SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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PREPARATION OF KUANTAN BAUXITE FOR RARE EARTH ELEMENTS EXTRACTION

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Preparation of Kuantan Bauxite for Rare Earth Elements Extraction**". 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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Date : 3 July 2017

Witness by

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Date : 3 July 2017

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

°C	Degree Celsius
%	Percent
M	Molar
K	Kelvin
cm	centimetre
ml	millilitre
L	Litre
g	gram

ABBREVIATIONS

REE	Rare Earth Elements
LREE	Light Rare Earth Elements
HREE	Heavy Rare Earth Elements
XRF	X-ray Fluorescence
XRD	X-ray Diffraction
AAS	Atomic Absorption Spectrometry
ICDD	International Centre for Diffraction Data
ICSD	Inorganic Crystal Structure Database
ICP-MS	Inductive Couple Plasma- Mass Spectrometer
IUPAC	The International Union of Pure and Applied Chemistry

PENYEDIAAN BAUKSIT KUANTAN UNTUK PENGEKSTRAKKAN LOGAM NADIR BUMI

ABSTRAK

Proses Bayer adalah proses mengekstrak alumina daripada bauksit. Proses ini melibatkan pelarutlesapan bauksit dengan larutan natrium hidroksida pekat yang panas. Dalam projek ini,pencirian sampel bauksit daripada Kuantan telah dilakukan. Sampel bauksit tersebut mengandungi majoriti Al_2O_3 pada 53.10%, Fe_2O_3 pada 36.88%, TiO_2 pada 5.35%, SiO_2 pada 3.87%, scandium pada 26 ppm, lanthanum pada 21.8 ppm dan cerium pada 19.8 ppm. Pelarutlesapan bauksit telah dilakukan dalam keadaan bertekanan (autoklaf) pada suhu 145°C dengan natrium hidroksida 5.0 M selama 2 jam dengan kadar penaikkan suhu under 4°C setiap minit. Perolehan aluminium dicatatkan pada 12.54% mungkin disebabkan rendahnya kepekatan natrium hidroksida dan tempoh rendaman yang rendah. Lumpur merah dihasilkan kemudiannya tertakluk kepada pengudaraan larut lesap dengan larutan ammonium klorida 0.37 M pada suhu 70°C dengan nisbah pepejal dan cecair sebanyak 1/4. Sisa selepas tindak balas berakhir didapati mengandungi besi yang lebih tinggi iaitu daripada 38.54% kepada 42.22%. Ini adalah yang mungkin disebabkan oleh kealkalian yang tinggi lumpur merah pada pH 10-12 yang menyebabkan ammonium klorida tidak dapat meneutralkan dan menukarkan besi ke dalam spesies boleh larut yang lebih dipilih pada pH yang lebih rendah. Pengudaraan oksigen juga mungkin menyumbang kepada pemendakkan ferum kerana daripada keputusan XRF yang menunjukkan pengudaraan menggalakkan pemendakkan ferum oksida lebih daripada pemendakkan logam lain.

PREPARATION OF KUANTAN BAUXITE FOR RARE EARTH ELEMENTS EXTRACTION

ABSTRACT

Bayer process is a process of extracting alumina from bauxite. This process involves leaching of bauxite with hot concentrated sodium hydroxide. In this project, the characterization of bauxite sample obtained from Kuantan was done. The bauxite sample contain Al_2O_3 in the majority at 53.10%, Fe_2O_3 at 36.88%, TiO_2 at 5.35%, SiO_2 at 3.87%, scandium at 26 ppm, lanthanum at 21.8 ppm and cerium at 19.8 ppm. Alkaline leaching of bauxite was done in an autoclave pressure reactor at 145°C with 5.0 M sodium hydroxide under a soaking time of 2 hours with a rate of temperature rise at 4°C per minute. The recovery of aluminium was recorded at 12.54% due to the low concentration of sodium hydroxide and low soaking period. The red mud produced was then subjected to aeration leaching with 0.37 M ammonium chloride solution at temperature 70°C with solid to liquid ratio of 1 to 4. The residue after reaction ended was found to contain higher iron from 38.54% to 42.22%. This was most probably due to the high alkalinity of red mud at pH 10-12 that cause ammonium chloride unable to neutralize it and convert iron into soluble species which are favorable at lower pH. The aeration of Oxygen also could be considered as a contributor to the precipitation of iron as it seems from the XRF result the aeration promotes precipitation of iron oxides more than precipitation of other metals.

CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, bauxite mining has seen an abrupt increase of popularity in Malaysia, especially in Kuantan. Bauxite is the main source ore for production of alumina which is produced through Bayer Process, that subsequently produce pure aluminium through alumina smelting in the of Hall-Heroult electrochemical process. The main minerals of aluminium in bauxite are gibbsite, boehmite and diaspore.

The top producer globally for bauxite is Australia accounting for around 30% of the total world bauxite production with China at second place at around 21%. Bauxite is important as the main ore of aluminium that has a broad range of application such as in food packaging, conducting electricity, building construction, sports gear and transportation. It is also widely known that aluminium is the most common metal and the third most common element after silicon and oxygen on Earth.

In the extraction of alumina, the residue produced as wastes are called red mud composed of gangues such as iron oxides, silicon dioxides, titanium dioxide and traces of Rare Earth Element such as scandium and vanadium. Due to the content of aluminium in bauxite, about 1-2 tonnes of red mud will be produced for one tonne of alumina produced. The solid waste of red mud has rusty red tint because of its high ferric oxide content. Around 150 million tonnes of red mud that can constitute problem environmentally are being produced annually around the world according to International Aluminium Institute. Red mud discharging is hazardous to the environment due to the fact that it has high alkalinity (pH around 12), abundance of heavy metals and also might contain small amount of radioactive elements.

1.2 Properties of Bauxite

Bauxite is a not a mineral but rather a rock which consists of group of aluminium hydroxides formed from a laterite soil that has been severely leached of silica and other soluble materials in a wet tropical or subtropical climate. It is most well-known as the primary ore of aluminium used as feed material for Bayer process to produce alumina. It is also said that bauxite has no specific composition. Some minerals may contained in bauxite includes gibbsite $Al(OH_3)$, boehmite AlO(OH), diaspore AlO(OH), hematite, magnetite, quartz, siderite, goethite and sodalite. REEs are also present in bauxite as mineral phases or as ions that are either absorbed on the surface of minerals or replacing similar ions in the lattice of some matrix minerals (Li et al., 2013). The general properties for bauxite are also listed in Table 1.1.

1.3 Rare Earth Elements

Rare Earth Elements are a group of seventeen chemical elements that occur together in the periodic table (www.geology.com). The group consists of yttrium and the 15 lanthanide elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium). Scandium is found in most rare earth element deposits and is sometimes classified as a rare earth element. The International Union of Pure and Applied Chemistry (IUPAC) also include scandium in the definition of rare earth elements.

Scandium and yttrium are considered rare earth elements since they frequently present in the same ore deposits as the lanthanides and exhibit similar chemical properties. Figure 1.1 shows the REE in the periodic table of elements.

Table 1.1: Properties of bauxite (www.geology .com)

Properties	**Identification**
Color	White, gray, sometimes stained yellow, orange, red, pink, or brown by iron or included iron minerals
Streak	Usually white, with occasional iron stain
Specific gravity	2.0 – 2.5
Diaphaneity	Opaque
Cleavage	None
Chemical composition	Varied but consistently rich with aluminium oxides and aluminium hydroxides
Mohr scale hardness	1 – 3
Luster	Dull or Earthy
Transparency	Opaque
Crystal System	Amorphous
Tenacity	Brittle

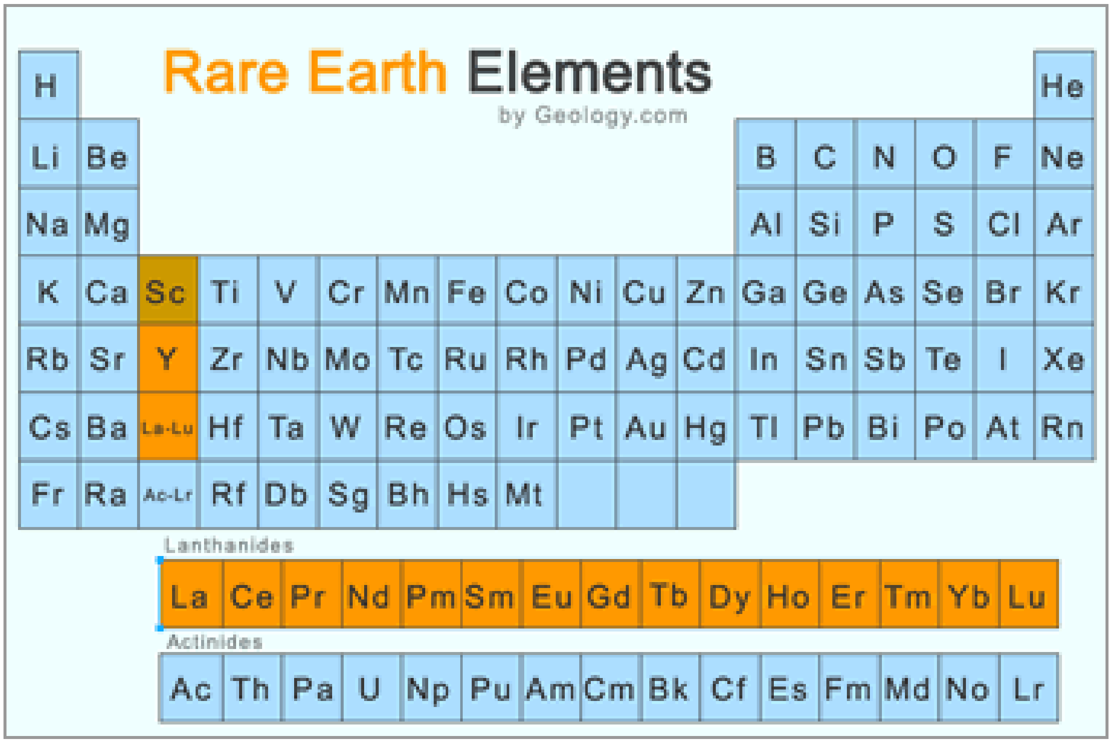

Figure 1.1: Periodic Table of Elements with REE Highlighted in Orange (www.geology.com)

Although the name implies that they are rare, two of the least abundant REE which are Thulium and Lutetium are nearly 200 times more common than gold. However, the difficulty of mining these metals were due to the ores not usually found in concentrations economically feasible for extraction.

REE is also typically subdivided into two classes which is light rare earth elements (LREE) and heavy rare earth elements (HREE). The electron configuration of a particular REE will define it as being LREE or HREE. The LREE are defined as lanthanum, atomic number 57 through gadolinium, atomic number 64. The LREE have in common increasing unpaired electrons, from 0 to 7, with none of it having paired electron. The HREE are defined as terbium, atomic number 65 through lutetium, atomic number 71, and also yttrium, atomic number 39. All of the HREE differs from the first eight lanthanides or LREE in that they have 'paired' electrons (a clockwise and counter-clockwise spinning election). Yttrium is included in the HREE group based on its similar ionic radius and similar chemical properties. Scandium is quite an anomaly as although it is trivalent, its other properties do not behave similarly enough to be classified either a LREE or HREE.

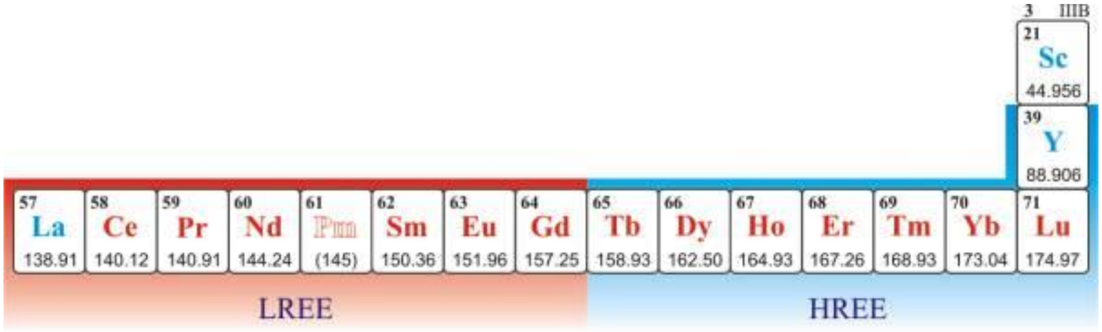

Figure 1.2: The Classification of REE into LREE and HREE (www.periodni.com)

1.4 Problem Statement

Although processing bauxite yields high alumina content, there are as much or twice the amount of red mud produced. The disposal of red mud has adverse effect to the environment. Therefore the need to reduce waste from alumina production is not to be overlooked. One way to minimize waste is by utilization of the materials that might go into wastes. There have been a number of studies that worked on extracting elements that may be present in red mud such as iron, titanium, vanadium, scandium and others (Vachon et al., 1994, Borra et al., 2015, Yang et al., 2015;). From an ICP-MS analysis of the Kuantan bauxite sample, there are substantial concentration of scandium at 26 ppm. Scandium is considered economically exploitable at around 20 to 50 ppm. This brought interest to prepare the condition at which extraction of scandium or other REE are conducive. To achieve this, iron must be removed as much as possible because presence of iron makes it difficult for extraction of scandium as they have similar ionic radii. Earlier studies have worked out leaching of red mud with sulphuric acid (H_2SO_4) and hydrochloric acid (HCl). This project aims to observe whether leaching with ammonium chloride can replicate the result of the study or not.

The relatively low content of scandium compared to the main components of red mud such as iron, aluminium and titanium makes it hard for a direct recovery. Therefore, leaching of bauxite with hot sodium hydroxide and subsequently aeration leaching of red mud to remove iron will be conducted. This will be the focus for this project which is to prepare red mud for extraction of REE. This, in the long run might allow companies to profit from production of REE and also reduce stockpiles of red mud wastes.

1.5 Objectives

There are some objectives that this project aims to achieve that are listed as follows;

1. To characterize the raw Kuantan bauxite for the processing of alumina by pressurized alkaline leaching.
2. To study the effect of aeration leaching of red mud with ammonium chloride in iron removal for the extraction of REE.

1.6 Thesis Outline

This thesis contains five chapters. Chapter 1 includes the introduction of the research background and also provides the objectives and problems statements related to the project. Chapter 2 reviews the literature and studies on extraction of elements from red mud and removal of iron from red mud. Chapter 3 explains the materials and experimental methods of the research. These include materials selection, sample preparation, and experimental setup. Chapter 4 discussed the data analysis and interpretation. The data were obtained from the samples using XRD, XRF AAS, and other methods. Finally, Chapter 5 is about the overall conclusion of the project and recommendations for improvement in future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Bauxite is the main ore of aluminium used for extraction of alumina by Bayer process. Although bauxite can also be processed to alumina using lime sintering process and sodium carbonate (Deville Pechiney process), alkaline leaching with sodium hydroxide was accepted as the most economical. The residue produced as by-product, known as red mud or bauxite residue is considered as wastes and need to be managed more strategically. The composition of red mud is quite interesting with trace elements such as Rare Earth Elements (REE) namely scandium. One of the classifications of bauxite is (1) bauxite on igneous and metamorphic rocks (2) bauxite on sediments, carbonate rocks and stratified rocks. It is found that, carbonate rock or better known as karst bauxite, have higher concentration than other types of bauxite. Therefore, the red mud generated from karst bauxite is also more enriched in REE compared to ones generated from other bauxite. A good example is from a study by Wagh and Pinnock, (1987) that found a sample of Jamaican bauxite contain scandium in the form of scandium oxide at around 87 ppm to 113 ppm and was enriched in red mud at range of 200 ppm to 390 ppm. It is also found from an Inductive Couple Plasma- Mass Spectrometer (ICP-MS) analysis that the Kuantan bauxite sample provided for this project, that it has economical content of scandium. The multitude of uses and lack of distribution in high concentration of Scandium makes it expensive, thus, justifying the interest towards bauxite red mud as a secondary resource of Scandium.

Figure 2.1: Bauxite Rock Sample (www.pitrukrupamineral.com)

2.2 Bauxite Mining

The mining of bauxite is rather simple and generally by open cast method. As with other ore, mining of bauxite starts with the removal of overburden which is typically a few metres of rocks and clays that varies from one point to another. Then, the bauxite ore is recovered usually using excavators and some cases by blasting. The ore was then transported to the processing plant. The processing part of bauxite does not need complex circuit as the bauxite mined is usually of acceptable grade. Some simple processing method used to improve the quality of bauxite by removing clays was also applied such as crushing, washing, and wet screening as implemented by Aras Kuasa Sdn. Bhd. shown in Figure 2.3. The clays and some other impurities removed were then disposed of in tailing ponds. Some rehabilitation effort can also be done such as replanting with local species to re-establish natural vegetation. Finally, the ore was either sold as bauxite or transported to refineries to be processed until pure aluminium metal was obtained.

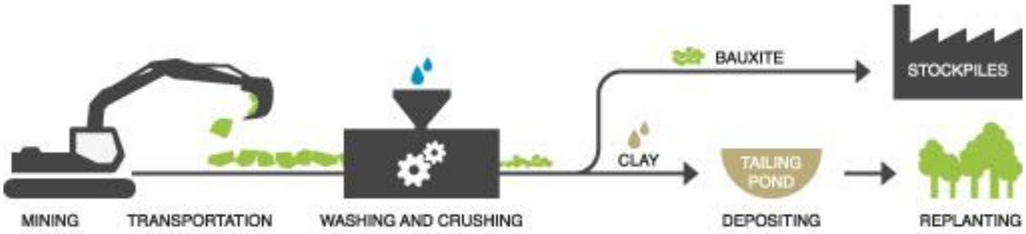

Figure 2.2: Summary of Bauxite Mining (www.hydro.com/en/)

Figure 2.3: Processing Plant for Bauxite in Aras Kuasa Sdn. Bhd.

2.3 Bayer Process

After mining, the next step for bauxite is to extract alumina (Al_2O_3). Majority of the world nowadays uses the process invented in 1887 by Austrian scientist Karl Josef Bayer for production of alumina from bauxite. This process involves digestion of bauxite with hot concentrated caustic soda/ sodium hydroxide that produces saturated solution of sodium aluminate. A typical equation for the reaction can be represented as;

For Gibbsite,

$Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow Na^+ \, Al(OH)_{4(aq)}^-$ **Equation (2.1)**

For Boehmite and Diaspore,

$AlO(OH)_{(s)} + NaOH_{(aq)} + H_2O \rightarrow Na^+ \, Al(OH)_{4(aq)}^-$ **Equation (2.2)**

Bauxite ores with high gibbsite content will warrant a reaction temperature of around 135ºC- 150ºC while high boehmite content need higher temperature at 205ºC-245ºC. Diaspore needs the highest temperature, above 250ºC.

Following digestion, the mixture is passed through a series of pressure-reducing tanks, of which the solution is flashed to atmospheric pressure. The insoluble red mud is then separated from the sodium aluminate solution. Residues of different sizes are removed according their effective methods. These residues are then washed, combined, and discarded. The clarified solution is further cooled in heat exchangers, enhancing the degree of supersaturation of the dissolved alumina, and pumped into tall, silolike precipitators.

Then, the supersaturated sodium aluminate is cooled to allow crystallization of $Al(OH)_3$ and aluminium hydroxide crystals are also introduced to hasten the separation of crystals. These seed crystals attract other crystals and forms agglomerates that are transferred to the next step. Fine sized particles would be thickened, filtered and recycled as seed crystal for future precipitation. This step is the reverse of the dissolution step which is;

$Na^+ \ Al(OH)_{4(aq)}^- \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)}$ **Equation (2.3)**

The sodium hydroxide produced can be recycled for future digestion.

Lastly, the agglomerates would be calcined which is a thermal treatment (excess of 1000 ^oC) process that drive off chemically combined water to produce pure alumina. This step is described by equation;

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ **Equation (2.4)**

Usually bauxite as feed material for Bayer process contains around 30-60 wt% Al_2O_3 and the red mud would still contain around 10-25 wt% Al_2O_3. The alumina production will then become feedstock for Hall-Heroult process, an electrochemical treatment process to obtain pure aluminium from alumina.

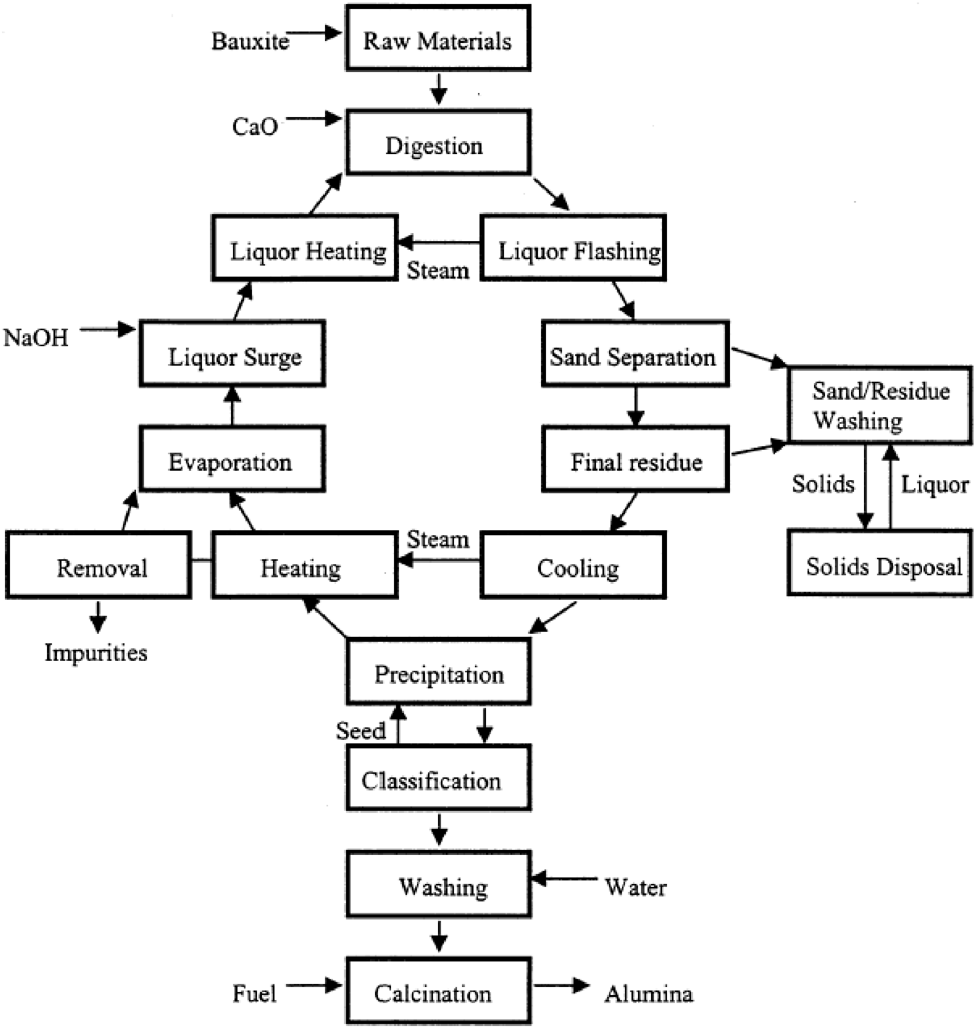

Figure 2.4: Summary of Bayer process (Hind et al; 1998)

2.4 Hall-Heroult Process

Hall-Heroult process is the major industrial process used to extract aluminium. It was discovered almost simultaneously by two independent scientists, Charles Martin Hall in United States of America and Paul L.T Heroult in France. In this process, pure alumina usually obtained from product of Bayer process will be dissolved in molten cryolite.

Cryolite was chosen as the electrolyte due to relatively low melting point, it also dissolves alumina well, conducts electricity, dissociates electrolytically at higher voltage than alumina and has a lighter density than aluminum at the temperatures required by the electrolysis. A steel vessel with carbon lining (cathode) and graphite rods (anode) is usually used for the process. When electricity is passed through the electrolytic cell which consists of carbon electrodes, the chemical bonds between aluminium and oxygen were broken and oxygen is formed at the anode. This oxygen formed reacts with the carbon of the anode to form carbon monoxide and carbon dioxide. Meanwhile, pure aluminium is deposited at the cathode. In this method of production of aluminium for every 2 kg of Al produced, approximately 1 Kg of carbon anode is burnt. The overall reaction is;

$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$ **Equation (2.5)**

Reaction at cathode;

$Al^{3+} + 3e^- \rightarrow Al$ **Equation (2.6)**

Reaction at anode;

$C + 2O^{2-} \rightarrow CO_2 + 4e^-$ **Equation (2.7)**

Aluminium produced is then sold according to the current global price which like in this case 1,949.99 USD/t at 26 May 2017. The price of aluminium for the span of five years can be seen in Figure 2.5.

Figure 2.5: Price of Aluminium from 2012 to 2017 (www. Infomine.com)

2.5 Kuantan Environmental Problem

Bauxite mining in Malaysia has been taking place as early as 2000 in Teluk Ramunia, Johor (Minerals and Geoscience Department Malaysia) without any controversy arising. 15 years later, bauxite mining in Kuantan has created a different scenario within a short period of time. Various environmental problems arose within a short period of time that led to widespread community outrage as a result of extensive and aggressive mining which include transporting and stockpiling of bauxite in huge quantities (Abdullah et al., 2016). Mining activities usually are conducted in remote locations or well defined buffer zones but some mining activities in Kuantan disregard this, with some mining done close to school areas. It was made rather difficult for the authorities to regulate and control bauxite mining activites in Kuantan as illegal individual miners outnumber the legal miners that were actually following the regulations set by the law.

The issue for Kuantan resident was the air pollution due to dust. Dust sized less than 10 micrometer can be inhaled deep into respiratory system which were great health concerns. Large dust particulate also causes great discomfort. This was even more the case with bauxite as they contain high iron oxide that gives the highly visible red colour. Public roads, housing areas and buildings were tainted red as the dust were deposited as seen in Figure 2.6. Aside for air pollution, water pollution in the form of river pollution was also reported as the result of uncontrolled mining of bauxite. The sources of water pollution in Kuantan were mainly attributed to extensive land clearing, extraction of bauxite leading to soil erosion and sedimentation; washing of bauxite and effluent from the bauxite washing pond which flows into the nearby river; and stockpile of bauxite in large quantities without a proper drainage system. River pollution might eventually lead to contamination in drinking water which makes it unsafe for consumption.

To rectify the situation, authorities had impose a moratorium in 15 Jan 2016 until 15 April but extended twice to 15 July then to 14 Sept and now to 30 June 2017. No activity except stockpile clearing can be done. This was also why the processing plant in Figure 2.3 appeared to be abandoned as no mining activity was allowed to be conducted. Stricter rule was imposed where lorries must report to be checked at checkpoints. Failure to do so will mean no access to Kuantan port. It is also required for lorries to be washed when exiting the mine site into public roads or they will not be cleared by the checkpoint.

Figure 2.6: Public Road Polluted with Dust (www.thestar.com.my)

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2.6 Red Mud Waste

As discussed before, the residue from Bayer process were called red mud and usually treated as wastes. The main characteristic of red mud was its high alkalinity which must be considered in disposal or utilization of red mud. Many studies have been reporting ways to utilize red mud instead of the common practice of stockpiling the red mud. One of the uses of red mud that have been receiving attention, are those reported on the utilization of red mud for building materials production such as cement, bricks, roofing tiles and glass-ceramics. Red mud is considered as a raw material for production of these materials. An example of the research would be Ribeiro et al., 2010 which concluded "non-calcined red mud is an interesting candidate for use in mortars and concretes for non-structural applications, partially replacing the cement in the mixture." Garhard B also patented a method for manufacturing fired bricks with 50-90 wt% of red mud alongside clay and a water fixing agent. The potential of red mud from Birac Alumina Industry, Serbia as a pigment for use in the building material industry for standard concrete mixtures was also observed by Ceblik., 2007. Red mud was added as a pigment in various proportions (dried, not ground, ground, calcinated) to concrete mixes of standard test blocks (ground limestone, cement and water). The idea to use red mud as pigment was based on its relatively fine particles of red mud and characteristic red colour. Ekrem., (2006) studied the possibility of using red mud for the preparation of stabilization material. From testing, it was found that compacted clay samples containing red mud and cement–red mud additives as compared to natural clay samples, have a high compressive strength, decreased hydraulic conductivity and swelling percentage. Therefore, it was concluded that red mud and cement–red mud materials are suitable for the purpose of stabilization of clay liners in geotechnical applications. An interesting usage of red mud includes the potential usage as catalyst as studied by Kurtoğlu and Uzun., (2016) whereby red mud can be simply converted into an exceptionally active and stable catalyst for hydrogen production from ammonia. From the results obtained, it was found red mud was able to convert ammonia into hydrogen and nitrogen at constant conversion for more than 72 h at 700 °C.

2.7 Red Mud Content

Many study reported on the mineral content of bauxite after processing for alumina such as a characterization result from Cablik., (2007) for samples of monohydrate bauxite from Jamaica after Bayer process. The red mud sample contains high concentration of iron oxide Fe_2O_3 (48.50%), SiO_2 (11.53%), Al_2O_3 (14.14%), CaO (3.96%), TiO_2 (5.42%), and V_2O_5 (0.116%). An analysis by Borra et al., 2015 shows content of Fe_2O_3 (44.6%), Al_2O_3 (23.6%), SiO_2 (10.2%), CaO (11.2%), and TiO_2 (5.7%). Its XRD analysis reported presence of minerals such as hematite, goethite, gibbsite, diaspore, calcite and cancrinite. Meanwhile, a characterization by Wang et al., of red mud of Australian origin shows a composition of Fe (28.4%), Al (11.4%), Si (5.3%), Na (4.8%), Ti (4.5%), and Ca (2.0%). Newson et al., (2006) reports the characterization of red mud from United Kingdom as containing of Fe_2O_3 (36.31%), SiO_2 (18.25%), Al_2O_3 (23.43%), CaO (4.38%) and TiO_2 (5.97%). This shows that after leaching with sodium hydroxide, not all aluminium will be extracted and some will leave in the red mud as waste and also that eventhough different source bauxite has different elemental composition, after Bayer process iron is consistently the major elements in red mud.

2.8 Extraction of Various Metals from Red Mud

2.8.1 Aluminium Extraction from Red Mud

The aluminium in red mud can be extracted further by many ways. One of it is through leaching with acids as studied by Vachon et al., (1994). Organic acids and mineral acids such as sulphuric acid, citric acid and oxalic acid were used separately or as a mixture. The optimum recovery of alumina at 96% was reported by mixing citric acid and oxalic acid at a ratio of 2 to 1 with addition of sulphuric acid to modify the pH to 1.5. Compared to leaching with sulphuric acid alone at pH 1.0, the mixed leaching agent was found to be more efficient in recovery but higher in cost due to high price of organic acid. Another interesting way to recover Al from red mud was through bioleaching (Vachon et al., 1994). Bacteria found in wastewater sludge and fungi such as *Aspergillus niger*, *Penicillium notatum*, *Penicillium simplicissimum* and *Trichoderma viride* were tested in the bioleaching experiments. It was found that up to 75% of aluminum can be recovered in a 10% v/v initial red mud concentration using the acids generated by *P. simplicissimum*. Borra et al., (2015) found that leaching of red mud with acid which decreases the pH of red mud will cause dissolution of Al and Si to occur simultaneously. This correlation might be the result of the dissolution of sodium aluminosilicate that contains both Al and Si.

2.8.2 Iron Recovery from Red Mud

As mentioned before, most of the red mud has iron oxide as its major constituent which ranges from 6.8 wt% to 71.9 wt% dependant of the initial iron concentration in bauxite. One of the basic ways to recover iron is by physical processing which is magnetic separation. Although this method has been practiced for a while dating back to 1970, the recovery performance back then was poor. The usage of high gradient superconducting magnetic separation (HGSMS) system was considered as a highly efficient way to separate magnetic particles in liquid suspension due to its stronger magnetic field compared to ordinary ferromagnetic-core electromagnets. Various contents of iron oxide such as hematite or goethite will affect the efficiency of magnetic separation system. Therefore, the type of iron content should be considered before utilization of magnetic separation.

Another way found to remove iron from red mud is through leaching of red mud with oxalic acid (Wang et al., 2015). Oxalic acid ($H_2C_2O_4$) leach with red mud will cause iron and aluminium to be extracted substantially which Wang solved by increasing selectivity towards iron by adding sulphuric acid.

2.8.3 Scandium Extraction from Red Mud

There are a few studies reporting on the extraction of elements from red mud. As example, Piga et al., (1993) studied the recovery of scandium by combining pyrometallurgical process and hydrometallurgy process. At range of temperature of 800°C-1000°C, red mud and mixture of coal, lime and sodium carbonate under reduction sintering conditions were processed. Next, alumina releaching with hot water was done to produce a brown mud. The brown mud was comprised mostly of iron and its slag has valuable content with scandium and after separation of iron in the brown mud, it was leached with sulphuric acid (H_2SO_4). The leach liquor is then hydrolysed at 140°C to recover titanium. After removal of titanium, the solution can be treated with solvent extraction or precipitation to recover scandium. Direct leaching of red mud for scandium with mineral acids was also done by Wang et al., (2013) and Ochsenkühn-Petropulu et al., (1996). Wang found that sulphuric acid (H_2SO_4) works better than nitric acid (HNO_3) and hydrochloric acid (HCl). However, Ochsenkühn-Petropulu found that nitric acid works best. This difference was then reported by Wang to possibly be due to their differing mineralogical composition.

The effect of acid concentration for red mud leaching was also studied by Borra et al., (2015). The higher the acid concentration is, the higher the dissolution of elements. As example, iron is dissolved at less than 5% with usage of 0.5M acid concentration to an increase of 60% at 5.0 M of acid. It is also worth to note that dissolution of iron shows a correlation with the dissolution of scandium. Borra et al., (2015) also found that a recovery of 50% of the scandium is possible without too much concentration of iron dissolved. However, the case is different when trying to increase the recovery of scandium to above 50% as major part of iron is inevitably dissolved. Therefore, it can be understood that complete recovery of scandium without the disruption of iron would be impossible. Scandium may exist in iron oxide lattice which explains why scandium cannot be completely soluble in acid unless iron dissolved completely. Scandium might also exists in other minerals, is enriched in the outer layer of iron oxide particle or adsorbed on the surface of iron oxide particles which is why iron dissolution is minimal at under 50% of recovery of scandium but increases rapidly at above 50% scandium recovery.

The alkalinity of red mud is a problem posed by many researchers. Borra et al., (2015) concluded that washing of red mud by water with the aim of reducing pH to help reduce amount of acid needed to neutralize or raise pH of red mud for further leaching, was not very efficient. After 4 runs of washing with water, the pH did not budge from 10 which might be attributed to the buffering action of sodium aluminosilicates contained in the sample. Therefore, leaching with hot water is not an important step for extraction of metals and other valuable elements. Habashi (1997) also reported that the pH value of leach liquor from washing red mud with 1000 times of its mass of distilled water still result in a high pH which is 10.5. Therefore, other neutralization method should be taken into consideration rather than simply diluting with water.

2.9 Pourbaix Diagram for Iron

Pourbaix Diagram also known as the Eh/Ph diagram depicts the thermodynamic equilibrium states for a system of metal-electrolytes. The top part of the diagram describes the oxidizing conditions of a metal and the lower part describes reducing conditions. Left side of the diagram shows acidic condition meanwhile right side shows alkaline conditions. Pourbaix diagram can help predict the species that will be stable at certain conditions. A simplified Pourbaix Diagram for iron is as follows;

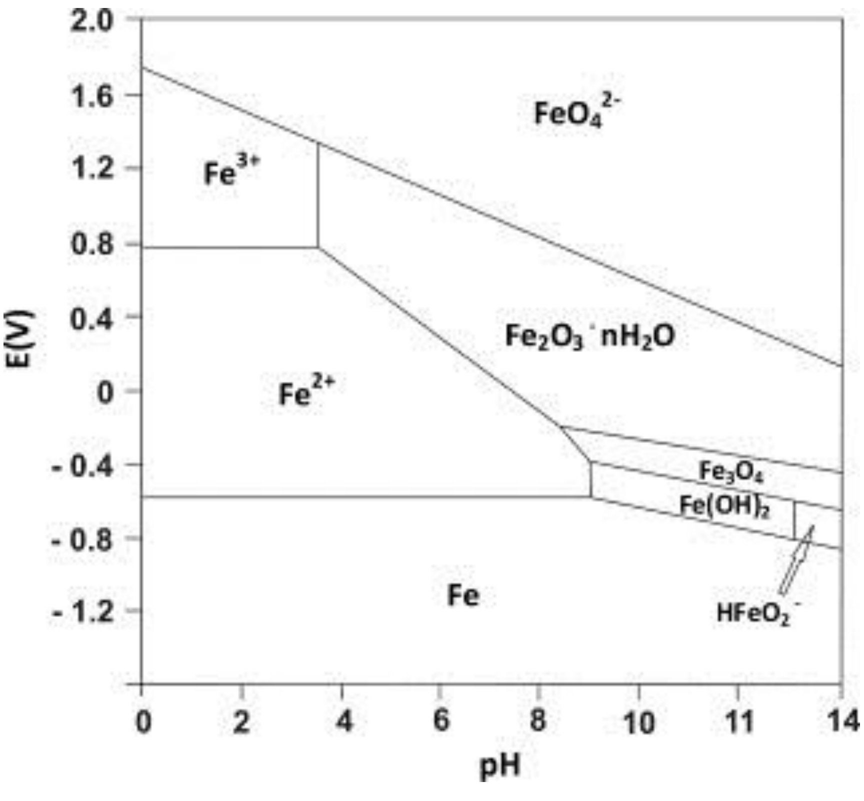

Figure 2.7: Pourbaix Diagram for Iron at 25°C (Tekerlekopoulou et al., 2013)

From the diagram, it can be understood that Fe can present in aqueous solution as one of three species which are Fe^{2+}, Fe^{3+} and FeO_4^{2-}. Fe^{3+} requires high pH of 0-3, Fe^{2+} present at pH range of 0-8 and FeO_4^{2-} exist throughout 0-14 but only at higher potential. Fe will exists as solid or in other words precipitated as residue as Fe_2O_3, Fe_3O_4 and $Fe(OH)_2$. It must be noted that some limitations of Pourbaix diagram such as it provides no information about the kinetic parameters of the corrosion reactions, the diagrams take into consideration of pure metals and aqueous solution at standard conditions which are temperature 298K, pressure 1 bar and it also does not take account non ideal behaviour of aqueous solution.

2.10 Becher Process

This process was invented in Australia by Robert Gordon Becher in 1960. It is applied in upgrading ilmenite ore from 55% TiO2 to about 94% TiO2 by reduction with charcoal. Becher process involves two main steps termed “reduction” and “aeration”. In the reduction step, or also known as carbothermal reduction process, ilmenite in the phase of pseudobrookite is heated with coal at about 1100°C for between 13-16 hours producing reduced ilmenite; an intermediate phase consisting of a titanium oxide matrix embedding metallic iron.

Oxidisation with dissolved oxygen from air will cause leaching of metallic iron from reduced ilmenite with ammonium chloride (NH_4Cl) acting as catalyst for rusting. The formation of magnetite is most preferred as it can easily be separated from TiO_2 by means of magnetic separation. Then the mixture is washed with sulphuric acid to remove traces of metallic iron. This process is limited by the slow mass transport rates of oxygen that has low solubility. For this project, it will focus on the potential ability of ammonium