SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

ACID LEACHING OF AMANG FOR EVENTUAL RECOVERY OF TITANIUM UNDER DIFFUSION LIMITED SYSTEM

By

MOHAMAD AMIR SYAFIQ BIN MANSOR

Supervisor: Dr. Norazharuddin Shah Bin Abdullah

Dissertation submitted in partial fulfillment

of the requirements for the degree of Bachelor of Engineering with Honours

(Mineral Resources Engineering)

Universiti Sains Malaysia

JUNE 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Acid Leaching of Amang for Eventual Recovery of Titanium Under Diffusion Limited System**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any examining body, institution or university.

Name of student	: Mohamad Amir Syafiq Bin Mansor	Signature:
Date	: 21 June 2017	

Witnessed by

Supervisor	: Dr. Norazharuddin Shah Bin Abdullah	Signature:
Date	: 21 June 2017	

ACKNOWLEDGEMENTS

First of all, I am grateful to Allah S.W.T for the great health and wellbeing given to me that was necessary during the process of completing this whole project. I finally managed to complete this project within the period of time given.

I wish to express my sincere thanks to my supervisor, Dr. Norazharuddin Shah Bin Abdullah for all his guidance, support, suggestion, encouragement and even providing me with all the necessary facilities for the research.

Not to forget, a lot of thanks to all the lecturers for delivering all the knowledge that I personally require in order to work on this project.

I also offer my sincere gratitude to all technical staffs of PPKBSM who have always been helping me with the experimental work as well as providing me with all the laboratory supplies required. Next, big thanks to my parents for the encouragement, support and attention. I am also grateful to my partner who supported me throughout the venture.

Last but not least, I also place on record, my sense of gratitude to one and all, who directly or indirectly, have lent their hand in this project.

TABLE OF CONTENTS

Contents **Page**

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

SYMBOLS

°C	Degree Celsius
%	Percentage
μm	Micrometre
g	Gram
kg	Kilogram
ml	Millilitre
M	Molarity/Concentration

ABBREVIATIONS

XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
LOI	Loss of Ignition
PSD	Particle Size Distribution

CHEMICAL FORMULA

H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid

KEBOLEHLARUTRESAPAN AMANG DENGAN ASID BAGI TUJUAN PENGEKSTRAKAN TERUS TITANIA MELALUI SISTEM PENYEBARAN TERHAD

ABSTRAK

Kebolehlarutresapan 'Amang' dengan asid telah diuji dengan menggunakan asid hidroklorik dan asid sulfurik sebagai ajen larut resap tanpa kehadiran pemangkin. Pengurasan sampel diuji pada keadaan yang paling terhad di mana efek pergolakan tidak disertakan sepanjang perjalanan projekdan kinetik dipelajari melalui sistem penyebaran terhad. Proses pencirian amang dilakukan melalui kaedah yang berbeza termasuklah PSD, XRF, LOI dan SEM. Analisis XRF menunjukkan bahawa wujud beberapa komposisi yang memberikan nilai peratusan yang tinggi termasuklah TiO_2 (34%), Al_2O_3 (15%), SiO_2 (18%), Fe_2O_3 (15%) dan ZrO_2 (8%). Analisis XRD pula membuktikan kehadiran elemen dalam bentuk sebatian kompleks yang mengandungi elemen titania seperti rutil dan ilmenit. Analisis SEM pula membuktikan sebatian kompleks yang mengandungi komposisi titania wujud dalam keadaan bebas daripada elemen asing kecuali besi. Kinetik pelarutlesapan bijih besi dijalankan dengan memanipulasi beberapa parameter seperti kepekatan asid, nisbah cecair dengan pepejal dan suhu. Ujian dijalankan dengan menguji hanya satu faktor pada satu masa. Kepekatan asid pada 4M memberi nilai pengurangan berat sebanyak 1.25% selepas 4 jam. Sementara itu, pada nisbah 1:7 pula memberi nilai hanya 0.56% apabila diuji menggunakan asid dengan kepekatan 2M. Apabila efek suhu pula dikaji, asid pada suhu 80 ^{o}C memberi nilai yang tertinggi iaitu 3.18%. Ujian pada sisa sampel menggunakan analisis XRF memberi nilai peratusan yang sama dengan nilai asal. Manakala analisis XRD menunjukkan bahawa komposisi ilmenit ($FeTiO_3$) telah berubah fasa kepada TiO_2 pada dua fasa yang berbeza iaitu of rutil dan brookite.

ACID LEACHING OF AMANG FOR EVENTUAL RECOVERY OF TITANIUM UNDER DIFFUSION LIMITED SYSTEM

ABSTRACT

Leaching process of ‘Amang’ was carried out by using hydrochloric acid and sulfuric acid as leaching agent without any presence of catalyst. Leaching were tested at the worst condition where no agitation included in the whole process and kinetics was studied under diffusion limited system. Amang was characterized using a few techniques including PSD, XRF, XRD, LOI and SEM. XRF analysis shows that some elements presents in amang give a high percentage by weight including TiO_2 (34%), Al_2O_3 (15%), SiO_2 (18%), Fe_2O_3 (15%) and ZrO_2 (8%). From XRD, major peak shown indicates the existence of major mineral bearing the titanium metal that is rutile and ilmenite. SEM of polished section proves that titanium bearing mineral was already liberated from other elements excepts for iron so it can be leached directly. The leaching was conducted by manipulating different parameters such as acid concentration, solid to liquid ratio and temperature. The novelty of the experiment is to test one factor at a time. At room temperature, two parameters were tested by using different concentration of sulfuric acid and different volume of acid to leach 10g of amang. 4M of acid concentration give higher weight loss of 1.25% after 4 hours of leaching. Meanwhile, ratio of 1:7 gives the highest weight loss of 0.56% when leached using 2M of sulfuric acid for 4 hours. Varying the temperatures, 80 ^{o}C of 2M sulfuric acid give highest weight loss of 3.18% after 4 hours of leaching. Testing the residue of amang after sample using XRF give the same amount of element in weight percent as raw sample. XRD analysis of leached residue shows that ilmenite has been leached because only TiO_2 can be detected in two different phases of rutile and brookite.

CHAPTER 1

INTRODUCTION

1.1 Background

Amang is a local term used for a tailing from others mine which contains heavy minerals that haven't been process by that industry. This is because of the insufficient technology to process that heavy minerals contains in the bulk of ore at that current time. Sometimes, it was because of the price of the mineral that was too low and cause the recovery process is not profitable to the company.

Since the bulk of the ore is all tailing of their mineral industry, amang comes in liberated size particles that are less than 75 microns. Amang was rich of rare heavy minerals such as Zircon ($ZrSiO_4$), Tin (SnO_2), Rutile (TiO_2) and also Ilmenite ($FeTiO_3$). The main titanium bearing minerals was rutile and ilmenite which is also the major constituents of amang.

Acid leaching is one of the extractive metallurgy processes. It is a process of extracting valuable minerals from solid bulk ore by dissolving them into a liquid named acid and leave for a certain period to allow reaction and contacts between the solid and liquid. Examples include the dissolution of gold from a low grade heap of low grade soil. Acid leaching can occur in heap leach pads or in situ.

Under diffusion limited system, leaching is studied at a worst condition where no stirring condition is applied during the test. Kinetics is the study of the movements of the particle or the rate of reaction of the process. There are some weight loss from solid movement to the solution showing there are reaction occurring.

1.2 Problem Statements

Physical processing approaches usually only separates the different type of the mineral but not the titanium element. A pyro metallurgical approach was one of the techniques used to obtain the titanium metal or compounds but there are some problem related to that approaches including high cost for a complete recovery.

The beneficiation of titanium is being actively practiced in the industry by doing hydrometallurgical process where many factors are taken into considerations. Problems rose due to acid and energy consumptions when using this approach.

In this project the acid leaching of amang was studied by altering different parameter at a time. The factor affecting the acid leaching such as acid concentrations, acid dosage by altering the solid to liquid ratio and temperature of reaction were studied.

During the whole leaching process, the optimum time taken for amang to leach in the acid was monitored and the solid residue were analysed to see the reaction under diffusion limited system where no stirring were included. The weight loss and analysis of the residue is discussed to further explain the effectiveness of the leaching project.

1.3 Objectives

The objectives of this project are:

1. To characterize the sample of amang obtained from the site.
2. To investigate the possibility of titanium recovery or enrichment from amang using sulphuric acid leaching.
3. To study the effect of a number of variables (i.e., acid concentration, solid to liquid ratio and the temperature) under diffusion limited system.

1.4 Scope of Study

The study is done by conducting the leaching process without including stirring or agitation effect. 3 different parameters were chosen to be studied including acid concentration, liquid to solid ratio and temperature. For the first parameter, leaching was done using 2M, 3M, 4M and 5M.

Two types of acid were used in the experiment which is hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). Under the same temperature, the leaching was also experimented at different liquid to solid ratio. Finally, the sample was test for leaching under different temperature starting at normal room temperature, 40 ^{o}C, 60^{o}C and 80^{o}C.

The leaching is done by testing one parameter at a time to make it easier and simpler analysis of result. Several analysis were done for both raw sample and solid residue after leaching including LOI, SEM, XRD, XRF, PSA and weight loss of sample. The fraction of solid dissolved in acid was calculated by comparing the final weight of amang with the original weight before leaching being done.

1.5 Flow of Dissertation

This dissertation starts with chapter 1 explaining on the experimental background, problem statements, objectives and scopes of study are cited. Then, followed with chapter 2, where all literature review on acid leaching of titanium bearing ore leaching were previously being done.

Chapter 3 describe all the methodology and the full flow of the project. Next, chapter 4 represented all the results obtained from the experiment and their prior discussion. Lastly, in chapter 5, conclusions were cited and recommendations for future work were included.

CHAPTER 2

LITERATURE REVIEW

2.1 Amang Background

‘Amang’ which is known as a tin tailing, was usually left abundant in ex-mining area. It is rich in heavy minerals containing various rare earth elements (Hamzah, Ahmad and Saat, 2009). Further beneficiation of amang doesn’t have enough technology and the recovery cost that doesn’t allow the process was the reason why amang left as a tailing at that time.

At a point when Malaysia was the biggest exporter of tin bearing ore in the world, the processing of the associated heavy minerals or amang, specifically focussing on titanium bearing mineral including ilmenite and rutile, was also a major industry(Teh and Lokman, 2002). Nowadays, the approach of titanium extraction was getting higher as the increased in demands from industry.

Major constituents of amang are usually heavy minerals. Heavy minerals refers to minerals with a specific gravity (SG) greater than that of quartz (SG = 2.7) (Reyneke and Van Der Westhuizen, 2001). Some heavy minerals like monazite (Ce, La, Nd, Gd, Th PO4), zircon ($ZrSiO_4$), ilmenite ($FeOTiO_2$), xenotime (YPO_4) and struverite ($Nb.Ta.TiO_2$) are used in minerals industries.

Although some species may be more of an environmental concern than others, the leaching process is indiscriminant such that all constituents (e.g., major or minor matrix components as well as inorganic, organic and radionuclide contaminants) are released under a common set of chemical phenomena which may include mineral dissolution, desorption and complexation, and mass transport processes.

2.1.1 Sources of Amang

Usually, former tin mining areas would be rich in ‘amang’, the tin tailing that contained heavy minerals. After years, all of this tailing content will be economically beneficial to the mineral industries. Other researchers found that beach sand and rock are also the mineral resources of heavy minerals other than ex mining area (Hamzah, Ahmad and Saat, 2009).

A lot of amang was produced, in particular in the two main tin producing areas in Peninsular Malaysia, that is the Kinta Valley in the Ipoh area to the north and the Klang Valley in the Kuala Lumpur area to the south (Teh and Lokman, 2002). Amang doesn’t need undergo the process of mineral dressing (processing), also called ore preparation, milling, and ore dressing or ore beneficiation.

2.1.2 Characterization of Amang

The physical characteristics of the heavy minerals usually studied under the binocular microscope, while mineralogical and textures were studied using polished sections under the reflected light microscope. The EPMA (electron probe micro analyser) was later used to identify more precisely the heavy minerals, their intergrowths textures, inclusions and their chemical compositions (Teh and Lokman, 2002)

There is no regular pattern for the mineral content in the soils. Usually, zircon content in amang is higher than ilmenite and monazite. The mineral accumulation that forms those different type of mineral may depend on the activity like smelting process previously, and they was not forming a uniform pattern throughout the area (Hamzah, Ahmad and Saat, 2009).

Titanium rich mineral in amang was usually ilmenite and rutile with the formula of FeTiO3 and TiO_2. Ilmenite in its pure form is $FeTiO_3$, but also often contains some Mg and Mn, so that the formula can be more fully expressed as (Fe, Mg and Mn) TiO3. Fe_2O_3 is usually present in the form of hematite in titanium bearing mineral.

At high temperatures complete solubility exists between Fe_2O_3 and $FeTiO_3$, but miscibility decreases at low temperatures resulting in exsolution products as previously described. Ilmenite may also contain considerable amounts of Fe_3O_4, and sometimes also Al_2O_3, in solid of grains at high temperatures.

Ilmenite has a theoretical composition of 52.7 % TiO_2 and 47.3 % FeO based on calculation. Some of the ilmenite grains in the sample under investigation appear optically essentially unaltered and micro-analyses of these grains are comparable to the composition of theoretical ilmenite (Reyneke and Van Der Westhuizen, 2001).

Table 2.1: Number of grains of individual heavy minerals from sample locations in the Kinta Valley (Teh and Lokman, 2002)

Sample	**Ilmenite**	**Monazite**	**Zircon**	**Topaz**	**Rutile**	**Pyrite**
1	60	1	2	13	11	30
2	160	6	80	19	21	50
3	92	2	10	14	1	35
4	32	20	2	0	32	15
5	31	0	0	5	31	12
6	42	5	3	5	42	23
7	77	4	21	0	17	10
8	85	13	101	14	98	1
Total:	479	51	217	70	243	176

2.2 Production and Uses of Heavy Mineral in Amang (Titanium)

The unique properties of heavy metals is dominantly expanding its application especially titanium are needed to supply the required functionality in many high-tech components, green technologies and material industries of high-temperature superconductors, secondary batteries, hybrid cars, etc. (Jha *et al.*, 2016). Titanium is the ninth most abundant element and occurs mainly in a form that can be mined as ilmenite (FeO. TiO2) (95%) and rutile (TiO2) (5%) minerals. The current world production capacity of ilmenite and other titanium feed stocks for production of titanium oxide pigment, titanium metal, welding electrodes etc. is around 7 million tonnes per annum (Sahu *et al.*, 2006).

2.2.1 Industry Demand

All valuable minerals contains in amang have various uses in industries depending on their unique properties. For example, Zircon is a valuable mineral used as raw material in various industries such as foundry, ceramics, and refractory. In Bangladesh, almost 300 tonnes of zirconium flour is consumed every year in ceramic industries which are the entire amount being currently imported. Ilmenite fines is a by-products generated by the titanium slag and iron industries consisting of titanium dioxide, which is commonly used for the manufacture of white pigment for paint, plastic, paper and fabrics (Hamzah, Ahmad and Saat, 2009).

Usually, the processing cost or beneficiation cost are very high because if the equipment and materials used during the extraction process. However, all those expensive and complex processing costs are only tolerated by some part of the industries such as the aerospace and biochemical industries, where the advantages of using titanium outweigh the expense (Agatzini-Leonardou *et al.*, 2008).

2.2.2 Uses of Titanium

Titanium metal mechanical properties which is extraordinarily strong and exceptionally lightweight as strong as steel with only 60% of its weight and is bio inert and resistant to corrosion (Agatzini-Leonardou *et al.*, 2008) used in high technology of metal casting.

Titanium is also an ideal material for medical implants in the human body since it is chemically inert, does not react with human body fluids, and after a proper surface treatment the bone is able to adhere to it. So, from a physiological viewpoint, pure titanium is consider as one of the optimum choice as an implant material since it does not contain other elements which may be toxic for the body. (Krallics *et al.*, 2014).

Other than that, TiO_2 is an important inorganic chemical reagent that is widely used in white pigment, plastic, paper, and photo catalyst (MENG *et al.*, 2016). Titanium dioxide is also used in the manufacture of paints, varnishes, lacquer, paper, paperboard, printing inks, rubber, floor covering, ceramics, food and pharmaceuticals (El-Hazek *et al.*, 2007).

2.3 Beneficiation of Titanium from Ore

The methods of metal extraction can be classified as either pyro metallurgical or hydrometallurgical. Meanwhile, as the technology being develops, the conventional method of metal extraction is the pyro metallurgical process where technologies being installed to enhance the beneficiation process.

After mining, the ore is crushed and roll-milled into a fine pulp, which is then concentrated by flotation using chemical reagents. The concentrate formed is smelted and electrolytically refined (Jonglertjunya and Rubcumintara, 2013).

2.3.1 Beneficiation of Titanium using Pyrometallurgy

Shortage of natural rutile has encouraged research efforts to convert ilmenite into high titanium slag or synthetic rutile which actually represent the major feedstock for the chlorination process. Pyro metallurgical production of this feedstock includes mainly ilmenite smelting and roasting.

Smelting produces a high titanium slag and a low manganese iron by-product and this is mainly conducted in South Africa, Canada and Norway (El-Hazek *et al.*, 2007).In spite of high power consumption, smelting of ilmenite or titanium-bearing ore has several advantages over the synthetic rutile route by chemical process.

It converts iron oxide as part of the concentrate to value-added iron metal and slag containing enriched titanium. This technology can use low-grade ilmenite with zero waste generation (Sahu *et al.*, 2006).

The essential mineral wellsprings of titanium are rutile, anatase (both TiO2), ilmenite (FeTiO3) and leucoxene (a weathered ilmenite of variable centralization of TiO2 yet like pseudorutile Fe2Ti3O9). These titaniferous minerals alongside their esteem included items like Synthetic Rutile and TiO2 slag constitute "Titanium Feedstocks" for TiO2 color, Ti metal and welding anodes businesses.

Not at all like in different enterprises, the request driver for titanium minerals is not the metal, but rather the TiO2 colour a claim to fame synthetic. Of the aggregate titanium feedstock use on the planet, around 93 % is expended in TiO2 color, with just around 3 % is used in metal generation.

India's overwhelming mineral sands assets are among the biggest and furthermore one of the wealthiest grades on the planet and ilmenite also included (Sahu *et al.*, 2006).

The nation's Ilmenite asset base stands at 348 million tons of Ilmenite (18% of the aggregate world stores) alongside 18 million tons of Rutile, 21 million tons of Zircon, 8 million tons of Monazite, 107 million huge amounts of Garnet and 107 million tons of Sillimanite (El-Hazek *et al.*, 2007).

2.3.2 Beneficiation of Titanium using Hydrometallurgy

Different titanium metallurgical procedures have been checked on and analysed for titanium dioxide and titanium metal, predominantly concentrating on the future improvement of hydrometallurgical procedures. It is perceived that ilmenite is winding up plainly progressively critical because of the quick consumption of normal rutile.

Many procedures are industrially utilized or proposed to overhaul ilmenite to manufactured rutile. The majority of these procedures include a blend of pyrometallurgy and hydrometallurgy and are for the most part costly (Sahu *et al.*, 2006).

There are two different commercial processes for the production of TiO_2, i.e., the chloride process and sulfate process. The current annual production capacity of titanium oxide pigment worldwide is approximately 6.5 million tonnes (Jia *et al.*, 2014)

Due to dispersed distribution of Ti components in various fine grained mineral phases and the content is not high, so it is difficult to recover the titanium dioxide through traditional separation processes (He *et al.*, 2016).

Hydrometallurgical processes offer easy and eco-friendly approaches of recovering valuable metals from solid industrial wastes (MENG *et al.*, 2016). Different techniques were suggested by many researchers for improving of the leaching process of titanium bearing mineral.

The improvement in leaching process is achieved by the chemical and physical modification of reduced ilmenite, modification in leaching process parameters, varying the quality and quantity of acids, and addition of other soluble and insoluble ions (Gireesh *et al.*, 2015).

A variety of problem such as high energy cost, shortage of high grade ores, processing of low and complex ores and exploitation of smaller deposits have prompted the development of low temperature hydrometallurgical processes for the extraction of base metals from their ores and concentrates.

The conventional hydrometallurgical processes for the extraction of a base metal from a named ore or concentrate consist of a catalytic sulphating, roasting, leaching of the metallic values, solvent extraction and selective stripping (Baba *et al.*, 2009).

The marketed thermo-compound chloride procedures, for example, Kroll and Hunter procedures are group operations and need higher review common rutile or redesigned manufactured rutile and slag as the bolster and the contribution of cost delicate chlorination and thermo steps (Baba *et al.*, 2009).

Numerous changes for the thermo-substance forms have been made, yet they hold minimal potential for noteworthy cost diminishments past current innovation. The improvement of the electro-synthetic procedures for direct diminishment of TiO2 and electro-slag as encourage material and in-situ electrolysis has made some progress (Zhang and Nicol, 2010).

Be that as it may, some trying issues, for example, redox cycling, nourishing, energy, control warm adjust must be settled before scaling-up to business applications (He *et al.*, 2016).

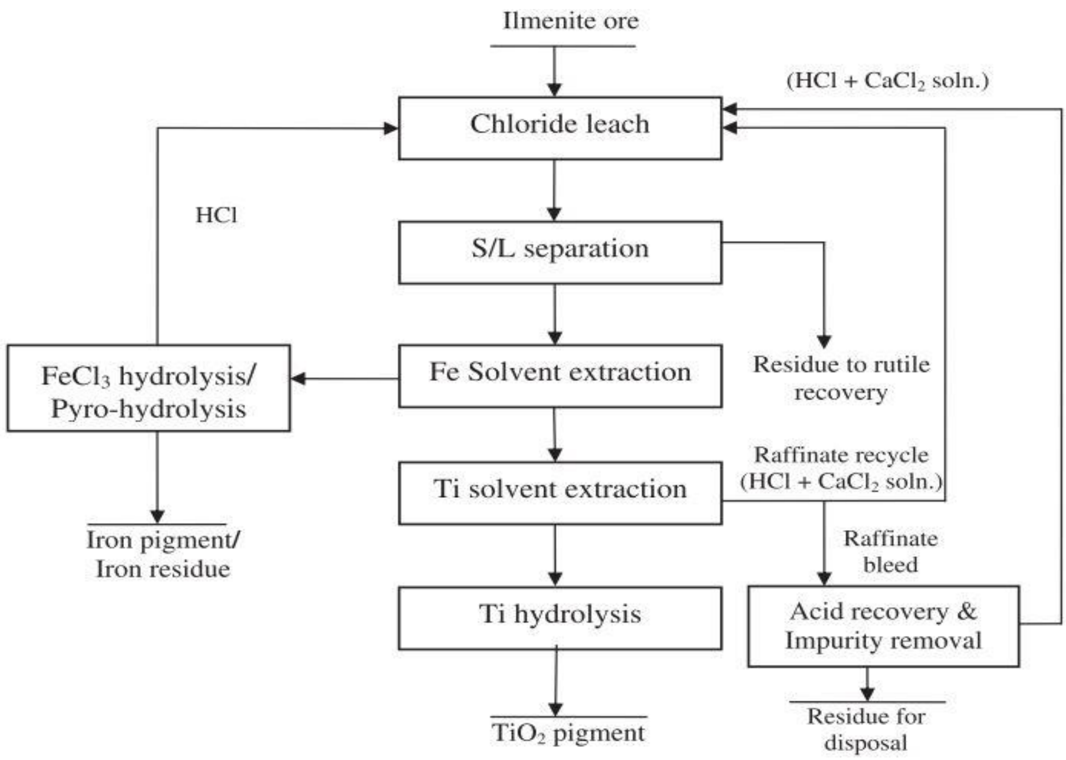

Figure 2.1: Proposed flow sheet for TiO2 pigment production by leaching ilmenite ores with acid in high chloride solutions and purification of the leach solution by SX (Das *et al.*, 2013)

Coordinate hydrometallurgical filter procedures are beneficial in handling bottomless ilmenite minerals, low vitality utilization and create adequately high caliber of color review TiO2 items for an extensive variety of uses and significant request. Novel BHP Billiton sulfate forms have been produced to enhance filtering techniques, partition of metals by dissolvable extraction, diminished squanders and reusing acids, and extremely encouraging for business applications in future (He *et al.*, 2016).

Coordinate chloride filtering forms have been examined seriously, including refinement by dissolvable extraction and recovering HCl by hydrolysis or pyro hydrolysis. Burning drain with high selectivity and titanium dioxide nano-innovation has additionally been produced. Promote advancement of direct draining ilmenite combined with dissolvable extraction for titanium colour and metal creation, is prescribed (Gireesh *et al.*, 2015).

2.4 Leaching of Titanium Using Acid

It has been reported that metal oxide can be soluble in a chemical reagent (e.g. sulfuric acid). However, the percentage of metal extraction varies depending on the interactions of the operating conditions such as the nature of mineral particles, initial pH, temperature, particle size and pulp density (Jonglertjunya and Rubcumintara, 2013).

The higher efficiency of sulfuric acid over others may be a reflection of the better performance of sulfuric acid at the chosen concentration (1 M), or may indicate that the released Ti is more stable in the sulfuric acid solution, potentially as a result of the a fore mentioned complex formation (Pepper, Couperthwaite and Millar, 2016).

2.4.1 Effect of Acid Concentration

Dissolution of titanium from their bulk ore such as ilmenite can be summarised by reaction which implies that a high sulfuric concentration would aid dissolution (Zhang and Nicol, 2010).

The reaction temperature of the whole system, H_2SO_4 concentration, and concentration of ferrous ions (Fe^{2+}) also had significant effects on the enrichment of TiO_2. Controlling the dissolution of one metal, would affect the rate of overall process.

With increasing reaction temperatures, the dissolution of iron from ilmenite was enhanced, while the titanium loss was reduced because of the limited free oxygen released into the solution.

Increasing the concentration of Fe^{2+} also had an adverse effect on the beneficiation of TiO_2 for most industries. In comparison, the dissolution of iron from ilmenite was accelerated by increasing concentrations of H_2SO_4,up to 40 wt. %.(Jia *et al.*, 2014).

The sample leaching present an increase in dissolution of Ti depending, mainly, upon the concentration of acid and solid to liquid ratio.(Agatzini Leonardou *et al.*, 2008). The effect of H2SO4 concentration on the leaching of titanium from its paste was investigated at 150°C at 375rpm stirring speed and 9:1 acid: ilmenite paste mass ratio.

The H_2SO_4 concentration used was varied from2Mto 8M. The fraction of titanium leached vs. time plots for the different H_2SO_4 concentrations was illustrated in Fig. 2.1. The concentration of the acid has a significant effect on the leaching of the ilmenite paste but in no case was the fraction of titanium extracted more than 89% (Nayl, Awwad and Aly, 2009)

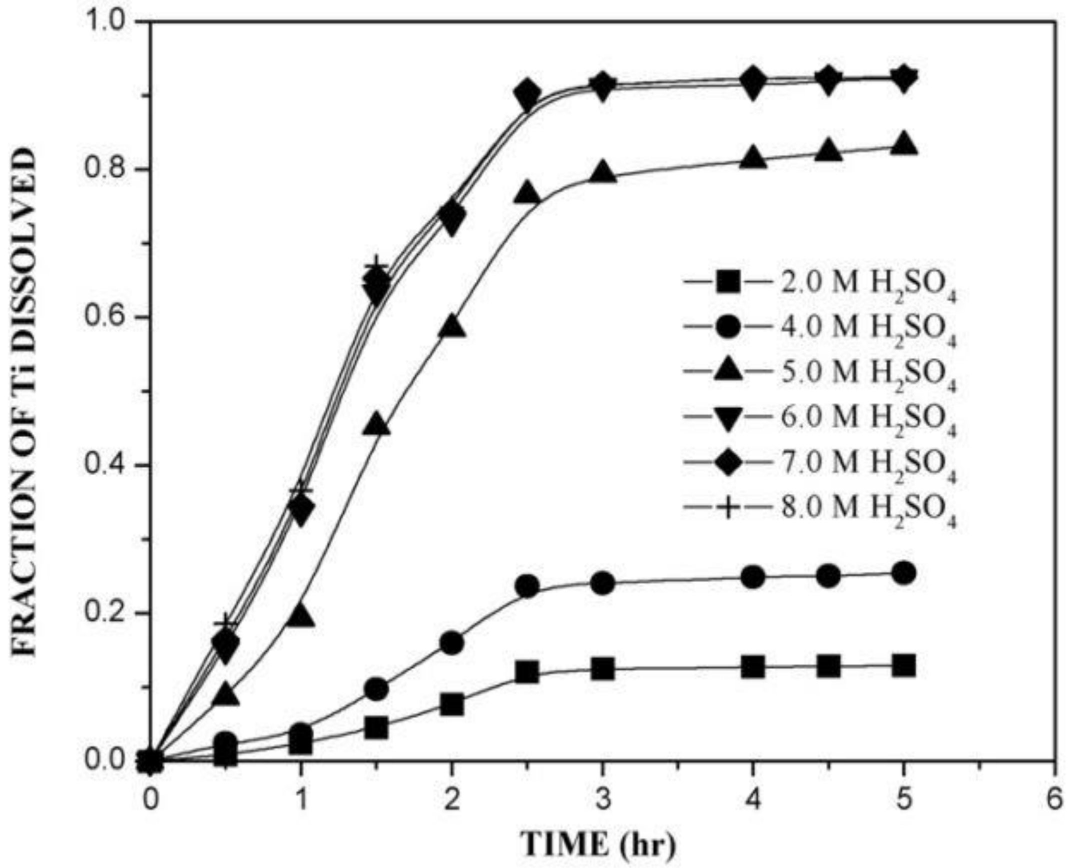

Figure 2.2: Effect of H_2SO_4 concentration on the leaching of Ti at 150◦C (Nayl, Awwad and Aly, 2009)

As the acid concentration increases, the leaching performance also increases. This is due to increased quantity of acid content for removal of iron in ilmenite. As the time for leaching increases, the amount of iron removed from the ilmenite also increases (Gireesh *et al.*, 2015)

Pourbaix diagrams for titanium suggest that leached Ti is most likely present in the form of TiO^{2+} (Chen *et al.*, 2005) which could form complexes in solution with anions contributed to solution from the acids used, such as with sulfate or chloride (Izci and Hosǵün, 2007).

Complexation of the liberated TiO^{2+} could potentially enhance the dissolution of Ti containing phases from bulk of sample in order to maintain equilibrium as ‘free’ TiO^{2+} is removed from the system (Izci and Hosǵün, 2007).

2.4.2 Effect of Solid to Liquid Ratio

The effect of pulp density on leaching was determined by varying the pulp density in the range of 3.3%–15% (w/w) and keeping the other conditions same which means testing only one factor at a time. The ratio was to compare the amount of solid use to the volume of acid been feed to the solid.

The increase in pulp density decreased the leaching of the ore gradually. The two phases are in intimate contact, the solid sample can diffuse from the solid to the liquid phase, which causes a separation of the components originally in the solid.

The leaching efficiency of Ti and Fe decreased from ~96% with a pulp density of 3.3% to 86% and 90% with a pulp density of 10%, respectively. A very low Ti leaching efficiency of 60% was obtained with 15% pulp density due to the hydrolysis of the dissolved Ti in the solution during leaching (Das et al., 2013).

From Fig. 2.3, it is clear that leaching efficiency of titanium is strongly dependent on the acid to ilmenite sample mass ratio. However, the fraction of titanium dissolved was found more or less similar for acid to ilmenite ratios 5:1, 6:1 and 8:1, where the increase in the amount of oxalic acid did not change the amount of titanium dissolved (Nayl, Awwad and Aly, 2009).

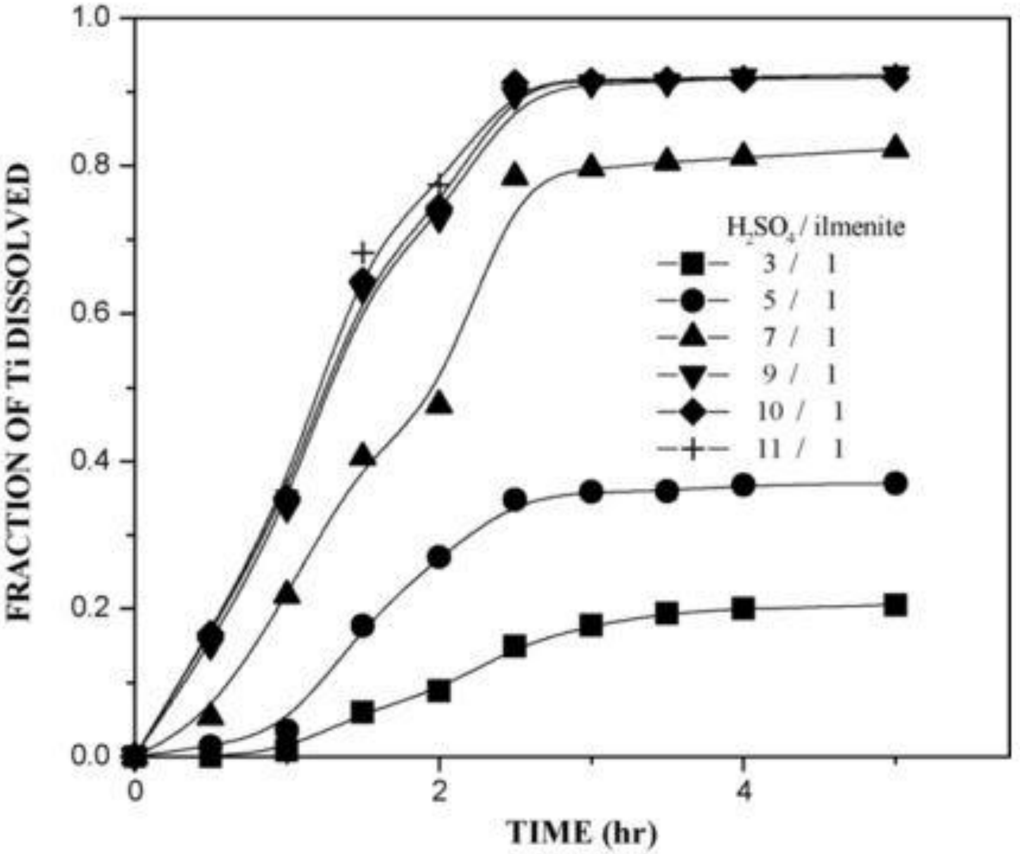

Figure 2.3: Effect of H2SO4/ilmenite paste mass ratio on the leaching of Ti in 6M acid solution at 150˚C (Nayl, Awwad and Aly, 2009)

2.4.3 Effect of Temperature

For a heterogeneous reaction between a solid and a solution, unless the reaction is purely chemically controlled, the reaction is actually a combination of activation energy and diffusion since diffusion also varies with temperature. Furthermore, the temperature dependence of diffusion of ions in a liquid also follows the Arrhenius rate equation (Haverkamp, Kruger and Rajashekar, 2016).

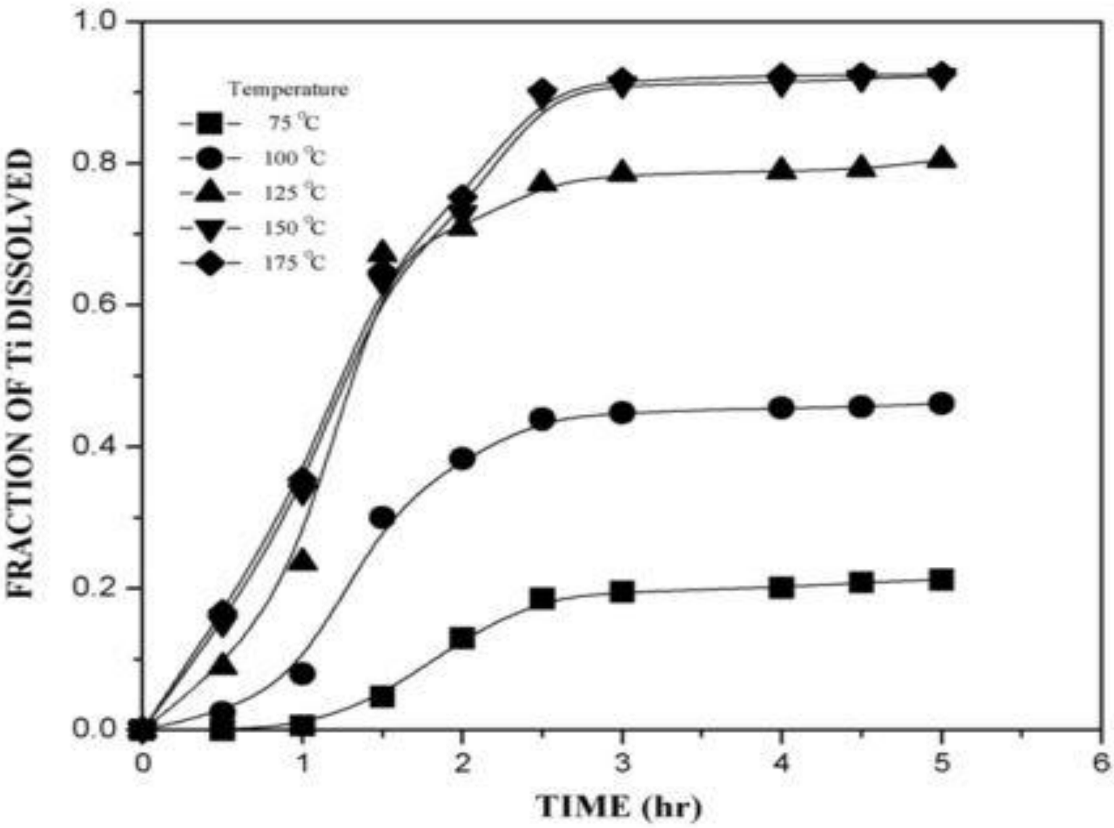

Figure 2.4: Effect of temperature on the leaching of Ti in 6M H_2SO_4 solution (Nayl, Awwad and Aly, 2009)

From the results shown in Fig. 2.3, it can be observed that titanium was largely dissolved at 150◦C, after three hours reaction period. At higher temperatures, the fraction of titanium dissolved was found to decrease, a behavior which can be related to hydrolysis of the formed soluble titanium oxalate in solution (Nayl, Awwad and Aly, 2009).

The titanium extraction degree was 99.84% when leached for 45 min at a leaching temperature of 160C with average particle size of 30.5 lm and initial acid concentration of 36%. It was found that iron and calcium were almost completely dissolved in the acid when the titanium extraction degree was 99.84%, while part of magnesium and aluminium in the spinel still existed in the leaching residue and silicon in the form of SiO_2 remaining in the residue (Zheng *et al.*, 2016).

The titanium extraction degree obviously increased with increasing reaction temperature, higher initial acid concentration and smaller particle size. The results indicate that these three parameters were of significance to the leaching kinetics, and that the reaction temperature was the most important factor followed by acid concentration and particle size (Zheng *et al.*, 2016).

Temperature of the leaching process increases, the reaction also increases. The rate constant for the leaching reaction at 40 °C was 2.16×10^{-3} min^{-1} while at 70 °C the rate constant improved to a value of 4.79×10^{-3} min^{-1}. This is due to increased mobility of ions in solid/liquid phase (Gireesh *et al.*, 2015).

Metal recovery was facilitated by higher acid concentrations, elevated reaction temperatures, longer reaction times, and an excess of acid relative to sample (Pepper, Couperthwaite and Millar, 2016).

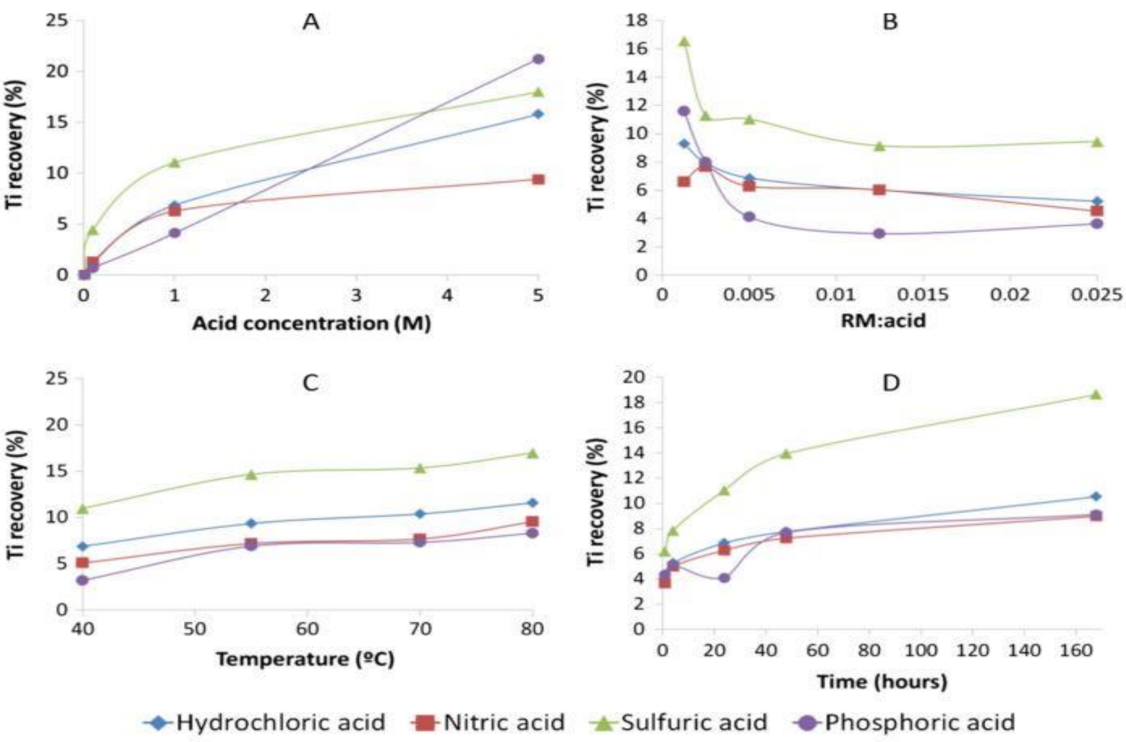

Figure 2.5: Variations in Ti recovery under different experimental conditions; the acids used were hydrochloric, nitric, sulfuric, and phosphoric (Pepper, Couperthwaite and Millar, 2016)

2.5 Kinetics of Acid Leaching

Energy in hydrometallurgy manages the energy of filtering, adsorption and precipitation. Contemplating of draining energy is accomplished for the foundation of the rate expression that can be utilized as a part of outline, advancement and control of metallurgical operations. (Hamzah, Ahmad and Saat, 2009).

A heterogeneous compound response is a response that happens at the interface between two diverse concoction stages. We might be concerned just with responses between a strong stage and an answer stage.

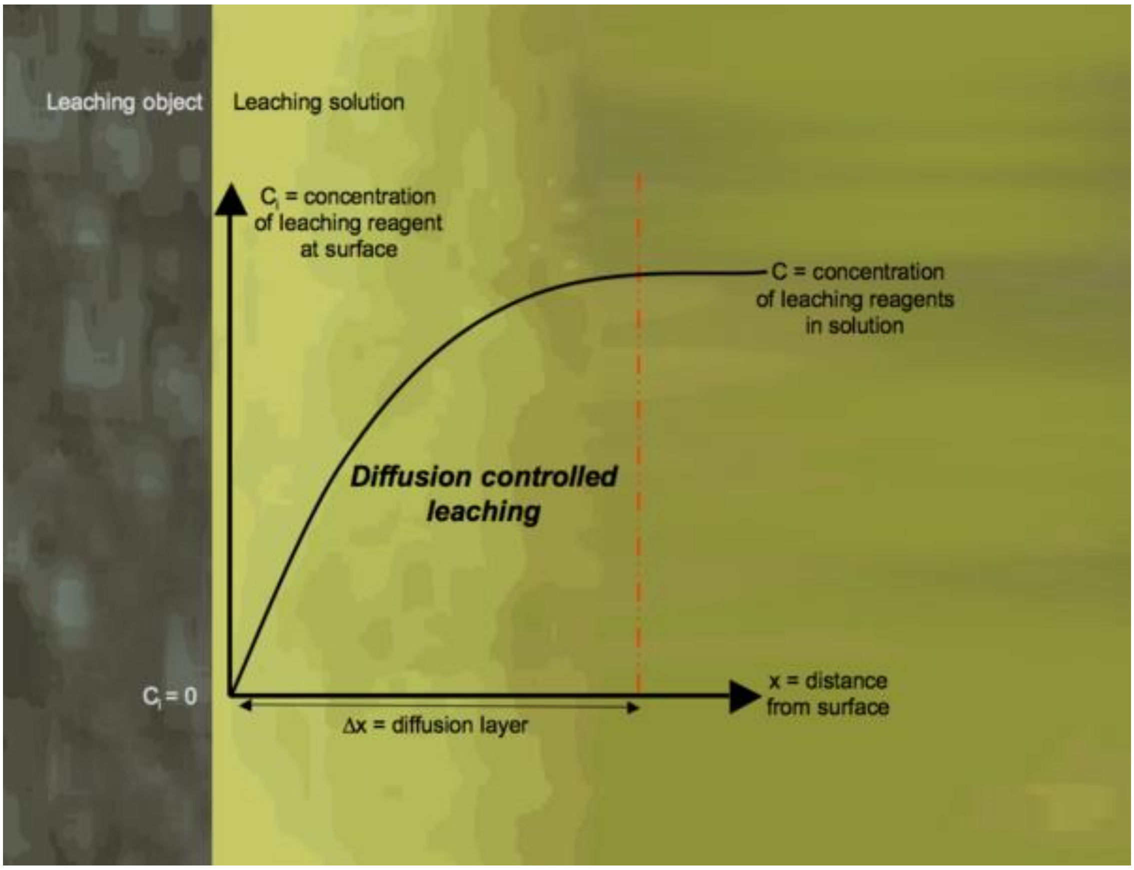

Figure 2.6: Schematic image of leaching according to shrinking core model.

When the chemical reaction on the surface is much faster than the diffusion, leaching becomes diffusion-controlled. In this case the reagent concentration at the surface becomes zero (Das et al., 2013).

The leaching mechanism might become diffusion-controlled when, during leaching, a porous product layer forms on the surface of the particle to be leached. This can for example happen in the case of leaching of sulfides where a layer of elemental sulfur can be deposited on the sulfide surface (Gireesh *et al.*, 2015).

The component of dispersion controlled filtering of a circular molecule is frequently called the contracting centre model. With an indistinguishable suppositions from for the contracting molecule show i.e. that the reagent fixation is steady and that circular and equivalent measured particles are drained, an expression for dissemination controlled filtering can be landed at by applying Fick's law (Chen *et al.*, 2005).

$$1 - 2/3\alpha - (1-\alpha)^{2/3} = \frac{2 \cdot M \cdot D \cdot C}{\beta \cdot \rho \cdot r_0^2} \cdot t$$

Where:

α = fraction leached
β = stoichiometric factor
M = molecular weight of leached mineral
ρ = density of particle
t = time of leaching
C = concentration of reagent
D = diffusion constant (gram/cm^2 or mole/cm^2)
r_0 = initial radius of particle at time zero

As is evident from the equation, the leach rate is inversely proportional to the square of the radius of the particle. The diffusion constant can be determined by plotting the left hand side against time in a diagram. Given the assumptions that C is constant and that volume changes has not been taken into account, this model is accurate until 80-90% has been leached out (Zheng *et al.*, 2016).

CHAPTER 3

METHODOLOGY

3.1 Flow of Process for Research Project

In this research, all the stages of process were decided based on previous work being done by other researchers. Overall, the process does exclude the comminution and grinding stage because the sample comes as a tailing of tin production where most of the sample particles were in their liberated size. In this project, amang which is a tin tailing from a tin production line was used as a solid sample tested for acid leaching process.

Amang was first characterized accordingly based on their physical, chemical properties and their mineralogical information. Sampling stages was done every time sample was taken from their bulk source, to ensure the sample was homogenous and representative of the whole sample. Physically characterized, amang was tested for particle size analysis using sieving process and the size was confirmed under microscope. Next, testing such as XRD, XRF, SEM and LOI was done to characterize the sample chemically and mineralogical.

Next, pre-run leaching were done using different type of acid which are hydrochloric and sulfuric acid. Optimum time and best type of acid decided from these stages of leaching. Once decided, leaching was done to the sample and three parameters were tested to justify all the objectives of this research. The efficiency of leaching were studied by analysing the solid residue according to their weight loss and their change in phases of compound by testing them using XRD, XRF and SEM. Overall, the flow of this research was simplified into Figure 3.1.

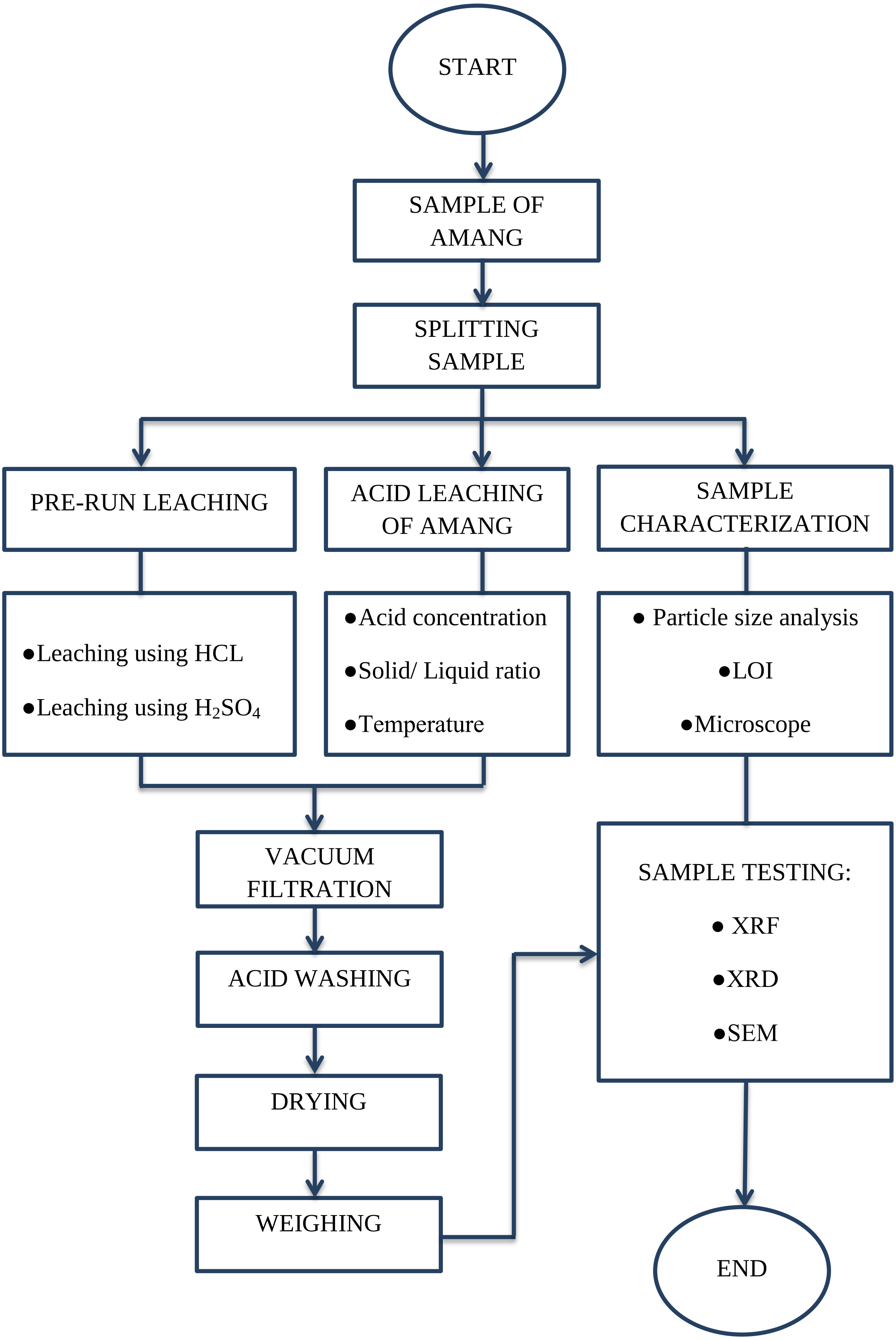

Figure 3.1: Flowchart of overall process of this project

3.2 List of Chemicals and Apparatus Used

3.2.1 Chemicals

For pre-run leaching stages, two types of acid were used and for parameter run only sulfuric acid was used. The information of chemical used in this project are being listed in Table 3.1. The preparation, usage, storage and disposal of both chemical were done following as regulated in the Material Safety Data Sheet (MSDS) that has been read before experiment being done.

Table 3.1: List of chemicals used in the leaching process

Chemicals	**Formula**	**Molarity (M)**
Hydrochloric acid	HCl	4
Sulfuric acid	H_2SO_4	2, 3, 4, and 5

3.2.2 Apparatus

Table 3.2: List of apparatus and equipment used in the leaching process

Apparatus / Glassware	**Description**	**Unit**
Beaker	100 ml	2
	600 ml	2
	1000 ml	2
Filter funnel	90 mm	1
Conical flask	500 ml	2
Measuring cylinder	500 ml	1
Pump filter	-	1
Water bath	-	1

Table 3.2 list all the apparatus and equipment used in this project. All apparatus were washed before and after being used cleanly to avoid any sample contamination. This is important to reduce the error produce in results and increase the reliability of the data obtained.

3.3 Sample Preparation

Amang sample obtained from the company can be directly leached without going through comminution and grinding stages. Most of the minerals in amang are already in their liberation size. Proper drying process need to be done during preparation stages before doing leaching.

All sample obtained from the company were dried in the oven at 80°C overnight to remove all the moisture content in the sample. This step is very crucial to remove all the possibility that might affect the result during weight loss analysis.

Next, the sample was split into desired amount according to the test and analysis. The splitting process was done by using John Riffler equipment. The samples were split at an amount where all part of the sample does represent the whole sample even at different weight.

Homogenous state of sample was important to increase the reliability of the results obtain from each test and analysis that being done. Only after both stages of preparation have been done, other step of the process would take place for including characterization and acid leaching process.

The first part in any ore dressing process will involve the crushing and grinding of the ore to a point where each mineral grain is practically free but not applicable for amang since the sample is in a tailing form.