SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

CHARACTERIZATION AND POTENTIAL INDUSTRIAL APPICATION OF GYPSUM RICH WASTE

By

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Dissertation submitted in partial fulfillment of the requirements for the degree of Bachelor of Engineering with Honours (Mineral Resources Engineering)

Universiti Sains Malaysia

JUNE 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertetion entitled **"Characterization and Potential Industrial Application of Gypsum Rich Waste".** I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any other examining body or University.

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ACKNOWLEDGEMENTS

Praise to Allah, the most merciful, with His permission, I would managed to complete this research. The success journey of my thesis is the contributing from all people around me. I would like to immerse gratitude to everyone who contributed toward preparing and helping in making this project successful. I would like to express my deepest appreciation to my supervisor, Associated Prof Dr. Kamar Shah bin Ariffin for giving me useful advised and guidance throughout the whole process. The opportunity doing research under him is very wonderful and unforgettable.

I would like to thanks to School of Materials and Mineral Resources Engineering cause allow and support throughout the journey of this research. A big thanks to staff and technician for always committed in giving suggestion, assistant and stimulating encouragement which really help me in coordinating my research. This thesis would not be completed without moral and finance support from both of my parents. Their constant love and blessing motivated me to complete this thesis with determination. Last but not least, thanks to my senior, Siti Nur Asifa Binti Ramlan for always guides me throughout the process of completing the Final Year Project and many thanks also to my coursemate for always support and brain storm.

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LIST OF SYMBOLS AND ABBREVIATION

DSC	Differential Scanning Calorimetric
DTA	Differential Thermogravimetric Analysis
EDX	Energy Dispersive X-Ray
FGD	Flue Gas Desulphurization
FTIR	Fourier Transform Infrared Spectroscopy
LL	Liquid Limit
LOI	Loss Of Ignition
NUF	Neutralized Underflow
PI	Plasticity Index
PL	Plasticity Limit
REE	Rare Earth Element
SG	Specific Gravity
SEM	Scanning Electron Microscope
XRD	Xray-Diffraction
XRF	Xray-Fluorescent
WLP	Waste Leach Purification

PENGENALPASTIAN DAN POTENSI APPLIKASI INDUSTRI HAMPAS KAYA GYPSUM

ABSTRAK

Sisa buangan Gypsum NUF yang dihasilkan oleh pemprosesan elemen nadir bumi dicirikan dan dianalisa untuk membandingkan antara gypsum semulajadi dan menilai kesesuaian kualiti mereka untuk aplikasi perindustrian. Ia menggunakan Pembelauan Sinar-X(XRD), Analisis Spektrum Inframerah (FTIR), Mikroskop Imbasan Elektron (SEM), Analisis Pengimbasan Berbeza Calorimetrik (DSC) / Analisis Thermogravimetric (TGA) dan analisis Pendafluor Sinar-X (XRF). Ujian lain termasuk ujian pH, LOI, kelembapan, graviti spesifik dan indeks plastik juga dilakukan. Ikatan ciri getaran air pada 3606-3558cm^{-1} dan getaran sulfat pada 1151cm^{-1} dalam ujian FTIR menunjukkan kewujudan gipsum kontang ($CaSO_4.2H_2O$). Imej SEM juga menunjukkan kehadiran bentuk gipsum heksagon dan diikuti oleh komposisi Kalsium Oksida (CaO) dan Sulfit (SO_3) yang diperolehi dalam analisis XRF membentuk gipsum. Keputusan XRD juga menunjukkan kehadiran kristal fasa gipsum dan kalsit. Sisa kaya gipsum sesuai digunakan untuk industri pertanian dan papan gipsum kerana ia memenuhi semua spesifikasi industri. Kandungan Magnesium, Mg yang tinggi 5.87% sesuai untuk pertumbuhan tumbuhan kerana ia boleh bertindak sebagai garam larut untuk membekalkan nutrin. Ia juga sesuai untuk aplikasi papan gipsum kerana kandungannya tidak mengganggu proses penghidratannya. Kandungan silika (SiO_2) 0.62%, Chlorine (Cl) 2.8% dan Na (Sodium) 0.7% memenuhi spesifikasi industri pertanian dan gipsum. Kandungan besi dalam sisa gipsum cukup tinggi untuk aplikasi gred tinggi papan gipsum. Salah satu cara untuk mengurangkan kandungan besi adalah menggunakan kaedah pelarut asid organik. Nilai indeks keretakan yang diperolehi adalah sangat optimum iaitu 19.78 yang memberikan kekuatan yang baik untuk aplikasi papan gipsum.

CHARACTERIZATION AND POTENTIAL INDUSTRIAL APPLICATION OF GYPSUM RICH WASTE.

ABSTRACT

NUF Gypsum rich waste which is by product from REE processing was characterized and analyzed to compare between natural gypsum and evaluate their quality suitability for specific industrial application. They were analysed by using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetric (DSC) / Thermogravimetric Analysis (TGA) and X-Ray Fluorescene (XRF) analysis. Other test included pH test, LOI, moisture, specific gravity and plasticity test are also done. The present characteristic bond of water vibration at 3606-3558cm^{-1} and sulfate vibration at 1151cm^{-1} in FTIR test indicates the present of gypsum anhydrate ($CaSO_4.2H_2O$). The SEM photomicrograph also shown the presence of hexagonal shape of gypsum and followed by composition of Calcium Oxide (CaO) and sulfite (SO_3) obtained in XRF analysis which lead to formation of gypsum. The XRD results also indicate the presence of gypsum and calcite phase crystallinity. The gypsum rich waste is suitable to be used for agriculture and gypsum board industry since it met all the industrial specification. The high contain of Magnesium, Mg which is 5.87% is suitable for plant growth as it can act as soluble salt for the nutrient supply. It also suitable for gypsum board application since the content would not disturb the hydration process of gyspum board. The content of silica (SiO_2) 0.62%, Chlorine (Cl) 2.8% and Na (Sodium) 0.7% meet the specification of agriculture and gypsum board industry. The iron content in the gypsum waste is quite high for the high grade of gypsum board application . One of the way to reduce the iron content is by using organic acid leaching method. Plasticity index value obtained is significantly optimum which is 19.78 which lead to a good strenght for gypsum board application.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Gypsum is a sulphate mineral which occur under salt water that form million years ago with a chemical composition $CaSO_4.2H_2O$ (Calcium Sulfate Dehydrate). It is normally mines in open pit at many worldwide countries like China, United State, Spain, Iran and Turkey. China is the leaders in mining and producing the gypsum (Gypsum statistic portal, 2015). Gypsum has been used through the age for a construction, fillers and others. Throughout the age, the gypsum has been used in construction since the day of ancient Eqypt. In 19th century, gypsum is well known with its function in making gypsum board. Around 20th century, the industry of gypsum booms since World War I happened which brought the usage of gypsum into many building construction.

The fire-resistant properties of gypsum leads to a better and suitable for construct military housing (Piątkowska and Pala, 2013). It is also has durability properties which lead to a good instability of structure and it can be proven that the ancient Egypt that has been build 5,000 years ago. The softness of the gypsum properties lead to high usage of alabaster as material sculptural. However, in this modern days, people and researcher has discovered the usage of synthetic gypsum to replace the natural gypsum. Synthetic gypsum has approximately the same properties

like natural gypsum and it is broadly used in many industry like cement, paper, gypsum board and others (Rebbling *et al.*, 2016). Synthethic gypsum is obtained through the chemical process which in the form of by-product. The chemical process is usually the acid neutralizing industrial processes. It can also obtain by recycle the waste gypsum

that has been used. One of the famous type synthetic gypsum is called as Flue Gas Desulfurization (FGD) which is obtain from the fossil fuel plant when the pollutant gas is scrubbing with added calcium carbonate to eliminate the impurities. It left the gypsum by-product. The same properties of synthetic gypsum with natural gypsum leads the manufacturer to consume synthetic more than natural gypsum. The reasons is, sources of natural gypsum are conserved and need to mine them is reduced.

Besides, the material that are going to landfill will be reduced. The synthetic gypsum can be 100% recycle able which they can be reused or reprocessed over and over without loss of quantity. It can be said that synthetic gypsum used interchangeably with natural gypsum in many application. There are many application of natural gypsum and synthetic gypsum. One of them is in process of cement making. It can be used as a retarder to avoid or reduce the setting time (Wang *et al.,* 2012). Setting time is necessary to avoid faster hardening of the cement and it will enhance the quality of product since it meet the customer's specification.

They can also use in agriculture which the supply of nutrient is important for the growth of plant. The natural and waste gypsum composed of calcium which can be used as fertilizer for the soil (Pérez-López *et al.*, 2010). It will remain the soil with no erosion and water lodge since gypsum may also act as absorbance. Besides, synthetic and natural gypsum also famous in construction field. The making of plaster board and gypsum plaster has proved a good mechanical strength and also fire resistance. They are also been used in road construction road. It has experimentally proved that the mixture of phospogypsum which synthetic gypsum can also be used in construction of upper layer of road embankment (Chandara *et al.,* 2009). The lower layer can be construct by using phosphogypsum-ash mix with no binder.

In current literature, the usage of synthetic gypsum is only focus on certain industry application like construction, agriculture and so on. Exposure of the industrial specification for each type of product from synthetic gypsum is also less. Therefore, a study on applicability of synthetic gypsum to replace natural gypsum for many application was chosen. The differences or similarity data of synthetic gypsum and natural gypsum will lead to determine suitability for a variety of application.

1.2 Problem Statement

Potential of Gypsum often found in various industrial application which requires difference specification and quality. The difference formation and process of natural and synthetic gypsum may lead to a different physical and chemical properties of gypsum. The synthetic gypsum may have a different properties compared to natural gypsum. Therefore, it is important to evaluate both of the gypsum based on their minerology, chemistry, physical properties to determine their suitability for industrial application and for subsequently exploitation and processing as well for value-added potential.

1.3 Research Objective

The objectives of this research are:

1) To characterize the synthetic gypsum based on the mineralogy, chemistry and industrial technical properties and compare the properties with natural gypsum.

2) To determine their quality suitability for specific industrial applications.

3) To evaluate the potential of synthetic gypsum waste as an alternative industrial raw materials by comparing their properties with the industrial requirement.

1.4 Research Scope

This research is conducted to study the applicability of NUF gypsum rich by-product from Gebeng processing plant, Kuantan. The sample synthetic gypsum which is by-product from the acid neutralizing process which in a chemical process for REE production. The different properties of this gypsum waste makes this research significance to investigate and compare its use ability with natural industrial gypsum. This thesis will investigate the properties of synthetic gypsum and their potential as raw material in various industrial application.

1.5 Hyphotesis

At the end of the project, the objectives of the project need to be achieved. The mineralogy, chemistry, physical properties of synthetic gypsum is analyzed. Their suitability for industrial applications is determined and the potential of synthetic gypsum as an industrial raw materials can be evaluated by using all the results from different tests. The properties of all gypsum can be compared with well-known industrial specification.

CHAPTER 2

LITERATURE REVIEW

2.1 Gypsum

The word of gypsum is literally obtained from a Greek word which is gypsos with meaning of plaster. It also comes with English version which is called as Spear Stone which referring to crystalline projection. Gypsum is sulfate mineral with a chemical formula of $CaSO_4.2H_20$ (Calcium Sulfate Dehydrate). The color ranges from colorless, white, blue, reddish brown or gray depend on impurities present. Gypsum is famous with its crystal habit and the crystal is normally found perfectly inviolite without any broken part. Gypsum is commonly rock like mineral which can be extracted and process for many industrial application.

Gypsum normally found in a tier which the formation is under salt water that form million years ago. The mineral is obtained once the water is evaporated since gypsum composed of Calcium Sulfate ($CaSO_4$) and water (H_2O). The gypsum often begin in White Sand National Monument in New Mexico as the biggest deposit of gypsum in the world (Singh and Garg, 1997). The crystal of gypsum can be expand under ideal condition which can be as large as 4 feet diameter and 50 feet long. The gypsum is feeling balmy when touch and the crystal is merry widow easily from specimen if correlated with ordinary rocks.

Gypsum typically subsist various amount of $CaSO_4.2H_20$ (dehydrate), $CaSO_4.0.5H_20$ (Hemihydrate) and $CaSO_4$ (Anhydrate). The forming of hemihydrate is commonly done by calcination or heating the dehydrate Gypsum at temperature of 175℃

to remove 75% of water content. This process is usually done to make a plaster of Paris which about 25% remaining water in gypsum is vital. Upon continuously heat the hemihydrate, the gypsum will become anhydrate which is totally lost of water (Chandara *et al.*, 2009). This changeover cause the water to absorb to atmosphere and having a volume cutback.

$$CaSO_4.2H_2O \rightarrow CaSO_4.0.5H_2O + 1.5H_2O \qquad \text{Eq 2.1}$$

The rehydration process can be achieved recover to glean back the dehydrate gypsum. The dry powder or hemihydrate gypsum can be mixed with excess water and some additive. This process is beneficial in application of plaster board which in making the plaster cemented at the cardboard. By adding surplus of water, it will keep the gypsum with a fluidity which can be used for many manufacturing process. The end progress for drying the excess water can be contrived by self-evaporation or heating at temperature of 250^{o}C for 60 minutes. According to Malinowski (2014), the sundry amount of Calcium Sulfate with have adverse effect on the settling time for industrial cement application. Each of the phase have their own role in fasting and slowing the chemical reaction in cement manufacturing and other applications.

$$CaSO_4.0.5H_2O + 1.5H_2O \rightarrow CaSO_4.2H_2O \qquad \text{Eq. 2.2}$$

2.2 Types of Gypsum

Generally, gypsum consist of two types which are natural gypsum and synthetic gypsum. The natural gypsum is mostly occur naturally in many countries like China, United State and Spain. Gypsum also mined in 17 states like Texas, New Mexico and Utah. The second source of gypsum is synthetic gypsum which is obtained from byproduct of certain chemical reaction and from recycling the gypsum waste. In Poland, the amount of phospogypsum produced annually is over 2.5 million metric tons (Folek *et al.*, 2011). In Malaysia, the synthetic gypsum is used as raw material since there are no gypsum mine available.

2.2.1 Natural Gypsum

Natural gypsum is naturally occurring which $CaSO_4.2H_20$ (Calcium Sulfate Dehydrate) is accumulate in sedimentary layers on the sea bed. The repercusion from high temperature and pressure makes the Calcium Sulfate Dehydrate lost its water content and turns into Anhydrite ($CaSO_4$). In nature, gypsum occurs in a bed with a few meter thick. The range of hydration can be influenced by the temperature and pressure which topography and structure of deposits plays the role. There are also contain of chalk and clay in gypsum and contain of gypsum range from 75% to 95%.

Generally, there are 9.52 Kg of chemically combined water in hundred pounds of gypsum rock. Mostly, gypsum is mined in open cast and some by underground mining. The fines from the gypsum is screened then being crushed by jaw crusher. The crushed product is deliver to the grinder for further fine grinding (Plotegher and Ribeiro, 2016). The grinding process guide by the usage of cement clinker.

The fined grain of gypsum is further undergo calcination which about three quarter from its water content is removed producing hemihydrates gypsum. The temperature for calcine process is normally about 175℃. It is also famous with a name that called 'Plaster of Paris'. In application of recycling, the hemihydrates gypsum can be added with water to form back the gypsum. Normally, calcined gypsum become the based for gypsum plaster, gypsum board and other products

2.2.2 Synthetic Gypsum

The synthetic gypsum attempts a safe, economic and recyclable products to supplant the natural gypsum. Synthetic gypsum commonly have the common properties like natural gypsum which is result from some research. Synthetic gypsum can also cut down the pressure demand on the natural resources of gypsum and it can be achieved by two ways which are by recycle and by-product form chemical reaction. (Doleželová *et al.*, 2018). There are five different product of synthetic gypsum obtain which are FGD, Phospogypsum, Titanogypsum and Citrogypsum.

FGD is obtained from a power station plant which are the end product from the reaction of wet purification procedure with natural lime. This process took only a few hours and it can replaced the usage of natural waste. Another specialty for this product is it contains about 94% of gypsum compared to natural gypsum which contain only 83% of gypsum. The reaction happens when there are chemical reaction between the slaked quicklime with flue gas that happen in scrubbing towers. The SO_2 is washed while precipitated form of $CaSO_4.2H_20$ is collected. It is in the form of moist and fine crystalline powder.

Phospogypsum is mainly obtained from the reaction of sulpuric acid with sulphate mineral. Tricalcium Phosphate will react with sulphuric acid to form the phosphoric acid and Calcium sulphate. The calcium sulphates is present in dehydrate or hemihydrate as it influence by the phosphoric acid concentration and the temperature of the sulfuric acid. Some of the phospogypsum product is contain a deviant crystal shape and may contain a very small amount of trace natural radioactivity. However, the significant amount of the trace doesn't give any harm to human being. About 5 tons of phospogypsum is produced for every tons of phosphoric acid manufactured (Papastefanou *et al.*, 2006)

$$Ca_5(PO_4)_3X + 5\ H_2SO_4 + 10\ H_2O \rightarrow 3\ H_3PO_4 + 5\ (CaSO_4 \cdot 2\ H_2O) + HX \qquad \text{Eq. 2.3}$$

Next, Titanogypsum is along the chemical based synthetic product of gypsum. This product is obtain from the process of Titanium dioxide. Processing of Titanium Dioxide involved two processes which are chloride and sulphate process. However, only sulphates process produced the gypsum. the contain of gypsum is about 55% which also called as 'White Gypsum'. Citrogypsum is obtain from the reaction between Citric acid with lime to produced Calcium Citrate and wash. The acidification with sulphuric acid will diminishe the pure citric acid and form the gypsum. Contain of gypsum is about 40% which can be further purified by the gypsum processed.

Fluoroanhydrite is another type of synthetic gypsum. The anhydrite is obtain from the reaction of fluorite with sulphuric acid. Contain of gypsum is about 66%. There are also some organic acid that can reborn the gypsum like formic and oxalic acid. Additionally, the products that end with sub-product Sulphuric acid are possibly to obtain

the gypsum product. The synthetic gypsum is always to cover the basic need of gypsum raw material.

2.3 Application of Gypsum in Industry

As stated by U.S Geological Survey (2005), the gypsum end-use statistic increase for Podrtland cement claim by 3 million tons. The second largest demand for gypsum is agriculture and sundry by 1 million tons and followed by plaster industry by 6 thousand tons. The number of demand in tons for each type of product increase by years. It shows and proves that gypsum is one of the industrial mineral that can be used in multipurpose application. By that reason, industry nowadays more preferably demand for the synthetic gypsum rather than natural gypsum to ensure the sources of natural gypsum are conserved and need to mine them is reduced.

Table 2.1: The percentage of gypsum uses in industry.

No.	Industry	Percentage of Uses
1.	Portland cement	50%
2.	Agriculture and miscellaneous	15%
3.	Plaster of Paris	12%
4.	Gypsum Board	10%
5.	Fillers and pigment uses	5%
6.	Glassmaking	4%
7.	Paint and joint compound	2%
8.	Others	2%

Gypsum can be adopted in the production of cement or Poland cement. Synthetic gypsum may also take part to reinstate the usage of natural gypsum in usage of setting retarder for cement since environmental concern and lack of natural deposit of natural

gypsum (Chandara *et al.*, 2009).The properties of dehydrate, hemihydrate and anhydrate is correlated with the performance of cement product. The presence of hemihydrate will always reduce the setting time of cement while presence of anhydrate totally boost the setting time. Upon cooling of the clinker in cement making, a small amount of gypsum will introduced to control the rate of hardening. The retardation mechanism is when cement is started to hydrate, gypsum will react with clinker to form calcium sulfoaluminate hydrate which form protection on cement particles to hinder the hydration

Table 2.2: Industrial specification of Gypsum retarder in cement.

Characteristics	**Specification (% w/w)**
$CaSO_4.2H_2O$ (Purity)	90
Cl as NaCl	0.1
Moisture (Free water)	15
Total P_2O_5	0.5
Sulfate (SO_3)	48
Calcium Oxide (CaO)	30-36
PH	6
MgO	0.5
Size Distribution	
Passing through	100
250 Micron	50

Gypsum can also be used in agriculture as fertilizers forms. This product has been applied in United State for about 250 years. Gypsum is soluble for plant nutrient, calcium and sulfur thus it reduce the loss of nutrient and tendency for soil erosion to be happened. Without calcium, the mechanism would fail due to lack of calcium supplied. A little changes for amendment for acidic soil reclamation can also include in the usage of gypsum. It will treat the toxicity through neutralized the soil and reduce the PH of soil. The gypsum may applied at the surface and being leach down to the subsoil. By putting gypsum in soil, they will retain the soil to drain without having any water lodge due to combinations of high sodium, water and clay (Papastefanou *et al.*, 2006).

Table 2.3: Industrial specification of gypsum in agriculture.

No.	Properties	Industrial Specification (%)
1.	MgO	10
2.	Na_2O	<0.8
3.	Soluble Chloride	<0.1
4.	Ca	24.5
5.	Sulphur (S)	16.1
6.	Phosporus (P)	0.03
7.	Potassium (K)	0.36
8.	Magnesium (Mg)	6.0

Next, gypsum can also use in making plaster of Paris. The expeditious setting of Calcium Sulfate Hemihydrate will produced the gypsum plaster. Gypsum plaster usually used to form the surface of wall smooth and it is actually different with the plaster or mortar used as agent glue in construction. It is commonly known as Plaster of Paris due to the plenty of deposit of gypsum found beneath Paris. In order to obtain a solid mass of gypsum, water need to be added. Present uses of plaster can be used in many manufacture of plaster board, fibrous plaster, plaster cornics and plaster moulding. Each

has their own function like smudging two sheet of cupboard, agent of hardening, decorative agent and so on.

Among others, gypsum also known for their usage in making gypsum board. It usually used as aarch for ceiling, wall for building material and commercial structures. It has strong fire resistant, monolithic surface and fastener heads covered with a joint treatment system.The slurry of gypsum is design by adding water in calcined gypsum. The slurry is the placed at between of paper in a board machine. The calcium sulphate will recrystallize once the board is pass through the conveyor line. It is spontaneously having mechanical and chemical bond. The final product of gypsum board can be cut and being dry by using a dryer.

Gypsum can also be used as filler for paint, paper and so on. It has a low density and constant weight that lead to thicker coat. It can totally reduce the weight of the paper and increased the gloss. Gypsum filler can also have high dispersibility which can be efficient in solvent mixing. Gypsum has also wide usage in making ceramics like earthenware, porcelain, stoneware and so on. It can act as filler of as the plaster for making the surface of ceramics smooth.

2.4 Gypsum Board Industry

The gypsum board has been widely used nowadays to replace the asbestos for the wall of ceiling and so on. The usage of the gypsum board are widely used in 21st century during world war I. Good technical and mechanical properties of gypsum board make them suitable for housing and building construction on that time. The high fire and thermal resistance make them suitabe for a heat resistant building construction purpose (Rozanna *et al.*, 2005). It also act as replacement the usage of plywood, hard and

fibreboard whch has nearly low grade or quality. The replacement usage of gypsum board will gradually decrease the consumption of gypsum raw material and its mining.

The usage of gypsum board in replacing the asbestos is the right chosen since it is lighter than the previous one (Ghazi Wakili *et al.*, 2007). The asbestos is heavy and not practicable for the construction purpose plus lead to dificulties in transportation. China and India are the leading producer of gypsum board with over 1.30 miillion metric tons produced in 2016. The gypsum board is also used in many applications like marble, ceramic tile, backling materials and exterior building which some of the industry will add additives during the process making of plaster board to improve the impact resistance and sound attenuation qualities.

The raw material which is obtained from the mining of gypsum is sent to the processing plant for processing and treatment. However, for synthetic gypsum. it is by-product from the acid neutraliation processed. Last 1980s, all the natural gypsum are used for gypsum board production untill new technology processing the gypsum board introduced in Europe back in 1960s. to start the process of wall board production, the synthetic gypsum or natural gypsum are crushed into powder and heated up to 350℃ to remove the combined water and mositure. It is also called as calcination which also refers to removing three fourth of the water. The gypsum is turn into hemihydrate and the excess removal of water need to be done in order to obtained anhydrate of gypsum.

Anhydrate of gypsum is crucial for feeding in gypsum board plant since it will give an optimum result during hydration process (Erbs *et al.*, 2018). The calcined or hydaretd gypsum is added with water and additives to form a slurry . The slurry is the fed into board machine which consist of continuos layers of paper. Once the face and back paper become mechanically bonded to gypsum core, the machine wrapped the edges

of the paper . The board is then dried and recrystallized when it is conveyed by conveyor line. The board is cut into length and conveyed through dryers to remove the mositure.Ater driven-off the mositure, the board is trimmed and cut to its final lenaght . Two different core is combined together to form a double sheet of gypsum board and it is prepared for storage and shippping.

2.5 Gypsum plaster industry

Gypsum plaster has been widely used in industry to replace the plastering using sand cement. It is also a modern day solution to replace the old method of plastering construction industries, due to its excellent and unique properties, it is commercialized and caught attention in construction industies. It has excellent properties of insulation, thermal and acoustic insulation, the gypsum plaster also has impact resistance and protection against the fire, mositure and vapors. It also has a minimum curing time and subsequently will reduce the cost of processing it. Since it has a good protection of insulation, it is very suitbale to be used for housing construction since it can keeps the houses cool during summer and hot during winters due to its low thermal conductivity (Bicer and Kar, 2017).

The market of gypsum plaster is divided into two which are manually applied plaster and auto-applied plaster. Most of construction field nowadays are demand for machine-applied gypsum since it is easier to applied for palstering and finishing purposed (Lamrani *et al.*, 2017). The demand of the gypsum plaster are also for residental and non residental. In residential area, the demand is very high since the finishng of gypsum plaster will give a smooth surface on the wall of cosntruction. It is diifers with using the sand cement as the finishing since it give a very rough surface. The demand for non-

residential is at medium scale which the quality of finishing is not as impotant factor to be determined.

The demand for gypsum plaster also increased to replace the plaster material in cement industry and also to reduce a new construction by repair the exiting infrastructure using gypsum plaster (Pervyshin *et al.*, 2017). The gypsum plaster is chosen by construction industry since it has low duration of water curing and crack doesnt exist during the hydration of the gypsum plaster. The gypsum waste also has light weight and has low thermal conductivity which lead to to the decreasing structural loading. The price of gypsum plaster is slightly more expensive than the sand cement gypsum. The gypsum waste has reached the global market like in North America, Latin America, Asia Pacific, Europe and others. It also due to the growth of construction industry in these country which consume the gypsum as raw material for the industry. The demand for residential houses in Germany and France also increased the demand of gypsum plaster.

Untill now the gypsum plaster is demand around world. In kazhakstan, the gypsum is very popular in usage for cooking material and ware. This is due to the good heat absorber and also the the firing properties. As we know, the cooking ware must be made from a very high quality of material. Before this, the utilization of the ware is made from the ceramics which it is actual consume a lot of cost to develop it. The alternative by using the gypsum is the best choice since it is cheeper and readily availabe.

2.6 Rare earth Extraction

The rare earth has been widely extract by using the process of laching and acid neutralization. Rare earth are commanly extract in Australia, China and Afghanistan. In Malaysia, the extraction is not allowed due to the avoidance from the people. The extraction may be in a large scale which will contribute to the exposure of the rare earth

element to the surrounding. Folek s, et. al. (2014) state that the limit for rare earth spreading to the environment is about 5 baqueral (bq). However, in Malaysia, got one processing plant which lead the process of processing rare earth mineral. The rare earth is not mined at Malaysia.

The extraction of rare earth is started by mining the deposit. Then they will undergo crushing and another few process of size reduction. The size reduction is important in order to have an optimum processing or seperation process. Then the ore of rare earth will be washed and feed into the process of leaching. The leaching process is done since the rare earth mineral are almost similar to the physical and chemistry properties which lead to a dificulty of processing it. It is done by introduce the process with ore concentrate, concentrated sulphuric acid and also the natural gas. The process will proceed with cracking stage at 400℃. It will produce the gas off treatment to the surrounding. The treatment is by using the calcium carbonate ($CaCO_3$).

Then, it will procedd with neutralization stage with the Magnesium Oxide. The neutralization stage will produce another source of gypsum. The dissolve REE will go to the Extraction and seperation stages which include the Hydrochloric (HCL) acid and the Calcium Carbonate ($CaCO_3$). Another by-product of gypsum is then obtained by the extraction and seperation stages. The extraction of REE product are very important since it can produce a valuable product of REE for industrial application like in making electronic appliance and also another type of products. However, people get worried with the radiation from the REE. The radiation of REE will give adverse effect to the human health and also to ecosyatem (Hammas, Horchani-Naifer and Férid, 2013). However, the serious care has been taken in order to reduce or avoid the contaminat of REE.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The sample of waste gypsum is obtained from REE mineral processing located in Gebeng, Kuantan. It is by product from the acid neutralization which is also known as neutralized underflow (NUF). The sample waste gypsum per received are accordingly analyzed and characterized as sample received. It is in the form of wet cake. The cake has been dried in an oven furnace to remove the percentage of water by 70% for subsequent testing. The raw gypsum and waste were characterized for their minerology, chemistry and physical properties. These tests are done to investigate the properties of synthetic gypsum for their similrity and differences with the natural gypsum for a various industrial application.

Minerology or phase composition and crystallinity are analyzed using X-ray Diffraction (XRD) and chemical analysis using X-Ray Fluorescene (XRF). The texture and morphology of the synthetic gypsum is determine by Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX). Infrared (FTIR) test is conducted to determine the grade and concentration or also known in determination the purity of waste gypsum. The Differential Differential Scanning Calorimetic (DSC) and Thermogravimetric Analysis (TGA) test is done based on thermal behavior of synthetic gypsum sample which influence by absorption and transmission of the heat.

The test such as free water or moisture, Loss of Ignition, pH, Specific gravity and plasticity test also carried out to investigate the industrial technical properties of synthetic gypsum. The physical test is very important for a plaster board and gypsum

plaster in industry. Industry is concern on the strength of material as it has been used in many building and construction field. The other test like chemistry and minerology not only used for characterization purpose, but is also useful in determination its suitability for industrial application like in agriculture since the properties like grain size, trace element found and other component are the crucial data needed.

3.2 Flowchart of Research Work

The received gypsum waste sample are examined and analyzed to determine their composition, minerology and physical properties as shown in **Figure 3.1.**

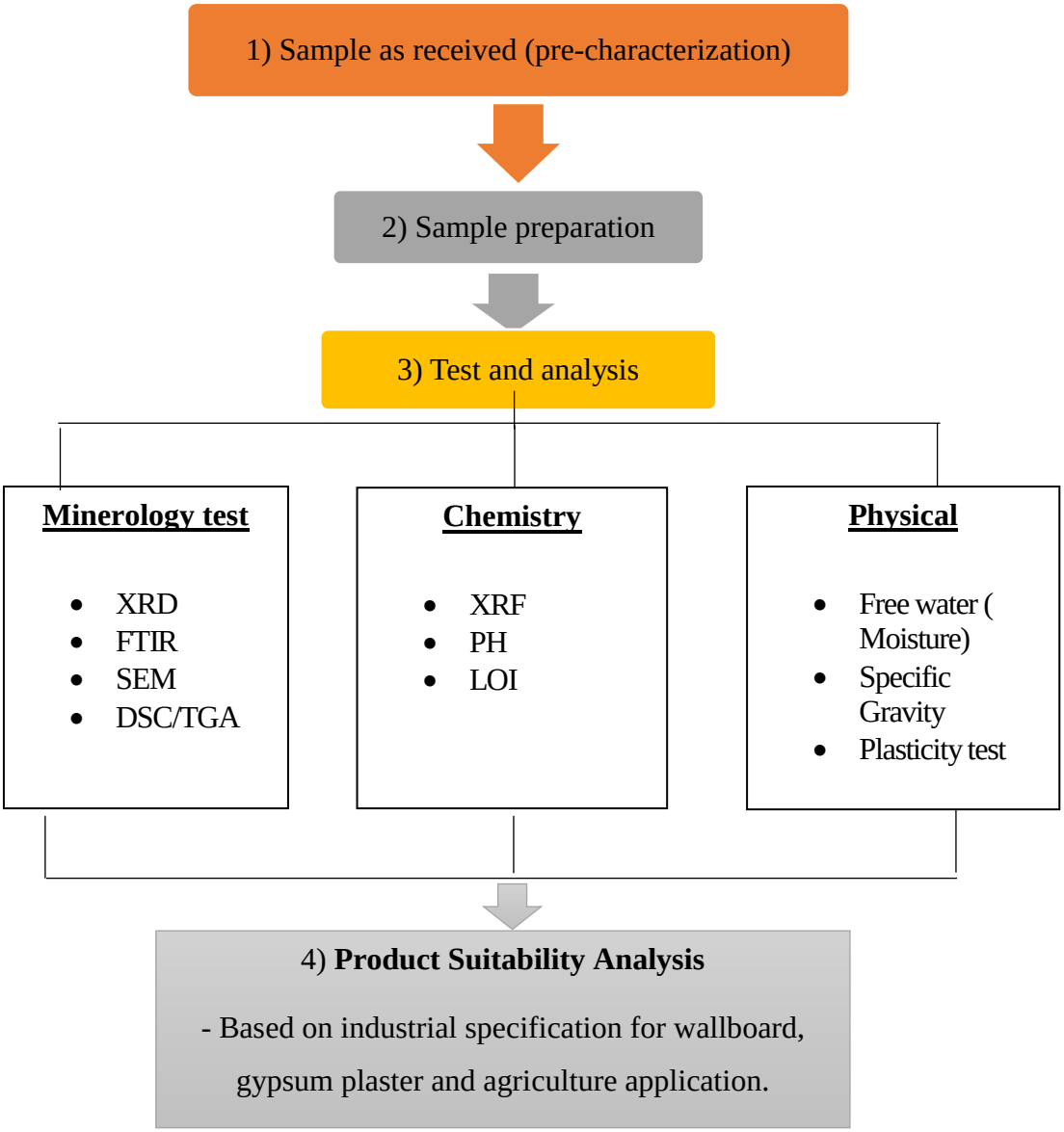

Figure 3.1: Flowchart of research work

3.3 Material

The disposal waste which is rich with gypsum is obtained from a company located in Gebeng, Kuantan and mainly involved in the process of extracting REE. The plant processed the REE concentrated which rich with REE containing phosphate mineral from MT Weld mines in Australia. The processing method is illustrated in **Figure 3.3** where the concentrated is first mixed with concentrated sulfuric acid and cracked or roasted at high temperature in rotary kiln. This material then leached with water and excess sulfuric acid which neutralized with magnesium and filtered to remove impurities like iron phospogypsum and the solution is then neutralized. The purpose of leaching process is to remove the phosphate. The REE obtained is like Sm, Eu, Gd, Ln, Ce, Pr and Nd element. It involved many stages of separation process since these element have almost similar physical and chemical properties that lead to the application of leaching process instead of via physical separation.

The by-product from the extraction process of REE is mainly gypsum rich by-product. The Sulphur dioxide from cracking and leaching are treated to form a gypsum compound which called Flue Gas Desulphurization (FGD) waste. The iron phospogypsum from leaching and acidified water neutralized to form Water Leached Purification Residue (WLP) and Neutralization Underflow (NUF). For each tone of REE material produced, there will be about 12.41 ton solid residue of the waste. The wastes mainly consist of NUF (7.93 ton), WLP (2.85 ton) and FGD (2.63 ton). These by-products is produced from process of cracking, neutralization and extraction and separation stages in REE processing. Each of this waste contains a substance mainly gypsum with different types of REE element. It is also known as synthetic gypsum. In this research, the synthetic gypsum obtained is NUF type.

Figure 3.2: Location of waste material dumping site (synthetic gypsum by-product), (Googlemaps,2018).

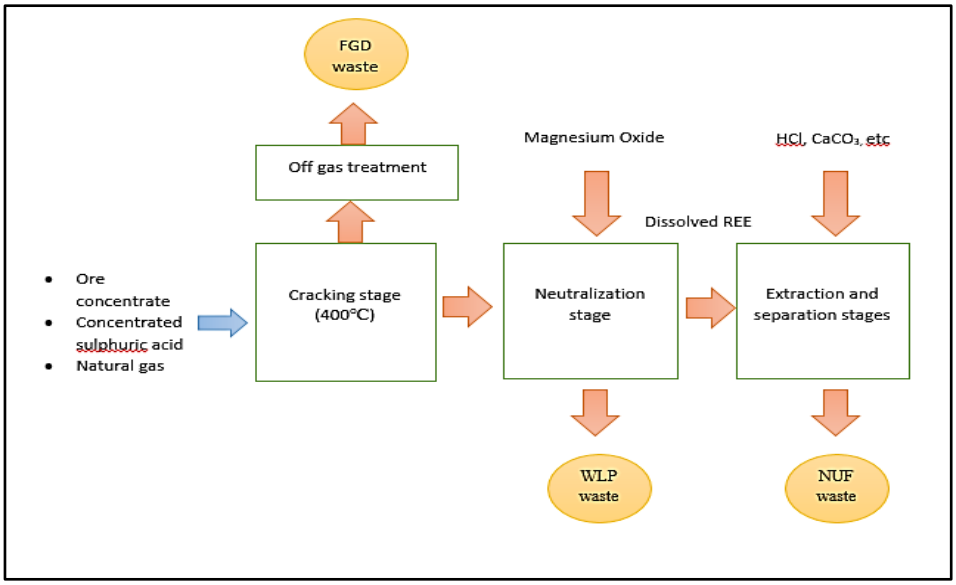

Figure 3.3: Process extraction of REE with gypsum as by-product.

3.4 Sample Preparation

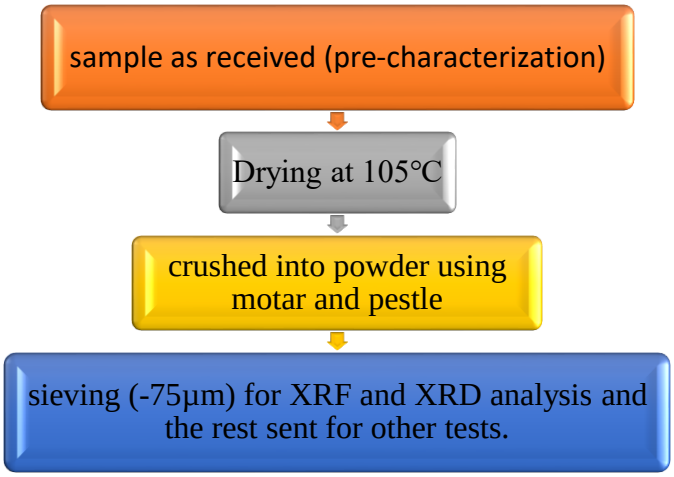

Figure 3.4: Flowchart of sample preparation

The sample preparation process of gypsum waste is illustrated as in **Figure 3.4**. The gypsum sample is first pre-characterized as per sample received. It is fine grain, high plasticity and a bit light yellowish and brown in colour as shown in **Figure 3.5**. The gypsum waste with weight of 1 Kg which in the cake form is then dried in furnace at temperature of 105°C. Oven drying method is the most accurate and standard laboratory test procedure. It is as preparation for the next test that are going to be conducted. The drying times may varies up to 24 hours or more depend on the water content. After the residue of water and moisture driven-off, the sample is sieved to size below 75µm for XRD and XRF analysis respectively. The rest of them is sent for another tests.

Figure 3.5: Sample as received NUF gypsum waste