## จุฬาลงกรณ์มหาวิทยาลัย



ทุนวิจัย

กองทุนรัชดาภิเษกสมโภช

รายงานการวิจัย

การพัฒนาผลิตภัณฑ์ที่ได้จากยิปขัมฟลูแก๊สแหล่งแม่เมาะ

โดย

สุพัตรา จินาวัฒน์

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## **Chulalongkorn University**

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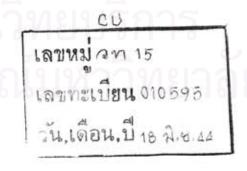
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Development of Products from Mae Moh Flue-Gas Gypsum

Supatra Jinawath

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ชื่อโครงการวิจัย

การพัฒนาผลิตภัณฑ์ที่ได้จากยิปชัมฟลูแก๊สแหล่งแม่เมาะ

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#### บทคัดย่อ

### การพัฒนาผลิตภัณฑ์ที่ได้จากยิปขัมฟลูแก๊สแหล่งแม่เมาะ

ยิปชัมฟลูแก๊สดีชัลเฟอร์ไรเชชัน (FGD) จากสถานีพลังงานแม่เมาะ ได้ถูกนำมาศักษา สมบัติจำเพาะทั้งเชิงกายภาพและเชิงเคมี ผ่านการล้างด้วยวิธีชะด้วยกรดและการตกตะกอนเพื่อให้สี จางลงและใช้เป็นวัสดุในการสังเคราะห์ β-เฮมิไฮเดรท แอนไฮไดรท์และมัลติเฟสพลาสเตอร์เทียบ กับยิปชัมจากธรรมชาติ นำพลาสเตอร์ที่สังเคราะห์ได้มาขึ้นรูปเป็นผลิตภัณฑ์ต่างๆ เช่น ยิปชัมบอร์ดและพลาสเตอร์ฉาบผนัง คุณภาพผลิตภัณฑ์สามารถปรับให้เท่าเทียมกับที่ได้จากยิปชัม ธรรมชาติและเท่าเทียมกับผลิตภัณฑ์ทางการค้า โดยอาศัยเทคโนโลยียิปชัม

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย Project Title

Development of Products from Mae Moh

Flue-Gas Gypsum

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#### Abstract

#### Development of Products from Mae Moh Flue-Gas Gypsum

The flue-gas desulfurization gypsum (FGD gypsum) from Mae Moh power station is characterized for its physical and chemical properties, precleaned by acid leaching and sedimentation to light coloured powder which is later used, in comparison with natural gypsum, as raw material for the syntheses of  $\beta$ -hemihydrate, anhydrites and multiphase plasters. Based on the commercial specification, these gypsum plasters are fabricated into product, i.e. gypsum board and projection plaster slurry. With the employment of gypsum technology, the product performance can be engineered to match up to that of the natural gypsum.

Key word : Anhydrite / β-hemihydrate / Desulfurization flue-gas gypsum / Gypsum plaster / Multiphase plaster / Projection plaster.



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### Chapter 1 Introduction



#### 1. Background

The desulfurization of flue gases from fossil-fuel fired power stations results in by-product called flue-gas gypsum (FG), flue-gas desulfurization gypsum (FGD gypsum) or desulphogypsum (DSG). FGD gypsum has been used mainly in the construction materials industry, and in fact all the FGD gypsum from coal-fired power stations is used for this purpose. Because of its white color, gypsum from coal-fired system is in the first instance, more suitable than the dark yellow gypsum from lignite-fired systems. However, due to its vast quantity produced, the precleaned FGD gypsum from coal-fired systems has been increasingly used in the building industry. Research and development in the utilization of FGD gypsum in other applications, i.e. fillers for plastics, adhesives and paint and also as coating slurries for paper industry are being carried out in leading industrialized countries.

The FGD gypsum from Mae Moh power station is of lignite-fired system and has been recently used only as retarder in portland cement industries which amounts to only ~4 wt% of the cement. Finding the possibility to preclean and turn it into more valuable gypsum plasters which have been proved to be of great benefit in terms of environmental concern is worthwhile attempted.

Flue gas gypsum obtained from the desulfurization of corroustion gases from power plants is a moist fine powder having a free water content ~10% and contains only minor quantities of impurities. The common impurities are soluble salts (Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>) and calcium sulfite, CaSO<sub>3.1/2</sub>H<sub>2</sub>O. Therefore, this gypsum can be used by the gypsum and cement industries without purification.

For building plaster and multiphase plaster, the flue-gas gypsum must be extra treated before calcination to get rid of the free water and in the case of multiphase plaster it is also necessary to modify the particle structure by means of agglomeration because both the fineness (p.s.d.) and the crystal structure of gypsum are important factors that determine its rheological properties (i.e., thixotropy). These stages of the process make the use of flue-gas gypsum less attractive when compared with natural gypsum. However the more stringent environmental protection measures and the lack of natural gypsum resources in some countries (e.g., Japan, Germany) have led to the use of this gypsum as a raw material by the gypsum industries. The progress of gypsum technology and the large quantites of flue-gas gypsum to be available in the future will put a strong impact on the recycling of flue-gas gypsum elsewhere and hence the cost of processing flue-gas gypsum and that of disposal by dumping are becoming more competitive.

- 2. Objective: To explore the possible applications for Mae Moh FGD gypsum by
  - Improving the precleaning of FGD gypsum to obtain lighter colored powder.
  - Synthesizing various forms of gypsum plasters, i.e., β-hemihydrate, anhydrite and multiphase plaster.
  - Fabricating gypsum plasters into products, i.e., gypsum board and projection plaster.
  - Improving certain properties of the above products, i.e., strength, water resistance, adhesion.

## Chapter 2 Theory

#### 2.1 Desulfurization process

#### Wet scrubbing (Chubu, 1985)

Flue-gas gypsum is obtained from the desulfurization of combustion gases of fossil fuels, such as anthracite, bituminous coal, lignite and oil, in large combustion plants, especially power stations. Countercurrent washing of the flue-gas with aqueous suspensions of limestone or lime to remove the SO<sub>2</sub> produces an almost insoluble CaSO<sub>3</sub>. ½H<sub>2</sub>O:

$$SO_2(g) + CaCO_3(s) + \frac{1}{2}H_2O \longrightarrow CaSO_3 \cdot \frac{1}{2}H_2O + CO_2(g)$$
 pH 7-8

In a 2<sup>nd</sup> circuit the pH is allowed to fall below 5 so that the suspended CaSO<sub>3</sub>. 1/2H<sub>2</sub>O is converted to soluble Ca(HSO<sub>3</sub>)<sub>2</sub> which is easily oxidezed by atmospheric O<sub>2</sub> to CaSO<sub>4</sub>.2H<sub>2</sub>O so-called flue-gas gypsum.

$$2CaSO_3$$
. ½ $H_2O$  (s) +  $2SO_2$  (g) +  $H_2O \longrightarrow 2$  Ca(HSO<sub>3</sub>)<sub>2</sub> (soln) pH 5  
Ca(HSO<sub>3</sub>)<sub>2</sub> (soln) + O<sub>2</sub> +  $2H_2O \longrightarrow CaSO_4$  .  $2H_2O$  (s) +  $H_2SO_4$  pH 5

H<sub>2</sub>SO<sub>4</sub> acid produced reacts with the remaining limestone to form additional gypsum:

$$H_2SO_4 + CaCO_3$$
 (s) +  $H_2O \longrightarrow CaSO_4$  .  $2H_2O$  (s) +  $CO_2$  (g)

gypsum crystals are separated from aqueous gypsum suspension in hydrocyclones and vacuum drum filters or centrifuges. It is a moist, fine, fairly pure powder having a free water content < 10%. About 5.4 t of gypsum are produced per tonne of sulfur in the fuel.

The net reaction: (Scholz, 1984)

$$SO_2(g) + CaCO_3(s) + \frac{1}{2}O_2(g) + 2H_2O \longrightarrow CaSO_4.2H_2O(s) + CO_2(g)$$

#### 2.2 Chemistry and Physics of Calcium Sulfate Hydrate

#### · Structure of calcium sulfate

The crystal structure of calcium sulfate consists of chains of alternate Ca<sup>2+</sup> and tetrahedral SO<sub>4</sub><sup>2-</sup> ions. For the most part these CaSO<sub>4</sub> chains remain intact during phase changes.

In calcium sulfate dihydrate the water of crystallization is embedded in between the layers, forming a layer lattice and thus allowing easy clevage along these planes. When calcium sulfate is dehydrated from dihydrate to hemihydrate, the volume decreases, and wide channels that run parallel to the CaSO<sub>4</sub> chain are formed. It is in definite positions in these channels that the water of crystallization is loosely bound. This water is able to escape relatively easily, which explains the facile conversion to anhydrite III. Anhydrite II exhibits the closet packing of ions, which makes it the densest and strongest of the calcium sulfates. However, lacking empty channels, it reacts only very slowly with water.

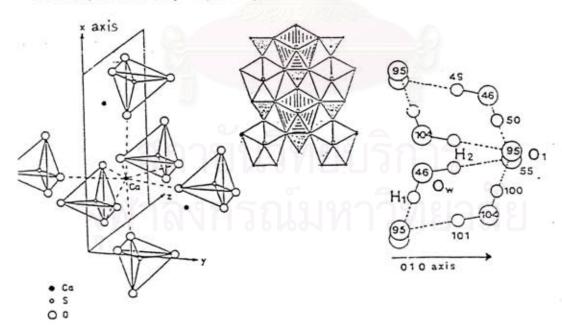


Fig. 2.1 Schematic drawing of the crystal structure of CaSO<sub>4</sub> octahedral coordination of Ca cation by [SO<sub>4</sub><sup>2-</sup>] anions (Kirfel and Will, 1980).

Fig. 2.2 The water molecule of gypsum projected on the (001) plane (Pedersen and Semmingsen, 1982).

Table 2.1 Phases in the CaSO4-H1O system (Wirsching, 1975).

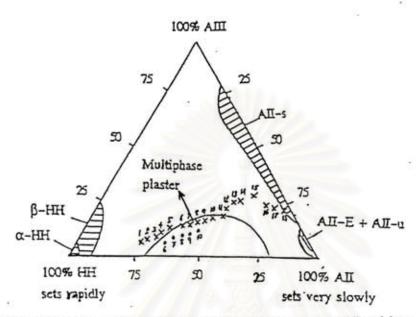
Characteristic	Calcium sulfate dihydrate	Calcium sulfate heminydrate	Anhydrite III	Anhydrite II	Anny- drite I	
Formula	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaSO + 1/2 H2O	CaSO <sub>4</sub>	CaSO.	CaSO,	
Molecular mass M.	172.17	145.15	136.14	136.14	136.14	
Thermodynamic stability, *C	< 40	metastable*	metastable*	40-1180	> 1180	
Forms or stages		two forms: α β	three stages: $\beta$ -anhydrite III $\beta$ -anhydrite III' $\alpha$ -anhydrite III	three stages: All-s. slowly soluble anhydrite All-u. insoluble anhydrite All-E. Estrichgips		
Other names, often based on the application	gypsum raw gypsum synthetic gypsum chemical gypsum byproduct gypsum set gypsum hardened gypsum	α-form: α-hemihydrate autoclave plaster α-plaster β-form: β-hemihydrate stucco plaster β-plaster plaster of Paris [26499-65-0]	soluble anhydrite	raw anhydrite natural anhydrite anhydrite synthetic anhydrite chemical anhydrite byproduct anhydrite calcined anhydrite	high-tem- perature anhydrite	
Synthesis condi- tions: tempera- ture, °C, and atmo- sphere	₹40	α-form: > 45. from aqueous solution β-form: 45-200 in dry air	α- and β-AIII: 50 and vacuum or 100 in air β-AIII': 100 in dry air	200-1180	> !180	
Production temperature. *C	< 40	α-form: 80-180 β-form: 120-180	β-AIII and β-AIII': 290 α-AIII: 110	300-900, specifically AII-s: < 500 AIII-u: 500-700 AIII-E: > 700	not pro- duced commer- cially	

<sup>·</sup> Metastable in air saturated with water vapor

Table 2.2 Physical properties of the CaSO<sub>4</sub> · x H<sub>2</sub>O (Wirsching, 1975).

Property	Calcium sulfate	Calcium sulfate hemihydrate			Anhydrite JII	Anhydrite II	Anhydrite I .
	dihydrate	α-form		β-form			
Water of crystallization, wt%	20.92		6.21		0.00	0.00	0.00
Density e, g/cm³	2.31	2.757		2.619-2.637	2.580	2.93 - 2.97	undetermined
Hardness, Mohs	1.5		-		-	3-4	-
Solubility in water at 20°C. , g per 100 g of solution	0.21	0.67		0.88	hydrates to the hemihy- drate	(0.27)	
Refractive Indices n <sub>a</sub> n <sub>b</sub> n <sub>b</sub>	1.521 1.523 1.530		1.559* 1.5595 1.584		1.501 1.501 1.546	1.570 1.576 1.614	undetermined
Optical character	+				+	+	undetermined
Optical orientation	$n_{d} \mathbf{I} b$ $n_{d} = 52$		clip		clly	nale nale	undetermined
Axial angle 2V	58-60*		14*		≈ 0°	42-44*	undetermined
Lattice symmetry	monoclinic		rhomb	oohedral	hexagonal	rhombic	cubic
Space group	$C2/c = C_{13}^6$		C3,2	= D <sub>3</sub>	C622 = D6	Cemm = D17	undetermined
Lattice spacing, nm, a b c	1.047 1.515 0.628		0.683 0.683 1.270		0.699 0.699 0.634	0.696 0.695 0.621	undetermined

<sup>·</sup> Average



.3 Three-phase composition diagram of calcined gypsum (Wirsching, 1975).

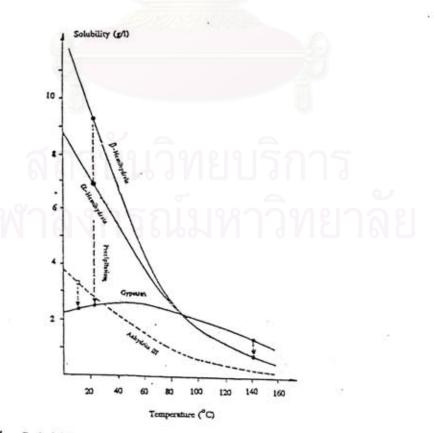


Fig. 2.4 Solubility curves for gypsum plasters (Lafarge, 1990).

Table 2.3 Heats of hydration (Wirsching, 1975).

Phase change		Heats of hydration per mole (gram) of dihydrate at 25 °C. J
β-CaSO <sub>4</sub> · 1/2 F	120 + 3/2 H10 (I) CaSO4 · 2H10	19 300 ± 85 (111.9 ± 0.50)
a-CaSO 1/2 F	120 + 3/2 H2O (I) CaSO 2H2O	17 200 ± 85 (100.00 ± 0.50)
β-CaSO III	+ 2H,O (I) CaSO - 2H,O	$30200\pm85(175.3\pm0.50)$
α-CaSO III	+ 2H2O (I) CaSO4 - 2H2O	25 700 ± 85 (149.6 ± 0.50)
CaSO,II	+ 2H,O (1) CaSO - 2H,O	16 900 ± 85 (98.0 ± 0.50)

Table 2.4 Heats of dehydration (Wirsching, 1975).

Phase change			ydration per mole or hydration products:
		J/mol	kJ/t
CaSO + 2H2O - B-CaSO + 1/2H	(0 + 3/2 H <sub>0</sub> O (g)	86 700	597 200
CaSO4 - 2 H2O - a-CaSO4 - 1/2 H		84 600	582 700
CaSO - 2H2O - B-CaSO III	+ 2H,O (g)	121 800	895 700
CaSO4 2H2O - CaSO4III	+ 2H2O (g)	117 400	863 100
CaSO4 · 2 H.O - CaSO417	+ 2H,0 (g)	108 600	798 000

Table 2.5. Chemical composition of some calcium sulfates (Wirsching, 1975).

	Natural gypsums			Natural Flue anhydrites gyps		Phosph	ogypsums -	Fluoro- anhydrite	
	1	2	3	4	5	6	7	8	9
Mineralogical analysis	34	4	1/14 2/14						
CaSO - 2H2O	91.6	96.4	6.0	3.8	97.5	93.0	97.6	96.5	0.0
CaSO, II	6.4	0.9	88.3	83.7	0.0	0.0	0.0	0.0	94.7
MgCO,	0.1	0.6	2.0	3.6	0.0	0.0	0.0	0.0	0.0
CaCO,	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 <sub>3</sub>	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
ScO	0.07	0.16	0.07	0.14	0.0	0.06	2.05	0.05	0.0
Fe,O, + Al,O,	0.01	0.08	0.01	0.39	0.27	0.27	0.70	0.93	0.27
HC1-insoluble residue	0.10	0.47	0.10	2.49	0.32	1.51	1.00	0.68	0.69
Na <sub>2</sub> O	0.02	0.01	0.04	0.11	0.01	0.47	0.14	0.02	0.03
Total P.O.	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 SC	,			0.11 ZnO
					0.01 CI				0.69 K <sub>2</sub> O
Organics	0.0	0.0	0.G	0.0	0.03	0.08	0.03	6.04	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

<sup>1)</sup> 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.

#### Dehydration and Rehydration

Gypsum is useful as an industrial because

- it readily loses its water of hydration when heated, producing partially or totally dehydration calcined gypsum,
- when water is added to this calcined gypsum, it reverts to the original dihydrate-the set and hardened gypsum product.

#### Dehydration (Table 2.4)

$$\begin{array}{c} \text{heat} \\ \text{CaSO}_{4}.2\text{H}_{2}\text{O} \xrightarrow{\hspace*{4cm}} \text{CaSO}_{4}.1/2\text{H}_{2}\text{O} + 3/2\text{H}_{2}\text{O} \uparrow \\ \text{heat} \\ \text{CaSO}_{4}.2\text{H}_{2}\text{O} \xrightarrow{\hspace*{4cm}} \text{CaSO}_{4} & + 2\text{H}_{2}\text{O} \uparrow \end{array}$$

The phase conversion of CaSO<sub>4</sub>.2H<sub>2</sub>O upon heating is illustrated by DTA in Fig. 2.5.

#### Rehydration (Table 2.3)

$$CaSO_4.1/2H_2O + 3/2H_2O -----> CaSO_4. 2H_2O + heat$$
  
 $CaSO_4 + 2H_2O -----> CaSO_4.2H_2O + heat$ 

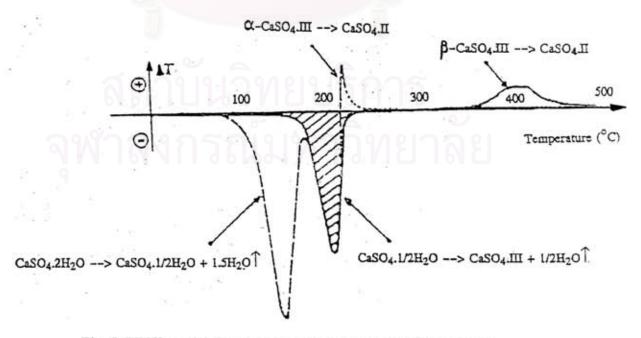


Fig. 2.5 Differential thermal analysis of gypsum (Lafarge, 1990).

#### 2.3 Production of gypsum plaster

#### Industrial Dehydration of Gypsum

Industrially it is most important that dehydration is achieved in the shortest time with the lowest energy consumption, i.e., that the costs be held to minimum. Because of kinetic inhibitions calcination is carried out at much higher temperatures than those used in the laboratory (Table 2.1). Rarely are pure phases produced during manufacture; rather, mixtures of phases of the CaSO<sub>4</sub>-H<sub>2</sub>O system are produced. Three types of calcined anhydrite II (anhydrous gypsum plaster or overburnt plaster) are manufactured, depending on burn temperature and time:

- 1) anhydrite II-s (slowly soluble anhydrite), produced between 300 and 500°C
- 2) anhydrite II-u (insoluble anhydrite), produced between 500 and 700°C
- anhydrite II-E (partially dissociated anhydrite: floor plaster. Estrichgips), produced above ≈ 700°C.

In use the difference among these products lies in the rates of rehydration with water (Table 2.1), which for anhydrite AII-s fast, for anhydrite II-u slow, and for anhydrite II-E in between, a little faster than anhydrite II-u. Transitions between these different stages of reaction are possible. Gypsum plasters are produced by calcining natural gypsum in the kiln.

The two wellknown commercial processes are:

- Rotary kiln process (Fig. 2.6)
  - 2. Kettle kiln (Fig. 2.7 and 2.8)

The degree of size reduction is determined by the calcining unit or the intended use of the gypsum:

rotary kiln	0-25 mm
kettle	0-2 mm
kettle with combined drying and grinding unit	0-0.2 mm
conveyor kiln	4-60 mm
gypsum and anhydrite for cement	5-50 mm

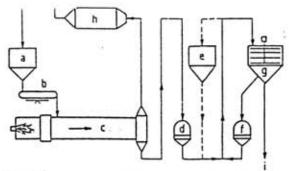


Fig. 2.6 Production of  $\beta$ -hemihydrate plaster by the rotary kiln process

a) Silo for gypsum rock; b) Weigh-belt feeder; c) Rotary kiln with combustion chamber; d) Primary mill; e) Start-up and shut-down bin; f) Fine mill; g) Air classifier; h) Electrostatic precipitator; i)  $\beta$ -Hemihydrate plaster

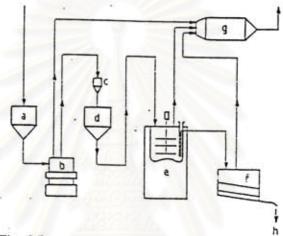


Fig. 2.7 Production of β-hemihydrate plaster by the continuous kettle process with combined drying and grinding a) Silo for gypsum rock; b) Drying-grinding unit; c) Cyclone; d) Kettle feed bin; e) Continuous kettle: f) Cooling bin (hot pit); g) Electrostatic precipitator; h) β-Hemihydrate plaster

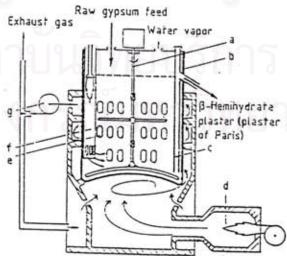


Fig. 2.8 Kettle with submerged combustion burner for continuous production of β-hemihydrate (plaster of Paris) a) Agitator; b) Outer casing of kettle; c) Ascending pipe for stucco plaster discharge; d) Combustion chamber; e) Cross pipes for hot gases; l) Submerged pipe with submerged combustion burner; g) Ventilating fan for exhaust and circulating gas

(Fig. 2.6-2.8; Wirsching, 1975)

Projection plaster is made from multiphase plaster of which the industrial production is illustrated in Fig. 2.9.

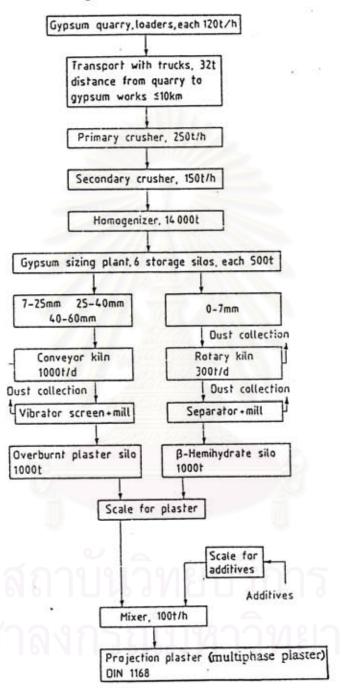


Fig. 2.9 Flow diagram for production of projection plaster with a conveyor kiln (Knauf, 1961).

#### Drying of FGD gypsum (Wirsching, 1984)

After filtration of the aqueous suspension from the hydrocyclone, the obtained FGD gypsum is moist, finely divided crystal with a free water content about 10% in form of absorbed surface water which is removed at temperature below 70°C and above this temperature, calcination occurs resulting in the loss of combined or chemically bonded water (~20%, Table 2.2 and 2.5). The relationship between exhaust gas temperatures with drying is shown in Fig. 2.10; The higher the drying temperature is, the higher the total water loses with the gas outlet and the lesser the combined water and free moisture remain.

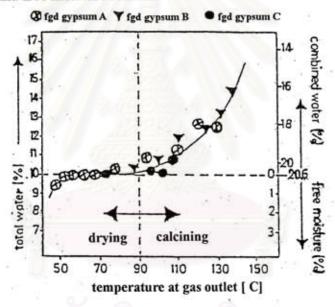


Fig. 2.10 Relationship between exhaust gas temperatures with drying and with calcination of the FGD gypsum (Wirsching, 1984).

#### · Agglomeration of FGD gypsum

Size and shape of crystals of FGD gypsum depend on the desulfurization process. The particle shape range from cubic (bulk density 1.2 ton/m³) to lath or rod shaped (bulk density 0.5 ton/m³) and the size from small crystals (20-60 µm) to maximum 200 µm while those of natural gypsum are massive or rocklike structure (Fig. 4.2). The moist finely divided particle size and structure of the FGD gypsum crystal cause the disadvantage in handling, storage and application. 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 ~2.3 g/cm³, Table 2.2). They are as follows:

1.) Agglomeration by means of pelletizers

2.) Agglomeration by means of extrusion presses

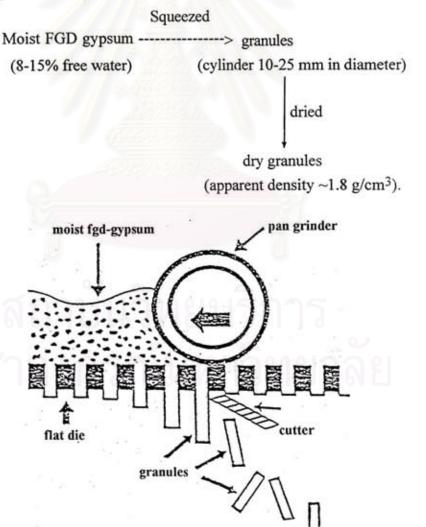


Fig. 2.11 Agglomeration of FGD gypsum by means of extrusion press producing granules (Wirsching, 1984).

#### 3.) Agglomeration by means of compacting presses (Gebr, 1977)

#### Pressed

FGD gypsum -----> Briquets (high strength > 500 N, (dry or semidry) apparent density 
$$\sim 2.15 \text{ g/cm}^3$$
).

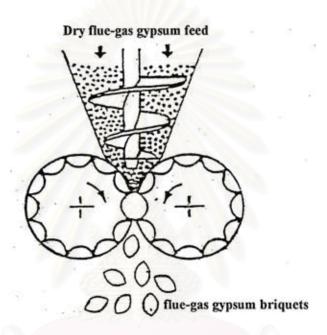


Fig. 2.12 Agglomeration of FGD gypsum by means of a compacting press producing briquets (Wirsching, 1984).

The SEM of the FGD briquet reveals a solid structure of which the original crystals have intergrown into a rocklike body and nothing is left of the FGD gypsum particle, initial size and shape (Fig. 4.2). Hence the unfavorable particle size and shape of FGD gypsum are successfully dealt with by compaction under high pressure and its thixotropic properties are completely eliminated. By this technique, FGD gypsum can be used in the same way as natural gypsum.

Table 2.6 Properties of calcined gypsum\* (Wirsching, 1975).

Mode of production	Type of plaster	Sieve residue	Combi- ned wa-	g plaster/	Water- to-plaster	Setting min	time,	Strength of set and hardened gypsum			Density of dry	Uses
		> 0.2 mm, %	ter, %		ratio, 100/E	initial	final	flexural strength, N/mm <sup>2</sup>	com- pressive strength, N/mm.2		gypsum, kg/m³	
Natural gypsum						1		-				
Rotary kiln	fl-plaster (plaster of Paris)	1.0	4.1	137	0.73	13	28	4.8	11.2	19.1	1069	gypsum building components, special building plasters
Kettle -	#-plaster (plaster of Paris)	3.3	5.6	156	0.64	9	22	5.2	14.0	26.8	1133	gypsum building components, special building plasters
Conveyor kiln	multiphase plaster (construction plaster)	36.6	8.0	167	0.60	6	35	5.1	15.5	25.9	1225	muchine-applied plaster, multiphase plaster
Autoclave	α-plaster (molding plaster)	0	6.2	263	0.38	10	22	12.3	40.4	92.0	1602	molding plaster, industrial plaster, dental plaster
Flue-gas gypsum												-5
Rotary kiln (Knauf process)	β-plaster	3.1	3.4	135	0.74	9	21	4.7	11.0	21.5	1064	premixed pluster, bonding pluster, jointing pluster, gypsum building components
(Knauf process)	β-plaster	2.6	5.2	139	0.72	14	28	5.2	13.5	19.5	1070	premixed plaster, bonding plaster, jointing plaster, gypsum building components
Conveyor kiln (Knauf process)	multiphase plaster	26.2	2.0	177	0.56	6	20	6.7	20.8	34.1	1353	machine-applied plaster, multiphase plaster
Autoclave (Nitto Gypsum process		0	6.0	270	0.37	13	26	12.0	45.0	90.2	1580	molding plaster, industrial plaster, dental plaster

<sup>\*</sup> The tests of the properties are carried out in accord with DIN 1168. The water-to-plaster ratio is calculated on the basis of quantity of gypsum plaster, g. in 100 g of water. In German this is called the Einstreamenge and represented by E.

Table 2.7 Phase compositions, in %, of overburnt plaster, plaster of Paris, and multiphase plaster\* (Wirsching, 1975).

0	Plaster of Paris (rotary kiln)	Over- burnt plaster (con- veyor kiln)	Multiphase plaster, a mixture of plaster of Pa- ris and over- burnt plaster
Dihydrate, CaSO <sub>4</sub> ·2H <sub>2</sub> O	0-0.5	0-2	0-2
β-Hemihydrate, β-CaSO <sub>4</sub> ·1/2H <sub>2</sub> O	75	6	26
β-Anhydrite III, β-CaSO <sub>4</sub> III	19	18	14
Anhydrite II. CaSO <sub>4</sub> II**	5	74	58

Impurities not considered.
 Consisting of reaction stages AII-s (slowly soluble A), AII-u (insoluble A), and AII-E (Estrichgips)

Table 2.8 Gypsum building materials and their properties (Wirsching, 1975).

	Plasterboard, 9.5 mm thick	Finished gyp- sum projec- tion plaster	
Apparent density and porosity			
Density, kg/m <sup>3</sup>	900	1200	
Pore volume. %	60*	50	
Pore radius, µm	≈ 99% > 0.05	≈ 99% > 0.05	
Climatic properties			
Heat conductivity J, WK <sup>-1</sup> m <sup>-1</sup> (DIN 4108)	0.21	0.35	
Heat penetration coefficient b (equivalent)			
1/2-h test. J s-1/2 m-2 K-1	412	1172	
2-h test	439	1410	
Resistance to transmission of			
water vapor µ (DIN 4108)	8	10	
Water vapor absorption coefficient a, m/h			
untreated surface	2.29		
rough fiber coated	2.98	2.5	
wallpapered	2.66		
Heat expansion and equilibrium moisture content			
Linear coefficient of thermal expansion a, K-1	13 × 10 <sup>-6</sup>	20 × 10 -6	
Equilibrium moisture content at 20°C and 65% relative humidity, wt%	0.5	0.3	
Modulus of elasticity, N/mm <sup>2</sup>	3000	2800	

<sup>·</sup> Core

Table 2.9 Application properties of projection plaster, bonding plaster, and premixed plaster\* (Wirsching, 1975).

Property	Projection plaster	Bonding plaster	Lightweight plaster
Water: plaster ratio	0.45-0.55	0.60-0.70	0.55-0.65
Initial setting, min	60-120	50-90	50-90
Final setting, min	170 - 220	80 - 200	100 – 170
Strength of set and hardened gypsum, N/mm <sup>2</sup>	1000 177000	40-200	100-170
Flexural strength	1-2	1-2	1-2
Compressive strength	4-6	3-5	3-7
Apparent density of dry gypsum, kg/m3	1000 - 1200	850-1000	900-1100
Coverage, m2 per 100 kg of plaster	9-10	13-14	12-13

<sup>\*</sup> Tests conform to German (DIN) standard 1168 [48]

# Chapter 3 Experiment

#### 3.1 Materials and Methods

- 3.1.1 Materials: 1. Mae Moh FGD gypsum (light brown coloured, lignite fired system, wet scrubbing desulfurization technique)
  - 2. Natural gypsum (Thai Gypsum Plaster Co. Ltd.)
  - 3. H<sub>2</sub>SO<sub>4</sub> acid
  - 4. Sodium lignosulfonate
  - 5. Methylcellulose
  - 6. Vinyl acetate
- 3.1.2 Methods: 1. Precleaning of FGD gypsum

Due to the colour of impurities contaminating in the FGD gypsum, the as received has to be washed prior to calcining process. Fig. 3.1 is the illustration of the segregation sequence occurring after addition of H<sub>2</sub>SO<sub>4</sub> acid and Fig. 3.2 is the flow chart for the precleaning.

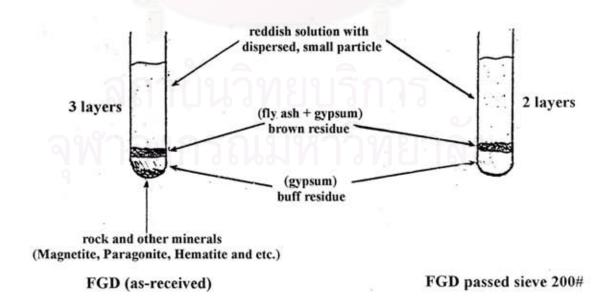


Fig. 3.1 Sequence of segregation.

After the trial runs (Fig. 3.1), the procedure for precleaning of the FGD gypsum was designed based on the information of drying in Fig. 2.10 as in the flow chart:

#### 1.) Precleaning of FGD gypsum

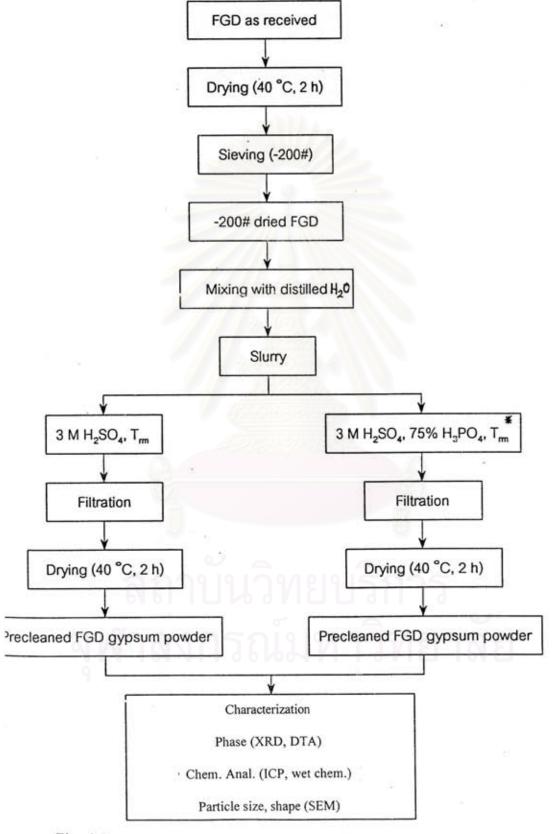


Fig. 3.2 Flow chart for the precleaning of FGD gypsum.

<sup>\*</sup> omitted due to no improvement of result.

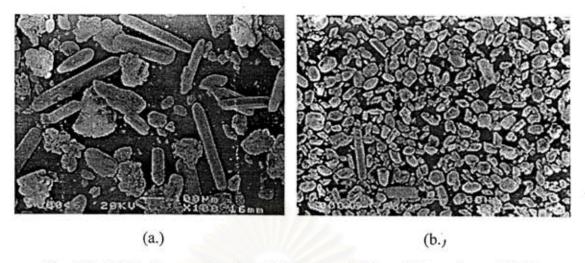


Fig. 3.3 SEM micrographs of a.) FGD (as-received) and b.) precleaned FGD

#### 2.) Syntheses of β-HH and anhydrite III (AIII)

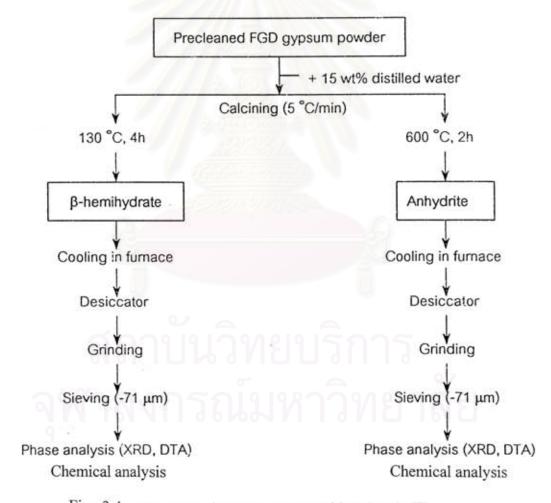


Fig. 3.4 Flow chart for the syntheses of β-HH and AIII.

The procedure illustrated as the flow chart of the above figure, was designed following the information of Table 2.1, 2.6, 2.7 and references 11-14 with some modification after a number of trial run (Table 2A, 3A, 4A and 5A).

#### 3.) Preparation of multiphase plaster

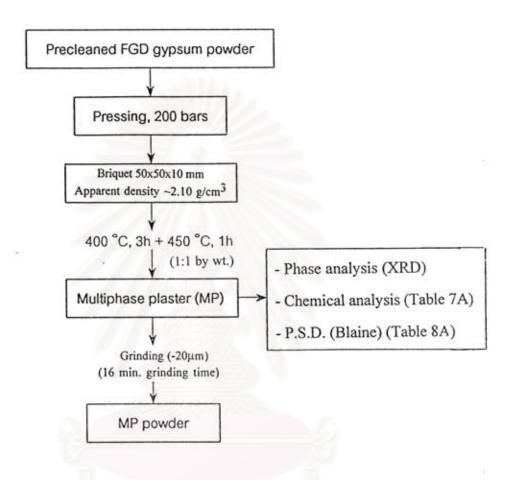


Fig. 3.5 Flow chart for the preparation of MP.

The procedure illustrated as the flow chart, was designed according to the composition in Fig. 2.3, Table 2.7 and the synthesis condition of Table 2.1 and Fig. 2.12 with some modification after a number of trial run (Table 7A and 8A).

#### 4.) Fabrication of gypsum boards from β-HH and MP

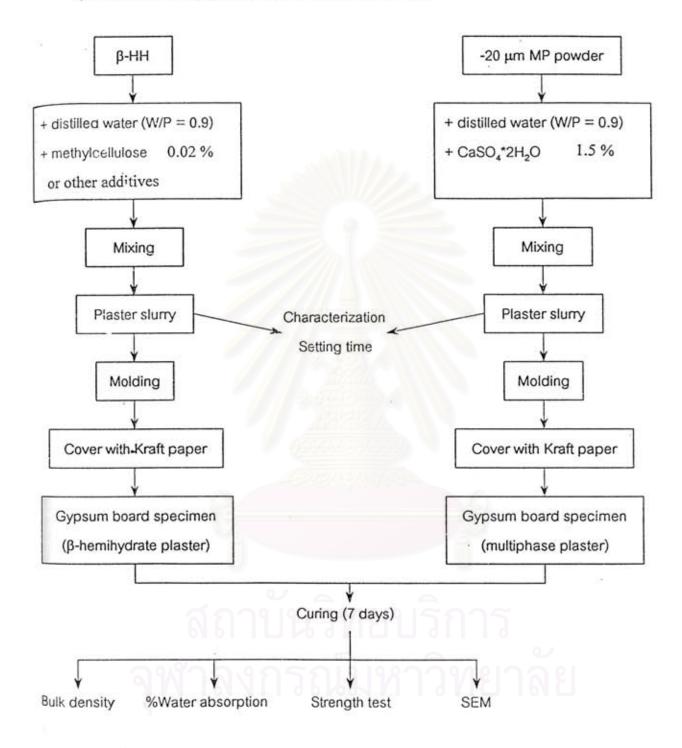


Fig. 3.6 Flow chart for the fabrication of gypsum board test specimens.

The above flow chart is designed based on the test specimen with required properties of gypsum building materials mentioned in Table 2.8, 2.6, and with some modification.

i

#### 5.) Preparation of projection plaster

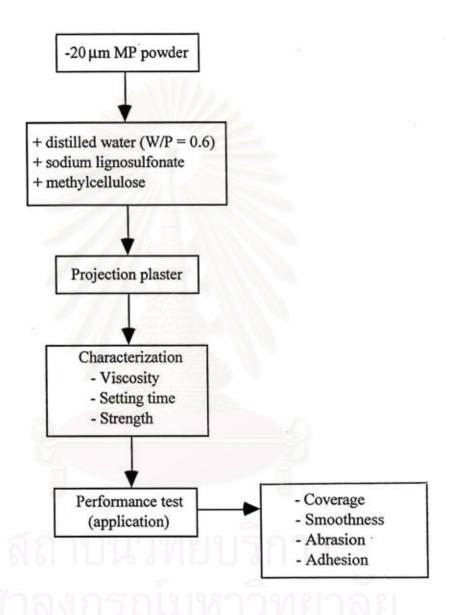


Fig. 3.7 Flow chart for the preparation of projection plaster.

The procedure according to the flow chart of Fig. 3.7 was designed following the flow diagram of Fig. 2.9, information from Table 2.7, 2.8, 2.9 and 8A also with some modification.

# Chapter 4 Results and Discussion

#### Precleaning of Mae Moh FGD gypsum

Table 4.1 is the precleaning conditions of FGD gypsum. The best condition is to wash the as-received FGD gypsum with 1 ml, 3 M H<sub>2</sub>SO<sub>4</sub> acid at room temperature since it gives both the light colour and high % recovery. The precleaned FGD is of buff colour which can be lightened by blending with natural gypsum.

#### · Characteristic of Mae Moh FGD gypsum

#### Chemical composition

Table 4.2 is the summarized properties of Mae Moh FGD gypsum (asreceived) as compared with the natural one. It can be seen that the as-received FGD
gypsum contains higher content of mineral gypsum (93.33%) than the natural gypsum
(80.07%) because after separating the inclusion impurity which is mainly fly ash from
the FGD gypsum by sedimentation technique (Fig. 3.1), nearly all of the remaining
portion is gypsum. In the case of the natural one, limestone or dolomite is the
common associate mineral (Fig. 4.3 and 4.4).

The DTA of gypsums in Fig. 4.1 reveal the free water content of the as received FGD gypsum which can be reduced or eliminated after aeration and also the dolomite mineral in the natural gypsum. Fig. 3.3 and 4.2, SEM micrographs reveal the wide particle size distribution of the rod shaped crystals of the as-received FGD gypsum and the massive or rocklike natural gypsum. They also show the narrower particle size distribution of the precleaned FGD gypsum and the closeness of the massive structure between natural gypsum and FGD briquet.

The XRD and EDS results in Fig. 4.3, 4.4, 4.5 and 4.6 confirm that the impurities, i.e. talc, magnetite and calcite in the as-received FGD gypsum are completely separated out from the precleaned FGD gypsum and are in good

agreement with its chemical analysis, Table 4.3, which shows that the precleaned FGD gypsum is 95.8% purity (based on % H<sub>2</sub>O). The value of combined water is 20.05% but the CaO content is a little bit higher than those of the commercial ones (Appendix, Table 6A). This maybe due to the presence of CaCO<sub>3</sub> and CaSO<sub>4</sub> in the as-received FGD (Fig. 4.1 and Fig. 4.3), CaCO<sub>3</sub> will react with H<sub>2</sub>SO<sub>4</sub> during precleaning to form CaSO<sub>4</sub> hence this amount will add up to the previous CaSO<sub>4</sub> and result in the high value of CaO (34.4 %) compared with the low value of combined water of CaSO<sub>4.2</sub>H<sub>2</sub>O.

#### · Preparation of gypsum plasters

#### Phase analysis

Fig. 4.7 shows the XRD patterns of β-hemihydrate (β-HH), anhydrite III (AIII) and multiphase (MP) plasters synthesized according to the process illustrated in Fig. 3.4 and 3.5. The XRD of β-HH reveals traces of anhydrite at 130°C, 4 h calcining (also see Table 2A) while that of anhydrite shows a complete transition of dihydrate (DH) to anhydrite at 600°C, 2 h heat treatment (see Table 3A) and the XRD of multiphase plaster shows the mixture of 2 phases, β-HH and AIII at 450°C, 1 h (corresponding to composition point 6-10 in Fig. 2.3 and the chemical analysis in Table 7A).

#### Characteristic of gypsum products

#### Setting time and strength of gypsum boards

Table 4.4 is the summarized results of the retarding effect of various additives upon the setting time of the gypsum board specimens prepared from  $\beta$ -HH according to the procedure described in Fig. 3.6. The results are shown in parallel with those of the natural gypsum prepared in the same way. The results show short initial and final setting times (Table 2.6) characteristic of  $\beta$ -hemihydrate plaster for all types of the additive used. Considering the amount of addition upon the strength (Fig. 4.8a), effects on bulk density (Fig. 4.8b) and  $\frac{\alpha}{\alpha}$  water absorption (Fig. 4.8c), of the set

specimens, citric acid is the most effective retarder of all. Although all the plots between flexural strength and content of additive (Fig. 4.8a) show the same trend, the rate of strength decrease is quite different and is characteristic of the particular additive therefore, in application, the optimum content has to be aware. Table 4.5 is the summation of the accelerating effect of the dihydrate on the setting time and flowability of gypsum board specimens made from multiphase plaster and it also shows the short initial and long final setting times (Table 2.6) characteristic of multiphase plaster. The optimum content of dihydrate considered from the product performance (Table 4.5 and Fig. 4.9a - 4.9c) is around 1.5% for both multiphase plasters from FGD gypsum and from natural one.

The role of additives in controlling flowability, setting and strength development of the plaster is complicated and to some extent related to surface chemistry. This finally results in the modification of crystal morphology of the rehydrated plaster as shown in the SEM micrograph, Fig. 4.10.

# Setting time, viscosity, coverage and abrasive resistance of projection plaster

Table 4.6 is the typical properties of projection plaster prepared from multiphase plasters which were synthesized from differnt sources, FGD and natural gypsums. The target viscosity, coverage and setting times are 600-800 cps (Rixom and Maivaganam, 1986), 9-10 m<sup>2</sup>/100 kg and 60-120 min (initial), 170-220 min (final) (Table 2.9), respectively. To improve abrasion resistance, vinyl acetate is employed. The best combination for this experiment is 0.75 wt% sodium lignosulfonate (as water-reducing agent and retarder): 0.125 wt% methylcellulose (as binder and water-retaining agent): 0.50 wt% vinyl acetate (as abrasion resisting and air entraining agent) since it gives a good performance, i.e. flow property, smooth surface, good coverage and good abrasion resistance with suitable setting time for application (Fig. 4.11-4.13). Because of these unique properties, machine-applied projection plaster has been produced to enable a fast plastering which can be operated by one person.

Table 4.1 Precleaning condition of FGD gypsum.

Suspension	3 M H	<sub>2</sub> SO <sub>4</sub> (ml)	Res	idue
(5 ml)	Tm (27°C)	100°C	Colour	wt% Recovery
FGD	0.00	-	Brown	95.0
(as received)	0.25	-	Brown	83.0
1 g	0.50	-	Brown	58.0
1440,4004	1.00	-	Light brown	62.0
	-	0.00	Brown	94.0
		0.25	Brown	68.0
	-	0.50	Brown	71.0
	-	1.00	Light brown	69.0
FGD	0.25	-	Light brown	87.0
(-200#)	0.50	-	Light brown	86.0
1 g	1.00*	-	Buff	76.0
	4//9	0.25	Brown	78.0
		0.50	Light brown	82.0
	//-/	1.00	Buff	57.0

<sup>\*</sup>The chosen condition for precleaning of Mae Moh FGD gypsum.

Table 4.2 Properties of Mae Moh FGD gypsum as compared with natural gypsum.

Characteristic	FGD gypsum (as received)	Natural gypsum (NG
Free water content (dried at 40 °C)	10-15%	-
Density (Archimedes methods)	2.58 g/cm <sup>3</sup>	2.35 g/cm <sup>3</sup>
Mean particle size (Laser light scattering)	66.92 µm	-
Particle size distribution	45 mesh (335 μm) 94.55%	- 3
(Sieve analysis, % finer than)	80 mesh (180 μm) 91,14%	-
	100 mesh (150 μm) 90.68%	-
	120 mesh (125 µm) 89.28%	-
	200 mesh (75 μm) 85.88%	
	325 mesh (45 µm) 45.28%	
	400 mesh (38 μm) 11.31%	1
Specific surface area (BET)	$4.84 \pm 0.15 \mathrm{m}^2/\mathrm{g}$	-
Mineral phases (XRD)	Gypsum + fly ash + other impurities	Gypsum + dolomite
Mineral content (app %)	93.33% Gypsum	80.07% Gypsum
	4.57% Fly ash	19.93% Dolomite
	2.10% Other impurities	
Color	Yellowish	White

<sup>\*</sup> From Table 1A

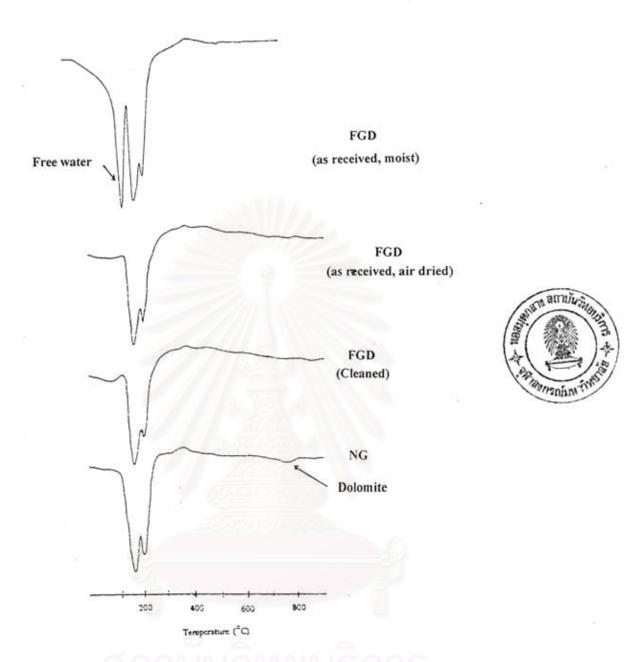


Fig. 4.1 DTA thermograms of Mae Moh FGD and natural gypsum. (Netzsch model Nr. 1.303003)

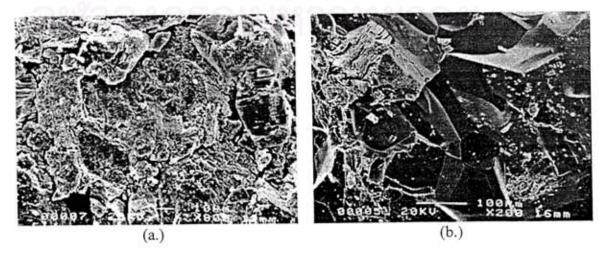
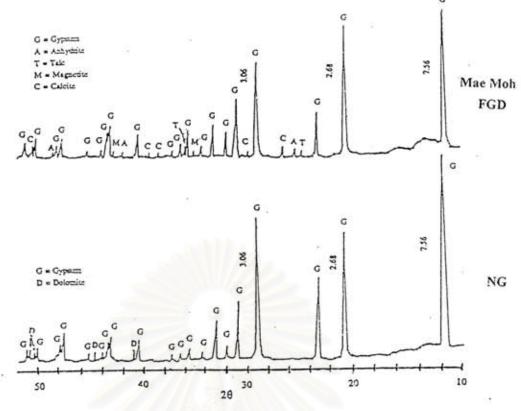
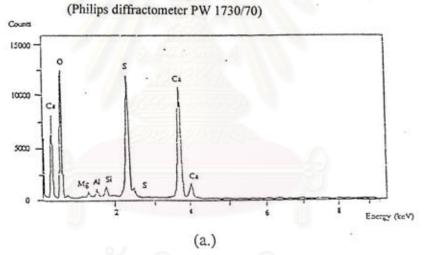


Fig. 4.2 SEM micrographs of a.) briquet and b.) natural gypsum.



Relative Intensity

Fig. 4.3 XRD patterns of FGD and NG (as-received).



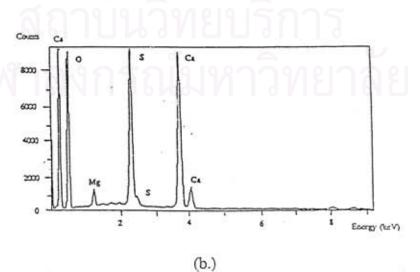


Fig. 4.4 EDS of a.) FGD and b.) NG. (JSM T 220 A, JEOL)

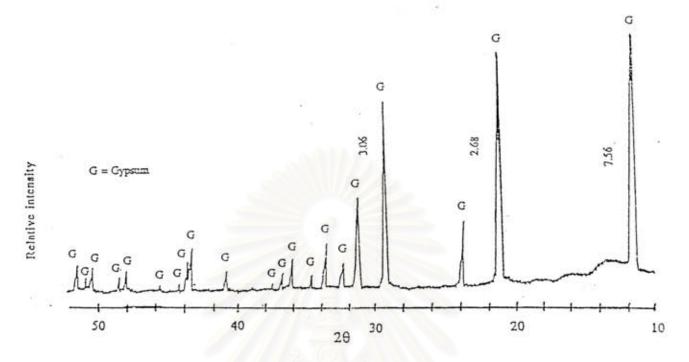


Fig. 4.5 XRD pattern of FGD (cleaned).
(Philips diffractometer PW 1730/70)

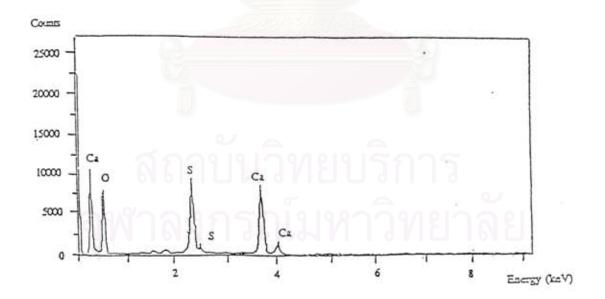


Fig. 4.6 EDS of FGD (cleaned). (JSM T 220 A, JEOL)

Table 4.3 Chemical analysis of Mae Moh FGD gypsum (precleaned) by ICP method.

											9	Combined	
	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO +	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>	water+	SO
%	0.62	0.31	0.23	0.26	34.4	<0.05	0.02	0.01	<0.01	0.01	0.01	20.05	46. 36
			100	- 12									
							14.7						
								***			-		



<sup>\*(</sup> see Appendix, Table 6A)

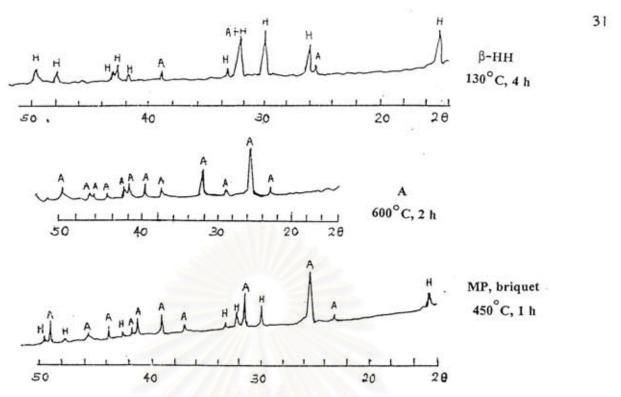


Fig. 4.7 XRD pattern of the synthesized β-HH, A and MP. (Philips diffractometer PW 1730/70)

<u>Table 4.4</u> Effect of additives on the setting time of gypsum board specimens from  $\beta$ -HH (humidity = 66%, room and water temperature = 21°C and 25°C,

pH of water = 7.10 and W/P = 0.9).

	Con	tent	Setting time (min.)							
Additives	(wt	%)	Init	ia!	Final					
	FGD	NG	FGD	NG	FGD	NG				
None	-	2	4.28±0.30	5.51±0.35	7.56±0.38	6.36±0.26				
Citric acid	0.02	0.02	6.49±0.36	8.35±0.40	10.11±0.25	9.41±0.25				
Ы	0.04	h rip a	8.57±0.28		13.20±0.39					
Methylcellulose	0.02	0.02	6.24±0.41	8.11±0.31	9.45±0.35	9.16±0.27				
9 7 1	0.04	I d'P N	8.18±0.35		11.26±0.40	-				
Acetic acid	0.20	0.20	5.56±0.40	6.21±0.29	8.38±0.30	7.13±0.24				
	0.40	0.40	7.42±0.25	8.51±0.35	10.45±0.29	9.55±0.30				
Potassium alum	0.20	0.20	5.50±0.20	6.17±0.37	8.16±0.27	8.40±0.21				
	0.40	0.40	7.31±0.31	8.44±0.26	10.24±0.20	9.36±0.41				
Sodium borate	0.20	0.20	6.10±0.31	6.21±0.20	9.30±0.38	7.33±0.28				
	0.40	0.40	7.54±0.34	8.48±0.39	11.12±0.41	9.39±0.32				

<sup>\*</sup> repeat with 5 tests in each composition.

target initail setting time 5-8 min.

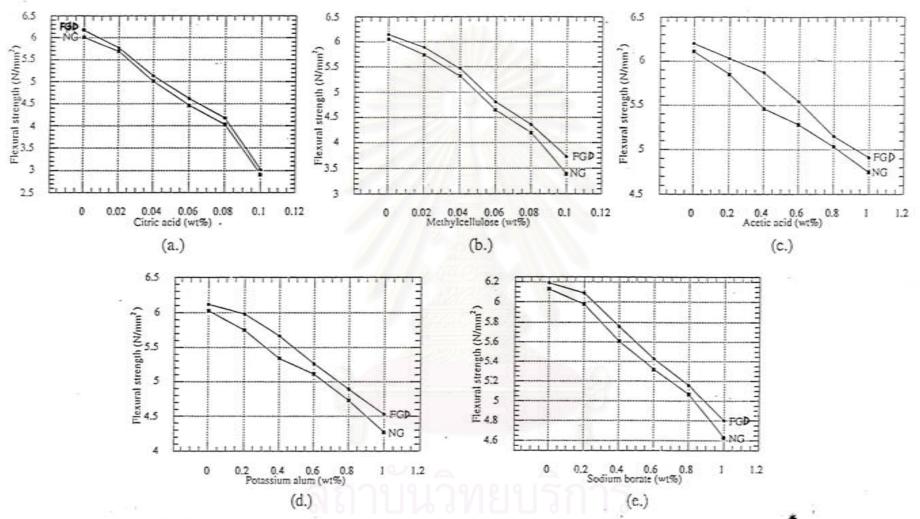


Fig. 4.8a Relationship between the content of additive and the flexural strength of β-HH.

a.) citric acid, b.) methylcellulose, c.) acetic acid, d.) potassium alum and e.) sodium borate.

<sup>\*</sup> Material testing machine, Instron Corporation (Series IX automated materials testing system 7.26.00)

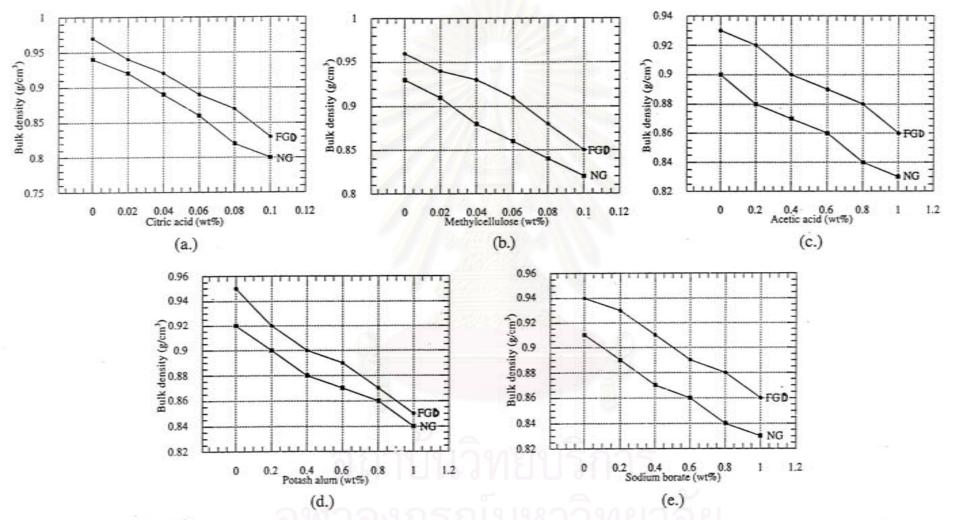


Fig. 4.8b Effect of additives on bulk density of β-HH. a.) citric acid, b.) methylcellulose, c.) acetic acid, d.) potash alum and e.) sodium borate.

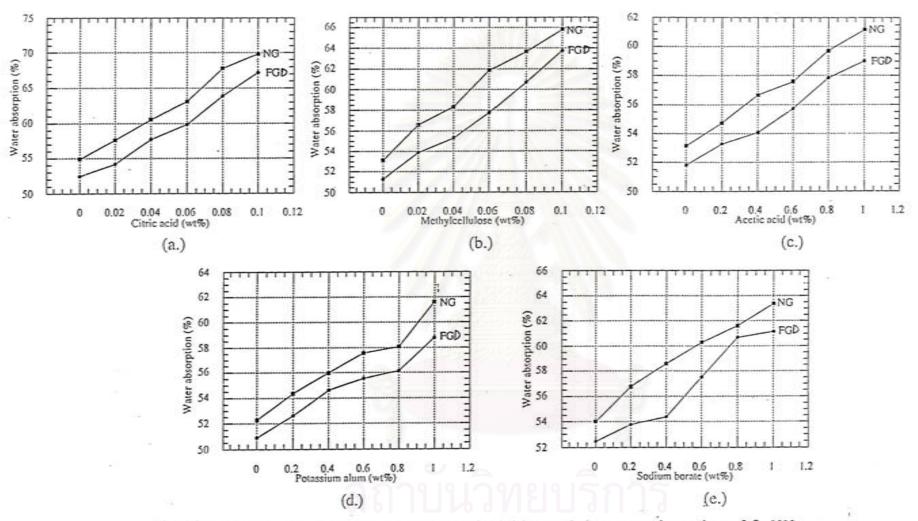


Fig. 4.8c Relationship between the content of additive and the water absorption of  $\beta$ -HH. a.) citric acid, b.) methylcellulose, c.) acetic acid, d.) potassium alum and e.) sodium borate.

<u>Table 4.5</u> Effect of calcium sulfate dihydrate on setting time of gypsum board specimens prepared from multiphase plaster (humidity = 77%, room and water temperature =  $21^{\circ}$ C and  $25^{\circ}$ C, pH of water = 7.29 and W/P = 0.9).

Calcium sulfate			Setting time (min.)					
dihydrate	Flowa	ability	Ini	tial	Fir	nal		
(wt%)	В	NG	В	NG	В	NG		
0.00	Good	Good	25.39	30.15	64.26	44.36		
0.50	Good	Good	18.58	24.40	52.17	35.15		
1.00	Good	Good	11.20	19.52	40.47	28.20		
1.50	Medium	Good	6.12	12.36	28.38	15.33		
2.00	Poor	Medium	2.01	7.14	22.50	11.45		

<sup>\*</sup> B = MP from briquet

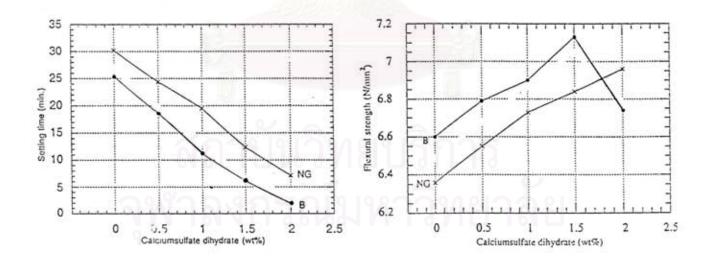


Fig. 4.9a Effect of additive content on initial setting time and flexural strength of MP test specimens.

<sup>\*</sup> the number of test sample was 3 (DIN 1168).

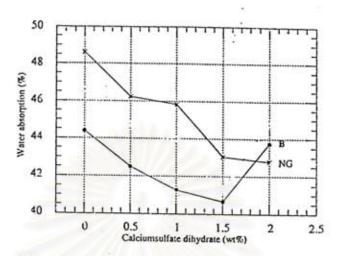


Fig. 4.9b Relationship between the water absorption of MP and the content of additive (calcium sulfate dihydrate).

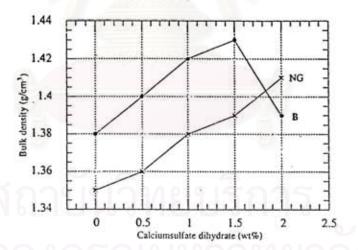


Fig. 4.9c Relationship between bulk density of MP and the content of additive (calcium sulfate dihydrate).

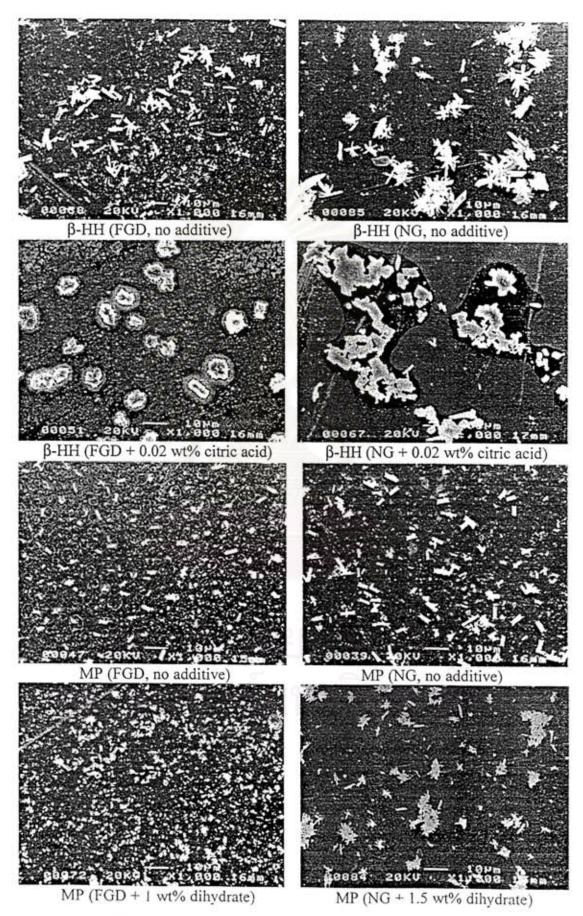


Fig. 4.10 SEM micrographs of rehydrated gypsum plasters in the presence of additives. (JSM T 220 A, JEOL)

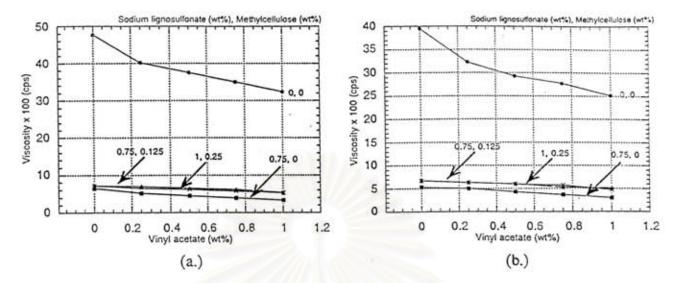


Fig. 4.11 Relationship between the content of sodium lignosulfonate + methylcellulose + vinyl acetate and viscosity of projection plaster prepared from a.) briquet and b.) NG.

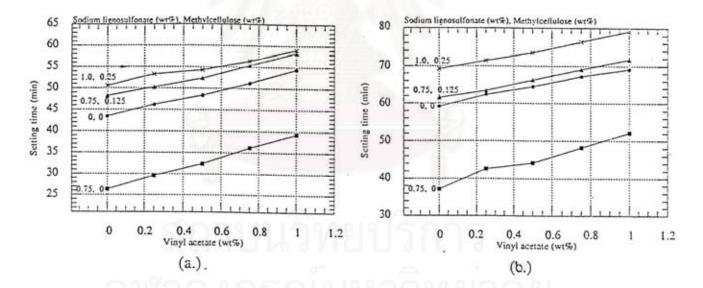


Fig. 4.12 Relationship between the content of sodium lignosulfonate + methylcellulose + vinyl acetate and initial setting time of projection plaster prepared from a.) briquet and b.) NG.

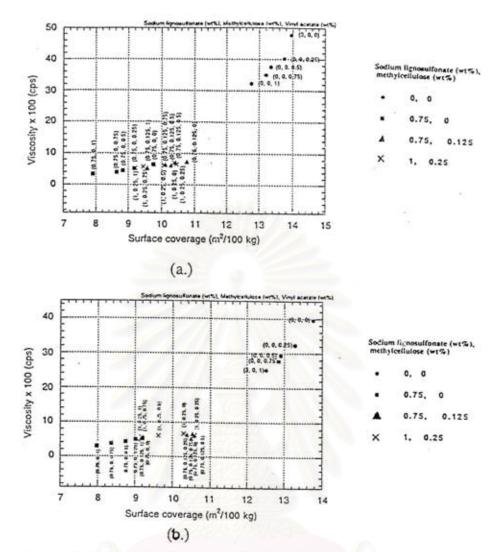


Fig. 4.13 Relationship between viscosity and surface coverage of modified projection plaster a.) briquet and b.) NG.

<u>Table 4.6</u> Typical properties of projection plaster with the combined additives.

(0.75 wt% sodium lignosulfonate : 0.125 wt% methylcellulose : 0.50 wt% vinyl acetate).

Sam ples	ηχ100 <sup>1</sup> (cps.)	Surface coverage	-0-0	g time <sup>2</sup> nin)	Flexural <sup>3</sup> strength	Water 4 absorption	Bulk 5 density	111	face <sup>6</sup> iness
		(m <sup>2</sup> /100kg)	Initial	Final	(N/mm <sup>2</sup> )	(%)	(g/cm <sup>3</sup> )	Gouge	Scratch
В	7.30 <u>+</u> 1.75	10.26±0.36	54.53 <u>+</u> 0.35	137.29 <u>+</u> 2.97	5.82 <u>+</u> 0.30	28.20±1.56	2.10±0.06	3H	НВ
P	7.17 <u>+</u> 1.64	10.33±0.65	60.36±0.19	159.05±3.35	4.90 <u>+</u> 0.57	28.57 <u>+</u> 1.75	2.10 <u>+</u> 0.05	2H	НВ
NG	6.70 <u>+</u> 1.76	10.45 <u>+</u> 0.51	61.25 <u>+</u> 0.32	140.11 <u>+</u> 3.45	4.05 <u>+</u> 0.42	30.38 <u>+</u> 1.84	2.07 <u>+</u> 0.04	2H	В

• the number of each test was 5.

According to 1. ASTM: D 2196-86, Brookfield viscometer model RVTD AO 4184

2. DIN 1168

3, 5. ASTM: C 472-93 4. ASTM: C 373-72 6. ASTM: D 3363-92a



## Chapter 5 Conclusion

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

- The gypsum plaster from FGD gypsum produced in the experiment is equivalent to that of the natural one in terms of performance and quality (excluded colour handicap).
- 2. Besides using directly as retarder in portland cement manufacture, Mae Moh FGD gypsum, with the application of gypsum technology, can be industrially utilized as gypsum plasters i.e., where colour is not handicap, as wall board, partition board, colour projection plaster, and etc. Where light colour product is required, the FGD gypsum has to be adequately quality controlled by the power plant i.e., using high quality limestone, installing effective dust precipitators, burners, precleaning by magnetic and cyclone separators prior to acid washing at the gypsum plant. However the FGD gypsum can be partially absorbed in the present manufacture of gypsum plaster products with little effect on manufacturing cost provided that there is no excessive transportation cost.

## **Future suggestion**

There are a lot of researches on by-product gypsum being carried out worldwide because of its abundance and more stringent environmental control.

Among these, the appropriate ones for Thailand are:

- The possible utilization of phosphogypsum which is becoming an urgent environmental problem.
- Technology for cost reduction in producing anhydrites and other plasters.
- New and better gypsum plaster products.

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## Appendix

Table 1A

Phase composition of FGD and NG.

Materials	%AIII	%НН	%AII	%DH	%Rest
(as-received)	1.78 <u>+</u> 1.65	-8.17 <u>+</u> 2.53	-6.43 <u>+</u> 2.73	93.33 <u>+</u> 2.93	6.67 <u>+</u> 2.81
(washed)	-2.08 <u>+</u> 1.98	-12.08 <u>+</u> 2.17	-0.09 <u>+</u> 2.48	95.55 <u>+</u> 2.81	4.45±2.56
. NG	-1.75 <u>+</u> 2.15	-6.82 <u>+</u> 1.86	-2.63 <u>+</u> 3.12	80.07 <u>+</u> 2.95	19.93 <u>+</u> 2.97

<sup>•</sup> The number of test sample was 5.

Table 2A

Phase composition of the β-HH from calcined FGD and NG at various temperatures and times.

Temperature (°C)	Time (hours.)	%.	AIII	%1	нн	%.	All	%1	DH	- %	Rest
		FGD	NG	FGD	NG	FGD	NG	FGD	NG	FGD	NG
120	2	15.34±1.87	9.02 <u>+</u> 4.03	62.37±2.63	60.17±1.98	4.77 <u>+</u> 2.28	0.77 <u>+</u> 0.45	13.07 <u>+</u> 1.65	10.11 <u>+</u> 3.14	4.45±2.28	19.93±2.97
120	3	8.71 <u>+</u> 2.63	8.70 <u>+</u> 1.86	69.42 <u>+</u> 1.83	63.32 <u>+</u> 2.35	7.91±2.45	0.89±0.76	9.51±3.07	7.16±2.67	4.45 <u>+</u> 2.28	19.93±2.97
120	4	3.72 <u>+</u> 2.54	2.66 <u>+</u> 2.26	76.00 <u>+</u> 3.24	70.87±3.48	8.21 <u>+</u> 3.01	0.94 <u>+</u> 0.90	7.62±2.64	5.60 <u>+</u> 2.41	4.45 <u>+</u> 2.28	19.93±2.97
130	2	10.68±2.03	7.45±3.21	78.65±4.01	70.76±1.32	5.55 <u>+</u> 2.81	1.07±0.87	0.67±0.65	0.79±0.21	4.45±2.28	-19.93±2.97
130	3	3.22 <u>+</u> 1.78	6.19 <u>+</u> 3.09	83.11 <u>+</u> 3.63	72.52 <u>+</u> 2.04	8.97±2.04	0.99±0.62	0.25±0.83	0.37±0.25	4.45±2.28	19.93±2.97
130*	4	1.36 <u>+</u> 1.14	2.87 <u>+</u> 1.64	87.42 <u>+</u> 2.43	75.89 <u>+</u> 3.36	6.23±1.83	1.21±1.13	0.54 <u>+</u> 0.18	0.10±0.23	4.45±2.28	19.93±2.97
150	2	23.93±1.85	14.00 <u>+</u> 3.21	59.01 <u>+</u> 3.02	52.40±1.87	11.73±2.75	12.55±1.04	0.88±1.13	1.12±1.00	4.45±2.28	19.93±2.97
150	3	16.61 <u>+</u> 1.93	11.27 <u>+</u> 2.78	63.64 <u>+</u> 2.78	56.99±1.14	14.68 <u>+</u> 3.13	10.14 <u>+</u> 2.17	0.62 <u>+</u> 0.98	0.87 <u>+</u> 0.76	4.45±2.28	19.93±2.97
150	4	12.75±2.14	11.04±2.04	68.84±1.65	60.66±1.35	13.22±1.64	7.97±3.02	0.74±1.12	0.40±0.65	4.45+2.28	19.93+2.97

The number of test sample was 5.

<sup>%</sup>based on chemical analysis. Thai Industrial Standard for Gypsum 595-2528, UDC 666-81

<sup>\*</sup> Chosen condition for the synthesis of  $\beta$ -HH.

Table 3A Phase composition of the anhydrite from calcined FGD and NG at various temperatures and times.

Temperature (°C)	Time (hours.)	%1	AIII	961	НН	%.	All	%1	DH	%	Rest
		FGD	NG	FGD	NG	FGD	NG	FGD	NG	FGD	NG
. 400	2	83.62 <u>+</u> 2.75	73.41±2.32	1.75±1.13	1.56±1.15	10.18±2.46	5.10 <u>+</u> 2.43	-1.71 <u>+</u> 1.58	-2.13 <u>+</u> 1.14	4.45 <u>+</u> 2.28	19.93 <u>+</u> 2.97
400	3	83.13 <u>+</u> 2.93	71.89±1.76	1.47±1.25	1.33±0.98	10.95±1.87	6.85±2.65	-2.22 <u>+</u> 2.14	-1.69 <u>+</u> 1.34	4.45±2.28	19.93±2.97
400	4	82.26±1.63	71.10 <u>+</u> 1.95	1.09±0.96	1.19±1.03	12.20±1.65	7.78±3.17	-1.09 <u>+</u> 0.94	-0.85 <u>+</u> 0.76	4.45 <u>+</u> 2.28	19.93±2.97
450	2	82.11 <u>+</u> 2.45	70.60 <u>+</u> 2.11	0.71±0.85	0.85±0.61	12.73±2.38	8.62 <u>+</u> 2.73	-1.24 <u>+</u> 1.76	-2.35 <u>+</u> 1.78	4.45 <u>+</u> 2.28	19.93 <u>+</u> 2.97
450	3	81.79±3.14	69.15±3.21	0.63±0.57	0.54±0.78	13.74±2.74	10.38±2.67	-2.01 <u>+</u> 1.84	-1.53 <u>+</u> 1.20	4.45±2.28	19.93±2.97
450	4	81.44 <u>+</u> 1.65	68.53±1.18	0.67±0.32	0.42 <u>+</u> 0.57	13.44 <u>+</u> 2.93	11.12±1.97	-0.86 <u>+</u> 0.75	-1.94 <u>+</u> 0.98	4.45±2.28	19.93±2.97
500	2	80.61±3.47	67.63±2.24	0.44±0.92	0.28±0.15	14.50 <u>+</u> 3.21	12.16±2.93	-1.47 <u>+</u> 1.09	-2.01 <u>+</u> 1.45	4.45 <u>+</u> 2.28	19.93±2.97
500	3	79.24±2.64	65.09±2.37	0.33±0.20	0.15±0.21	15.98±2.41	14.83±2.36	-1.81 <u>+</u> 1.74	-1.32 <u>+</u> 1.14	4.45±2.28	19.93±2.97
500	4	78.19±2.07	63.48 <u>+</u> 2.76	0.13 <u>+</u> 0.11	0.75±0.66	17.23±1.87	15.84±1.87	-2.23 <u>+</u> 2.11	-1.21 <u>+</u> 1.09	4.45 <u>+</u> 2.28	19.93 <u>+</u> 2.97
550	2	77.16±2.14	62.90 <u>+</u> 1.76	0.09±0.07	0.06±0.14	18.30 <u>+</u> 3.42	17.12 <u>+</u> 3.23	-1.51 <u>+</u> 1.42	-0.97 <u>+</u> 0.84	4.45±2.28	19.93±2.97
550	3	75.96±2.36	61.98±3.45	0.01±0.02	0.02±0.07	19.58±2.63	18.07±1.47	-1.13 <u>+</u> 1.07	-1.15 <u>+</u> 0.79	4.45±2.28	19.93±2.97
550	• 4	75.19±1.86	60.78±2.51	0.01±0.14	-2.08 <u>+</u> 1.63	20.35±2.59	19.26±2.53	-0.87 <u>+</u> 0.45	-1.99 <u>+</u> 1.65	4.45±2.28	19.93±2.97
500 ₩	2	74.10 <u>+</u> 2.05	57.52 <u>+</u> 2.30	-1.57 <u>+</u> 1.24	-1.77 <u>+</u> 1.87	21.45 <u>+</u> 1.69	22.55±2.41	-2.07 <u>+</u> 1.68	-1.83 <u>+</u> 1.07	4.45 <u>+</u> 2.28	19.93±2.97
600	3	72.80 <u>+</u> 2.33	55.05 <u>+</u> 1.87	-2.83 <u>+</u> 2.03	-3.03 <u>+</u> 2.01	22.75±3.15	25.02±2.83	-1.60 <u>+</u> 1.47	-1.06 <u>+</u> 0.75	4.45±2.28	19.93±2.97
600	4	70.67±1.98	53.85±2.25	-1.56 <u>+</u> 1.21	-1.08 <u>+</u> 1.01	24.88±1.73	26.22±1.76	-0.96 <u>+</u> 0.85	-1.65 <u>+</u> 1.23	4.45 <u>+</u> 2.28	19.93±2.97

The number of test sample was 5.

<sup>%</sup>based on chemical analysis.

<sup>\*</sup> Chosen condition for the synthesis of AIII.

Table 4A Particle size of  $\beta$ -HH (Blaine).

T (°C)	t (hours)	1 2 3	urface area <sup>+</sup> 4 m <sup>2</sup> /g)		nsity em <sup>3</sup> )	Mean particle size from calculation (µm)		
		FGD	NG	FGD	NG	FGD	NG	
120	2	4789.63±26.42	2325.17±17.25	2.40+0.02	2.59 <u>+</u> 0.03	5.22 <u>+</u> 0.15	9.96±0.21	
120	3	4621.10±35.50	2278.93±20.38	2.40 <u>+</u> 0.01	2.60 <u>+</u> 0.02	5.41 <u>+</u> 0.24	10.13-0.28	
120	4	4662.27±18.13	2191.84 <u>+</u> 24.69	2.41±0.05	2.60 <u>+</u> 0.03	5.34 <u>+</u> 0.21	10.53_0.13	
130	2	4403.54 <u>+</u> 22.28	2370.50±15.01	2.42 <u>+</u> 0.04	2.61 <u>+</u> 0.03	5.63 <u>+</u> 0.10	10.46±0.16	
130	3	4551.32±19.67	2122.07±21.26	2.41±0.04	2.62 <u>+</u> 0.02	5.47±0.19	10.79 <u>+</u> 0.11	
130	4	4192.66 <u>+</u> 30.45	2229.01±16.33	2.43±0.02	2.62 <u>+</u> 0.02	5.89 <u>+</u> 0.23	10.27±0.23	
150	2	3947.48 <u>+</u> 19.94	2258.74 <u>+</u> 22.29	2.42 <u>+</u> 0.03	2.62 <u>+</u> 0.01	6.28 <u>+</u> 0.27	10.98-0.22	
150	3	3985.19 <u>+</u> 25.07	2078.49±25.86	2.44±0.03	2.61 <u>+</u> 0.05	6.17 <u>+</u> 0.19	11.06-0.28	
150	4	3862.75±32.11	2049.66+29.51	2.42±0.02	2.63±0.04	6.42±0.25	11.13±0.20	

<sup>\*</sup> The number of test sample was 5, T = temperature, t = time.

Table 5A Particle size of anhydrite (Blaine).

T t (°C) (hours)	100	urface area <sup>†</sup> <sup>4</sup> m <sup>2</sup> /g)	Den (g/c	sity m <sup>3</sup> )	Mean particle size from calculation (µm)		
		FGD	NG	FGD	NG	FGD	NG
400	2	1446.34±25.07	1053.56±15.85	2.41±0.02	2.62 <u>+</u> 0.06	17.21±0.12	21.7÷±0.20
400	3	1405.07±39.47	1034.31±22.43	2.45±0.04	2.64+0.03	17.43±0.25	21.96-0.15
400	4	1399.86±11.16	1040.42 <u>+</u> 20.20	2.43±0.06	2.61 <u>+</u> 0.02	17.64±0.17	22.10 <u>+</u> 0.18
450	2	1372.19±27.03	1001.63±35.19	2.47±0.01	2.67 <u>+</u> 0.06	17.70±0.15	22.4÷±0.14
450	3	1374.23±25.49	1014.47 <u>+</u> 27.57	2.49±0.05	2.65±0.05	17.53±0.11	22.32±0.20
450	4	1350.58±20.58	1042.81±24.63	2.50 <u>+</u> 0.03	2.69±0.01	17.77±0.19	22.21±0.26
500	2	1345.91±31.20	983.65±36.48	2.53±0.06	2.71±0.02	17.63±0.29	22.51 <u>+</u> 0.19
500	3	1305.76±16.13	968.32 <u>+</u> 18.79	2.56±0.07	2.74±0.02	17.95±0.31	22.60±0.24
500	4	1335.21±19.24	963.21 <u>+</u> 26.65	2.52 <u>+</u> 0.02	2.75±0.03	17.83±0.24	22.65±0.21
550	2	1294.80 <u>+</u> 24.65	958.59 <u>+</u> 28.02	2.55 <u>+</u> 0.03	2.79±0.05	18.17±0.26	22.43±0.19
550	3	1289.53±32.51	955.43 <u>+</u> 32.47	2.54±0.03	2.76±0.07	18.32±0.27	22.75±0.27
550	4	1261.64 <u>+</u> 24.26	953.12 <u>+</u> 35.65	2.57±0.05	2.78±0.02	18.50 <u>+</u> 0.16	22.63±0.23
600	2	1229.61±30.66	947.04 <u>+</u> 21.34	2.58±0.05	2.77±0.03	18.76±0.21	22.86±0.14
600	3	1252.88±27.90	929.66 <u>+</u> 19.70	2.60±0.04	2.81±0.04	18.43±0.17	22.97±0.20
600	4	1211.26 <u>+</u> 28.31	927.75 <u>+</u> 34.55	2.61±0.04	2.80+0.05	18.98±0.31	23.11±0.27

<sup>\*</sup> The number of test sample was 5, T = temperature, t = time.

<sup>+</sup>Air permeability apparatus (Blaine, model 7201)

<sup>+</sup> Air permeability apparatus (Blaine, model 7201)

Table 6A Oxide Analysis Of Natural And Synthetic Gypsum

	SYNTHETIC	SYNTHETIC	NATURAL	NATURAL
	1	2	1	2
CaO	32.02	34.17	31.45	32.05
so <sub>z</sub>	45.53	43.64	43.78	43.60
Mg0	0.06	0.07	0.22	1.12
Sro	0.01	0.03	0.04	0.36
Al,0,	0.05	0.13	0.55	0.22
Fe,O,	0.07	0.09	0.24	0.07
sio,	1.35	0.75	2.41	0.66
TiO,	<0.01	<0.01	<0.01	<0.01
MnO	<0.01	0.01	0.03	<0.01
P,0,	<0.01	<0.01	0.01	<0.01
к,0	<0.01	0.03	0.10	0.05
F	0.02	1.49	<0.01	<0.01
CO <sub>2</sub>	0.01	0.45	0.78	2.56
Chem H <sub>2</sub> O	20.36	19.32	19.75	19.24
Free H,O	0.06	0.09	0.10	0.08
LOI	21.08	20.24	20.86	22.04
TOTAL	100.18	100.03	99.69	100.17

Carbon dioxide and "chemical water" are included in the LOI. The results are reported based on the sample with the "free water" removed. The total is corrected for the oxygen that is replaced by fluoride.

ELEMENT AS WT % OXIDE	FGD-1	FGD-2	TIG-1
CaO	30-34	32-35	30-34
50,	45-48	40-44	38-42
MgO	<0.5	<1	<1
Sr0	<0.1	<0.1	<1
A1,0,	<0.1	<0.5	<1
Fe,0,	<0.1	<1	<1
Sio,	<0.1	<0.2	<0.5
K,0	<0.05	<0.1	<0.1
P,0 <sub>e</sub>	<0.05	<0.2	<0.1
TiO,	Trace	Trace	<2
V.O.	Trace	Trace	<0.5
Cr,0,	Trace	Trace	<0.1
H <sub>2</sub> O "combined" (250°C)	18-21	18-21	18-21
co,	<0.2	<1	1-3

From Proceeding of 2<sup>nd</sup> International Conference on FGD and Chemical Gypsum, P. 23.4, P. 26.7, May 12-15, 1991, Canada.

Table 7A Phase composition of MP prepared from bulk materials (B, P 50x50x10 mm., NG 2.36-3.35 mm.).

Samples	T (°C)	t (hours)	%AIII		%НН			%AII			%DH			
			В	P	NG	В	P	NG	В	P	NG	В	P	NG
1	300	1.	6.08+2.15	8.70±2.17	3.77±2.50	70.87±1.50	65.05±1.84	76.49+1.84	23.14+2.23	26.24+2.85	19.74+2.85	-6.78±2.34	-4.67±2.13	-8.93 <u>+</u> 2.13
2	300	2	7.90+2.37	.9.33±2.38	5.03±2.76	66.21±1.94	61.78+1.91	71.77±1.91	25.89+2.06	28.89±3.06	23.20+3.06	-3.14+2.01	-3.69±2.75	-5.14 <u>+</u> 2.75
3	300	3	8.50±2.01	10.24±0.95	7.24+2.38	61.90±3.01	58.57±2.47	68.42+2.47	29.60±0.74	31.19+2.17	24.34+2.17	-10.03±3.75	-7.87±1.69	-6.73 <u>+</u> 1.69
4	350	1	10.91±2.65	12.90±1.60	9.44±1.29	57.63±3.15	50.35±2.33	63.84+2.33	31.46+2.39	36.75±2.29	26.72+2.29	-2.65±1.54	-10.13±1.37	-3.08±1.37
5	350	2	12.58±0.93	13.86±1.49	10.02±0.78	53.10±2.78	46.57±2.61	61.10+2.61	34.32+2.64	39.57±0.87	28.88±0.87	-5.78±1.63	-5.40±0.98	-10.15±0.98
6	350	3	13.40 <u>+</u> 2.78	14.46+2.28	10.76±1.54	50.71±0.69	43.76+0.76	55.97±0.76	35.89±1.73	41.78+2.91	33.27±2.91	-7.74 <u>+</u> 2.12	-1.78±1.02	-5.02±2.02
7	400	Ť	14.89±1.64	15.22±2.37	12.20±1.13	46.95±2.84	39.03±1.90	51.42+1.90	38.16+1.12	45.75±2.80	36.38+2.80	-1.98+0.48	-2.65±1.41	-7.13±1.41
8	400	2	15.11±1.50	16.89±3.14	13.80±3.07	42.02+2.21	35.87±2.13	47.75±2.13	42.87±1.55	47.24±2.53	38.44+2.53	-3.65±1.54	-5.28±2.63	-1.60 <u>+</u> 1.03
9	400*	3	16.23±2.65	18.37±2.70	15.25±2.38	38.16±2.13	32.75±2.84	43.72±2.84	45.61±2.64	48.88±3.42	41.03±3.42	-6.37 <u>+</u> 2.02	-5.30±3.10	-2.23±1.10
10	450 *	1	17.95±3.02	21.43+2.41	15.87±2.49	32.65±2.47		40.88+2.79				-11.14 <u>+</u> 2.85	-3.32 <u>+</u> 2.58	-9.75 <u>+</u> 2.58
11	450	2	19.11±2.40	23.69+2.52	16.40+1.62	30.00±1.98	26.25+2.50	35.76+2.50	50.89±2.81	50.06+1.37	47.84±1.37	-9.63±2.13	-2.10+2.97	-7.21 <u>+</u> 2.97
12	450	3	21.37±2.57	24.64±1.77	18.17±1.57	27.47±1.63	22.74±1.66	32.73±1.66	51.16±3.14	52.62±2.65	49.01±2.65	-8.02±2.60	-1.81±2.60	-5.08±2.60
13	500	1	24.38±3.11	25.86±3.14	21.12±0.98	22.28+2.24	18.93±2.32	28.28±2.32	53.34+2.22	55.75±1.77	50.60±1.77	-3.11±1.48	-9.64±1.83	-4.79±1.83
14	500	2	25.71±2.98	24.44+2.69	23.69±2.01	19.84±2.52	16.28±1.61	25.09±1.61	54.45±2.76	59.28+2.33	51.22+2.33	-5.52±1.21	-11.13 <u>+</u> 0.75	-6.65±0.75
15	500	3	27.87±0.73	22.28±1.73	22.83+2.76	13.61±3.07	13.91±2.40	22.84+2.40	58.52±2.38	63.81±2.10	54.33±2.10	-4.98±2.34	-7.43±1.86	-10.11 <u>+</u> 1.86
16	550	1	24.48+1.47	20.74±1.02	20.96+3.14	10.27±2.67	9.86±0.77	17.85±0.77	65.25±1.69	69.40±2.45	61.19+2.45	-2.63 <u>+</u> 1.09	-6.41 <u>+</u> 2.59	-2.23±1.59
17	550	2	22.72±1.69	18.36±2.80	18.00±0.67	7.34±2.30	4.93±2.84	14.28±2.84	69.94±1.93	76.71±3.07	67.72±3.07	-8.07 <u>+</u> 3.11	-8.54 <u>+</u> 2.32	-3.65+2.32
18	550	3	21.57+2.20	16.62+2.21	16.22+2.76	3.71+2.15	1.59+2.63	10.71+2.63	74.72+0.89	81.79+2.39	73.07+2.39	-7.15+2.20	-3.60+0.60	-8.22±0.60

the number of each sample was 5, T = temperature, t = time.

% based on chemical analysis

B = Briquet specimen

P = Pellet specimen

NG = Natural gypsum specimen

(1:1 by wt. mixing)

<sup>\*</sup> Chosen condition for the preparation of MP.

<u>Table 8A</u> Effect of grinding time on the particle size of MP prepared from bulk materials (density of B =  $2.60\pm0.03$  g/cm<sup>3</sup>, P =  $2.64\pm0.04$  g/cm<sup>3</sup> and NG =  $2.79\pm0.04$  g/cm<sup>3</sup>)

Grinding time (min.)	Spe	ecific surface a (cm <sup>2</sup> /g)	area (Blaine)	Mean particle size from calculation (µm)			
	В	P	NG	В	P	NG	
0	19.59±0.30	19.40 <u>+</u> 0.21	18.15±0.37	1177.99±16.36	1171.15±15.27	1184.86±16.71	
1	24.97±0.41	25.48±0.50	21.99±0.24	924.49 <u>+</u> 12.85	892.67 <u>+</u> 13.58	978.43±13.80	
2	32.23+0.34	30.79±0.37	28.45±0.41	716.20±12.72	738.10 <u>+</u> 12.97	756.12±14.21	
4	41.36±0.85	39.18±0.76	35.96±0.55	558.35±10.44	580.45 <u>+</u> 13.93	598.37±14.93	
6	67.48±1.22	61.26±1.48	45.18±0.71	342.02 <u>+</u> 5.36	371.16 <u>+</u> 8.67	476.54±10.65	
8	116.55±3.11	123.51±2.13	71.44±1.73	198.68±7.02	184.53 <u>+</u> 4.28	301.10±7.38	
10	311.85±7.63	280.58±9.28	147.29±3.65	74.26±1.35	81.39 <u>+</u> 1.63	146.28±4.21	
12	769.23±11.84	688.70±12.76	364.49 <u>+</u> 9.81	30.87±0.58	33.64 <u>+</u> 0.71	59.46±1.63	
14	1442.31±18.65	1623.37±21.75	655.65±14.54	16.05±0.17	14.31±0.24	32.80±0.64	
16+	2307.69+29.88	2525.29±21.75	1164.34±23.60	10.49±0.20	9.87±0.19	17.47±0.21	
18	1775.15±30.02	1893.94+28.46	1955.03±32.13	13.73±0.24	12.51±0.23	11.56±0.15	
20	1214.57 <u>+</u> 21.38	1262.28±31.75	1536.10±27.83	19.60+0.32	18.63+0.30	14.37±0.19	

<sup>\*</sup> the number of test sample was ..

with mean partical size < 20µm.



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<sup>+</sup> Grinding time of 16 min. was chosen for obtaining MP powder



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