CHARACTERIZATION AND POTENTIAL UTILIZATION OF GYPSUM FROM LAO PDR

By

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SANGKHONE PANHYAVISY

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TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
BET	Brunauer, Emmet, Teller
BC	Before Christ
CIS	Commenwealth of Independant States
DSC	Differential Scanning Calorimetry
FGD	Flue gas desulphurization
EDX	Energy dispersive X-ray
LOI	Loss on Ignition
G_V	Gypsum from Vilaco
G_D	Gypsum from Donghene
Ma	Million years ago
NE	North-East
PPL	Plane-polarized light
PVC	Polyvinyl chloride
SEM	Scanning Electron Microscope
SW	South-West
TGA	Thermal Gravimetric Analysis
XPL	Cross-polarized light
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
XRM	X-Ray Mapping
USGC	United State Gypsum Company

LIST OF SYMBOLS

%	Percentage
ºC	Degree Celsius
d10	10% volume of the particles have a size value smaller than the given diameter
d50	50% volume of the particles have a size value smaller than the given diameter
d90	90% volume of the particles have a size value smaller than the given diameter
$H_2 SO_4$	Sulfuric Acid
$CaSO_4$	Calcium sulfate
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CO_2	Carbon dioxide
km	Kilometer
m	Meter
cm	Centimeter
mm	Millimeter
µm	Micrometer
cm^3	Centimeter cube
g	gram
rpm	Revolutions per minute
ppm	Pass per million
Mt	Million tone
ml	Milliliter

ppm	pass per million
Ǻ	Angstroms
wt%	Weight percentage
g/cm^3	Gram per centimeter cubed
MPa	Megapascal
cc	Milliliter
M	Million

PENCIRIAN DAN POTENSI PENGGUNAAN GIPSUM DARI LAO PDR

ABSTRAK

Tujuan kajian ini adalah untuk memberi tumpuan kepada penilaian kualiti dan pemprosesan optimuman batuan gipsum daripada persekitaran endapan geologi yang berbeza sebagai sumber yang berpotensi untuk pelbagai aplikasi industri hiliran. Sampel dari endapan gipsum telah diperolehi daripada dua sumber yang berbeza di wilayah Khammouan dan wilayah Savanakhet, Lao PDR. Sampel gipsum ini adalah tertakluk kepada penyiasatan makmal terperinci termasuk pencirian bahan mentah dan penghasilan gipsum untuk menilai dan menentukan serbuk gipsum yang telah dikalsinkan untuk setiap sumber gypsum. Berdasarkan dari asal-usul geologi kedua-dua sumber gipsum mempunyai cirian mineralogi, kimia dan fizikal yang serupa. Kedua-dua sumber dari kelas I (gred tinggi, 98% daripada $CaSO_4.2HO_2$), satu keperluan khas bagi pelbagai aplikasi industri seperti plaster, gentian dinding, simen, makanan dan farmaseutikal, dan desulphurization gas serombong (FGD). Walau bagaimanapun, kedua-dua gipsum tidak sesuai sebagai baja dan cat. Ini membuktikan bahawa kualiti produk akhir dan penyediaan sebahagiannya ditentukan oleh asal usul geologi sumber gipsum terutamanya faktor mineralogi batuan. Serbuk gipsum dihasilkan selepas penghancuran, pengisaran dan pengkalsinan pada beberapa suhu (110 º C, 150 ° C, 175 ° C, 200 ° C, 225 º C & 250 º C) didapati dalam bentuk $CaSO_4.0.5H_2O$ (hemi anhidrat), di mana air telah dikeluarkan. Keputusan ini disokong dari fizikal, kimia dan mineralogi pencirian pada kalsin gypsum. Luas permukaan BET daripada G_V adalah 3.02m^2 / g dan G_D = 3.03 m^2 / g, dan ketumpatan pukal G_V adalah 2.93g/cm^3 dan G_D = 2.94g/cm^3. Elemen utama terkandung adalah CaO (35% -37%), dan SO3 (40% -42%). Puncak utama hadir dalam difraktogram XRD adalah bentuk hemi-anhidrat dan analisis EDX menunjukkan kehadiran 3 unsur utama Ca, S dan O. Kajian ini membuktikan suhu pengkalsinan dalam julat 120 º C - 180 º C merupakan suhu pengkalsinan optimum yang menukarkan gipsum kepada produk gipsum yang mempunyai kualiti untuk kegunaan industry.

CHARACTERIZATION AND POTENTIAL UTILIZATION OF GYPSUM FROM LAO PDR

ABSTRACT

The aim of this research work is to focus on the quality evaluation and optimization processing of the gypsum rock formed from different geological depositional setting as the potential resources for many downstream industrial applications. Samples from naturally occurring gypsum deposits were sought from two different resources in Khammouan province, and Savanakhet province, Lao PDR. These gypsum samples were subjected to detailed laboratory investigations including raw material characterization and gypsum manufacturing in order to evaluate and determined the optimized calcined gypsum powder for each gypsum resources. Based from the geological origins of these two gypsum resources, they have similar mineralogical, chemical and physical characteristic. Both resources were found to be of class I (high grade with 98% of $CaSO_4.2HO_2$), which is a specification for many industrial applications such as plaster, wallboard, cement, food and pharmaceutical, and flue gas desulphurization (FGD). However, both gypsum are not suitable for agriculture as fertilizer and paint. This proved that the quality of the end-products and its preparation were partly determined by the geological origin of the gypsum resources especially the rock mineralogy. The gypsum powder produced after crushing, grinding and calcinations at several temperatures (110 ºC, 150 ºC, 175 ºC, 200 ºC, 225 ºC & 250 ºC) were found to be in the form of $CaSO_4.0.5H_2O$ (hemi anhydrate), where some water have been removed. This result is supported from the physical, chemical and mineralogical characterization on the calcined gypsum. BET surface area of G_V is 3.02m^2/g and G_D=3.03 m^2/g, and bulk density of G_V is 2.93g/cm^3 and

G_D = 2.94g/cm^3. The main element contain are CaO (35%-37%), and SO_3 (40%-42%). The major peaks present in the XRD diffractogram was in the hemi anhydrate form and EDX analysis shows the presence of 3 major elements of Ca, S and O. The suitable temperature for calcinations was found to be in the range of 120 ºC - 180 ºC at a retention time of 1- 3 hr, which is the optimum condition to produce good quality gypsum powder based product to meet industrial requirement.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Gypsum is one of the most commonly occurring minerals in soils of arid and semi-arid regions; gypsum is chemically exposed calcium sulfate ($CaSO_4.2H_2O$), a white or gray naturally occurring mineral which is a very important industrial mineral resource worldwide. Gypsum is found in nature, most commonly as the sparingly soluble salt $CaSO_4.2H_2O$, and often coexists with calcite (Mohammed and Rowellb, 2006).

Raw material gypsum ore is processed into a variety of products such as Portland cement additive, soil conditioner, industrial and gypsum wallboard (Testa and Lugli, 2000).

Some gypsum deposits contain only about 60 per cent gypsum, and these are not very suitable for producing a plaster; those containing more than 80 per cent would be most suitable (Bhavan, 2011). In the commercial production, system configuration plant setting is based on the following requirements:

Feed size: less than 2 mm with a moisture content of below 0.8%, required end-product fineness: 97% < 100 µm, which is ground and classified using a classifier integrated with a sharp top-size limitation.

To produce plasters or wallboard, gypsum must be partially dehydrated or calcite to produce calcium sulfate hemihydrates ($CaSO_4.0.5H_2O$). [In most plants, land plaster is fed to kettle calciners or flash calciners, where it is heated to remove three – quarters of the chemically bound water to stucco by calcinations at 120Cº to 180Cº (Ecofys, 2009)].

1.2 Significant of Study

Gypsum is available worldwide, and as in Laos, gypsum is widely used for construction material such as cement additive, ceiling and wallboard. In Laos, there are many gypsum resources. However, since gypsum is not locally produced in Laos, gypsum product is imported from Thailand, Vietnam and China. Gypsum is analyzed to obtain base information, but this is depends on the market requirement and specifications. Quality and production aspects of gypsum are subjected to various geological condition and deposition nature of the gypsum during formation. There are two gypsum deposits is studied which have wild area more than other resources, the ultimate market for the gypsum-based almost products often required detailed analysis and product specification. There are relative levels of chemical impurities, which usually restrict the generally high purity grade of gypsum-based products (32.57% CaO, and % 46.50 SO_3) , especially to be used in pharmaceuticals, plaster casts, wall board, dental prosthesis, fever medicine, some cement, fertilizer, paint filler, ornamental, medicine and food (as tofu coagulant).

1.3 Area of study

The area of study covered two deposits which located in mid-central of Laos, the first area is located in Bunghouana village, Xebangfai District, Khammouan Province (Vilaco deposit) with geographical coordinate of (17 º 10’37”N, 105 º01’41’’E), and second area is located in Outumphone District, Savanakhet Province (Donghene deposit) with coordinate of (16 º 33’00”N, 105 º14’59’’E).

Figure 1.1: Location of Vilaco and Donghene deposit

1.4 Objectives

The main objectives of this research are:

- To conduct evaluate the quality and characteristics of raw gypsum using based on mineralogy, chemical composition, and physical properties from different deposits for downstream industrial application and market.
- To investigate parameters requirements that determine optimum condition in preparation and processing of gypsum based product (hemihydrates and anhydrates gypsum).

1.5 Scope of Work

This research work is divided in to 2 main parts which will be addressed in detail in chapter 3. The first part will present the evaluation and characterization of raw material (gypsum) such as physical properties and chemical composition. Gypsum deposits from two different geological origins with diverse characteristic in (texture, color) were collected from two deposits, from Khammoun province and Svanakhet province, Lao PDR, where these samples were subjected to detailed laboratory investigation including mineralogy, petrography, chemistry and physical properties of raw material evaluation gypsum.

For second part, gypsum grinding performance of ground gypsum product (G G P) is evaluated using a ring mill, to study the particle size of gypsum powder.

The effect of particle size of gypsum powder that effect the calcinations quality is also study calcinations temperature, retention time and resulted quality of the produced calcined gypsum are also investigated and quantitative physical and chemical characteristic on composition of calcined gypsum and process gypsum are determined accordingly to ensure it meets industrial thermal properties, specification and requirement. This includes PSD density, surface area, mineralogy, chemical composition and moisture content.

CHAPTER 2

LITERATURE REVIEW

2.1 Gypsum

2.1.1 Formation of Gypsum

Gypsum is a sedimentary and a crystalline mineral and soft, its color is white to gray “chalk”, gypsum mineral consist of calcium sulfate and water and found in many parts in the world and occurred as crystals or as deposits in bed.

Gypsum is the most abundant calcium sulfate mineral that occur under normal sedimentary conditions (Mess and Dedappe, 2005).

Sedimentary gypsum beds were occurred during prehistoric periods in earth’s history. The vas beds in Michigan in US has occurred over a period more than 15-20 million years and stopped forming over 390 million years ago. It is formed in shallow sea basin. The geological areas are called evaporation basins and occur in tidal flats along coastlines, in lagoons, deltas, hot springs, volcanic areas, and even on plant roots.

Gypsum can be formed by oxidation, this chemical reaction forms when oxidation of existing sediments causes gypsum to form and gypsum is replaced by other mineral in the sediments. These gypsum deposits were became sedimentary rock beds when they were cemented together.

Gypsum formation did not stop in prehistoric times, the crystals still occur when minerals crystallize as water evaporates (Testa and Lugli, 2000).

2.1.2 Occurrence of Gypsum

Gypsum occurs in many parts in the world and it is the most common of the sulfate mineral, it is formed as an evaporate mineral and found in alkaline lake mud, clay beds, evaporated seas, salt flats, salt springs and caves.

Gypsum is a common mineral with thick and extensive evaporate beds in association with sedimentary rocks. Gypsum is deposited from lake and sea water, as well as in hot springs, from volcanic vapors, and sulfate solutions in veins. Pure gypsum is white, but other substances found as impurities may give a wide range of colors to local deposits. Gypsum has been occurred to almost every geological age from mid-Jurassic to cretaceous times, the age between 167.7 ± 3.5(Ma) to 164± 4.0(Ma)

There are numerous gypsum deposits occurred in the United State, and North America as a whole. In New York, Utah, Colorado, Oklahoma and Mexico are a few deposits where excellent specimens have been found (Jacob, 2002).

2.1.3 Composition

2.1.3 (a) Terrigenous Components

Terrigenous components are those substances derived from erosion of a land area outside the basin of deposition, and carried in to the basin as solid as such quartz, feldspar, heavy minerals, clay minerals, chert or limestone pebbles derived from erosion of older rock (Folk, 1990).

2.1.3 (b) Allochemical Components

Allochemical components are those substance precipitated from solution within the basin of deposition, but they are abnormal chemical precipitates because in general they have been later moved as solid within basin and they have a higher degree of organization than simple precipitates like broken, whole shells, oolite calcareous, fecal pellets and fragments of penecontemporaneous carbonate sediment torn up and reworked to form pebbles (Folk, 1990).

2.1.3 (c) Orthochemical Components

Orthochemical constituents are produced chemically within the basin and showed little or no evidence of significant transportation or aggregation into more complex entities such as microcrystalline calcite or dolomite ooze, probably some evaporates, calcite or quartz or pore-fillings in sand stone and replacement mineral (Folk, 1990).

2.1.4 Classification of Gypsum Rock

Gypsum is a common mineral in the evaporate rocks and is deposited both in marine evaporative basins and lakes, the anhydrite deposits rehydrate again and transform to become gypsum rocks when it is exposed to weathering processes (secondary gypsum rocks). In general, gypsum rocks composed of gypsum and accompanied by lutites (clays and microcrystalline carbonates) such as minor celestite, quartz, anhydrite, and glauberite can be present (Guinea, 2009).

Gypsum presents a considerable variety in color, texture and structure. Pure white gypsum is common use, though grayish white, white browns , grays and more rarely pink may be noted in industrial (Lugo et al., 2008).

Geophysical technique such as resistivity survey is widely use in mineral gypsum rocks have been successfully identified with electrical resistivity tomography (ERT) profiles (Guinea et al., 2010a), and (Guinea et al., 2010b) elaborated a geoelectrical classification of gypsum rock that establishing a direct relation between its electrical resistivity value and the percentage of lutitic matrix on Table 2.1 (Maysounave, 2011).

Table 2.1: Geoelectric classification of gypsum

	Purity in gypsum (%)	Resistivity (ohm.m)
Lutites and gypsum rich Lutites	0-55	1-100
Transitional gypsum	55-75	100-700
Pure gypsum	75-100	700-1000

2.1.5 Mineralogy of Gypsum

Gypsum forms monoclinic crystals with a perfect {010} cleavage and certainly cleavages along {100} and {101}. Gypsum from anhydrite with lower Mohs hardness scale (1.5 to 2.0), and specific gravity (2.24 to 2.97 g/cm^3), pure gypsum is colorless, but may be yellow, red, and brown because depend on impurities of gypsum. Twinning is common along {100}, and forming “swallowtail twins.” Gypsum is relatively soluble in the fresh water (about 0.2 g/100 g of H_2O), and is easily dissolved or eroded in high humidity conditions or rainfall (Escavy et al., 2012).

Anhydrite forms orthorhombic crystals with perfect cleavages along {100}, {010} and a good cleavage along {001}. Anhydrite has a Mohs hardness scale (3.5), and a specific gravity of 2.97. Pure anhydrite is colorless, but the color change from colorless to dark gray (Elzeakogal et al., 2006).

2.1.6 Chemical Composition of Gypsum

The rock can be defined like a solid substance that occurs naturally because of the effect from three basic geological process such as magma solidification, sedimentation of weathered rock debris and metamorphism.

Gypsum rock is one group of sedimentary rock that occurs on Earth’s surface and formed by burial, compression and chemical modification of deposited weathered rock debris (Feng et al, 2002).

The Sulfates are a mineral group that consisting one or more metallic element and is combined by the sulfate compound (SO_4). All sulfate minerals are transparent to translucent and soft. Rarer sulfate exist consisting substitutions for the sulfate compound such as in the chromates (SO_4) is replaced by the compound (CrO_4). Two common sulfates are anhydrite and gypsum.

Calcium sulfate occurs in the natural condition in two common mineral form as gypsum ($CaSO_4.H_2O$), and anhydrite ($CaSO_4$). They are also found sometimes as a double salt in several compounds, such as syngenite ($CaSO_4KSO_4.H_2O$) and polyhalite ($2CaSO_4.MgSO_4.\ KSO_4.H_2O$) (Frank, 2002).

2.1.7 Physical Characteristics of Gypsum

Gypsum crystals are flexible but not elastic, which means that they can bend, but it cannot spring back, and stay bent. Typically colorless of natural gypsum, white or grey, but it can also be brown, yellow, and red, and monoclinic crystal system, with cleavage good in one direction and distinct in two others (Nesse, 2000).

2.2 Potential Utilization of Gypsum

The potential uses for by product of gypsum are the same like for the uses of naturally occurring gypsum, but only added problems of lower grade and impurities. Therefore, the material must be beneficiated in some manner before normal applications, some of potential uses for this by product gypsum (Oliver, 2012).

The general product from gypsum flowing are:

- ✓ Utilization for agricultural purposes – land plaster.
- ✓ Converting to sulfur or sulfuric acid and cement.
- ✓ Various calcined gypsum product
- ✓ Cement production (retarder)
- ✓ Road base stabilization
- ✓ Asphalt filler

2.2 .1 Gypsum for Construction Materials

Gypsum is useful in wide variety of applications demand for construction material since ancient times. Gypsum was used as a mortar in the Egyptian pyramids in 3000 BC. One of biggest deficiencies of gypsum as construction material is low resistant to water presence. Although, actually, this aspect can be partially solved by adding to the gypsum some compounds based on silicones or other polymer, namely in gypsum card boards. This way, gypsum can be submitted to humid conditions, but even so do not permit utilization in external environments because of its low resistance to long direct contact with water (Eires et al., 2008).

2.2 .1 (a) Gypsum Used in Portland cement

Cement is made by calcinations a mixture of about limestone and clay to form a calcium silicate clinker and add a small amount of gypsum about 3% to 5% to cement and concrete to slow down the drying time (Colak, 2002).

Portland cement clinker is a hydraulic material that consist of at least two-thirds by mass of calcium silicates ($3\,CaO \cdot SiO_2$ and $2\,CaO \cdot SiO_2$), the rest that consisting of aluminium- and iron-containing clinker phases and other compounds. The ratio of CaO to SiO_2 shall not be less than 2.0, and magnesium oxide content (MgO) shall not exceed 5.0% by massGypsum is contained in Portland cement under Centro Cuesta Nacional (CCN) show on Table 2.2.

Table 2.2: Typical constituents of Portland clinker plus Gypsum Cement chemist notation under Centro Cuesta Nacional (CCN)

Clinker	Centro Cuesta Nacional (CCN)	Mass (%)
Tricalcium silicate $[(CaO)_3 \cdot SiO_2]$	C_3S	45-75
Dicalcium silicate $[(CaO)_2 \cdot SiO_2]$	C_2S	7-32
Tricalcium aluminate $[(CaO)_3 \cdot Al_2O_3]$	C_3A	0-13
Tetracalcium aluminoferrite $[(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3]$	C_4AF	0-18
Gypsum($CaSO_4 \cdot 2\,H_2O$)		2-10

2.2 .1(b) Uses of Gypsum in Building

The gypsum is used wildly for building material construction by its diverse applications. The European production of gypsum attained about 21 millions in 1996, and industry has 220 factories that produce gypsum products. Gypsum has an important role in homes and buildings, and is one of the most important construction materials used for interior construction, gypsum building materials are used in many construction types as residential, non-residential, new or refurbished, the ranging from complex high-tech systems to easy to install products adapted for use by the general public. There are many products as plaster, plasterboards, which include a wide range of standard and specialty products, gypsum fiberboard and gypsum blocks, they are all used in the building sector (Mridul and Neeraj, 2010).

2.2 .1(c) Gypsum Concrete

Gypsum concrete is a building material that was used as floor underlayment used in wood-frame and concrete construction as fire rating, sound reduction, radiant heating, and floor leveling. It is a product from mixture of gypsum, Portland cement, and sand. The brand name is called Gyp-crete. Gypsum concrete has been used in the construction industry started in 1980s, because of the advantages over lightweight concrete. Gypsum concrete is light weight and fire resistant, but doesn’t shrink crack.

Gypsum concrete underlayments are current an important choice in complex construction, and they are used rapidly in commercial markets. The growth of commercial application is driven largely by recent increase in compressive strength performance. The compressive strength standards of minimum gypsum concrete underlayment, there are recording on historically was set at 1000 to 1500 psi, and has now nearly doubled to 2500 psi. While not all gypsum concrete underlayment manufacturers and applicators present minimum-strength 2500 psi of products, those that do provide architects with a practical, cost efficient flooring solution that reliably meets a wide range of performance and application requirements. This high strength of product withstands heavy construction traffic not including powdering, dusting chipping or cracking. They also present improved flow ability, and make them almost completely self leveling, reducing application time and finished floor preparation time (Brendan, 2010).

2.2 .2 Gypsum in Chemical Industry

In 2004 identifies gypsum as calcium sulfate and phosphogypsum. According to the National Institute for Occupational Safety and Health (NIOSH), it usually designates the byproduct produced from a manufacturing process as phosphoric acid (Reed, 1975).

The word "gypsum" is used to describe different phases of the same material, including anhydrite (calcium sulfate), selenite, calcined gypsum, and plaster of Paris (Reed, 1975), health council of the Netherlands, committee on updating of occupational exposure limits. This review presents data of dust gypsum and fibers. The information and study data relating to oral exposure to gypsum or anhydrous calcium sulfate and using of gypsum in bone implants is generally not included in this review (Chen et al., 2005).

2.2 .2(a) Flue Gas Desulphurization (FGD) Gypsum

Flue Gas Desulphurization (FGD) gypsum results from the emissions cleaning process known as (FGD), at coal fired electricity generating stations. This cleaning of flue gases is carried out using a finely ground limestone (or lime), which reacts with sulphur dioxide emissions to produce very pure gypsum. The synthetic gypsum has a higher purity (96%) more than natural gypsum, normally purity (80%) gypsum although higher purity natural gypsum occurred in England. The primary purpose of this for reducing of acid precipitation from the atmosphere, the desulphurization process produces carbon dioxide, and reaction taking place in wet scrubbing using a $CaCO_3$ (limestone) slurry produces $CaSO_3$ (calcium sulphite) and can be expressed as:

$$CaCO_3 \text{ (solid)} + SO_2 \text{ (gas)} \rightarrow CaSO_3 \text{ (solid)} + CO_2 \text{ (gas)} \quad (2.1)$$

Other sources of by-product gypsum are available. The main examples of these are titanogypsum and fluorogypsum (Andrew, 2007). The annual production of the three main types of by –product gypsum is given in Table 2.3 (Wrap, 2006).

Table 2.3: Sources of by-product gypsum (Sources: Wrap, 2006)

Type of by-product gypsum	Current utilisation	Current UK production (Million tonnes per annum)
FGD gypsum (from removal of sulphur dioxide from flue gases of coal-burning power stations using FGD)	Virtually all sold on for use in plasterboard or related products	1.4
Titanogypsum (from TiO_2 pigment production)	Majority utilised in plasterboard or landspreading	0.48
Fluorogypsum (from the manufacture of hydrofluoric acid)	Used in cement and floor screed	0.04

United State Gypsum Company (USGC) continues to develop specification and guidelines covering the chemical and physical of synthetic gypsum to help forecast end use suitable in wallboard manufacturer. The guidelines are based in part on past experience with natural and synthetic gypsum. The most wall board manufacturers in North American have developed guidelines based in part on its unique history and particular experiences with synthetic gypsum.

USGC's general guidelines of FGD gypsum along with guidelines from the German Gypsum Association are shown in Table 2.4. The guidelines are not all inclusive list all of gypsum property important to the wallboard manufacturer. The guidelines serve as a starting point in negotiating sale agreements between the wallboard manufacturer and synthetic gypsum supplier. The product specification agreement at USGC is improved to each individual source depending in large part to the percent usage at the wallboard facility, type of synthetic gypsum and capabilities of supplier (Henkels and Gaynor, 1996).

Table 2.4: FGD gypsum guidelines

	USG	German Gypsum Association
Purity ($CaSO_4 2H_2O$) (% min)	95	95
SO_3 (% min)	44.2	-
Free Moisture (% max)	10	10
Flash (% max)	1.0	-
SO_2 (% min)	1.0	-
Calcium Sulfite (% max)	1.0	0.25
Chloride (max.ppm)	120	100
Total water Soluble Salts (max.ppm)	600	-
Average Particle size (min. microns)	20	-
Surface Area (cm^2/gram)	3500 max	-
pH	6-8	5-9

2.2 .2(b) Fertilizer

Gypsum has been used for more than 200 years as a soil amendment and fertilizer. Gypsum (Calcium Sulfate - $CaSO_4$) is one of those rare materials that perform in all three categories of soil treatment such as an amendment, conditioner, and fertilizer. Application of gypsum to agricultural soils has a long history to improve soil structure, compacted soil, decreases pH of sodic salts, loosen soil, etc

Agricultural gypsum and two types of FGD products that contain calcium sulfate ($CaSO_4$) were applied about 0, 14 to 60 lbs of sulfur per acre to an agricultural soil. Growth of a new planting of alfalfa was increased 10 % to 40% by the treatments compared to the untreated control. Calcium may also improve the growth of plants under sodic conditions. Understanding of important nutrients such as potassium and phosphate also helps reduce sodium binding to cell walls and plasma membranes.

A minimum calcium activity relative to sodium in the soil that required to insures calcium saturation of electrovalent binding sites on the plasma membrane surfaces (Jonathan and Michael, 1995).

2.2 .2(c) Production of Sulfuric Acid from Gypsum

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. Sulfuric acid amount around 200 million metric tons is manufactured per year in around the world, Asia 35%, North America (including Mexico) 24%, Africa 11%, Western Europe 10%, Eastern Europe and Russia 10%, Australia and Oceania 7%, South America 7%, most of them from strong SO2 (~10%) gas. A majority of it is used for making phosphate fertilizers amount (~60%), but it has a numerous of other uses (Davenport et al., 2006).

Roast the gypsum moderately in an oven, "waters of hydration."

$$CaSO_4 2H_2O \longrightarrow CaSO_4 + 2\ H_2O \qquad (2.2)$$

The anhydrous calcium sulfate can be processed to obtain a separation or extraction of its sulfur content. Heat the gypsum in a kiln to 600 to 900 degrees C in the presence of a reducing atmosphere such as hydrogen or carbon monoxide to produce calcium oxide and sulfur dioxide by using hydrogen

$$CaSO_4 + H_2 \longrightarrow CaO + H_2O + SO_2 \qquad (2.3)$$

Therefore, the gypsum is converted to calcium oxide (lime) and sulfur dioxide, both very useful products. The sulfur dioxide can then be further processed in at least two commercially profitable ways (Vincent, 2010).

2.2.2 (d) Gypsum in the Mining Industry

For a long time ago about 170 years, gypsum was mined in south western Virginia in U.S.A since1830 until 2000. Several long-term, underground mining operations in New York, Kansas, and Ontario ceased operations in the early of the 21st century.

Nowadays, most of the world’s gypsum is produced by surface-mining operations. In North America, five underground gypsum mines were in operation in 2004. Two mines are located in Indiana, and one each in Iowa, Michigan, and Ontario, Canada. Four additional underground gypsum mines are ceased operations early in the21st century after extensive periods of operation (Elzeakogal et al., 2006).

2.2.2(e) Gypsum Plaster

Gypsum plaster or plaster of Paris is produced by heating gypsum to about 150℃ to 180°C

$$2CaSO_4\cdot 4H_2O + Heat \rightarrow 2CaSO_4\cdot H_2O + 3H_2O \text{ (released as steam)} \qquad (2.4)$$

When the dry plaster powder are mixed with water, it reforms in to gypsum and setting of plaster about 10 minute after mixing is complete about 45 minutes.

Gypsum plasters are used in dental and orthopedic applications. Dentists use the plaster to make impressions of teeth and gums to produce joint, crowns, and dentures. Orthopedic plasters are used in bandages and casts to immobilize broken limbs. Newer, more innovative applications include its sue engineering where gypsum is used to promote bone and tissue re growth. It is used as bone- Void filler, in which cast pellets of high purity gypsum provide a temporary framework for tissue re growth (Pereira et al., 2011).

Nowadays, gypsum-based plasters are the most common interior coating of walls and ceilings of buildings. Name of gypsum plasters in the European standard is EN 13279-1 (gypsum binders and plasters), they are produced gypsum plasters in a factory ,and made with synthetic binders usually called synthetic gypsum plasters are also used for the interior coating of walls and ceilings (Pereira et al., 2011).

2.2.2(f) Food and Pharmaceutical

Gypsum is naturally occurring calcium sulfate, gypsum is refined and food safe for use as a tofu coagulant. Gypsum is the traditional ingredient used by the Chinese as their tofu coagulant (Oshri and Benny, 2012).

Food and pharmaceutical grade gypsum ($CaSO_4.2H_2O$), calcium sulphate is made from hydrate of gypsum by fine grinding high purity white gypsum containing about 20% water of crystallization.

In increasing volume, calcium sulfate products supplies the food, beverage and pharmaceutical industries as an economical source of supplement calcium, and used in enriched breads, cereals, baking powder, yeast foods, bread conditioners, canned vegetables and artificially sweetened jellies and preserves.

Application of pharmaceutical, calcium sulphate is extensively used as a diluents serving as an excellent inert extender while it supplies dietary calcium.

Food grade gypsum is certified halal and suitable for consumption by Muslims, and guaranteed to meet the specifications of food chemical codex.

Gypsum is an approved additive on food and drug administration (FDA) “general recognized as safe” (GRAS) listing of food additive (Lizhang, 2012).

2.2.2(g) Filler in Paint

The filler grade of gypsum powder is white color and some grades have a reflectance of over 90. Oil absorption is 20 to 25. Gypsum is not widely used as filler but some is used as a filler in paint, gypsum is mined in Ontario no filler grade material is produced (Hewitt, 1997).

2.3 Gypsum in Commercial

2.3.1 World Gypsum Consumption

Demand of gypsum depends largely on the strength of the construction industry particularly in the United States about 95% is used for building plasters, Portland cement manufacture, wallboard products, etc. In 2009, the world wide consumption of gypsum has declined due to a significant of the housing and construction markets continued to drop, with an apparent decrease of about 17%.

China produced more than three times the annual amount of gypsum from the United States, the second ranked of world producer. Iran is in the third rank of world production and is a major supply in gypsum for construction in the Middle East region.

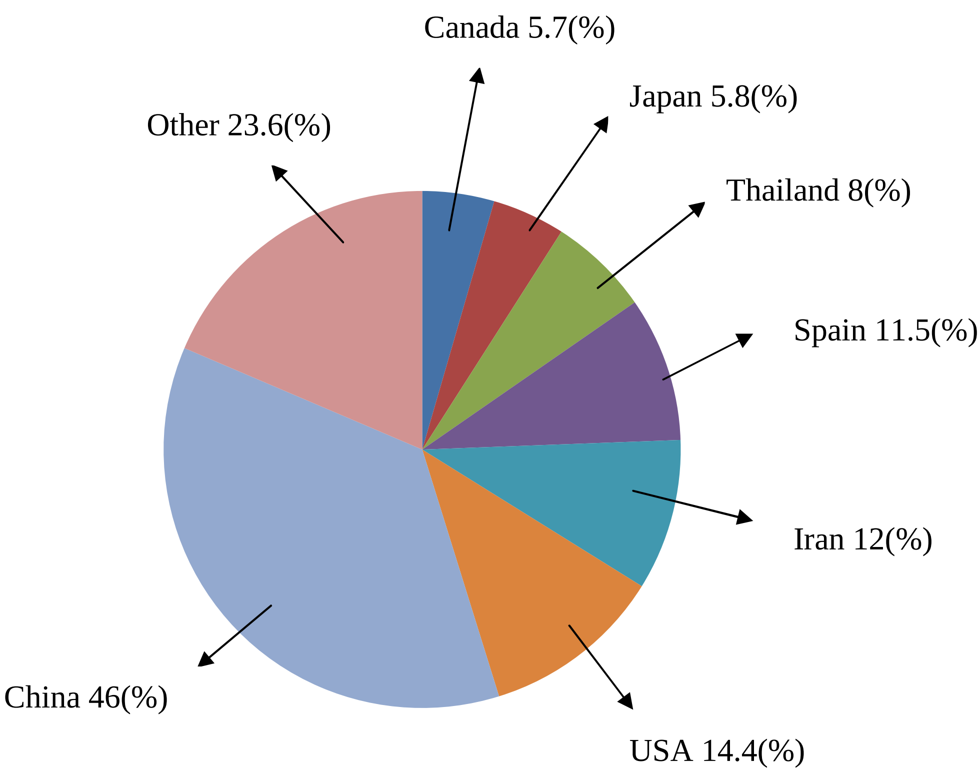

Figure 2.1: Annual world gypsum production in 2009 (million tons**)**
(Sources: Freedonia Group, 2009)

From Figure 2.1, Spain is the leader of European producer; the rank is number fourth of the world, and can supply crude, products to most for Western Europe region. Use of wallboard in Asia increase, with new gypsum product plants, heightened production in this region. As more cultures recognize the economics and efficiency of wallboard, gypsum production is expected to increase worldwide (Freedonia Group, 2009).

The United States is the leader of the world in the gypsum international trade and exporting products of gypsum wallboard to 69 countries and territories. Industry shipments of gypsum wallboard in the United States (including imports) were an estimated 4.57 billion square feet in 2010, down about 7% compared with 4.89 billion square feet in 2009 (IBIS World, 2009).

In addition, the United States continued to remain the biggest volume consumer of products manufactured from world gypsum products. The United-States represented about 50% in the world demand of 2009. Companies in US alone employ 10,000 individuals with have annual full capacity sales more than $10 billion of products (Bizminor, 2009).

The leading crude and products States are, (in decreasing order), Nevada, Iowa, California, Oklahoma, Texas, Arkansas, New Mexico, Indiana, and Michigan, which together accounted to about 79% of total output. In the United States, 46 companies produce gypsum by 55 mines in 18 States, and 9 companies calcined gypsum by 57 plants in 29 States (U.S. Geological Survey, 2010).

Gypsum resources in domestic are sufficient but unequally distributed. Large volume imports from Canada expand domestic supplies for wallboard manufacturing in the United States, normally in the eastern and southern coastal regions.

Some crude gypsum imports from Mexico supplement domestic supplies for wallboard manufacturing along portions of the U.S. western seaboard. Large gypsum deposits occurred in the great lakes region, the mid-continent of this region, and several Western States. Foreign deposits are very large and widely distributed; 86 countries produce crude gypsum. Crude gypsum about 187 million tons was mined in 2009. Of that, amount 15 million tons was mined in North America.

Nowadays, the composite industry includes 8 manufacturing entities that ship more than 99% of all the gypsum board, gypsum panels, and gypsum plaster products sold in the United States and Canada. These 8 producers together control almost about 75% of the global plasterboard market**.** Moreover, there is an enormous market opportunity to sell gypsum into the agricultural market. Gypsum allows farmers to reduce or eliminate tillage in farm soil, thereby generating substantial carbon credits back to the farmers. In addition, it Increases drought tolerance of plants (Gypsum market, 2011).

2.3.2 Gypsum- Based Product

Global natural gypsum production in 2006 was estimated to be 125 Mt representing an increase 2% compared in 2005, when production totaled 122 Mt. This represented the third year in a row that worldwide gypsum production increased to record breaking levels. In 2006, 84 countries produced gypsum, 10 countries of which about percent of the total world production. More than 200 million metric tons per year of synthetic gypsum is generated worldwide (Roskill, 2004).

However, only a small portion of that gypsum is consumed. The United States remained the largest producer of crude gypsum in 2006 with 21.1 Mt, followed by Spain with 13.2 Mt. Spain, where it is estimated that gypsum deposits underlay 12% of the surface area, is the largest European producer of crude gypsum. Iran was third in gypsum production with 13.0 Mt, followed by Canada with 9.5 Mt, Thailand with 8.4 Mt, and Mexico with 7.0 Mt. North American production accounted for almost 32% of total crude gypsum production (Roskill, 2007).

Although the use of gypsum wallboard increased worldwide, only industrialized nations, such as United States, used gypsum primarily for wallboard products. In developing countries, especially in the Middle East and Asia, most gypsum was used in the production of cement or as a plaster product. Annual world production of gypsum from 1999 to 2012 is between 100.000 to 165.000 thousand metric tons (Robert, 2013) as shown in Figure 2.2

Annual world production of gypsum from 1924 to 2012 shown in Appendix A (Page 149)