

การผลิตเต็นท์สโตนจากยิปซัมฟลูแก๊ส



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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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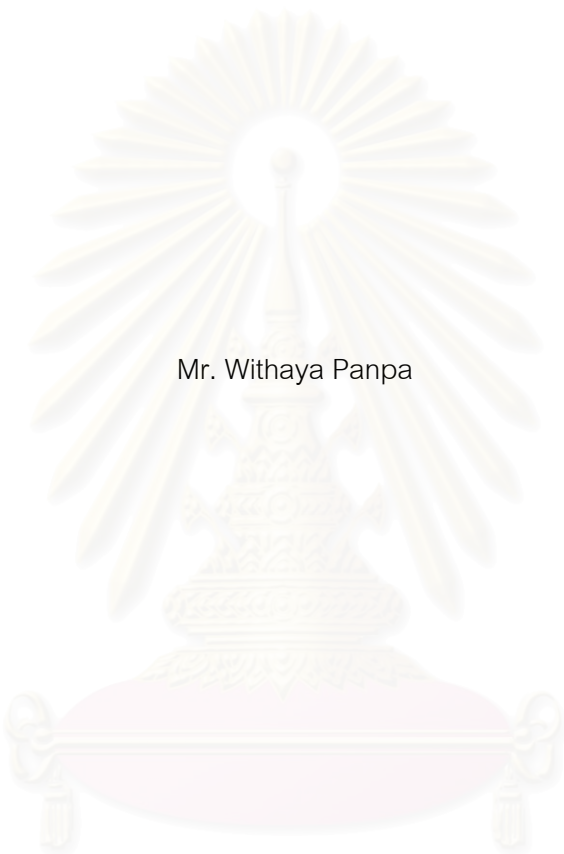
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PRODUCTION OF DENTAL STONE FROM FLUE-GAS GYPSUM



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ยิปซัมฟลูแก๊สเป็นวัสดุเหลือทิ้งที่ได้จากกระบวนการกำจัดแก๊สซัลเฟอร์ไดออกไซด์ของโรงงานไฟฟ้าแม่เมาะ จ.ลำปาง ได้ถูกนำมาผ่านกระบวนการล้างด้วยวิธีอัลตราโซนิกและการชะด้วยกรด โดยยิปซัมฟลูแก๊สที่ผ่านการล้างแล้วจะมีความบริสุทธิ์ประมาณ 97 เปอร์เซ็นต์และมีสีอ่อนลงอันเนื่องมาจากสิ่งเจือปนส่วนใหญ่ เช่น เถ้าลอยและเหล็กออกไซด์ได้ถูกกำจัดออกไป ยิปซัมฟลูแก๊สที่ผ่านการล้างแล้วได้ถูกนำไปสังเคราะห์เป็นอัลฟา-เฮมิไฮเดรต โดยการชุบก้อนของยิปซัมฟลูแก๊สที่ผ่านการอัดด้วยแรง 180 บาร์ลงไปในสารละลายของโซเดียมซัลไฟด์และกรดซัลฟอนิก ต่อจากนั้นนำไปผ่านกระบวนการสังเคราะห์ด้วยหม้อออโตเคลฟ ที่ความดัน 6 บาร์เป็นเวลา 1 ชั่วโมง เฮมิไฮเดรตที่สังเคราะห์ได้มีความบริสุทธิ์ประมาณ 94-99 เปอร์เซ็นต์ ผลึกที่ได้มีค่า aspect ratio ต่ำ ทำให้มีการไหลตัวดี ในการเตรียมที่อัตราส่วนน้ำต่อพลาสติกเท่ากับ 0.32 เดินทัลสโตนที่ผลิตได้จากยิปซัมฟลูแก๊สที่ผ่านการล้างด้วยวิธีอัลตราโซนิกและไม่ใช้สารเติมแต่งในการสังเคราะห์อัลฟา-เฮมิไฮเดรต จะมีคุณสมบัติเทียบเท่ากับที่ผลิตได้จากยิปซัมธรรมชาติ โดยมีความทนต่อแรงอัดเท่ากับ 28.75 เมกะปาสคาล



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ปีการศึกษา 2545

ลายมือชื่อนิสิต.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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Flue-gas gypsum, a waste product obtained from desulfurization process of the Mae Moh power plant, Lampang, was precleaned by ultrasonication and acid leaching method. Precleaned FGD gypsum had a purity of approximately 98% and a light color because impurities such as fly ash and iron oxide, were removed. It was transformed to α -hemihydrate by classical vapor process. In this technique, the FGD gypsum briquettes pressed at 180 bars were impregnated in solution of either sodium succinate or succinic acid, and calcined to α -hemihydrate in an autoclave at a steam pressure of 6 bars for 1 hour. The α -hemihydrate obtained had α -HH content of 94-99% and was consisted of low-aspect-ratio crystals, resulting in a good flowability. At a water to plaster ratio of 0.32, the dental stone having equivalent properties to those of natural gypsum was successfully produced from ultrasonicated FGD gypsum without additive and had a maximum compressive strength of 28.75 MPa.

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Chapter 1

Introduction

Motivation

The development of industry results in a large quantity of waste product, including gas, water and solid waste. Residues from industrial productions directly affect environment and storage. To protect environment and decrease landfilling of waste product, the utilization for residual materials is a best method.

One of solid waste products from the power generating industry which is suitable for recycling is flue-gas gypsum (or FGD gypsum). It is produced by the gypsum-forming reaction between gaseous sulphur dioxide from combustion of fossil fuels and calcium compounds. The big source of FGD gypsum in Thailand is from the Mae Moh power plant, Lampang. The FGD gypsum from the Mae Moh power plant is of lignite-fired system and is produced about 3 million tons/ a year¹. It is used as a secondary or replacement material and has been recently used as retarder in portland cement industries which amounts to only ~4 wt% of the cement. Research and development in the utilization of FGD gypsum in other application, i.e. pottery plaster, filler material, gypsum board, projection plaster and etc. are being carried out on industrial scale².

In medical application, for example dental plasters have long been produced from high purity, natural gypsum and no attempt from the FGD gypsum has been reported. This product is utilized in a large volume and is cost attractive in comparison with other industrial plasters. The dental gypsum products are classified into 5 types depending upon application and their properties³. Especially, Type III is applied for denture model making which is used in a large quantity, hence it has a high price. To increase the potential for utilization of the Mae Moh FGD gypsum, this research is dealing with an attempt to produce dental stone (Type III) from FGD gypsum for denture model application.

Objectives

- To synthesize α -hemihydrate (α -HH) from Mae Moh FGD gypsum and study on the properties of the synthesized α -HH
- To produce dental stone from the synthesized α -HH for denture model making

Scope

The scope of this research covered the study on the production of α -HH from Mae Moh FGD gypsum by classical vapor process. In this process, crystallization modifiers, succinic acid and its salt, were used to control crystal size and shape. Then α -HH obtained was formulated to dental stone (Type III) having properties in conformity with ISO 6873. Moreover, the dental stone powder obtained was made into a denture model by casting on impression materials for performance testing.

Benefit

- An effective environmental problem-solving,
- Decrease the quantity of waste product from power plant storage,
- Increase in the potential of both utilization and value of flue-gas gypsum which was a waste from the power plant,
- Saving the reserve of gypsum ore for future uses.

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Chapter 2

Literature review

2.1 Desulfurization processes

2.1.1 Wet scrubbing

The technology employs an alkaline sorbent slurry which is predominantly lime or limestone based because it gives reasonably good SO_2 removal and rather good utilization (Chubu, 1985 and Stromberg and Jonsson, 1985).^{4,5} A scrubbing vessel or scrubber is located downstream of the boiler in which intimate contact between gas and sorbent is carried out, a process which readily removes over 90% of SO_2 from the flue gases. The resulting solid is predominantly calcium sulfite which can be further oxidized to calcium sulfate dihydrate which can be sold as a by-product to the building industry where it finds application as plaster board. The schematic diagram of the wet scrubbing is shown in Fig. 2.1

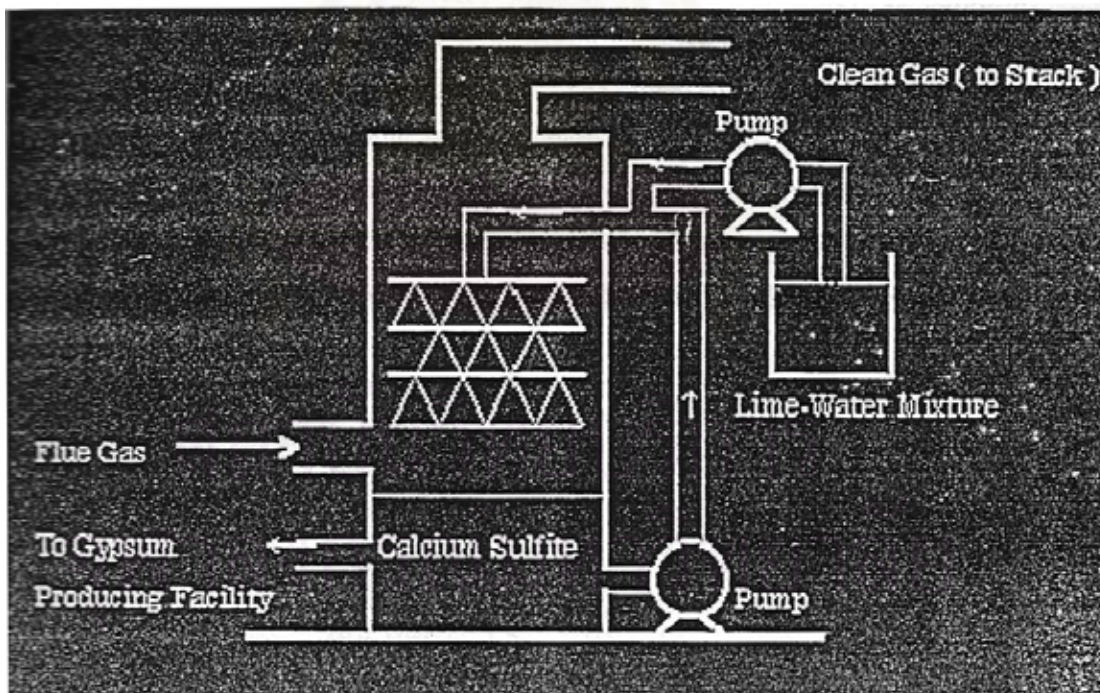


Fig. 2.1 Schematic diagram of the wet scrubbing.

There are quite a number of developments in this technology to increase overall efficiency, for example, regenerative flue gas reheating and natural draft cooling tower. Holter and Gibhard (1989)⁶ had reported a process for making FGD gypsum. The process comprised treating the flue gas in a wash tower with a wash water suspension containing calcium oxide, calcium hydroxide or calcium carbonate and converting the scrubbed SO_2 by oxidation with input atmospheric oxygen and by crystallization to calcium sulfate dihydrate crystals. After that the calcium sulfate dihydrate was separated by a cyclone separator and the crystal suspension was dewatered. By control of the amount and partial pressure of the suspension flow, the grain size of the calcium sulfate dihydrate crystal was precisely adjusted.

2.1.2 Spray dry scrubbing

This technology also employs a sorbent slurry or solution, however, the by-product is dry and removal efficiency about 80 to 90%. The slurry of sorbent, alkaline based, is sprayed into the scrubbing vessel in very fine droplets and dried (typically having a free water content of about 4 to 12% by weight) as it contacts the flue gas. At this point the sorbent reacts with the SO_2 . The dry sorbent is picked up by the gas stream and carried into the dust collector for removal. The schematic diagram of the dry scrubbing is shown in Fig. 2.2.

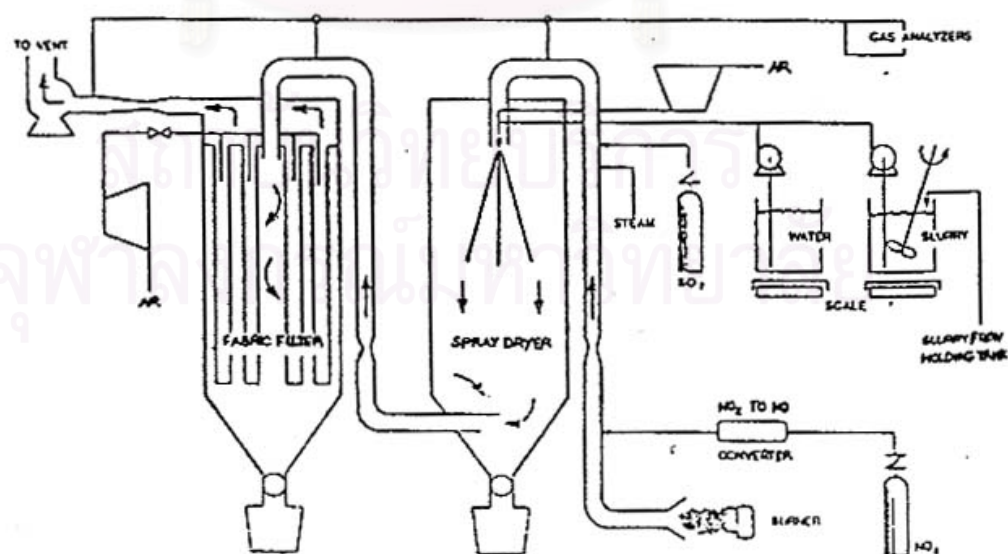


Fig. 2.2 Schematic diagram of the dry scrubbing.

Stromberg and Hans (1988)⁷ had reported the disadvantage with spray dry scrubbing in obtaining a high SO₂ removal. Because of the relative short residence time under wet condition in the spray dry scrubber and because of the low dissolution rate of limestone, a high SO₂ removal would not be reached in the spray dry scrubber, if nothing was done to enhance the dissolution of limestone. However, that limestone could be as efficient as slaked lime for SO₂ absorption during the dry reaction period. Bjerle, Klingspor and Karlsson (1984)⁸ had reported very good SO₂ removal with limestone as an absorbent in spray dry scrubbing, when operating at low approach temperatures.

2.1.3 Sorbent injection

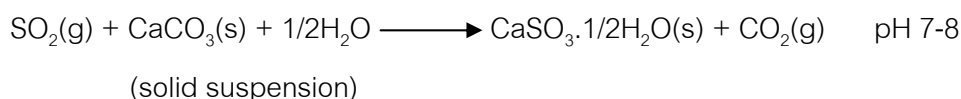
The technology of calcium sorbent injection is developed technology and is the lowest in term of capital outlay of all the available SO₂ removal technologies. The sorbent can be added dry into one of three locations (Theodore and Buonicore, 1976)⁹.

- into the furnace (gas temperature 850 to 1250 °C).
- into the economizer region (gas temperature 550 to 950 °C).
- after air heaters (gas temperature close to saturation).

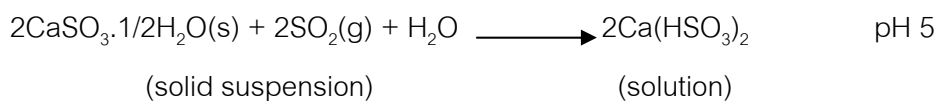
However, because of relatively poor contact between the sorbent and SO₂, efficiency is generally in the range of 30 to 60% and hence, sorbent use is much higher. The residual sorbent and ash mixture is not a commercial product as with wet and spray dry scrubbing. Klingspor, Karlsson and Bjerle (1983)¹⁰ had reported that the research was underway with efficiencies expected to reach as high as 80% if techniques like humidification of the flue gas or other additive into the gas stream proved successful.

2.2 Reaction of desulfurization processes

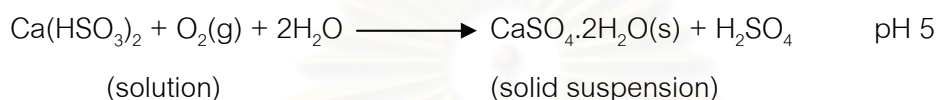
Almost all of these processes are operated by the countercurrent washing the flue gas with aqueous suspensions of limestone or lime to remove the SO₂. The reaction takes place at pH 7-8 (Scholz, 1984)¹¹ and produces an almost insoluble calcium sulfite (CaSO₃·1/2H₂O).



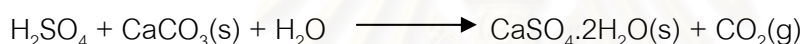
In the second step, the pH is allowed to fall below 5. So, the suspended calcium sulfite is converted to soluble calcium bisulfite ($\text{Ca}(\text{HSO}_3)_2$).



This calcium bisulfite is easily oxidized by atmospheric oxygen to calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or gypsum so-called "Flue-gas gypsum".



The sulfuric acid (H_2SO_4) produced reacts with the remaining limestone to form additional gypsum.



Gypsum crystals grow and are separated from the aqueous gypsum suspension in hydrocyclones and vacuum drum filters or centrifuges. The product is moist fine powder, fairly pure powder having high percentage of calcium sulfate that contains only minor quantities of impurities which are specific to process such as soluble salts (Na^+ , Mg^{2+} , Cl^-) and calcium sulfite (Knauf, 1983)¹² and is almost pure white color (Hamm and Huller, 1982).¹³ Chemical composition of FGD gypsum is as shown in Table 2.1. About 5.4 tons of gypsum are produced per ton of sulfur in fuel.

The net reaction:

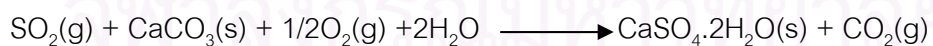


Table 2.1 Chemical composition of some calcium sulfates.¹⁴

	Natural gypsums		Natural anhydrites		Flue-gas gypsum	Phosphogypsums			Fluoro- anhydrite
	1	2	3	4	5	6	7	8	9
	Mineralogical analysis								
CaSO ₄ ·2H ₂ O	91.6	96.4	6.0	3.8	97.5	93.0	97.6	96.5	0.0
CaSO ₄ II	6.4	0.9	88.8	83.7	0.0	0.0	0.0	0.0	94.7
MgCO ₃	0.1	0.6	2.0	3.6	0.0	0.0	0.0	0.0	0.0
CaCO ₃	1.9	1.3	3.1	5.3	0.0	0.0	0.0	0.0	0.0
Chemical analysis									
Combined water	19.1	20.1	1.3	0.8	20.6	19.5	19.2	19.2	0.0
SO ₃	46.4	45.4	55.1	51.0	45.8	43.2	45.4	46.9	56.4
CaO	33.6	32.5	40.3	38.7	32.1	32.2	32.5	32.1	40.8
MgO	0.05	0.28	0.95	1.71	0.04	0.01	0.01	0.01	0.13
SrO	0.07	0.16	0.07	0.14	0.0	0.06	2.05	0.05	0.0
Fe ₂ O ₃ + Al ₂ O ₃	0.01	0.08	0.01	0.39	0.27	0.27	0.70	0.93	0.27
HCl-insoluble residue	0.10	0.47	0.10	2.49	0.32	1.51	1.00	0.68	0.69
Na ₂ O	0.02	0.01	0.04	0.11	0.01	0.47	0.14	0.02	0.03
Total P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	1.01	0.11	0.30	0.0
F	0.0	0.0	0.0	0.0	0.04	1.76	0.14	0.29	0.92
Others					0.20 SO ₂				0.11 ZnO
					0.01 Cl				0.69 K ₂ O
Organics	0.0	0.0	0.0	0.0	0.03	0.08	0.03	0.04	0.0
Ignition loss	0.54	0.71	2.08	4.45	0.4	1.38	0.34	0.43	0.14
Total	99.89	99.71	99.95	99.79	99.81	101.45	101.62	100.95	100.18
pH	6	6	6	6	6	3.1	9	4.2	10-12

1) Zechstein gypsum; 2) Keuper gypsum; 3) Zechstein anhydrite; 4) Keuper anhydrite; 5) Mitsubishi process; 6) From Moroccan raw phosphate, dihydrate process; 7) From Kola raw phosphate, dihydrate/ hemihydrate process, after rehydration to dihydrate; 8) From Moroccan raw phosphate, hemihydrate/ dihydrate process; 9) From hydrofluoric acid production, Zechstein is an Upper Permian deposit; Keuper, an Upper Triassic.

2.3 Agglomeration of Flue-Gas Gypsum¹⁵

Size and shape of crystals of FGD gypsum depend on the desulfurization process. The particle shape ranges from cubic (bulk density 1.2 ton/m³) to lath or rod

shaped (bulk density 0.5 ton/m^3) and size from small crystals ($20\text{-}60 \mu\text{m}$) to maximum of $200 \mu\text{m}$ while those of natural gypsum are massive or rocklike structure. The moist finely divided particle size and structure of FGD gypsum crystal cause the disadvantage in handling, storage and application. Moreover, the thixotropic behavior makes it unsuitable for the manufacture of multiphase plaster. Therefore, it must be treated further to overcome this problem. Various agglomeration techniques have been developed to convert the finely divided crystals of FGD gypsum into a lump product closely resemble of the natural one (apparent density $\sim 2.3 \text{ g/cm}^3$) by any one of the following processes:

2.3.1 Agglomeration by means of pelletizers

Pellets are produced when the FGD gypsum is agglomerized in pelletizers (Fig. 2.3). The bonding agent is required for this type of agglomeration, for instance calcium sulfate hemihydrate, which is added to the moist finely divided FGD gypsum. At least 25% of hemihydrate and the adequate amount of water for hydration have to be added to ensure that the pellets will have the required strength. The moist FGD gypsum does not have to be dried first. The pellets produced are 10 to $25 \mu\text{m}$ in diameter, have a free water content of 8 to 10%, and an apparent density of about 1.6 g/cm^3 .

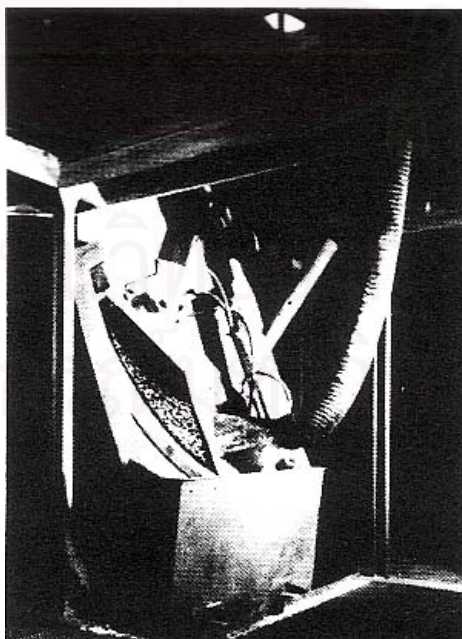


Fig. 2.3 Agglomeration of flue-gas gypsum by means of pelletizers producing pellets.

2.3.2 Agglomeration by means of extrusion presses

Granules are produced when the FGD gypsum is agglomerated by means of an extrusion press (Fig. 2.4). The starting material is the moist, finely divided FGD gypsum with a moisture content of 8 to 15% depending on the size distribution and the structure of the particles. The moist FGD gypsum is squeezed through a flat die by means of a pan grinder. The granules obtained are cylindrical and have a diameter of 10 to 25 mm. Initially the granules are moist and of low strength.

The granules have to be dried immediately to achieve a higher strength. Belt driers are very suitable for this since, mechanically, they do not put much strain on the fresh soft granules. The dried granules have an apparent density of approximately 1.8 g/cm³.

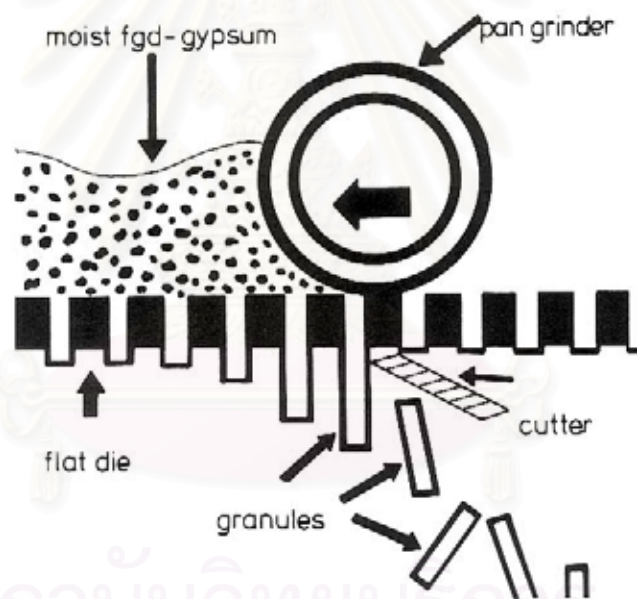


Fig. 2.4 Agglomeration of the flue-gas gypsum by means of an extrusion press producing granules.

2.3.3 Agglomeration by compacting presses

The manufacture of briquettes by agglomeration with a compacting press is a process recently developed to produce a lumpy FGD gypsum. When the process was being developed, it became apparent that the finely divided FGD gypsum would have to be in the dry state. By using suitably designed press rollers, such as corrugated press rollers closed at the ends (cigar-shaped), as shown in Fig. 2.5, FGD gypsum briquettes

can be produced that have a strength of more than 500 N and an apparent density of 2.15 g/cm^3 . Natural gypsum has an apparent density of 2.3 g/cm^3 . These FGD gypsum briquettes are therefore very much like a product made from natural gypsum. Because of their high strength and high density the briquettes are exceptionally abrasion resistant and can be stored in the open. Neither frost nor rain has any disturbing effect on them.

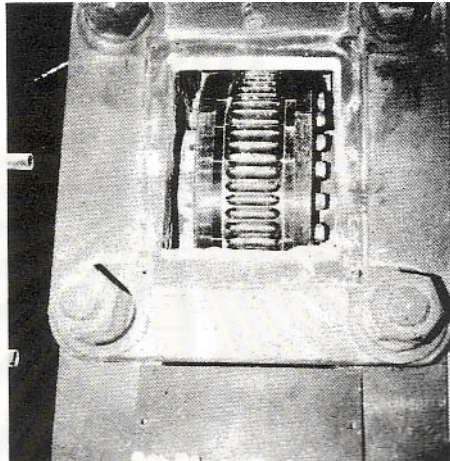


Fig. 2.5 Cigar-shaped corrugated press roller of a compacting press.

A further advantage of this process is that no bonding agents or additives are needed to agglomerate the finely divided FGD gypsum. Also it is found that the briquettes easily detach from the mold without any leftover material sticking to the press. Wear and tear of the rollers are slight because of the relatively soft gypsum grain (Mohs hardness 2). The operational dependability of the process has proved to be very good. The following figures show the process of compaction (Fig. 2.6), a compacting press in operation (Fig. 2.7) and flue-gas gypsum briquettes in storage (Fig. 2.8). In addition to agglomeration by roller press, uniaxial press (Fig. 2.9) can produce briquettes with high apparent density

Fig. 2.10 shows finely divided and compacted flue-gas gypsums. Special difficulties are caused by the very different bulk densities of the moist finely divided flue-gas gypsum from approximately 0.5 to 1.2 ton/m^3 . The process of compaction will overcome this deficiency and will produce a uniform product with a bulk density of about 1.0 to 1.1 ton/m^3 .

From what has been said, and considering all the flue-gas gypsum agglomeration processes, it can be concluded that, if a compacting press is used for compaction, a product of a lumpy structure very similar to that of lumpy natural gypsum is obtained.

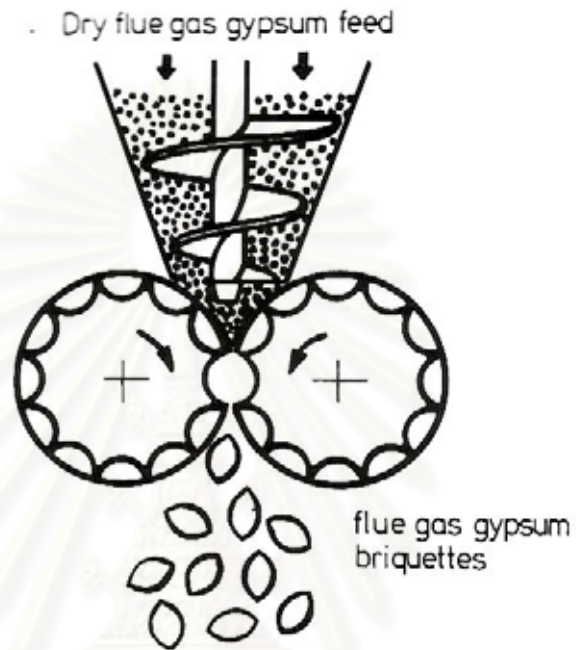


Fig. 2.6 Agglomeration of flue-gas gypsum by means of a compacting press producing briquettes.

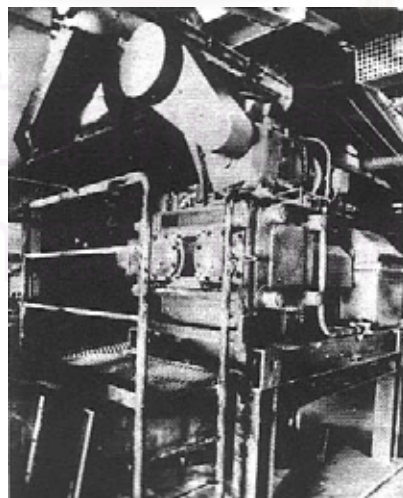


Fig. 2.7 Compaction press in operation, capacity 4 ton/h.



Fig. 2.8 Flue-gas gypsum briquettes in storage.

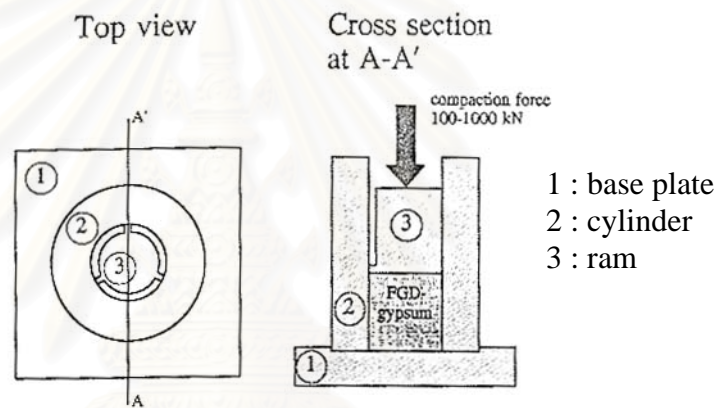


Fig. 2.9 Schematic presentation of the compaction die.¹⁶

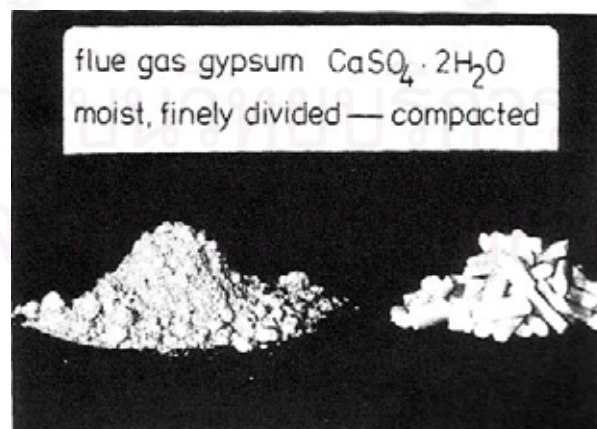


Fig. 2.10 Comparison of finely divided and compacted flue-gas gypsums.

2.3.4 Analyzing compacted flue-gas gypsum

Tests carried out on compacted flue-gas gypsum showed that nothing was left of the gypsum particles, initial size and shape. Scanning electron micrographs revealed that the flue-gas gypsum briquettes were of a solid structure, and the original gypsum crystals had intergrown into a rocklike body, as shown in Fig. 2.11 and 2.12. The original structure of the crystals could no longer be detected even after fine grinding of the briquettes. Thus, the unfavorable particle size and shape of the flue-gas gypsum were successfully dealt with by compaction under high pressure, and the flue-gas gypsum could be used in the same way as natural gypsum. Besides, its thixotropic properties were thus completely eliminated.

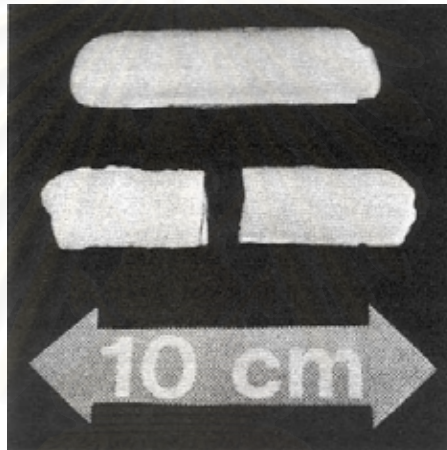


Fig. 2.11 Flue-gas gypsum briquettes in original size.



Fig. 2.12 SEM micrograph of the surface of a broken briquette : size and shape of flue-gas gypsum particles have disappeared.

2.4 Alpha-hemihydrate¹⁷

Alpha-hemihydrate (α -HH) and beta-hemihydrate (β -HH) are the results of the calcining of gypsum. The principal constituent of them are the calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$). Depending upon the method of calcination, different forms of the hemihydrate can be obtained.

β -HH is produced by a simple heat treatment under atmospheric condition at temperatures of about 160 °C in a kettle or rotary kiln. If the heating is carried out under steam pressure in an autoclave, form of α -HH can be obtained. α -HH crystals (Fig. 2.13) are prismatic and more regular in shape and have a smoother surface than β -HH (Fig. 2.14).

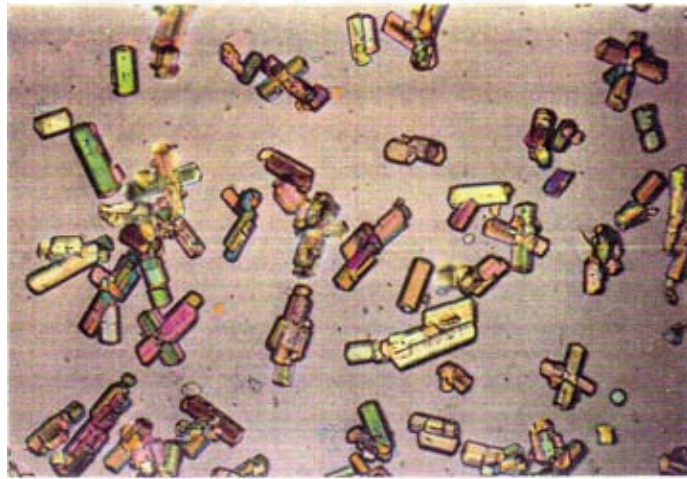


Fig. 2.13 Micrograph of α -HH crystals under polarized light.¹⁸

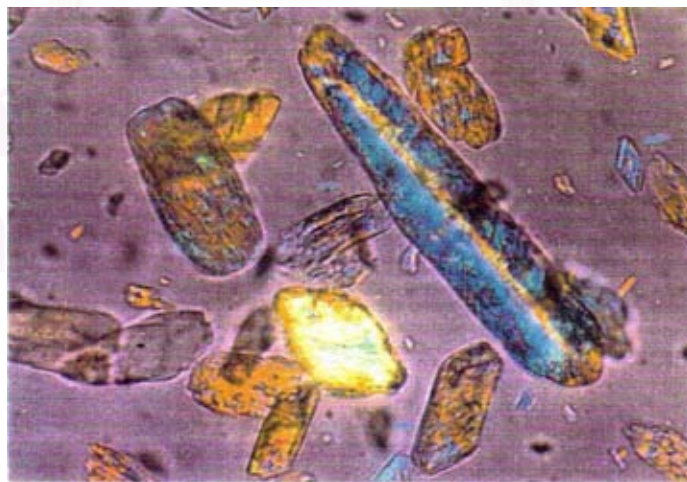


Fig. 2.14 Micrograph of β -HH crystals under polarized light.¹⁸

During the transformation to α -HH by a controlled hydrothermal treatment, totally-new clearly-defined crystals form. Their size lies in the range of 1 to 1000 μm , they are not porous and they do not disintegrate in contact with water. A plaster made of such a crystalline powder has a considerably lower water demand than β -HH. Thus, The product obtained from this plaster is much stronger and harder than that resulting from β -HH. Although particle size and the total surface area is one of the chief factors in determining the amount of gauging water required, the particle size distribution also plays an important role.

2.4.1 Production of α -hemihydrate

a) The classical vapour process (dry process)

Raw gypsum of appropriate quality in lump size is heated in an autoclave to temperatures between 110 and 150 $^{\circ}\text{C}$. The residence time can reach several hours, and depressurising, drying and grinding follows. Finally the material is heated again in order to eliminate residual dihydrate, with the process being carried out in batches. The method is robust and is therefore still used in most cases today.

b) The classical suspension process (wet process)

In this case, a suspension of fine particulate raw gypsum is heated in an autoclave. Generally, additives are used to control the crystal habits. The process can be carried out in batches, although the more economical continuous operation can also be used. Residence times are lower than those of the vapour process. The working temperature lies in the order of 135 $^{\circ}\text{C}$. Higher temperatures generate small crystals, and lower temperatures extend the necessary residence time. The process is able to use fine crystalline by-product gypsum (e.g. phospho-citro-titano-or FGD gypsum), which can be used wet off the filter. This process is more complex to control than vapour process.

c) Pressureless process (Autoclave-free process)

These processes use the fact that the vapour pressure is reduced in solution of an electrolyte. Since the vapour pressure of dihydrate is close to that of water, the dehydration can take place at atmospheric pressure, and therefore an autoclave is not needed. Many different salts, acids and even organic compounds have been proposed as appropriate electrolytes.

2.4.2 Action Mechanism of crystallization modifiers¹⁹

A preliminary study indicated that the addition of crystallization modifiers during dynamic slurry hydrothermal dehydration increases grain size and decreases aspect ratio of α -HH, which results in a decrease in water requirement and an improvement of strength. The mechanism is briefly described as follows:

α -HH belongs to the hexagonal crystal system and its crystal faces have different properties. In the absence of crystallization modifiers, α -HH grows in the C-axis direction more rapidly than in other directions and ends in the form of a fine needle crystal. The crystallization modifiers are selectively adsorbed on C-axis crystal faces and restrain growth of crystal in this direction. Thus, short prisms or even hexagonal plates are obtained.

Common organic crystal habit modifiers used in gypsum based systems are organic acids, amines and their derivatives; common inorganic crystal habit modifiers are divalent metal ions and divalent anions based on metallic elements (such as HPO_4^{2-} , AlF_5^{2-} and SiF_6^{2-}). The organic modifiers affect crystal growth by selective adsorption onto the growing C-axis crystal faces and restrain growth of crystal in this direction. Thus, short prisms or even hexagonal plates are obtained. The inorganic modifiers affect crystal growth by substitution in the growing lattice for either Ca^{2+} or SO_4^{2-} . The latter result in a gypsum crystal with co-crystalline impurities that is essentially a solid solution of a dilute second phase in the gypsum crystal.

2.5 Dental gypsum products²⁰

Dental gypsum products are classified into 5 types in accordance with International standard (ISO 6873) as shown in Table 2.2.

Table 2.2 Types of dental gypsum products and their physical properties.³

Type	Setting expansion (%) at 2 hours	Compressive strength (MPa) at 1 hour	
		Min.	Max.
I. Dental plaster, impression	0-0.15	4	8
II. Dental plaster, model	0-0.30	9	-
III. Dental stone, model	0-0.20	20	-
IV. Dental stone, die,high strength, low expansion	0-0.15	35	-
V. Dental stone, die,high strength, high expansion	0.16-0.30	35	-

The classification system used in this standard for dental gypsum products is based on their clinical application and is widely used, as described in the following sections.

Type I: Dental plaster (Impression plaster)

Type I, plaster form of β -HH, is used to make impressions (Fig. 2.15) of edentulous patients. Because it is hard and brittle, and does not deform elastically, it cannot be removed from the undercuts of teeth and therefore can not be used on edentulous patients. This material has a relatively short setting time of approximately 4 to 5 minutes when placed in the oral cavity. This is important, because a longer setting time might be uncomfortable for the patient. Additives are introduced to produce the shorter setting time. It has a relatively low expansion of 0.13%, in part because of the

higher w/p ratio of 0.6. The higher w/p ratio helps to ensure that the increase in temperature during the setting reaction will not be too high to damage the mucosal tissues. The minimal expansion is important from the standpoint of accuracy. The material is of minimal strength (27.5 MPa, or 4000 psi), which is beneficial because when the impression is difficult to remove, it must be broken in the mouth and then “glued” together out of the mouth in the correct relationship.

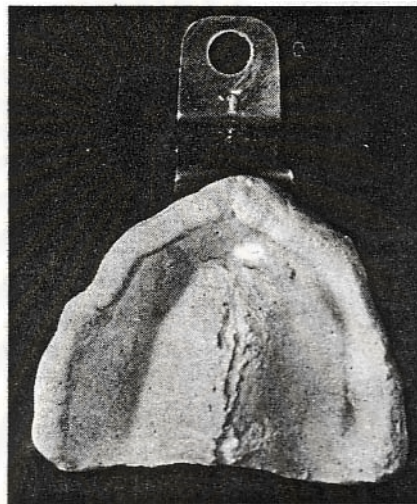


Fig. 2.15 Plaster impression of an edentulous upper arch.²¹

Type II: Dental plaster (Model plaster)

Type II, plaster form of β -HH, is used to make study casts or to mount stone casts in the articulator or in the denture flask. It normally is mixed with a w/p ratio of 0.5, and therefore sets with a higher expansion (0.3%) than type I plaster. This is of no clinical consequence, however. This plaster is stronger than type I because of the lower w/p ratio, which results in less overall porosity when the material has dried.

Type III: Dental stone

This stone is composed of α -HH. It is the common stone used to make casts of impressions for the production of dentures (Fig. 2.16) and treatment planning. It is harder and stronger than type II plaster, and hence more durable. The greater strength is a result of the lower w/p ratio of 0.3. The expansion of this material is between 0.15% and 0.20%, which, because of the additive used in the formulation, is less than that of

plaster. The dry strength of this stone is approximately 62 MPa (9000 psi). Dental stone originally is white. To distinguish its appearance from ordinary plaster, it usually is colored buff, although some manufacturers supply it in many pastel shades. The color is not a factor as far as the properties of the stone are concerned.



Fig. 2.16 Denture obtained from casting dental stone onto impression.

Type IV: Dental stone (Die, high strength, low expansion)

Type IV plaster is composed of α -HH and used as a die material (Fig. 2.17) on which wax patterns of inlays or crowns are produced. It has high-strength (79 MPa or 11,500 psi), high-hardness, and low-expansion (0.08%). The higher strength is a function of the low w/p ratio of 0.24 or less, used for these materials.



Fig 2.17 Die or investment for alloy casting.

Type V: Dental stone (Die, high strength, high expansion)

Type V gypsum products are the most recent additions to dentistry. It is composed of α -HH. Its production is the result of a need for dies with increased expansion to compensate for the greater shrinkage that occurs in many of the newer, high-melting alloys used for dental casting. The setting expansion approaches 0.3%, and is achieved by using a lower w/p ratio (0.18-0.22), which results in stronger gypsum product.

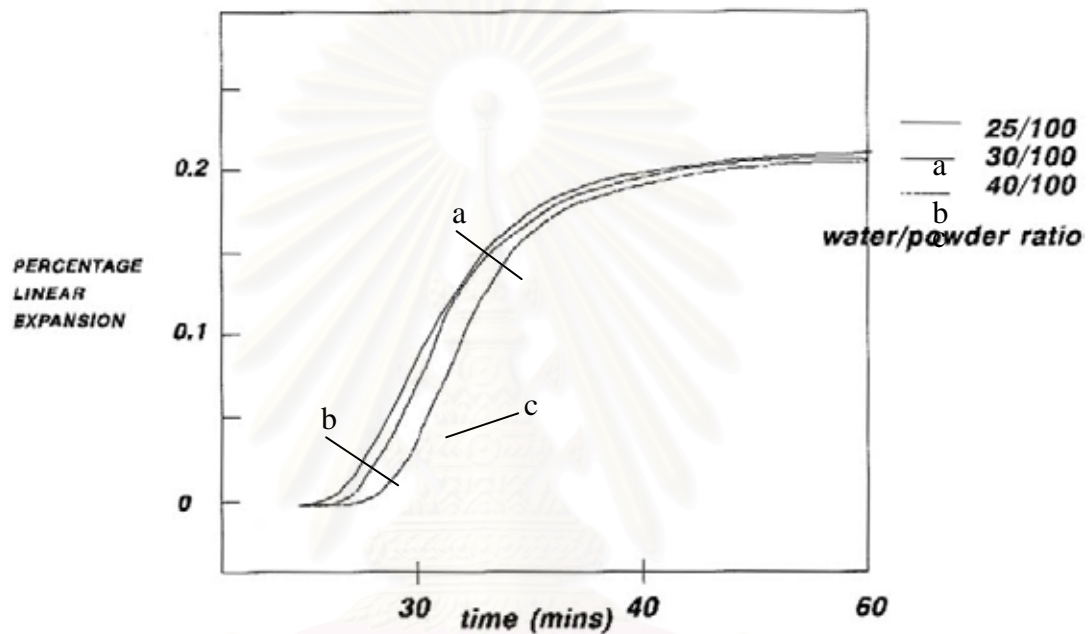


Fig. 2.18 Setting expansion of α -HH.²²

Denture model (Fig. 2.16), using dental stone type III is common in clinical application because its compressive strength is higher than type II. Normally, dental stone (Type III) with low water to plaster ratio (0.28-0.30) improves compressive strength but produces higher setting expansion, that results in a dimensional inaccurate cast. Fig. 2.18 represents setting expansion of α -HH at different water to plaster ratios. Mixes of decreasing water to plaster ratios feature increasing setting expansion due to the proximity of the spherulites. On the other hand, the effect of some additives (Table 2.3) is to reduce the setting expansion, probably due to modification of the morphology of gypsum crystals.

Table 2.3 Crystalline shape of gypsum found in various solutions.²³

Solution	Effect on setting expansion	Crystalline shape
Distilled water	(control)	Slender needle-like
Potassium sulfate (1%)	Reduction	Needle-like, relatively short and thick
Potassium nitrate (4%)	Reduction	Needle-like, short and thick
Potassium carbonate (1%)	Reduction	Mostly small and spheroid
Aluminum sulfate (4%)	None	Slender, needle-like
Potassium chloride (4%)	Reduction	Needle-like, short and thick
Rochelle salt (5%)	Reduction	Very short and massive
Sodium sulfate (4%)	Reduction (small)	Needle-like, short and thick

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Chapter 3

Experiment

3.1 Materials

- As-received Mae Moh FGD gypsum (from the Mae Moh power plant)
- As-received natural gypsum (Bunyawath, local)
- Sulfuric acid (H_2SO_4) 95-97%, Lab grade (Merck)
- Calcium carbonate (CaCO_3), Reagent grade (Scharlau)
- Sodium succinate ($\text{C}_4\text{H}_4\text{Na}_2\text{O}_4$), Lab grade (Fluka)
- Succinic acid ($\text{C}_4\text{H}_6\text{O}_4$), Lab grade (Fluka)
- Potassium sulfate (K_2SO_4), Lab grade (Fluka)
- Sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), Lab grade (Fluka)
- Sodium potassium tartrate, Lab grade (Fluka)
- Melamine, Commercial grade (Melment F 15G, skw. polymer)

3.2 Methods for characterization of the as-received and precleaned flue-gas gypsums.

Properties of the flue-gas gypsums were determined as follows:

Chemical compositions determined according to ASTM C471; mineral phases by means of X-ray spectroscopy (X-ray diffractometer, Bruker, D8 Advance); pH using pH meter (Mettler Toledo MP220); particle size distribution by wet sieve analysis and light scattering technique (laser type particle size analyzer CILAS 920); specific gravity by Archimedes' method and morphology by means of scanning electron microscopy (JEOL JSM 6400).

3.3 Precleaning of FGD gypsum

Two methods for washing FGD gypsum were selected, ultrasonication and acid leaching. Firstly, the FGD gypsum was sieved through a 200-mesh-sieve to get rid of coarse impurities. After that, 100 g of FGD gypsum was mixed with 200 cm³ of distilled water and sonicated for 3 min. Then the coloured top layer was removed after decantation. The remaining was filtered and dried at 45 °C for 2 hours. In the acid leaching, 100 g of FGD gypsum was mixed with 100 cm³ of distilled water and 100 cm³

of diluted sulfuric acid (3 molar). The mixtures were stirred with magnetic stirrer for 15 min. Then each suspension was filtered. This step was repeated 2 times. To make sure that the precipitate was neutral, pH of the last suspension was adjusted with CaCO_3 powder to ~ 7 . Then the neutralized precipitate was dried at $45\text{ }^\circ\text{C}$ for 2 hours. The precleaning process is shown in Fig. 3.1.

3.4 Synthesis of alpha-hemihydrate

Dry FGD gypsum from the precleaning was compacted by a hydraulic press with a compaction pressure of 180 bars to produce briquettes (size $50 \times 50 \times 10\text{ mm}$)⁽²²⁾. This experiment was run in parallel with natural gypsum which was used in lump form (about 100 mm in diameter) The FGD briquettes and natural gypsum lumps were impregnated by dipping in 10 wt% solution of either sodium succinate or succinic acid for 15 min⁽²³⁾. After that, the synthesis of α -HH was carried out in an autoclave at a steam pressure of 6 bars for 1 hour. The heating curve of the autoclave treatment is shown in Fig. 3.3. After autoclaving the synthesized α -HH was immediately dried at $100\text{ }^\circ\text{C}$ for 1 hour and ground with a laboratory grinding machine (FRITSCH Rotor Speed Mill Pulverisette 14) into α -HH powder. The production of α -HH is schematically presented in Fig. 3.2.

3.5 Production of dental stone (Type III)

α -HHs obtained from the above experiment were formulated into dental stone. The additives consisting of melamine, potassium sulfate, sodium citrate and sodium potassium tartrate were used to control flowability,²⁴ setting expansion, acceleration and retardation of setting time, respectively. A water to plaster ratio of 0.32 was used for dental stone since this was carried out in comparison with commercial product (Lafarge's). Accurate proportions of α -HH and distilled water were mixed with additives in a hand operated mechanical spatula using 100 turns in 30 seconds. The mixtures were kept still for 30 seconds and then mixed as previously for 60 seconds. After that physical and mechanical properties of dental stone produced from FGD and natural gypsums were determined according to ISO 6873³. The sequence of production is illustrated in Fig. 3.4.

3.6 Compatibility of dental stone with impression materials

Dental stone obtained was cast against silicone rubber and alginate impression materials. After 1 hour casting, the dental stone specimens were removed from impression materials and dried to constant weight at 45 °C. The hardness of various surfaces was measured by Vicker' s hardness tester using a 136° pyramid diamond indenter under a load of 300 g.²⁴ Furthermore, the compatibility of dental stone with impression materials was measured by reproduction of detail test. The test was carried out according to ISO 6873.

3.7 Effect of pigment on a colour of dental stone

Dental stones produced from α -HH (FGD, ultrasonicated, without additive), α -HH (FGD, acid leached, without additive) and α -HH (NG, without additive) were selected to be the samples for this experiment. The 0.05 wt% of organic green pigment was added to each of them and mixed at a water to plaster ratio of 0.32. Then the slurry was cast against glass to form specimen of size of 40x40x3 mm and dried at 45 °C for 2 hours. The colour of the cast was measured in terms of reflectance by UV/VIS spectrometer (PerkinElmer).

3.8 Phase analysis of calcium sulfate hydrate system ($\text{CaSO}_4 \cdot x\text{H}_2\text{O}$)²⁵

α -HH powder was dried at 75 °C for 30 min. Then about 1 g of it was accurately weighed on a watch glass to the 4th decimal (a). Four weights were needed for the following determinations:

a) Determination of soluble anhydrite (AIII, γ - CaSO_4)

1 cm³ of 80% ethyl alcohol was added to the content of α -HH (a) on first watch glass and the mixture was immediately dried at 75 °C for 30 min. Then it was cooled in desiccator and weighed. This weight was taken as b.

$$\% \text{ AIII} = (93.8/6.2) \times ((b-a)/a) \times 100$$

b) Determination of hemihydrate (HH, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$)

1 cm³ of distilled water was added to the content on the second watch glass and the mixture was left at room temperature for 30 min. After that a sample was

dried at 75 °C for 30 min. Then it was cooled in desiccator and weighed. This weight was taken as c.

$$\% \text{ HH} = (145.15/27) \times ((c-4b+3a)/a) \times 100$$

c) Determination of insoluble anhydrite (All, β -CaSO₄)

1 cm³ of distilled water was added to the content on the third watch glass and the mixture was kept in desiccator water level. After 7 days in desiccator, the sample was dried at 75 °C for 30 min, cooled in desiccator and weighed, respectively. This weight was taken as d.

$$\% \text{ All} = (136.14/36) \times ((d-c)/a) \times 100$$

d) Determination of calcium sulfate dihydrate (DH, CaSO₄.2H₂O)

The content on the fourth watch glass was heated at 350 °C for 30 min. Then it was cooled in desiccator and weighed. This weight was taken as e.

$$\% \text{ DH} = (172.17/36) \times ((4b-c-3e)/3) \times 100$$

$$\% \text{ Crystal water} = ((a-e)/a) \times 100$$

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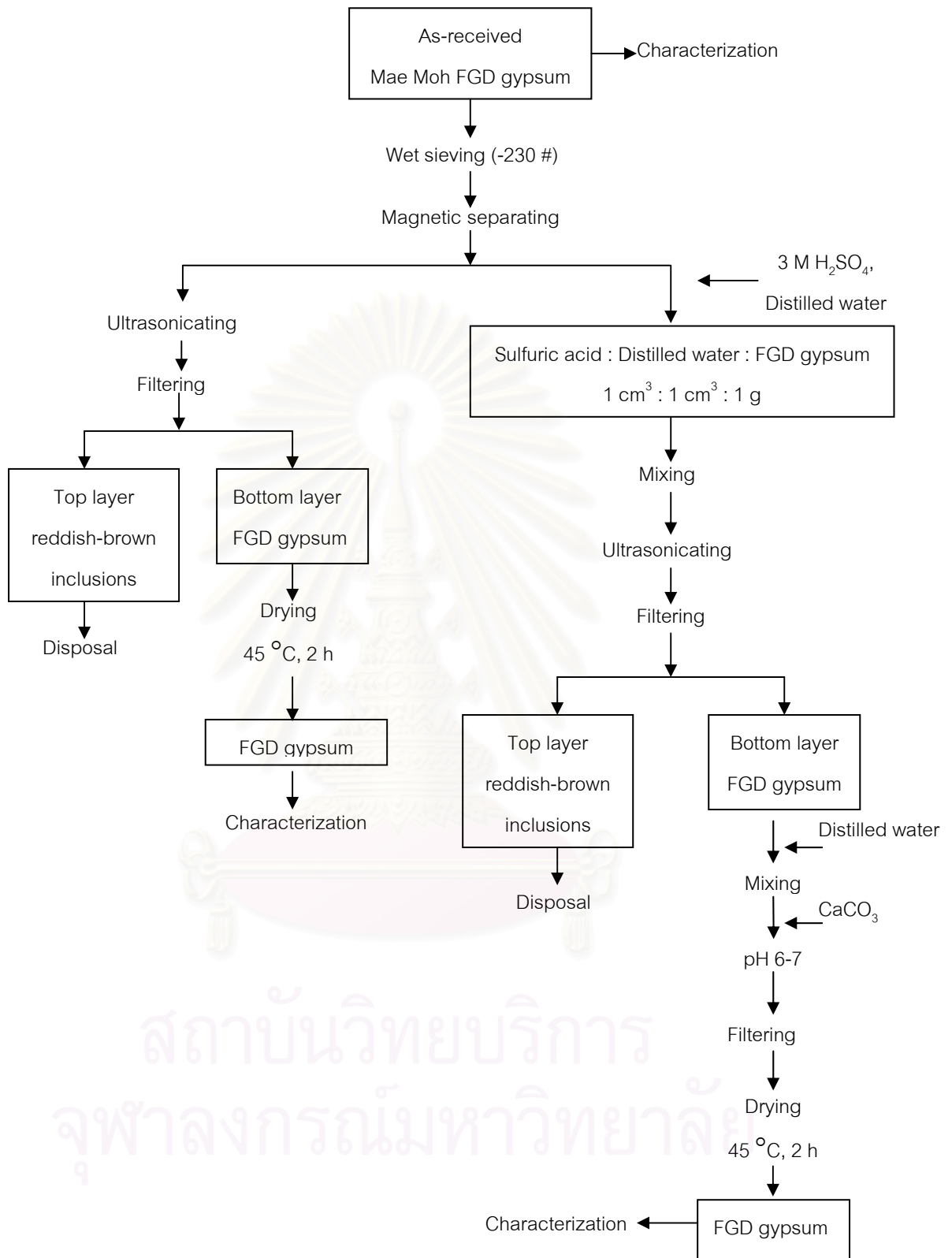


Fig. 3.1 Precleaning of Mae Moh FGD gypsum by ultrasonication and acid leaching method.

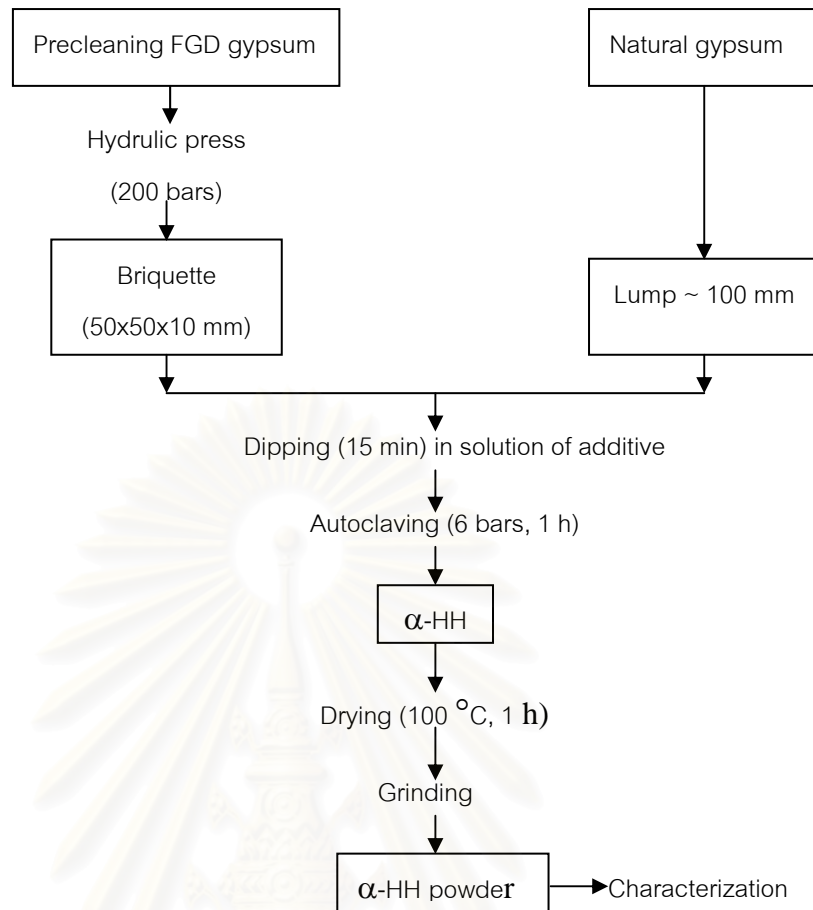
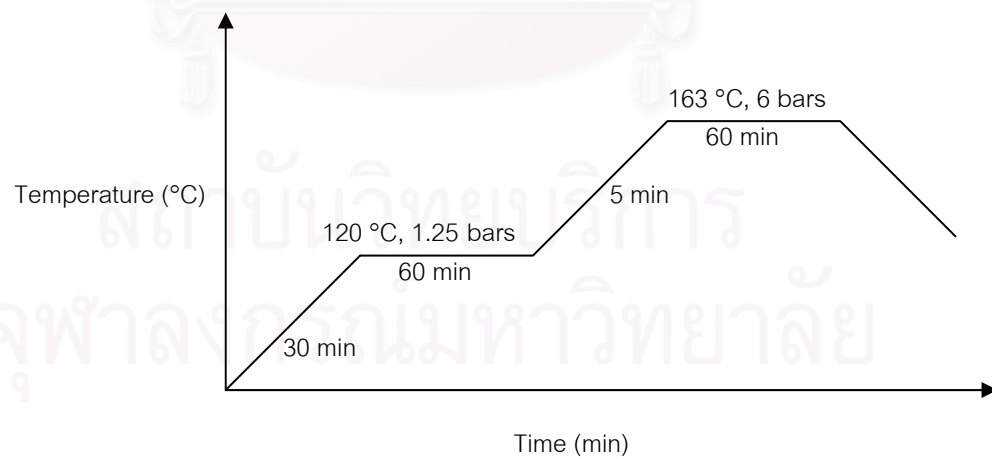
Fig. 3.2 Production of α -HH.

Fig. 3.3 Heating curve of the autoclave treatment.

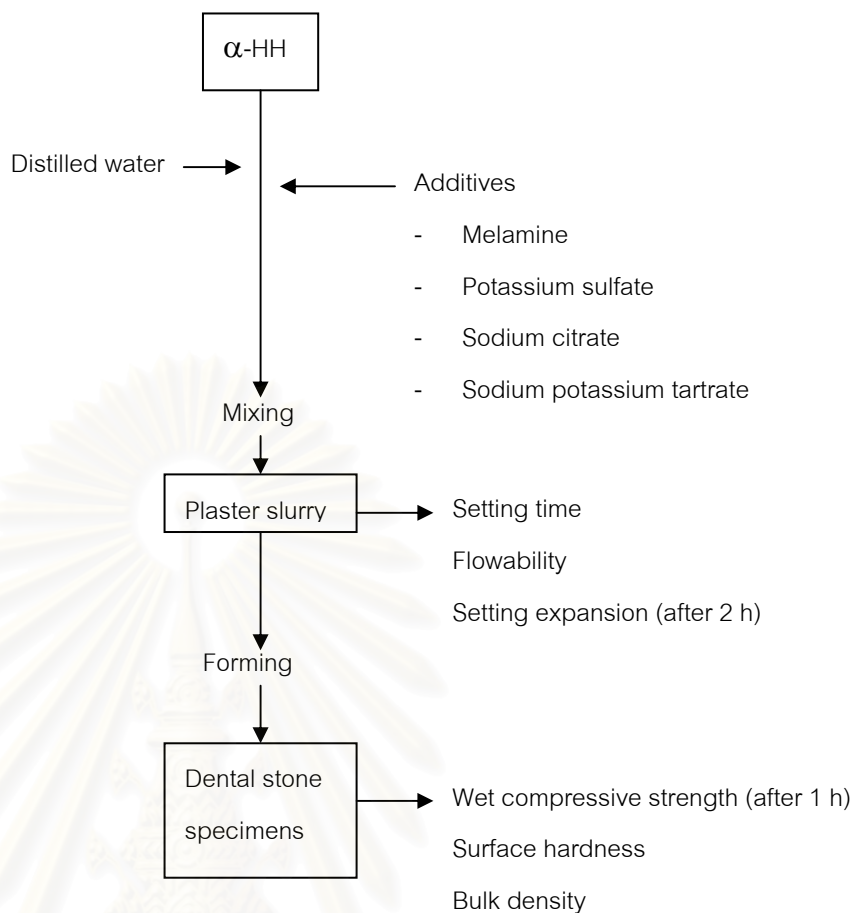


Fig. 3.4 Preparation of Dental stone from α -HH, synthesized under various conditions.

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Chapter 4

Results and Discussion

4.1 Precleaning of FGD gypsum

Table 4.1 Properties and characteristics of as-received FGD gypsum compared with natural gypsum.²⁶

	As-received FGD gypsum	Natural gypsum
Moisture (%)	1.30±0.23	-
Chemical compositions (%)		
Combined water	19.21	19.87
Insoluble residue + SiO ₂	1.63	0.36
Aluminum and Iron oxide (R ₂ O ₃)	0.92	0.28
Calcium oxide (CaO)	32.01	32.51
Sulfur trioxide (SO ₃)	43.98	45.70
Phase (by calculation, %)		
Gypsum (CaSO ₄ .2H ₂ O)	90.02	94.94
Anhydrite (CaSO ₄)	0.48	2.63
Calcium carbonate (CaCO ₃)	2.14	0.90
Wet sieve analysis (%)		
on sieve 50 mesh (>300 μm)	0.04	-
on sieve 100 mesh (300-150 μm)	0.02	-
on sieve 140 mesh (150-106 μm)	0.10	-
on sieve 200 mesh (106-75 μm)	1.61	-
on sieve 230 mesh (75-63 μm)	8.43	-
on sieve 325 mesh (63-45 μm)	18.04	-
Mean particle size (Laser light scattering, μm)	42.28	-
pH	6.65±0.38	7.13±0.10
Specific gravity (g/cm ³)	2.32±0.01	2.33±0.05
Color	reddish-brown	white

Table 4.2 Properties and characteristics of precleaned FGD gypsum.

	Ultrasonicating	Acid leaching*
Chemical compositions (%)		
Combined water (%)	20.41	20.63
Insoluble residue + SiO ₂	0.56	0.34
Aluminum and Iron oxide (R ₂ O ₃)	0.23	0.06
Calcium oxide (CaO)	32.57	32.64
Sulfur trioxide (SO ₃)	45.71	46.18
Phase (by calculation, %)		
Gypsum (CaSO ₄ .2H ₂ O)	97.54	98.52
Anhydrite (CaSO ₄)	0.60	0.62
Calcium carbonate (CaCO ₃)	0.99	0.53
Mean particle size (Laser light scattering, μm)	49.12	45.54
pH	6.82±0.42	6.22±0.18
Specific gravity (g/cm ³)	2.31±0.05	2.32±0.08
Color	light brown	yellowish brown

* Combination of ultrasonicating and acid leaching method

From Table 4.1, as-received FGD gypsum had a purity less than natural gypsum due to impurity such as quartz, calcium carbonate, iron oxide and other minerals. Of all the impurities, iron oxide largely affected the color of FGD gypsum. Calcium carbonate found in the FGD gypsum was as unreacted absorbent. To obtain a light color, the impurities in the FGD gypsum had to be removed by precleaning.

After precleaning by either ultrasonicating or acid leaching method, the precleaned FGD gypsums contained a higher content of gypsum than both the as-received and natural gypsums because the impurities, mostly as fine particles, were eliminated. Hence, the precleaned FGD gypsum had a light color, especially, the sample obtained from acid leaching method because of the dissolution of Fe⁺³ in the employed H₂SO₄ acid solution. Moreover, this method gave a slightly higher purity than that of the ultrasonicating. It is possible that the residual acid in the FGD gypsum reacted with both the residual CaCO₃ and the CaCO₃ added for neutralization resulting

in the increase in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ content. The samples of the as-received and the precleaned FGD gypsums are shown in Fig. 4.1

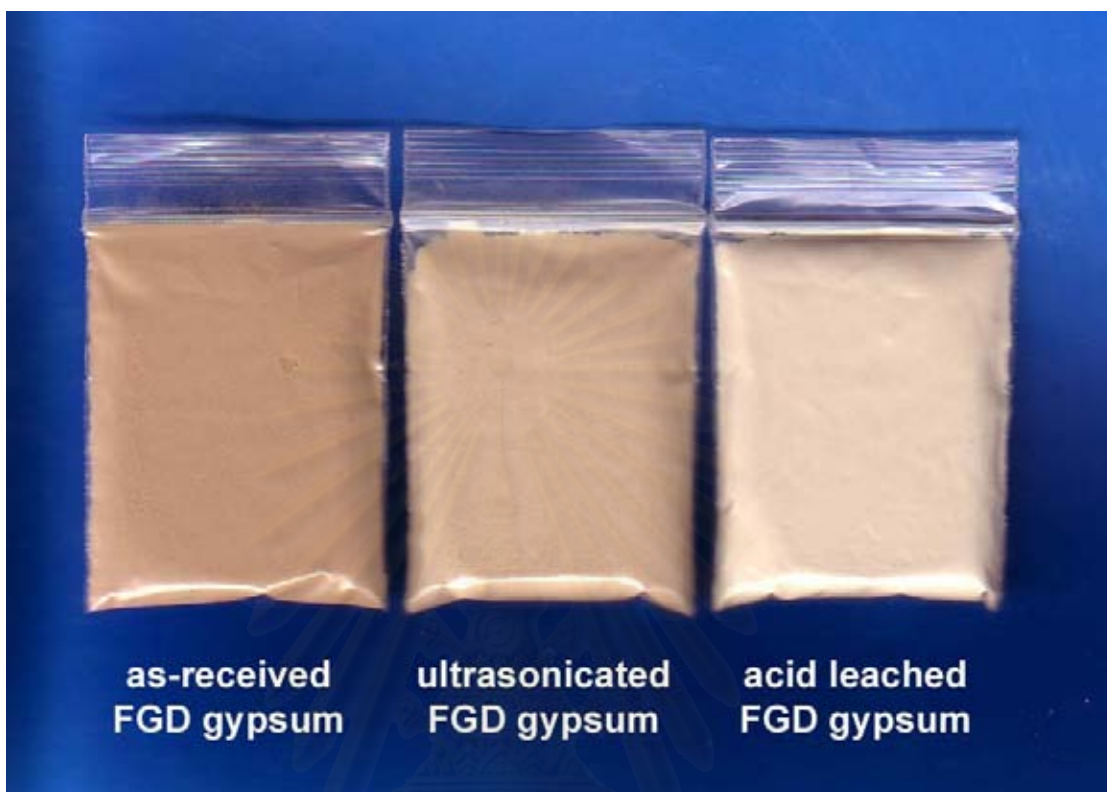


Fig. 4.1 Colors of as-received and precleaned FGD gypsum.

The as-received FGD gypsum (Fig. 4.2) was composed of tabular and rod-shaped crystals of DH ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, dihydrate), varying in size from 10-150 μm (average size $\sim 42 \mu\text{m}$). Its particle size distribution curve shown in Fig. 4.4 quite similar to those of the precleaned FGD gypsum (Fig. 4.6-4.7). However, there was a tendency toward narrow distribution of the precleaned FGD gypsums resulted from the reduction of the $< 10 \mu\text{m}$ fraction. After precleaned by ultrasonication and acid leaching, the DH content was raised to $>97\%$ and the color of precleaned FGD gypsum became pale (Fig. 4.1) and their particles (Fig. 4.3) had a smooth surface because the red inclusion, mainly fine-grained fly ash, was eliminated. The micrograph of the red inclusion (Fig. 4.4) clearly revealed the presence of fly ash as hollow spheres of different sizes, ranging from 0.3-60 μm (average size $\sim 14 \mu\text{m}$). The particle size distribution of the red inclusion was shown in Fig. 4.8. It was divided into 2 fractions, 0.3-4 and 4-60 μm . After

precleaning, some of them remained but in a much lesser extent. As fly ash consisting of glassy phase, the XRD pattern of the red inclusion (Fig.4.9) shows only the presence of gypsum, kaolinite and quartz.

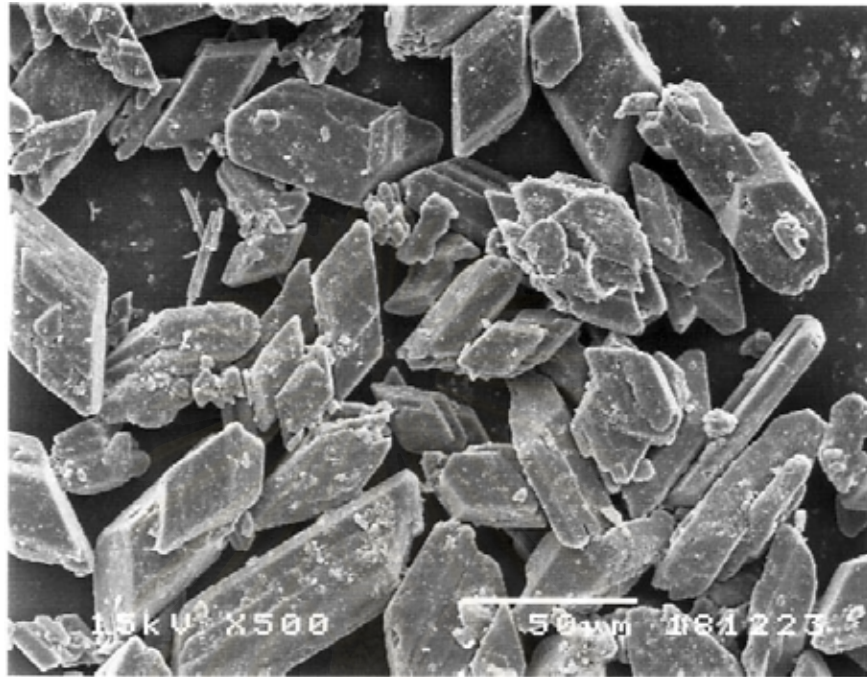


Fig. 4.2 SEM micrograph of the as-received FGD gypsum.



Fig. 4.3 SEM micrograph of the precleaned FGD gypsum.

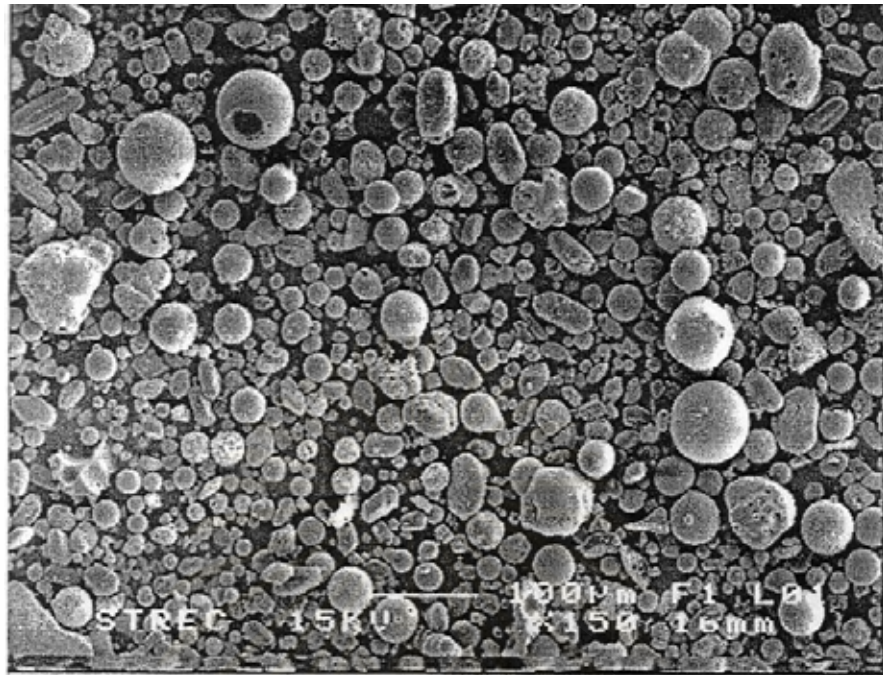


Fig. 4.4 SEM micrograph of the red inclusion.²⁶

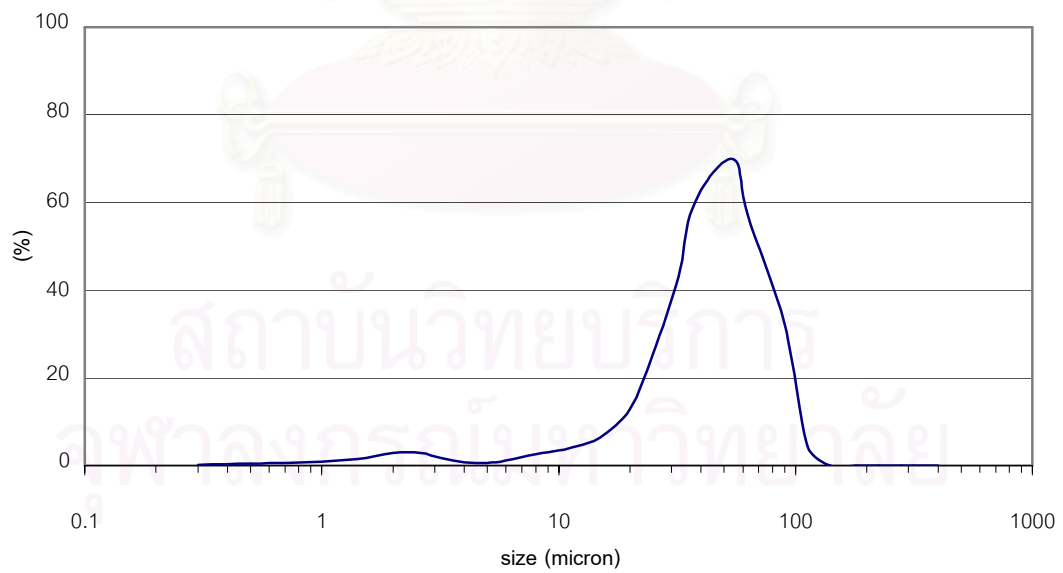


Fig. 4.5 Particle size distribution of the as-received FGD gypsum (no sieving).

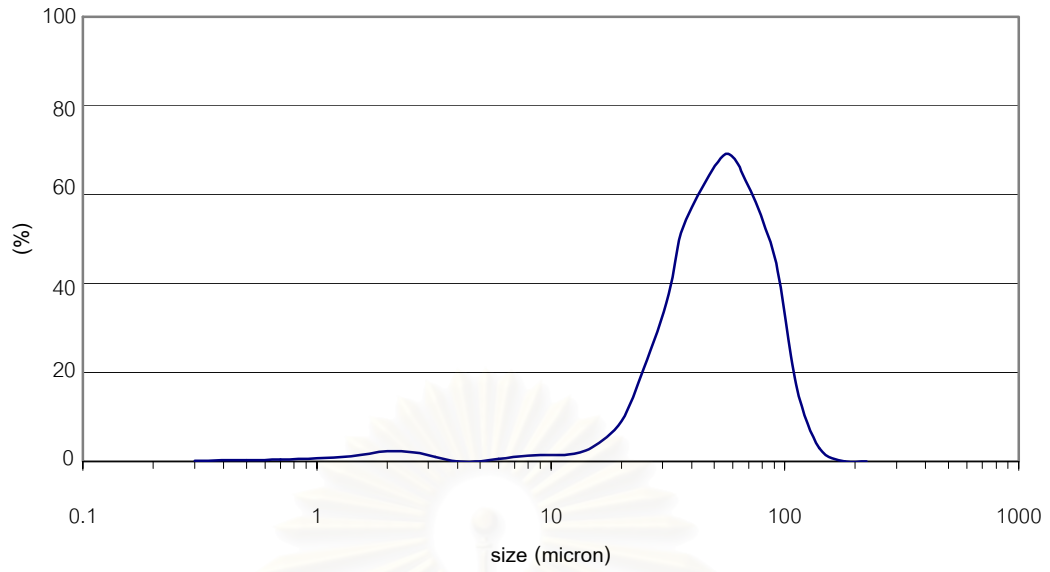


Fig. 4.6 Particle size distribution of the ultrasonicated FGD gypsum (-230 #).

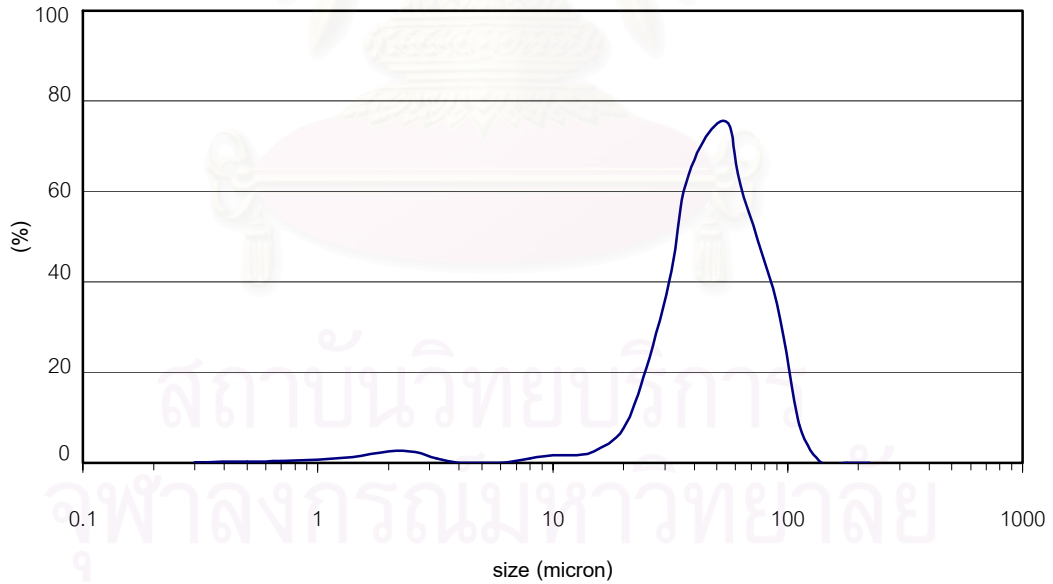


Fig. 4.7 Particle size distribution of the acid leached FGD gypsum (-230 #).

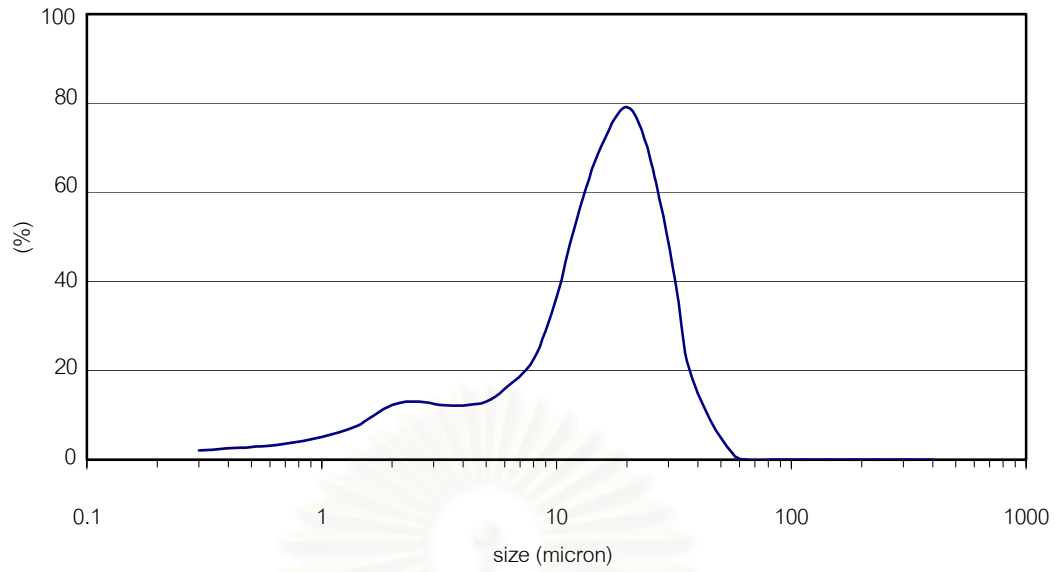


Fig. 4.8 Particle size distribution of the red inclusion (-230 #).

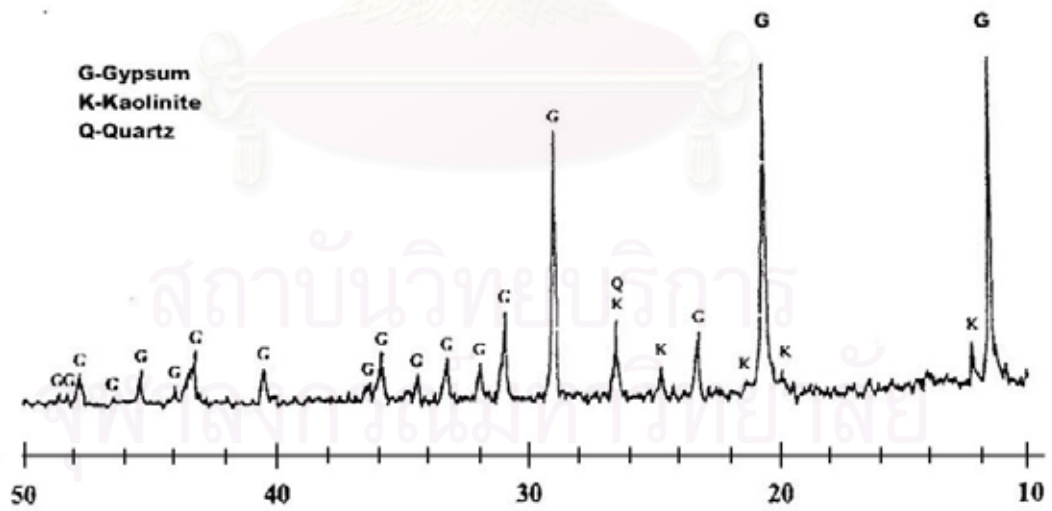


Fig. 4.9 XRD pattern of the red inclusion.²⁶

4.2 Synthesis of alpha-hemihydrate

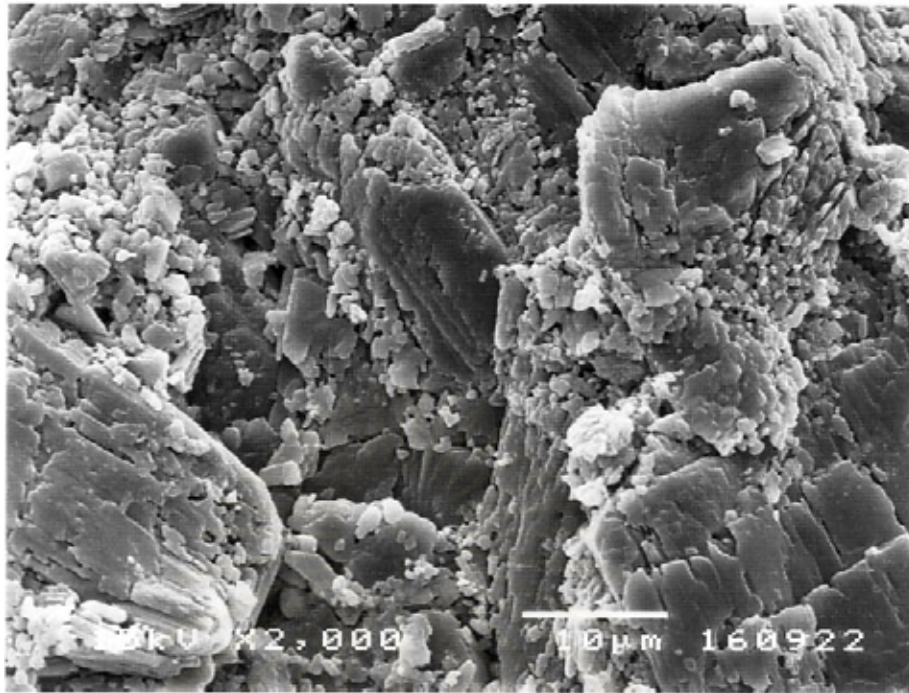
4.2.1 Microstructure of briquettes

Since the synthesis of α -HH in this research was by the classical vapour process, FGD gypsum in lump form or briquette was used. The FGD briquette (50x50x10 mm, bulk density = 2.33 g/cm³) is shown in Fig. 4.10.

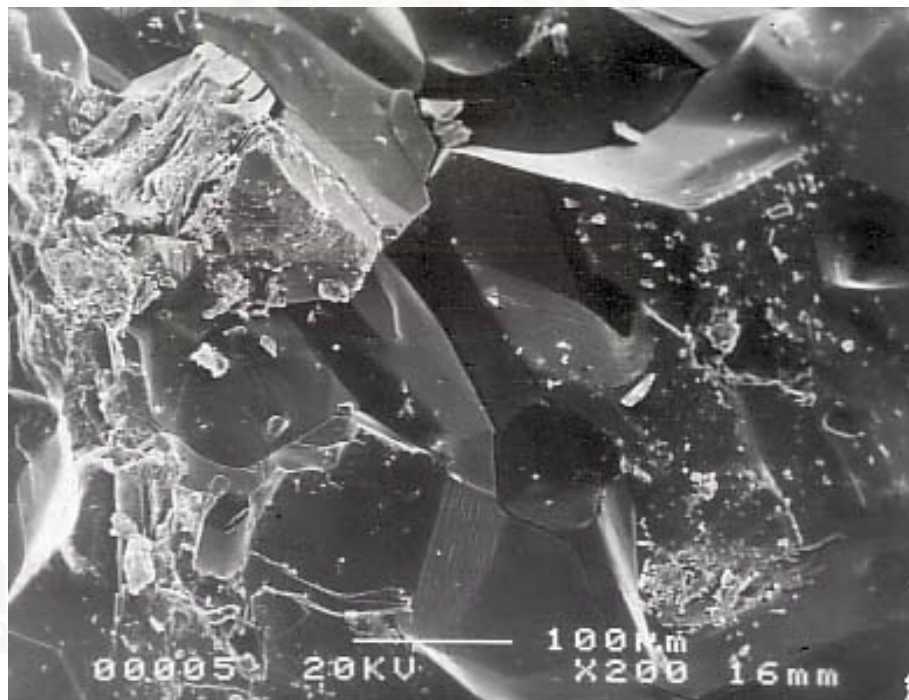


Fig. 4.10 FGD briquette pressed at 180 bars.

Due to the limitation of the press, the FGD briquettes produced in this research were compacted at a pressure of 180 bars which was lower than that of Wichit (1997).²⁷ However, they were able to withstand the vapor pressure in the autoclave during the synthesis of α -HH under nearly all conditions except when using succinic acid as additive. When the FGD gypsum briquettes were impregnated by dipping in succinic acid for 15 min, they broke into fine particles due probably to their low bulk density. The succinic acid easily penetrated into briquette and then reacted with residual CaCO_3 to form $(\text{CH}_2\text{COO})_2\text{Ca}$, hence CO_2 was released and disintegrated the briquettes. Comparatively, the FGD briquettes produced from the precleaned FGD gypsum by ultrasonically broke easier than those of acid leaching due to the higher content of CaCO_3 (Table 4.2). Therefore, the briquettes impregnated with succinic acid were covered with cloth to protect from slaking into the bottom of the autoclave.



(a) FGD gypsum briquette



(b) Natural gypsum²⁷

Fig. 4.11 SEM micrographs of fracture surface.

The microstructures of FGD gypsum briquette and natural gypsum lump are shown in Fig 4.11(a) and (b), respectively. Traces of the original rod shape crystals of FGD gypsum are still present under the compaction pressure of 180 bars, hence its thixotropic properties are not completely eliminated. As a result, the FGD gypsum is more thixotropic than the massive or rocklike natural gypsum.

4.2.2 Phase analysis of the synthesized α -HH

Table 4.3 Phase analysis from the calculation of synthesized α -HH.

Type of α -HH	Crystallization modifier	HH (%)	AIII (%)	AII (%)	DH (%)	Other (%)
Commercial product (Type III)		98.32±3.23	-	1.55±0.13	-	0.13±0.03
NG	-	97.10±4.46	-	1.20±0.10	-	1.70±0.01
	Sodium succinate	98.04±3.36	-	1.76±0.21	-	0.20±0.02
	Succinic acid	99.71±4.16	-	0.19±0.03	-	0.10±0.05
FGD (ultrasonicated)	-	96.70±4.14	-	1.36±0.43	-	1.94±0.13
	Sodium succinate	82.80±3.77	-	16.18±0.45	-	1.02±0.15
	Succinic acid	94.44±4.02	-	1.41±0.09	-	4.15±0.56
FGD (acid leaching)	-	99.05±4.07	-	0.55±0.05	-	0.40±0.23
	Sodium succinate	87.60±3.11	-	12.20±0.89	-	0.20±0.02
	Succinic acid	98.13±3.98	-	1.55±0.14	-	0.32±0.04

NG = Natural gypsum

FGD = Flue-gas gypsum

Commercial product (Type III) = Lafarge's product

From the results of Table 4.3, it was found that all the synthesized α -HHs from both the natural gypsum and the FGD gypsums contained some amount of A II and no AIII and DH. The A II content was very small (< 2 wt%) except in the case of sodium succinate (~12-16 wt%). The high content of A II in the α -HHs produced from the FGD gypsum with sodium succinate was well supported by XRD (Fig. 4.12) result and the fine needles in SEM micrographs (Fig. 4.13 (e) and (h)). This finding was in contrast to Wichit and Supatra (2000).²⁸

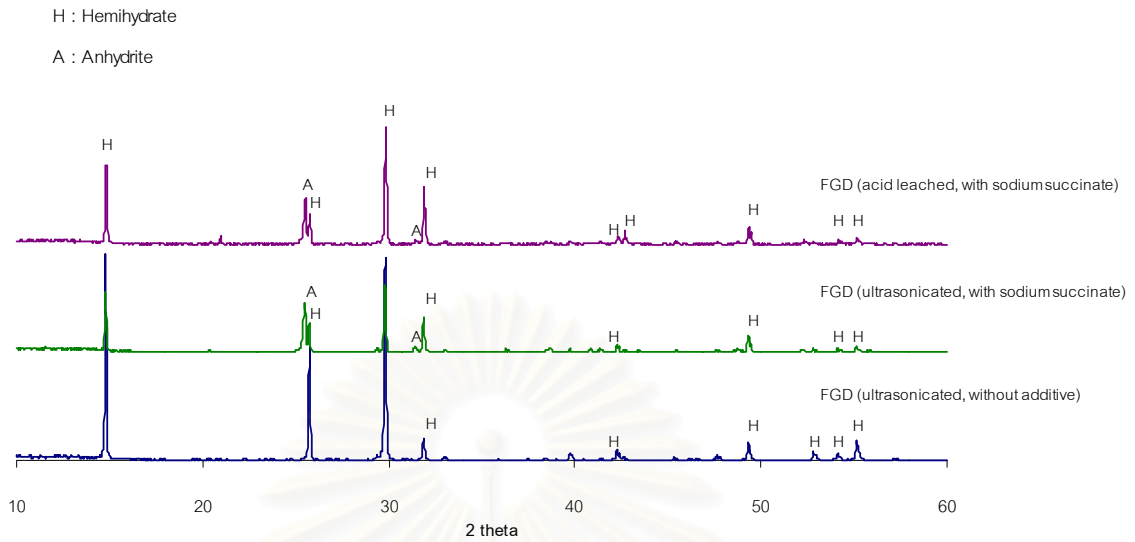


Fig. 4.12 XRD patterns of α -HH synthesized from FGD gypsum.

4.2.3 Microstructure of the α -HH powders

Fig. 4.13 showed the SEM micrographs of α -HHs synthesized under various conditions. It was found that all synthesized α -HHs had a different morphology. The shape of α -HH crystal was of great importance for the properties of gypsum products. It affected the water demand of plaster and the rheological properties. When using crystallization modifiers such as sodium succinate and succinic acid, they tended to reduce the aspect ratio of α -HH crystals and also increase in grain size. The low aspect ratio of α -HH crystals favoured flowability because of the less entanglement which decreased water demand, hence the mechanical strength and hardness of the hydrated plaster increased. On the other hand, the crystal having high aspect ratio caused poor flowability and an increase in water demand, resulting in low strength of the hydrated plaster. However, at the same water to plaster ratio, α -HH that produced high aspect ratio hydrated product proved to have a higher strength than the opposite one due to having a better interlocking of crystals. For example, all the α -HHs produced from natural gypsum (Fig. 4.13 (a), (b) and (c)) had a long and small to big prismatic crystal showing a much higher aspect ratio than those of the FGD gypsum. The morphology of α -HHs synthesized from FGD gypsum, especially the one with the acid leaching (without additive) shown in Fig. 4.13 (g) had a lower aspect ratio, and very larger

crystals with hollows due to fractures of some crystals. Obviously this feature of α -HH crystals was brittle. It seems that the additives induce stacking of the prismatic crystals which become cemented into big grain.

The α -HHs synthesized from The FGD gypsum with sodium succinate are shown in Fig. 4.13 (e) and (h). Besides α -HH crystals, which are short and thick they also revealed A II crystals as needle-like or plates with high aspect ratio. The morphology of α -HH from the ultrasonicated FGD gypsum, without additive, shows a long stripe of high aspect ratio crystals . Of all the morphologies, the α -HHs from the ultrasonicated FGD gypsums, with additive, show the least interlocking.



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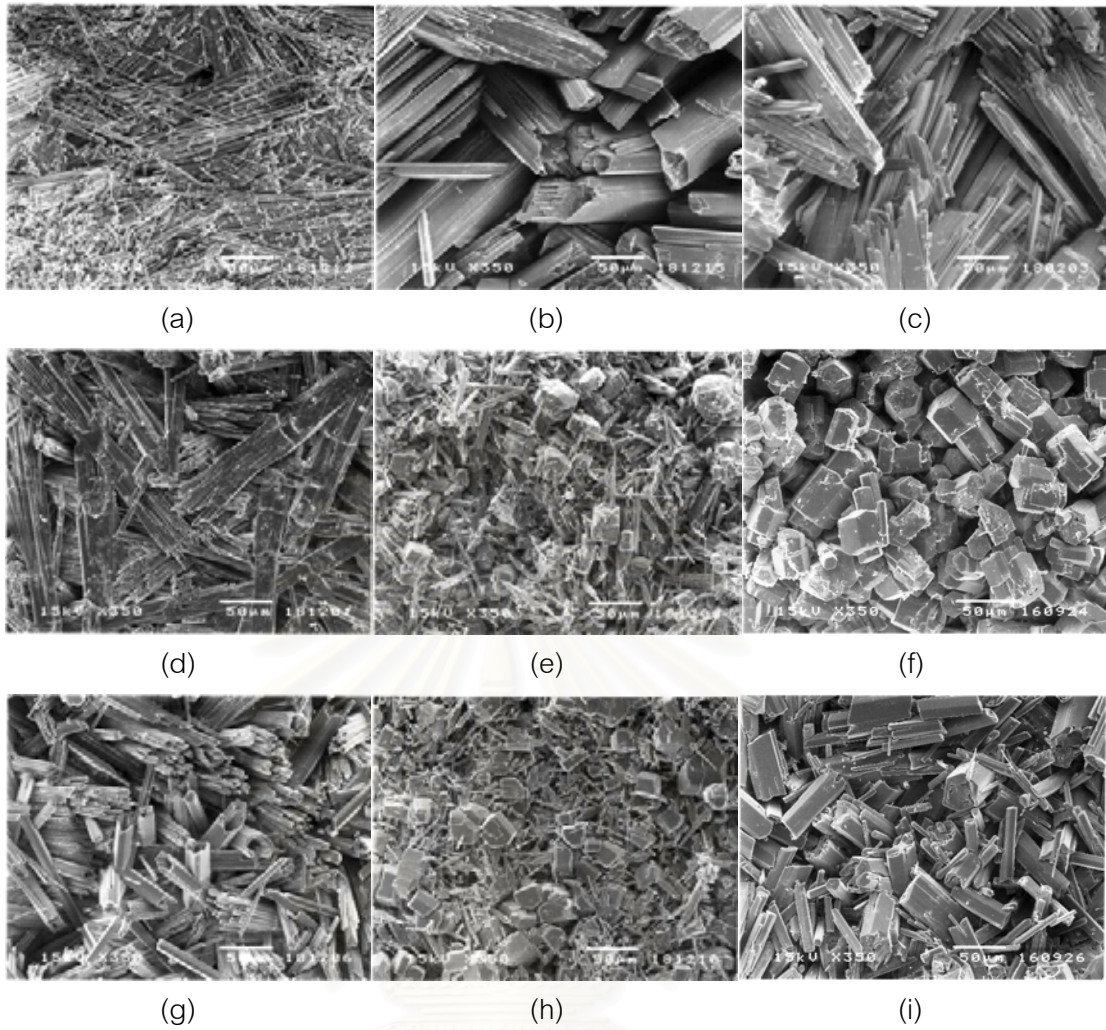


Fig. 4.13 SEM micrographs of α -HHs powders synthesized under various conditions.

- (a) NG (without additive)
- (b) NG (with sodium succinate)
- (c) NG (with succinic acid)
- (d) FGD (ultrasonicated, without additive)
- (e) FGD (ultrasonicated, with sodium succinate)
- (f) FGD (ultrasonicated, with succinic acid)
- (g) FGD (acid leached, without additive)
- (h) FGD (acid leached, with sodium succinate)
- (i) FGD (acid leached, with succinic acid)

4.3 Production of dental stone

All the α -HHs obtained under various conditions were ground with a laboratory grinding machine (FRITSCH Rotor Speed Mill Pulverisette 14) into powder. To obtain the comparable flow properties, the particle size distribution of the synthesized α -HHs was adjusted close to that of commercial dental product by varying the grinding condition and adding the coarse and fine sizes. The α -HH from the FGD gypsum with sodium succinate was selected to be the sample for this experiment. The particle size distribution of selected α -HH (under a feeding rate 23 g/min) was shown in Fig. 4.14. It showed that the synthesized α -HH from FGD gypsum had a lower percentage of fine size (1-7 μm) than commercial product. Therefore, the fine size (0.3-10 μm) was made by grinding the α -HH in planetary mill (FRITSCH Pulverisette) for 5 min, and added to the former. The adjusted particle size distribution was in Fig. 4.15. Fig. 4.16 showed the adjusted particle size distribution of all synthesized α -HHs in comparison with commercial product. Their average sizes were ~ 8 -10 μm .

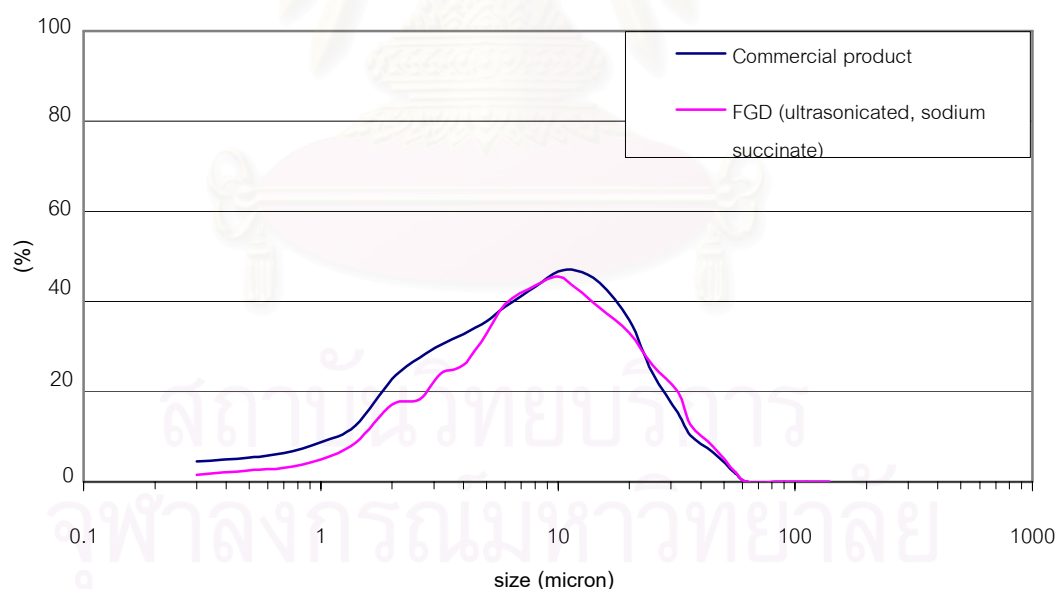


Fig. 4.14 Particle size distribution of the α -HH synthesized from FGD gypsum compared with the commercial product.

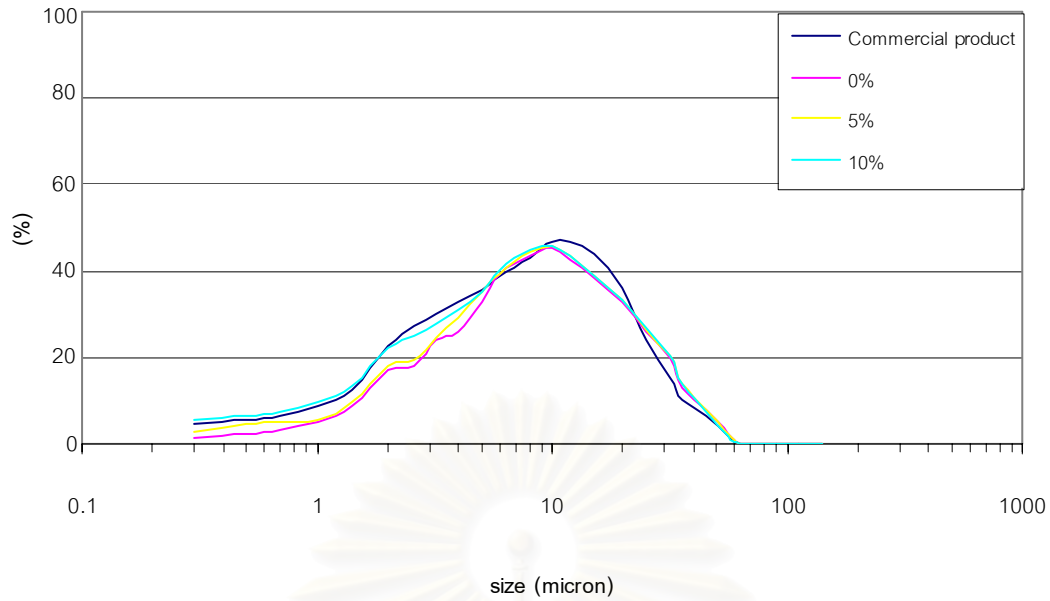


Fig. 4.15 Adjustment of particle size distribution of the α -HH produced from FGD gypsum with sodium succinate.

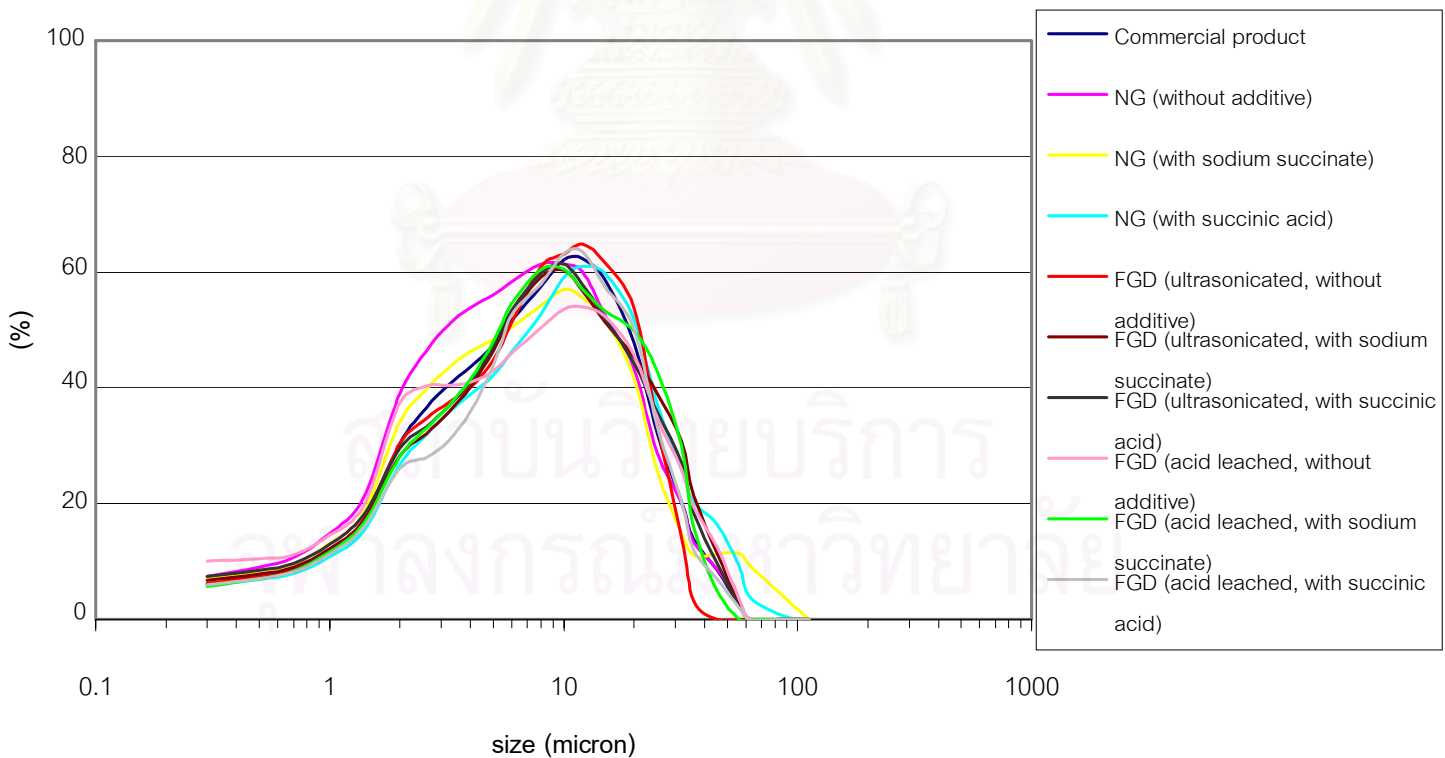


Fig. 4.16 Particle size distributions of α -HH products.

The properties of the dental stone formulated from the synthesized α -HHs were tabulated in Table 4.4 in comparison with those of commercial product. It was found that α -HH having high aspect ratio was difficult to work with, especially, those produced from natural gypsum. Their particles slowly sank into water and were difficult to mix with water. To obtain uniform and easy working plaster slurry, the plasticizer, melamine, was employed. In addition to improvement on flowability, melamine also reduced water demand, causing increase in compressive strength. Fig. 4.17 represented a typical water-compressive strength relation.

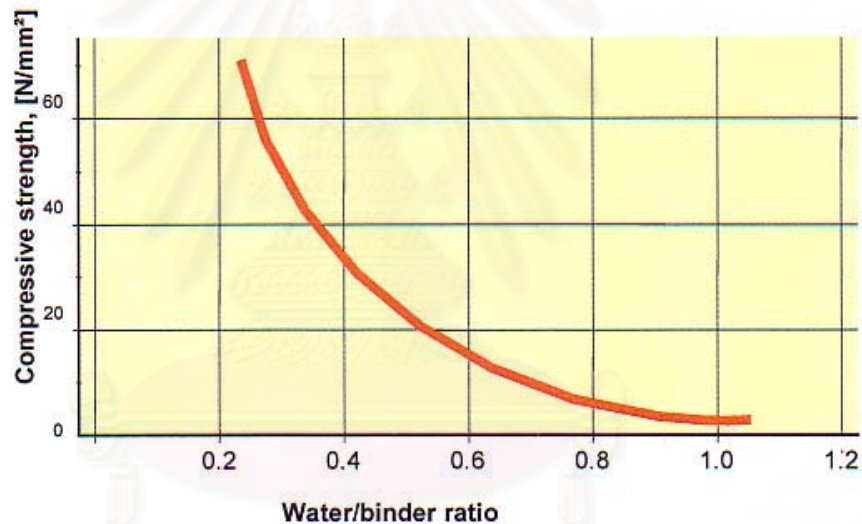


Fig. 4.17 Effect of melamine on compressive strength of the formulated dental stones.²⁹

Table 4.4 Percentage composition and physical properties of the formulated dental stones.

Type of α -HH	crystallization modifier	melamine (%)	potassium sulfate (%)	sodium citrate (%)	sodium potassium tartrate (%)	setting time (min.)	flowability (cm)	setting expansion (%) at 2 hours	Compressive strength (MPa) at 1 hour	bulk density (g/cm ³)
Commercial product						9.17±0.06	8.06±0.03	0.23±0.005	27.71±0.89	1.68±0.064
NG	-	0.30	0.10	0.005	0.01	10.05±0.07	8.20±0.05	0.20±0.005	27.91±1.02	1.67±0.019
	sodium succinate	0.25	0.10	0.01	0.01	10.01±0.17	8.10±0.02	0.17±0.011	29.17±1.00	1.69±0.017
	succinic acid	0.30	0.10	0.02	0.01	9.55±0.20	8.10±0.02	0.18±0.010	33.45±0.76	1.70±0.008
FGD (ultrasonicated)	-	0.02	0.10	0.02	0.01	9.42±0.16	8.10±0.03	0.19±0.005	28.75±0.90	1.67±0.007
	sodium succinate	0.10	0.10	0.02	0.01	9.55±0.38	8.20±0.05	0.20±0.005	13.56±0.82	1.63±0.010
	succinic acid	-	0.01	0.04	0.09	9.02±0.07	8.40±0.05	0.20±0.005	10.84±1.04	1.61±0.007
FGD (acid leached)	-	0.10	0.10	0.02	-	9.21±0.08	8.00±0.02	0.20±0.010	21.27±0.92	1.69±0.017
	sodium succinate	-	0.10	0.02	-	10.05±0.04	8.20±0.05	0.19±0.005	15.81±1.01	1.61±0.005
	succinic acid	-	0.05	0.04	0.04	9.10±0.06	8.40±0.02	0.20±0.005	12.18±1.00	1.68±0.007

Conditions of testing – Room temperature 25 °C, Consistency 32, according to ISO 6873.

4.4 Properties of dental stone

4.4.1 Physical properties

From the results of Table 4.4, the dental stone produced from α -HH (NG, without additive) had a compressive strength close to commercial product. Dental stones produced from α -HH (NG, with sodium succinate and succinic acid) and α -HH (FGD, ultrasonicated, without additive) showed somewhat a higher strength. However, all the formulated dental stones had a compressive strength in accordance with ISO 6873 except the ones from α -HH (FGD, ultrasonicated, with sodium succinate and succinic acid) which had a low strength. Besides the plasticizer, melamine, the strength of hydrated product was also affected by its microstructure and content of the α -HH. The dental stone produced from the α -HH of FGD with sodium succinate had a low compressive strength because of its low content of α -HH (Table 4.3).

Table 4.5 Hardness of dental stones with impression materials.

Type of dental stone		Vicker's hardness number (HV) of dental stone cast against		
		Glass	silicone rubber [*]	Alginate ⁺
Commercial product		19.7±0.55	19.5±0.70	17.1±0.77
NG	-	19.0±0.68	19.8±1.01	17.2±0.64
	sodium succinate	18.9±0.67	18.2±1.03	16.9±0.44
	succinic acid	21.0±0.87	21.2±1.24	20.6±0.80
FGD (ultrasonicated)	-	19.8±0.57	20.4±0.78	17.2±0.45
	sodium succinate	11.8±1.11	12.1±1.03	10.5±0.34
	succinic acid	11.1±1.01	11.5±0.91	8.3±0.87
FGD (acid leached)	-	16.5±0.88	16.2±0.56	14.8±1.22
	sodium succinate	12.8±0.56	13.8±1.01	10.6±0.55
	succinic acid	13.9±0.49	14.2±1.02	11.8±0.43

* Panasil, Germany

+ Oralghine, Italy

Condition of testing-Room temperature 25 °C, Consistency 32.

The hardness results (Table 4.5) for the dried dental stone cast against glass and various impression materials were related to the Vicker's hardness number (HV). The dental stone produced from α -HH (NG, without additive, with sodium succinate and succinic acid) and α -HH (FGD, ultrasonicated, without additive) had a surface hardness close to commercial product. The dental stones cast against glass had a surface hardness close to that cast against silicone rubber but showed slightly greater hardness than against alginate. The surfaces of dental stone cast against glass and silicone rubber showed a smooth and glossy surface, whereas those cast against alginate showed a rough surface with low hardness. Presumably the residual mixing water of alginate reacted with the surface of cast, resulting in the dissolution of dihydrates. However, Hsoda et al.²⁴ reported that the alginate gave appreciably softer surface for all the stones, due probably to the presence of residual hemihydrate and structural disturbance.

4.4.2 Microstructure of hydrated product

Fig. 4.18 showed the fracture microstructures of hydrated product. It was found that additives tended to reduce aspect ratio of dihydrate crystal. Succinic acid showed the lowest aspect ratio and smallest dihydrate crystal. It was noticed that the dihydrate microstructures in Fig 4.18 (h) and (i) were composed of laminated structure leading to less entanglement.

Supatra and Wichit (2000)²⁸ reported that sodium succinate and succinic acid tended to reduce the size of dihydrate crystal and caused grain cementation. However, succinic acid showed a smaller, shorter and tighter bound together of dihydrate crystal than sodium succinate, causing lesser interlocking, hence its hydrated product exhibited lowest strength.

The microstructures of dihydrate showed in Fig.4.18 (g) and (j) and Fig. 4.19 (enlarged) consisted of compact and voluminous crystals of low aspect ratio. This result was in contrast to Supatra and Wichit (2000),²⁸ due to the low bulk density of the FGD gypsum briquette and longer impregnation time which led to extreme reaction with succinic acid. This was confirmed by the high content of sodium citrate needed as retarder in the formulation. Normally, sodium citrate was a strong retarder and only 0.01

wt% could prolong setting time to 3-5 min, but in this experiment, the setting time of the formulated α -HH (FGD, with succinic acid) increased only 30 s – 1 min (from 5 min). According to Forsen,³⁰ succinic acid did not only act as crystallization modifier but also as a retarder. Since it is an organic acid, it is classified as a retarder of class IV³⁰ which is known to have a very sensitive range of application, a little overdose of it can suspend the setting. Moreover, the result of dihydrate microstructure (Fig. 4.19) was similar to that described by J. Kuhlmann and U. Ludwig,³¹ but they used a high content of A II as retarder. The hydrated product obtained in this case had a low strength because of the poor interlocking of the dihydrate crystals.

Since dental stone produced from FGD gypsum α -HH (acid leached, with succinic acid) had a light color and a good flowability without plasticizer (melamine). It was interesting to improve the strength by formulation with a lower water to plaster ratio. The results of Table 4.6 showed physical properties of this dental stone at different consistencies. It was found that without the aid of melamine, the minimum water used for the formulation could be reduced to 28 with a compressive strength of ~21 MPa and surface hardness number of ~15 HV. Fig. 4.21 showed hydrated microstructure of dental stone formulated at consistency 28 which was similar to that of consistency 32 (Fig. 4.19 (b)).

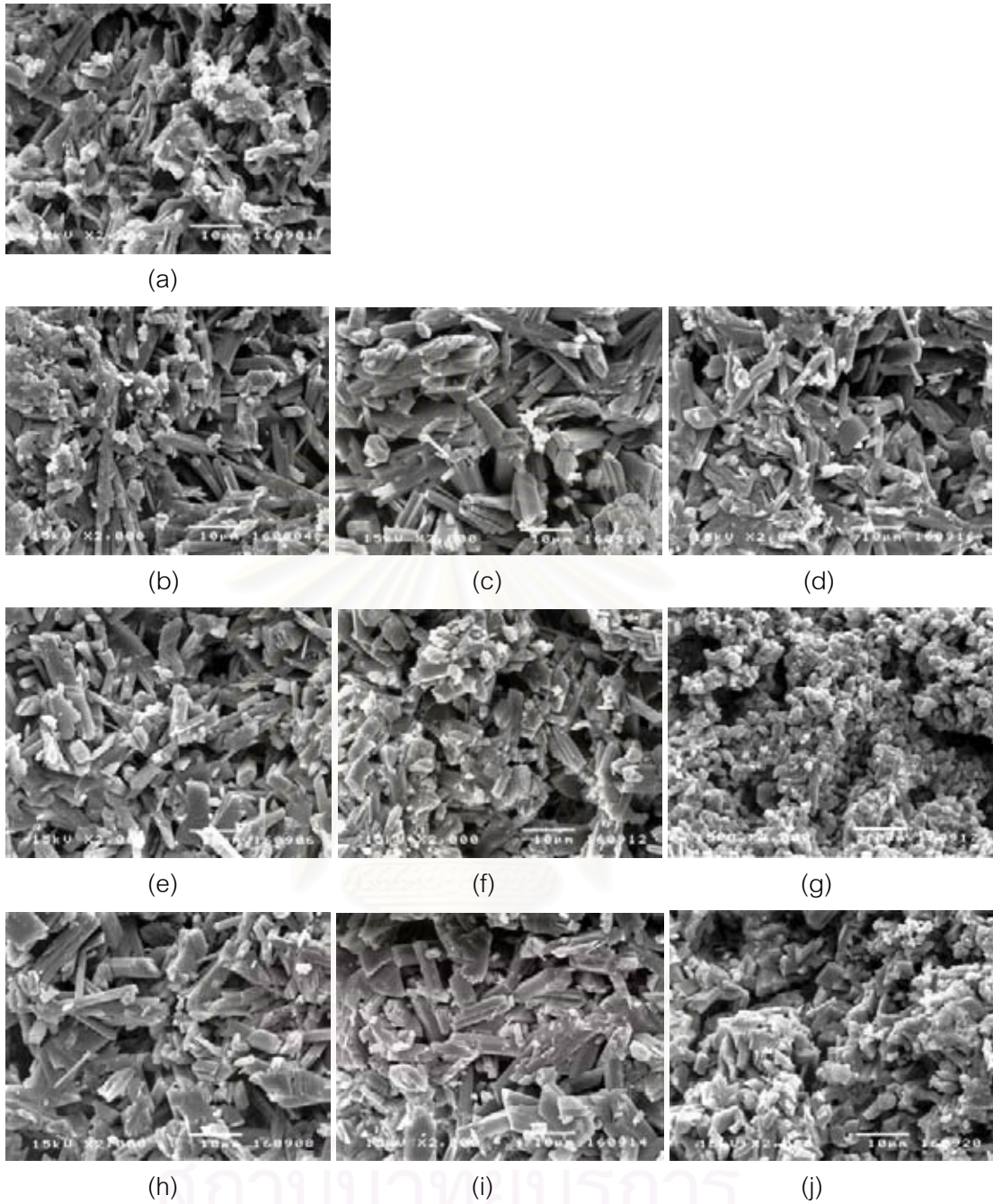
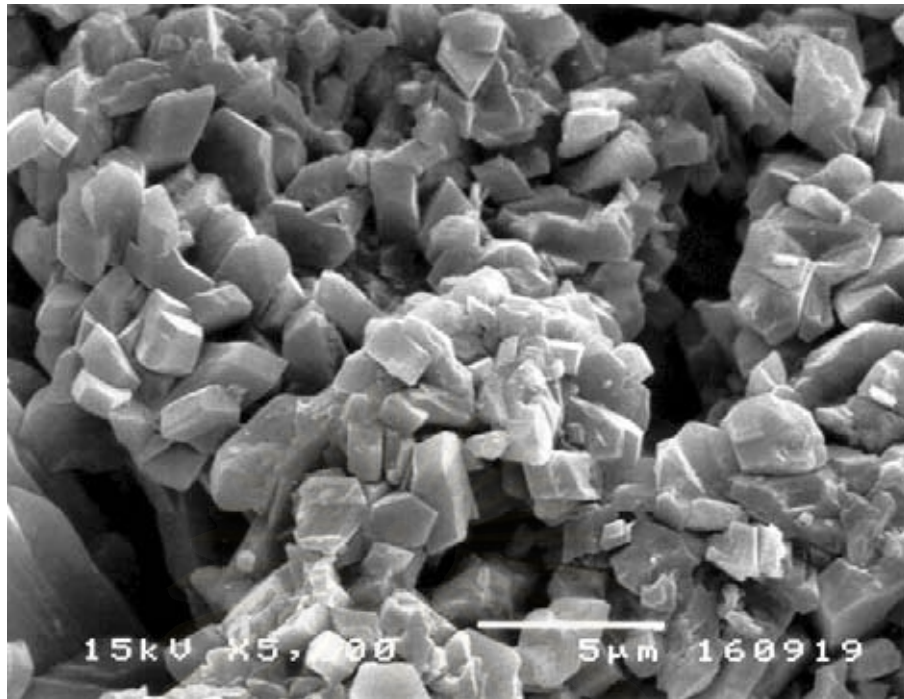
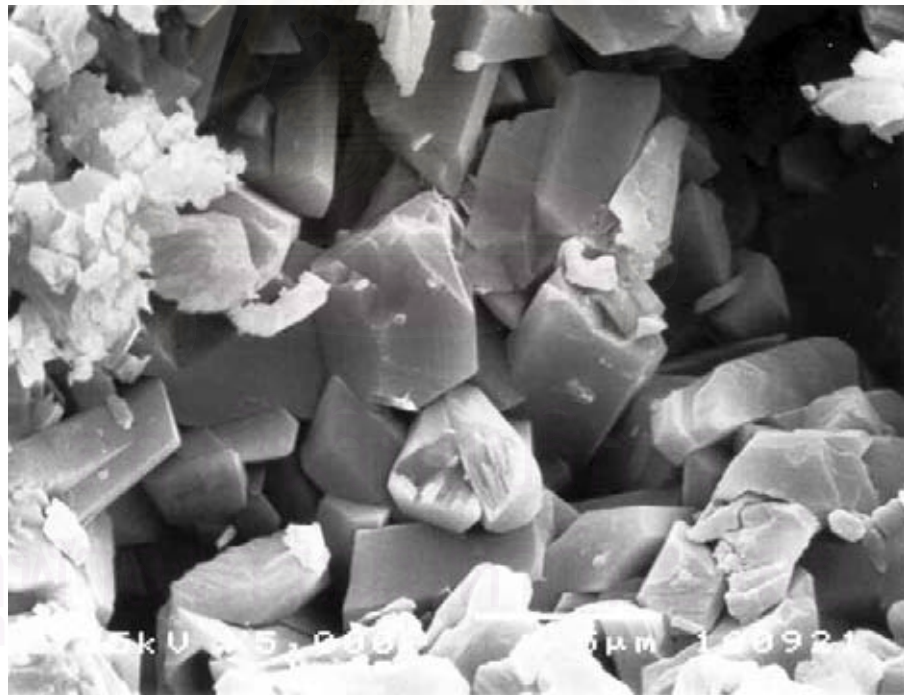


Fig. 4.18 SEM micrographs of hydrated product of dental stone.

- | | |
|---|---|
| (a) Commercial product | (h) FGD (acid leached, without additive) |
| (b) NG (without additive) | (i) FGD (acid leached, with sodium succinate) |
| (c) NG (with sodium succinate) | (j) FGD (acid leached, with succinic acid) |
| (d) NG (with succinic acid) | |
| (e) FGD (ultrasonicated, without additive) | |
| (f) FGD (ultrasonicated, with sodium succinate) | |
| (g) FGD (ultrasonicated, with succinic acid) | |



(a) ultrasonicated FGD gypsum



(b) acid leached FGD gypsum

Fig. 4.19 SEM micrographs of hydrated dental stone produced from FGD gypsum with succinic acid, showing dihydrate crystals.

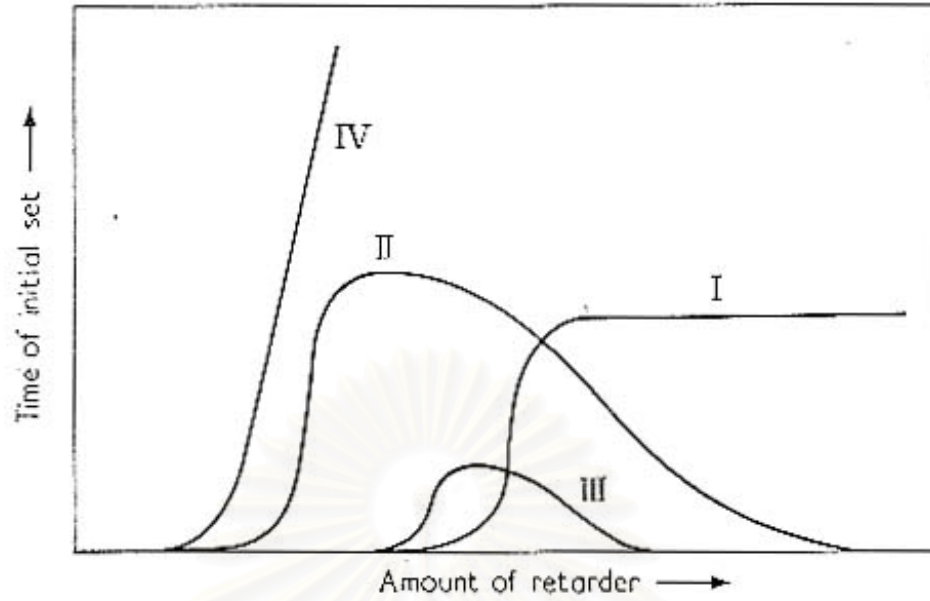


Fig. 4.20 Action of various retarders on portland cement clinker.³⁰

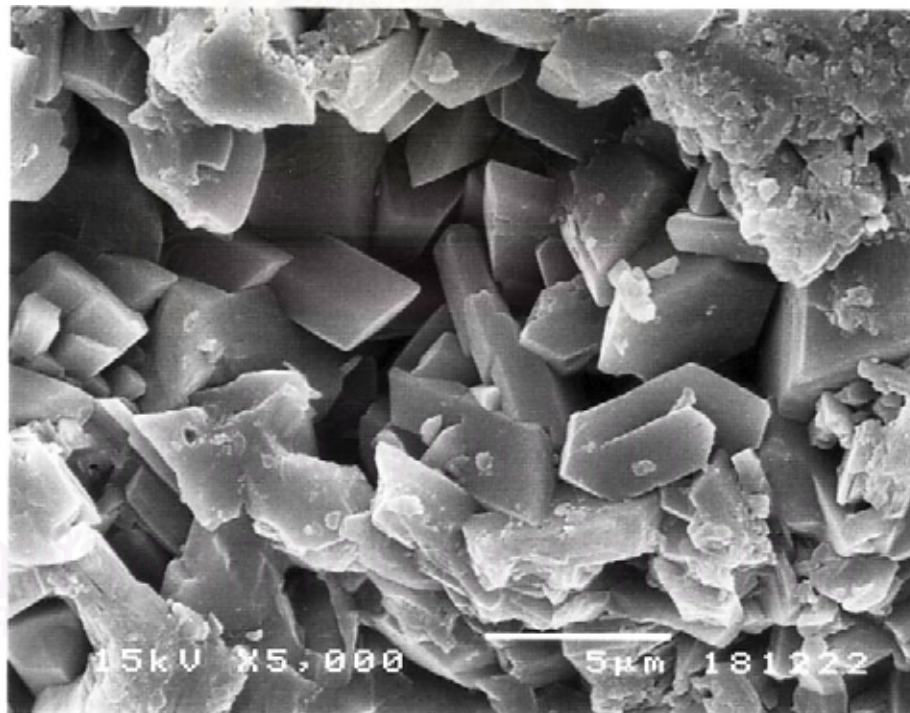


Fig. 4.21 SEM micrograph of dihydrate microstructure of dental stone formulated at consistency 28.

Table 4.6 Physical properties of dental stone produced from FGD gypsum (acid leached, with succinic acid) at different consistency.

Physical property	Consistency		
	32	30	28
Setting time (min.)	10.05±0.04	9.68±0.07	9.02±0.17
Flowability (cm)	8.40±0.05	8.20±0.02	8.05±0.04
Setting expansion (%) at 2 hours	0.19±0.005	0.195±0.005	0.205±0.005
Compressive strength (MPa) at 1 hour	15.81±1.01	16.25±0.85	21.43±1.03
Bulk density (g/cm ³)	1.61±0.005	1.69±0.016	1.76±0.005
Vicker's hardness number (HV)	12.8±0.56	13.1±0.91	15.0±1.05

4.4.3 Reproduction of detail

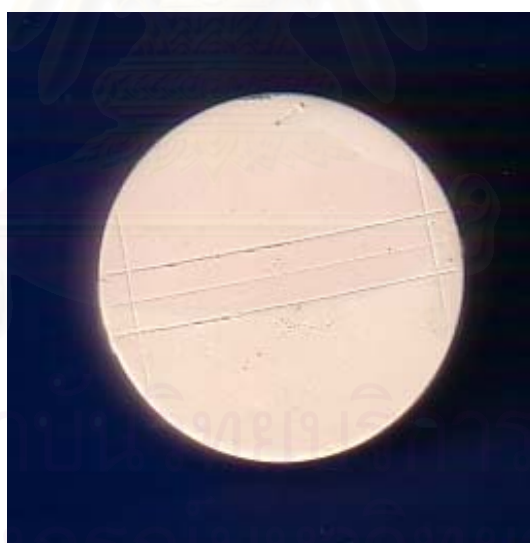


Fig. 4.22 Complete line on the surface of dental stone.

Fig. 4.22 shows a selected sample of dental stone produced from α -HH (FGD, ultrasonicated, without additive) cast from duplicating material, silicone rubber. The line on the surface of sample is used to determine a reproduction of detail. If the line is complete, dental stone meets requirement for the reproduction of detail according to

ISO 6873. On the other hand, if the test gives an incomplete line, the dental stone does not meet the requirement for reproduction of detail of this standard. All dental stones produced from FGD gypsum and natural gypsum in this research and commercial product which cast from both duplicating materials (silicone rubber and alginate) gave a complete line, as shown in Fig. 4.22

4.4.4 Color of dental stone.

Fig. 4.23 shows the reflectance/wavelength curves of dental stones with and without 0.05 wt% of organic green pigment in comparison with commercial product. The curve of commercial product and the dental stones produced are quite similarly but with a difference in percentage of reflection. The curves show reflectance peaks in the range of approximately 420-680 nm which covers the wavelengths for blue, green, yellow and red colors. However, the curves of all the dental stones produced from FGD gypsums are different from that of the commercial product. They obviously show lower reflectance peaks in range of approximately 420-550 nm which corresponded to the wavelengths for blue and green colors. Accordingly, the dental stones produced from the FGD gypsum have a strong yellowish tint, especially the one with no acid leaching.

Table 4.7 Numerical expression of color measured according to CIE L*a*b* system.

Type of dental stone	L*	a*	b*	Cab*	hab*
Commercial product	89.54	-10.35	-7.55	12.81	216.10
NG (without additive)	102.11	0.46	-0.34	0.57	323.36
FGD (ultrasonicated, without additive)	91.11	2.70	1.24	2.97	24.62
FGD (acid leached, without additive)	93.25	2.99	2.55	3.92	40.46
NG (without additive) + 0.05 wt% green pigment	91.52	-7.63	-5.92	9.66	217.84
FGD (ultrasonicated, without additive) + 0.05 wt% green pigment	86.02	-1.61	-1.11	1.96	214.64
FGD (acid leached, without additive) + 0.05 wt% green pigment	86.53	-4.61	-2.90	5.44	212.13

L* : lightness, a*, b* : space color, Cab* : chroma, hab* : hue angle

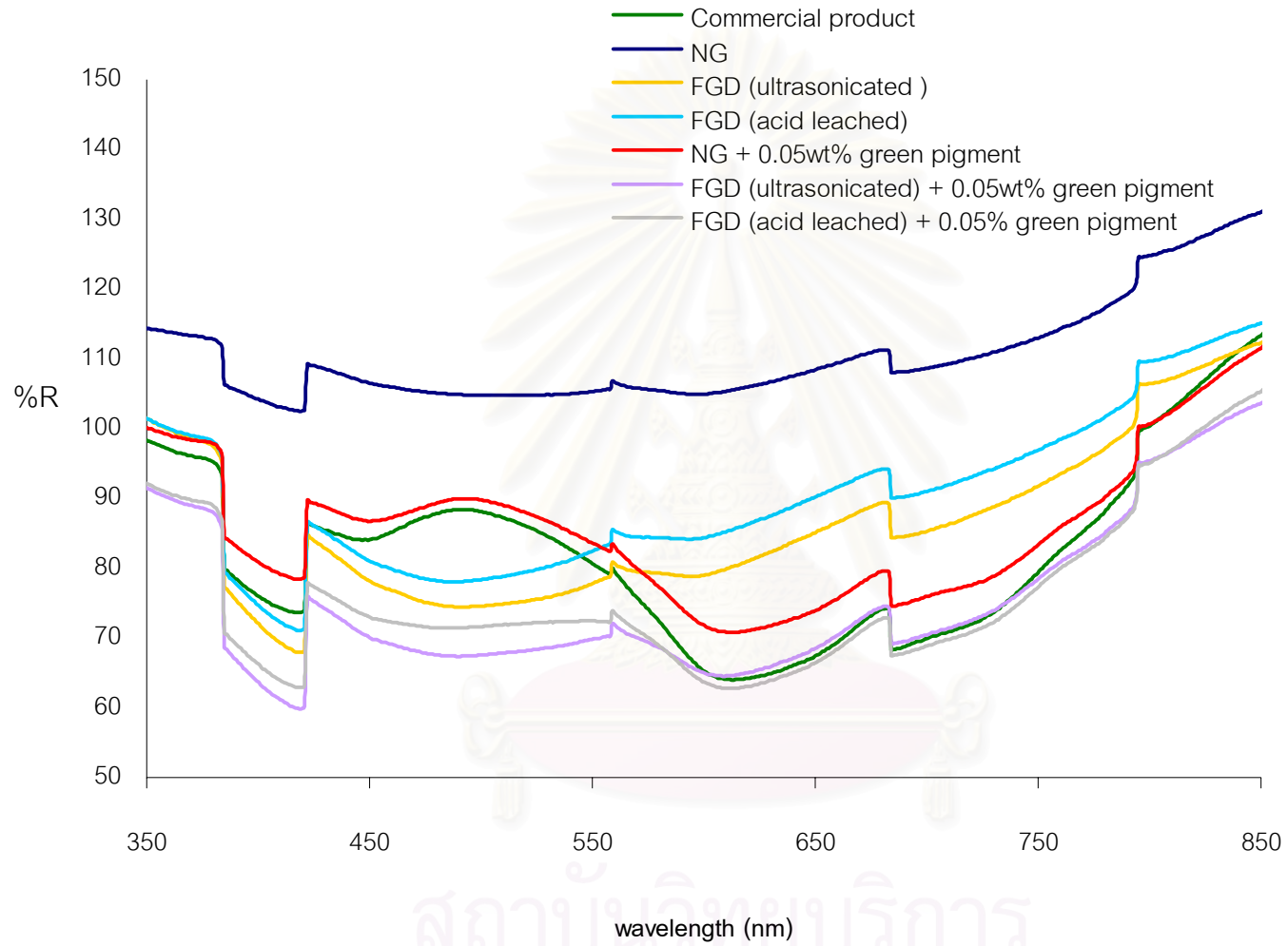


Fig. 4.23 Reflectance/wavelength curve of dental stone.

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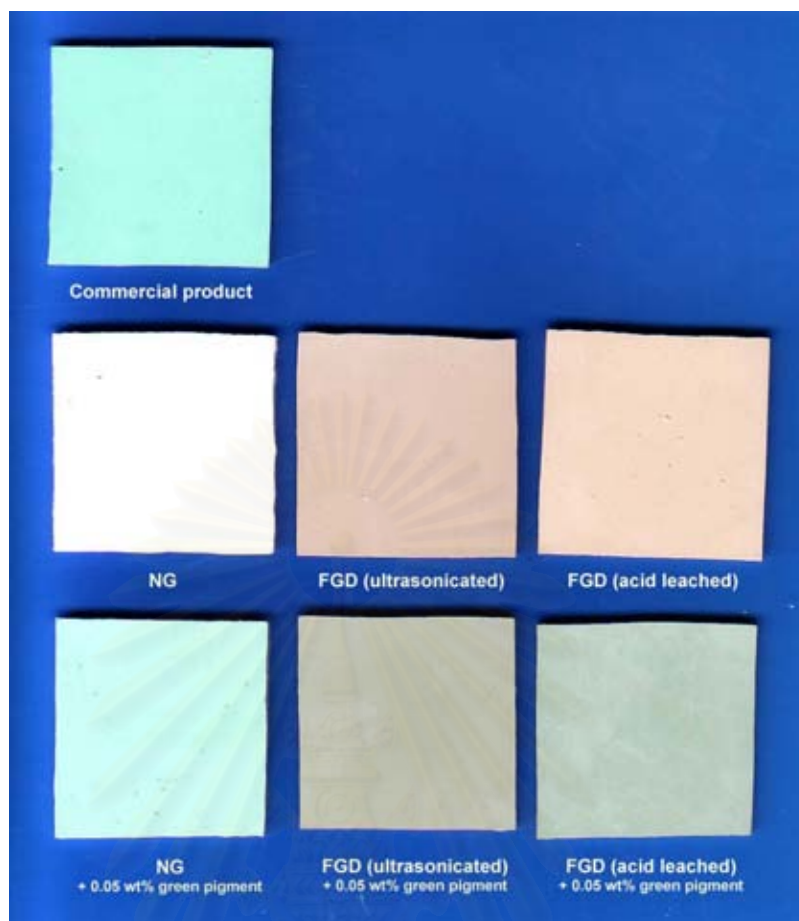


Fig. 4.24 Appearance of the formulated dental stones (with and without green pigment) compared with commercial product.

The values obtained from the reflectance/wavelength curve in CIE $L^*a^*b^*$ system are tabulated in Table 4.7. The dental stones produced from FGD gypsum have lightness (L^*) and hue angle (hab^*) close to commercial product but are different in space color (a^* and b^*) and chroma (Cab^*). The green colored product obtained (Fig. 4.24) had a lower saturation and percentage of green color than the commercial product.

Since the organic pigment was difficult to disperse. Therefore, the mixing method and type of mixer also affected a colored product obtained. In this research the dental stone produced and the organic green pigment were mixed with a different mixer (blender, National) from the commercial product (high speed mixer). This was another cause for the difference of color. However, it was obvious that the original color of the FGD gypsum strongly affected the color of the dental stones produced.

Chapter 5

Conclusions

From the experiment results, the following conclusion can be drawn:

1. Preparation of raw material

Precleaning by ultrasonication and acid leaching method can improve chemical and physical properties of FGD gypsum close to those of natural gypsum. Moreover, the purity of precleaned FGD gypsums (~98%) is higher than that of natural gypsum (~94%). However, the precleaned FGD gypsum has a brown tinge to its color.

2. Synthesis of α -hemihydrate

2.1 The compact mass of FGD gypsum briquettes and the content of CaCO_3 are significant when dipping in solution of succinic acid. Impregnated FGD gypsum briquettes of low density are prone to slake and not suitable for hydrothermal treatment by classical vapor process. High CaCO_3 in the briquettes is thought to respond for the high $\text{Ca}(\text{OH})_2$ in the system which leads to the acceleration of set, crystals of low aspect ratio and high A II content.

2.2 FGD gypsum can be used as substitute for natural gypsum in the synthesis of α -HH because high content of α -HH (94-99%) close to that of natural gypsum (97-99%) can be produced in this experiment.

2.3 Sodium succinate and succinic acid as crystallization modifiers tend to reduce the aspect ratio of α -HH crystals and shorter the crystal which is obviously seen in the α -HH produced from FGD gypsum.

3. Production of dental stone

3.1 α -HHs produced from the FGD gypsum requires a lower content of plasticizer (melamine) than that from natural gypsum due to having a lower aspect ratio of crystals. This morphology favours flowability because of the less entanglement. Hence, the morphology having a low aspect ratio can improve mechanical strength by formulation with lower water to plaster ratio.

3.2 According to ISO 6873, α -HH (FGD, ultrasonicated, without additive) can be used to produce dental stone (Type III) since the stone obtained has a high strength

(~28 MPa) and close to those of natural gypsum (~27 MPa) and commercial product (~27 MPa).

3.3 Dental stones produced from FGD gypsum are compatible with impression materials (silicone rubber, alginate) used clinically. They can completely reproduce the detail from impression materials and their surface hardness changes only slightly when cast against these materials.

3.4 Theoretically, the color does not affect the properties of dental stone. To protect the mistake of working, it is used to classify various types of dental gypsum products. Normally, dental stone (Type III) is usually produced into green or yellow product. In commercial, it has a different shade of green or yellow color. Therefore, the green color with a yellow tint present in dental stone produced from FGD gypsum should not be a problem in practical use.



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Appendices

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As-received FGD gypsum

Diameter at 10% : 15.93 μm
 Diameter at 50% : 40.34 μm
 Diameter at 90% : 72.05 μm
 Mean diameter : 42.28 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	0.10	0.32	0.53	0.89	1.46	2.67	3.57	4.01	4.21	4.35
q3	0.05	0.09	0.13	0.21	0.36	0.71	0.72	0.44	0.19	0.13
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	4.60	5.46	6.39	7.35	9.07	13.50	20.26	32.91	40.94	58.72
q3	0.29	0.63	0.87	1.10	1.62	3.23	6.35	10.75	14.30	16.71
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	76.81	84.85	98.53	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	17.35	14.32	8.04	1.41	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

Ultrasonicated FGD gypsum

Diameter at 10% : 21.49 μm
 Diameter at 50% : 46.00 μm
 Diameter at 90% : 82.49 μm
 Mean diameter : 49.12 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	0.08	0.25	0.41	0.70	1.16	2.13	2.76	3.00	3.00	3.00
q3	0.04	0.07	0.10	0.17	0.29	0.58	0.51	0.25	0.00	0.00
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	3.12	3.58	3.96	4.31	5.13	8.22	13.76	24.72	31.86	48.20
q3	0.14	0.34	0.36	0.41	0.78	2.28	5.26	9.41	12.85	15.52
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	66.04	75.34	94.74	99.21	100.0	100.0	100.0	100.0	100.0	100.0
q3	17.29	16.74	11.53	4.33	0.75	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

Acid leached FGD gypsumDiameter at 10% : 21.78 μm Diameter at 50% : 42.98 μm Diameter at 90% : 75.22 μm Mean diameter : 45.54 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.003.
Q3	0.06	0.23	0.39	0.69	1.19	2.31	3.06	3.32	3.32	32
q3	0.03	0.07	0.10	0.17	0.31	0.65	0.59	0.26	0.00	0.00
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	3.32	3.68	4.14	4.52	5.19	7.84	13.50	26.10	34.62	53.99
q3	0.00	0.26	0.43	0.43	0.62	1.91	5.27	10.60	15.02	18.03
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	73.76	82.49	97.60	99.79	100.0	100.0	100.0	100.0	100.0	100.0
q3	18.77	15.39	8.80	2.08	0.20	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

Fly ashDiameter at 10% : 1.96 μm Diameter at 50% : 13.61 μm Diameter at 90% : 26.95 μm Mean diameter : 14.36 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	0.71	1.92	2.92	4.43	6.54	10.23	13.10	15.25	17.52	19.98
q3	0.42	0.56	0.71	1.01	1.49	2.46	2.60	2.47	2.42	2.62
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	22.41	27.83	34.67	42.71	55.61	74.72	87.43	95.87	98.05	99.73
q3	3.17	4.49	7.30	10.50	13.76	15.82	13.56	8.14	4.41	1.79
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

Commercial productDiameter at 10% : 1.20 μm Diameter at 50% : 6.41 μm Diameter at 90% : 20.05 μm Mean diameter : 9.01 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.49	3.75	5.51	8.09	11.55	18.23	24.15	29.32	35.31	41.82
q3	0.90	1.08	1.27	1.76	2.50	4.56	5.50	6.06	6.54	7.11
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	47.63	57.83	66.38	73.38	81.46	89.95	94.39	97.48	98.48	99.67
q3	7.76	8.64	9.33	9.35	8.82	7.19	4.85	3.05	2.07	1.30
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

 α -HH (NG, without additive)Diameter at 10% : 1.00 μm Diameter at 50% : 4.85 μm Diameter at 90% : 15.57 μm Mean diameter : 6.84 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.81	4.59	6.76	9.95	14.23	22.60	29.93	36.28	43.50	51.03
q3	1.11	1.36	1.61	2.23	3.17	5.85	6.96	7.62	8.07	8.41
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	57.44	68.08	76.32	82.53	89.17	95.53	98.51	99.85	100.0	100.0
q3	8.76	9.22	9.21	8.49	7.42	5.51	3.33	1.35	0.32	0.00
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

α -HH (NG, with sodium succinate)Diameter at 10% : 1.07 μm Diameter at 50% : 5.82 μm Diameter at 90% : 21.40 μm Mean diameter : 9.74 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.76	4.36	6.34	9.21	13.01	20.45	26.84	32.36	38.69	45.31
q3	1.06	1.25	1.44	1.97	2.77	5.11	5.97	6.51	6.95	7.27
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	50.95	60.50	68.29	74.49	81.57	88.93	92.46	94.71	95.51	97.05
q3	7.58	8.13	8.55	8.33	7.77	6.27	3.88	2.23	1.66	1.69
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	98.58	99.24	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	1.71	1.37	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

 α -HH (NG, with succinic acid)Diameter at 10% : 1.26 μm Diameter at 50% : 7.37 μm Diameter at 90% : 24.33 μm Mean diameter : 10.69 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.51	3.72	5.40	7.81	11.01	16.94	22.15	26.76	32.16	38.01
q3	0.90	1.04	1.20	1.63	2.29	4.01	4.79	5.35	5.83	6.32
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	43.26	52.71	60.93	67.85	76.16	85.44	90.63	94.59	96.08	98.37
q3	6.94	7.92	8.88	9.15	8.98	7.77	5.61	3.87	3.05	2.47
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	99.64	99.91	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	1.40	0.55	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

α -HH (FGD, ultrasonicated, without additive)Diameter at 10% : 1.17 μm Diameter at 50% : 6.67 μm Diameter at 90% : 18.24 μm Mean diameter : 8.37 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.54	3.88	5.70	8.35	11.90	18.51	24.07	28.81	34.27	40.37
q3	0.93	1.13	1.33	1.83	2.59	4.56	5.21	5.61	6.01	6.72
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	46.08	56.80	66.30	74.26	83.57	93.03	97.66	99.77	100.0	100.0
q3	7.70	9.16	10.47	10.73	10.26	8.08	5.10	2.10	0.48	0.00
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

 α -HH (FGD, ultrasonicated, with sodium succinate)Diameter at 10% : 1.06 μm Diameter at 50% : 6.40 μm Diameter at 90% : 21.89 μm Mean diameter : 9.25 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.84	4.51	6.52	9.37	13.10	19.57	24.92	29.60	35.22	41.66
q3	1.11	1.28	1.46	1.95	2.71	4.44	4.99	5.51	6.16	7.06
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	47.63	58.19	66.59	73.06	80.19	88.01	92.94	97.03	98.35	99.70
q3	8.01	8.98	9.21	8.68	7.81	6.65	5.40	4.05	2.74	1.48
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

α -HH (FGD ultrasonicated, with succinic acid)Diameter at 10% : 1.13 μm Diameter at 50% : 6.54 μm Diameter at 90% : 21.52 μm Mean diameter : 9.24 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.62	4.06	5.94	8.65	12.25	18.52	23.80	28.42	34.00	40.52
q3	0.97	1.16	1.36	1.85	2.60	4.28	4.90	5.42	6.09	7.11
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	46.66	57.74	66.60	73.37	80.67	88.41	93.24	97.20	98.47	99.73
q3	8.20	9.37	9.66	9.04	7.96	6.55	5.27	3.90	2.62	1.37
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

 α -HH (FGD, acid leached, without additive)Diameter at 10% : 1.13 μm Diameter at 50% : 6.68 μm Diameter at 90% : 23.20 μm Mean diameter : 9.72 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.68	4.15	6.02	8.70	12.23	18.45	23.65	28.22	33.75	40.14
q3	1.01	1.18	1.35	1.83	2.55	4.24	4.82	5.35	6.02	6.96
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	46.08	56.58	64.89	71.27	78.36	86.42	91.81	96.50	98.05	99.64
q3	7.92	8.87	9.05	8.51	7.72	6.81	5.87	4.62	3.20	1.73
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

α -HH (FGD, acid leached, with sodium succinate)Diameter at 10% : 1.22 μm Diameter at 50% : 6.67 μm Diameter at 90% : 21.82 μm Mean diameter : 9.33 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.003
Q3	1.44	3.66	5.40	7.96	11.39	17.57	22.90	27.61	33.32	9.93
q3	0.86	1.06	1.26	1.26	2.48	4.22	4.95	5.52	6.23	7.21
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	46.06	56.79	65.11	71.52	78.85	87.69	93.60	98.16	99.31	100.0
q3	8.19	9.08	9.08	8.56	8.00	7.48	6.45	4.50	2.38	0.75
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

 α -HH (FGD, acid leached, with succinic acid)Diameter at 10% : 1.24 μm Diameter at 50% : 7.30 μm Diameter at 90% : 20.09 μm Mean diameter : 9.43 μm

x	0.30	0.50	0.70	1.00	1.40	2.00	2.60	3.20	4.00	5.00
Q3	1.49	3.71	5.42	7.90	11.19	16.94	21.48	25.43	30.39	36.44
q3	0.89	1.06	1.23	1.69	2.38	3.92	4.20	4.62	5.40	6.59
x	6.00	8.00	10.00	12.00	15.00	20.00	25.00	32.00	36.00	45.00
Q3	42.36	53.56	63.24	71.14	80.26	89.90	94.80	97.90	98.77	99.74
q3	7.89	9.46	10.54	10.53	9.93	8.14	5.34	3.05	1.79	1.06
x	56.00	63.00	90.00	112.0	140.0	180.0	224.0	280.0	315.0	400.0
Q3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
q3	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

x: diameter/ μm

Q3 : cumulative value/ %

q3 : population/ %

Approximate wavelength (in vacuum) and frequency ranges for the various colors

Color	Wavelength (nm)	Frequency (THz)
Red	780-622	384-482
Orange	622-597	482-503
Yellow	597-577	503-520
Green	577-492	520-610
Blue	492-455	610-659
Violet	455-390	659-769

1 terahertz (THz) = 10^3 GHz = 10^6 MHz = 10^{12} Hz,

1 nm = 10^{-3} μ m = 10^{-6} mm = 10^{-9} m.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Vita

Mr. Withaya Panpa was born on November 1st, 1976 in Lopburi Province. After graduation with a bachelor degree in Materials Science from faculty of Science, Chulalongkorn University in 1997, he was a lecturer at Rajaphat Institute for 2 years. He continued a further study for master degree in the field of Ceramic Technology at Chulalongkorn University in 2000 and graduated in April 2003.



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