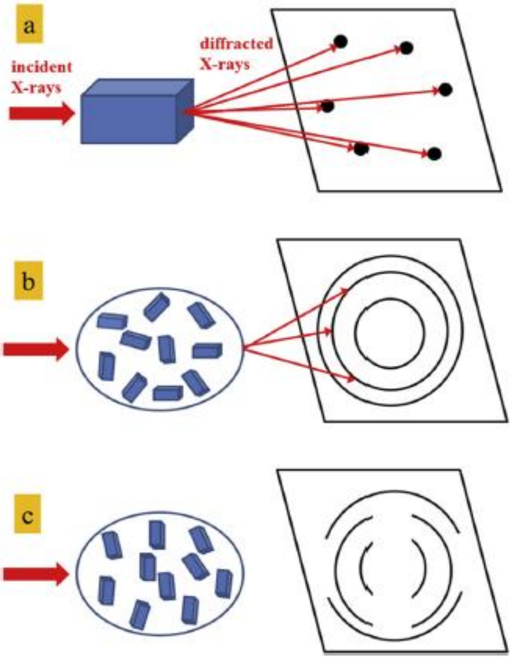

Figure 2.5: Schematic representation of the diffraction patterns on a plane detector from a (a) single crystal, (b) polycrystalline powder, (c) preferential oriented powder.

Information that can be collected from XRD data such as its microstructure or its texture and the crystallography. Usually XRD is used for phase identification by comparing the values of diffracted peaks with the ones tabulated in a database and can also determine the structure of a new compounds.

2.5.3.2. Rietveld Refinement Using XRD Data

The Rietveld technique analyses calculated vs experimentally derived X-Ray powder diffraction pattern for a phase modifying a wide-variety of crystallographic, chemical and modalabundance variables until the two come in agreement. The Rietveld method is a full-profile (rather than single peak), diffractogram-fitting technique that generates calculated diffractograms and attempts to match these to experimentally derived ones (Macchiarola *et al.*, 2007).

The strengths of the Rietveld technique are; (i) cost effective; (ii) relatively fast; (iii) suitable for homogeneous or heterogeneous sample; (iv) works with powdered materials; (v) effective at distinguishing between phases that may only differ subtly from one another and; (vi) capable of producing quantitative modal abundance for the phases being analysed (< 1 %).

Some limitations in Rietveld technique are include require atomic structure of phase to be known, if phases are missing, the results are relative weight percentages, not absolute weight percentage, and sometimes difficult to extract model data for samples containing two or more minerals of the same family. Best results are obtained when one has an understanding of mineralogy, crystallography and both the overall philosophy and approach to a successful Rietveld analysis.

The result of calculated X-ray diffraction profile that best fits an experimental one, both in terms of intensity, peak position and peak shape. For samples with amorphous content, a known quantity of an internal standard may be incorporated in the sample to calculate a weight fraction of amorphous content in addition to quantifying the crystalline phases.

2.5.4. Design of Experiment using ANOVA

The objective of the design of experiment (DOE) using ANOVA is to determine the influence of factors on output response and also to determine which variables are most influential on the output response (y). By using design of experiment, the effects of uncontrollable variables (z) can be minimized by setting the influential (x) (Shekhar). Figure 2.6 show the model of process of design of experiment.

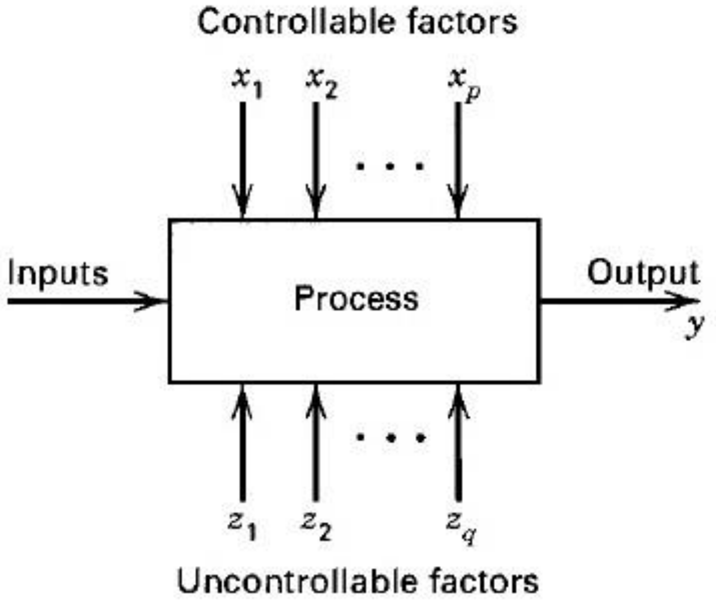

Figure 2.6: General model of a process or system

2.5.3.3. Full Factorial Design

Full factorial design is known as the most common and impulsive strategy of experimental design. The two-levels full factorial is the most simple form, there are k factors and L = 2 levels per factor. The samples are given by every possible combination of the factors values. Therefore, the sample size is N = 2^k. In this project the level used was three level. The three levels are called high (“h”), medium (“m”), and low (“l”) or, (“+1), (“0”) and (“-1”) (Cavazzuti, 2013).

Table 2.2.2: The example of 2^3 full factorial of experimental design

Experiment number	Factor level			Response variable	Two- and three-factors interactions			
	X_1	X_2	X_3		$X_1 \cdot X_2$	$X_1 \cdot X_3$	$X_2 \cdot X_3$	$X_1 \cdot X_2 \cdot X_3$
1	$-1\ (l)$	$-1\ (l)$	$-1\ (l)$	$y_{l,l,l}$	+1	+1	+1	−1
2	$-1\ (l)$	$-1\ (l)$	$+1\ (h)$	$y_{l,l,h}$	+1	−1	−1	+1
3	$-1\ (l)$	$+1\ (h)$	$-1\ (l)$	$y_{l,h,l}$	−1	+1	−1	+1
4	$-1\ (l)$	$+1\ (h)$	$+1\ (h)$	$y_{l,h,h}$	−1	−1	+1	−1
5	$+1\ (h)$	$-1\ (l)$	$-1\ (l)$	$y_{h,l,l}$	−1	−1	+1	+1
6	$+1\ (h)$	$-1\ (l)$	$+1\ (h)$	$y_{h,l,h}$	−1	+1	−1	−1
7	$+1\ (h)$	$+1\ (h)$	$-1\ (l)$	$y_{h,h,l}$	+1	−1	−1	−1
8	$+1\ (h)$	$+1\ (h)$	$+1\ (h)$	$y_{h,h,h}$	+1	+1	+1	+1

The advantage of full factorial designs is that they make a very efficient use of the data and do not confound the effects of the parameters, so that it is possible to evaluate the main and the interaction effects clearly. On the other hand, the sample size grows exponentially with the number of parameters and the number of levels (Cavazzuti, 2013). Figure 2.7 show the graphical representations for the 2^2, 2^3 and 3^3 full factorial design.

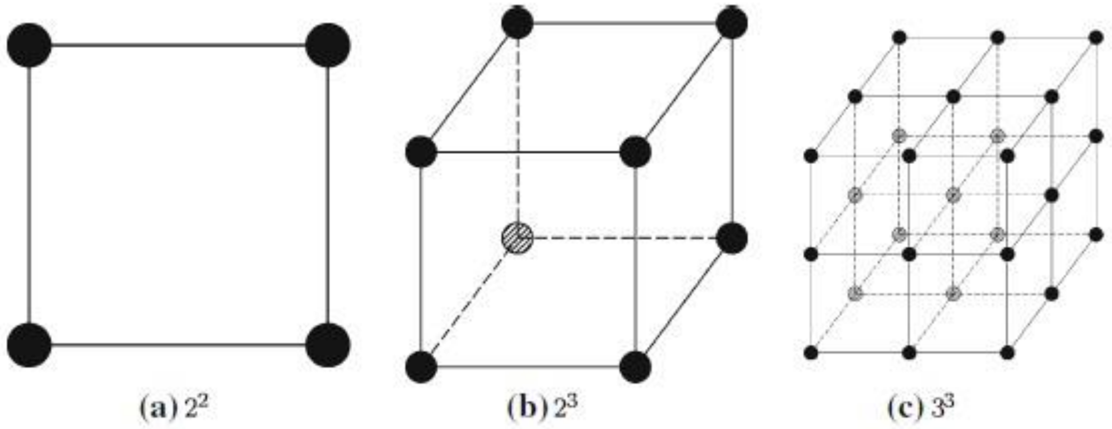
(a) 2^2 (b) 2^3 (c) 3^3

Figure 2.7: Example of L^k full factorial Experimental design

2.6. Site Background Description

2.6.1. Rahman Hydraulic Tin Sdn.Bhd. (RHT)

Rahman Hydraulic Tin Sdn Bhd (RHTSB) is one of the largest tin mine in Malaysia and also the only one that operate in open pit method. It located at mountainous area in old town Klian Intan, Hulu Perak, and have mining lease area at least 600 hectares. These areas are rich with minerals Cassiterite (SnO_2), Pyrite (FeS) and Hematite (Fe_2O_3).

Ores mining operation in Klian Intan ware believed start more than 300 years ago (1689). From the history note that found in 1800s, mine operation was carry out by Perak Royal family. At the early stage, this area was been conflict between Perak and Patani. When Tuan Toh Leh from Patani declares himself with title “Raja Reman”, he attacks Perak in year 1821. Both of them claim that area was their territory. Almost of the north area of Malaya were under Siamese power and when this conflict happen, the war was happen. After a long time war, finally this area was fall in Siamese territory and Raja Reman success to control Klian Intan mine.

When the British came to Malaya in 1903, they also show their interest to this area. In 1905, two European descend from British known as Mr Kemp and Mr Pearce, and both of them establish “Rahman Hydraulic Company Limited” and “Rahman Hydraulic Tin Company”. They form mining lease from Siamese to mine in that area. In 1907, both of them merge their company and known as “Rahman Hydraulic Tin Limited”. It was established in 30th May 1907. The conflict between Siamese and Perak was ended in 1909 when Siamese agree to sign the Anglo Declaration. In this declaration, the mine area will be give back to Perak territory with conceal from British. In the real situation, British still controlling the mine and all of the profit will go to British.

The mining operation was stop for a while when Japan attacks Malaya and continue back after the World War II. In 15th April 1966, the company changes their name to “Rahman

Hydraulic Tin Berhad", and Rahman Hydraulic Tin Berhads shares were listed into Kuala Lumpur Stock Exchange (KLSE) Main Board in 16th August 1973. Lastly, in 2004 the company change their name to "Rahman Hydraulic Tin Sdn Bhd" after Malaysia Smelting Corporation Berhad (MSC) one of the world‟s largest integrated producers of tin metal and tin-based product was acquisition of a 100% interest in RHTSB.

2.6.2. Geology of Tin Deposit of Gunung Paku in Rahman Hydraulic Tin Mine (RHT)

Gunung Paku in Palaezoic age belong to Baling Formation is mainly overlain with thick sequences of metasedimentary rock.

Figure 2.8 show the general geology of the Gunung Paku and its vicinity. The location of the Gunung Paku tin deposit of the Rahman Hydraulic Tin Sdn. Bhd located in the upper part of Perak state, near the Thailand border. The mine pit is located at about 5°38N, 101°50E which covers an area about 3 km x 1 km. The main rock beds overlying the mine open pit area are slate and silicified, while the north of the mine pit is phyllite. Formation of the superficial deposits that comprise recent river alluvium and old alluvium are due to mining activities, erosion and deposition (Ariffin, 2009).

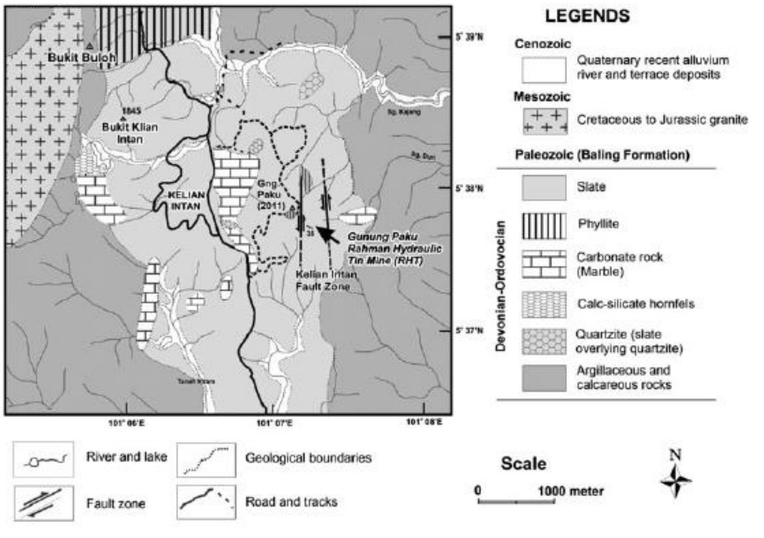

Figure 2.8: Geological map of the Gunung Paku tin deposit and Klian Intan area (Ariffin, 2009)

The tin-bearing zone at Gunung Paku obviously belief as structurally controlled mineralization and stratabound distribution. To be able to employed the mineralization zone, parameter such as for example mineralogy (alteration and sulphide minerals), colour of the mineral, concentration and the occurrence of the cassiterite must be looking attentively. Structurally, Gunung Paku tin deposit referred to as the Intan fault zone is clearly restricted in a mistake zone around 200–300 m wide (Khoo, 1989).

Cassiterite are the main ore of tin, it's among the abundant minerals in the planet earth crust and among a hardly any tin minerals. Tin are commonly occurring in high-temperature hydrothermal veins and commonly associated with siliceous igneous rocks. There are a common minerals associated during mineralization of tin such as quartz, bismuth, muscovite, wolframite, tourmaline, fluorite, arsenopyrite, and molybdenite. The most popular alluvial minerals contain in areas of several greisens is cassiterite. Greisen is the coarse-grained rock contain these minerals and formed by hydrothermal alteration of granitic rocks (Ariffin, 2009).

CHAPTER 3

METHODOLOGY

3.1. INTRODUCTION

This chapter will discuss and describes the flow of research work, procedure and steps of sample preparation, raw material, the experimental work and characterization of raw material and mill product. The sample used in this project is from Rahman Hydraulic Tin Sdn.Bhd.

Firstly, the received sample from Rahman Hydraulic mine will be taken for sampling and the sampling method used is cone and quartering. After sampling process is done, the sample was sieve to determine the size range. Then, the sample will be separated into two sections for a while which is Sample A (sample size 10 mm and above) and Sample B (sample below 10 mm) The sample size 10 mm and above will be liberated into smaller size using secondary crushing. After that, sample A and B will recombine again and undergo sieving process for the second time to determine the sieve size distribution.

The order of experimental work was decided by using Minitab 18 software. This software was used to design the experimental work which is milling process by manipulated the input in order to get the desired output. Eleven samples were run to complete the overall design.

Characterization of raw material and the mill product was an important study in this project. The raw material was characterized by using X-ray Fluorescence, X-ray Diffraction, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy. SEM was used to observe the morphology and texture of sample, while EDX provides the chemical composition of a material. Elemental composition of mineral also can be determined by using X-ray Fluorescence. Flowchart representing the overall experimental work conducted in this project can was shown in Figure 3.1.