CHAPTER 3

MATERIALS AND METHODS

A. Synthesis of α-HH

3.1 Materials

1. As-received Mae Moh FGD gypsum (from the Mae Moh power Plant, Thailand)
2. As-received Lippendorf FGD gypsum (from the Lippendorf power Plant, Germany)
3. As-received natural gypsum (from the Bunyawath mine, Thailand)

The above materials were characterized for chemical and phase compositions (Wet chemical analysis), phase analysis (X-ray diffraction, JEOL JDX 3530), and morphology (Scanning electron microscope, JEOL JSM T 220A). The results are presented in Table 3.1, Fig. 3.1, and Fig. 3.2, respectively.

Table 3.1 Chemical and phase compositions of gypsum raw materials (ASTM C 471).

Compositions		Raw materials			
		FGD-AR	FGD-WA	FGD-GER	NG
Air-dried sample					
Combined Water	%	18.52	20.05	20.36	19.87
SiO_2 + Insoluble Residue	%	1.79	0.55	0.32	0.36
Aluminium and Iron (R_2O_3)	%	0.90	0.32		0.28
Calcium Oxide (CaO)	%	32.47	32.01	32.86	32.51
Sulfur Trioxide (SO_3)	%	42.30	46.36	46.24	45.70
By Calculation					
Gypsum	%	88.49	95.80	97.26	94.94
Anhydrite	%	1.95	3.08	1.72	2.63
Calcium Carbonate ($CaCO_3$)	%	5.08	Nil.	0.85	0.90

FGD-AR = as-received Mae Moh FGD gypsum
FGD-WA = precleaned Mae Moh FGD gypsum (acid treated)
FGD-GER = as-received Lippendorf FGD gypsum
NG = Natural gypsum

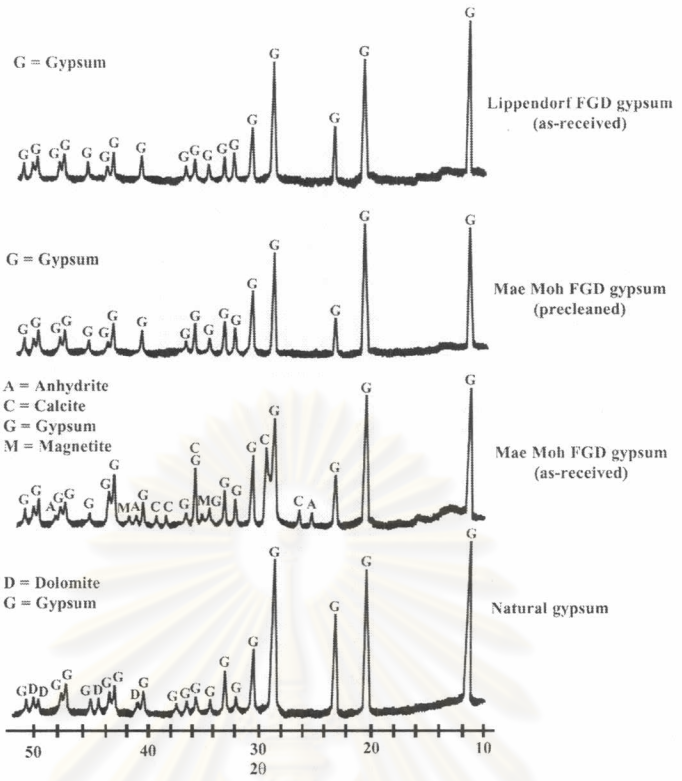
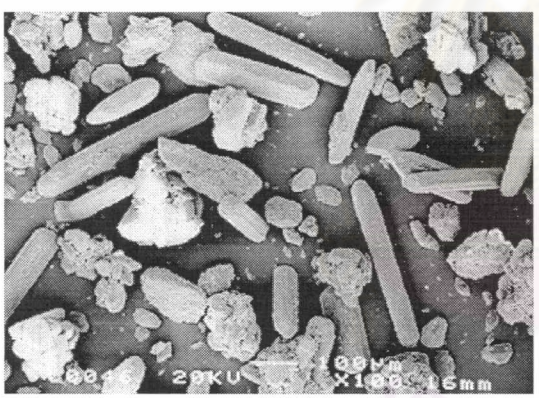
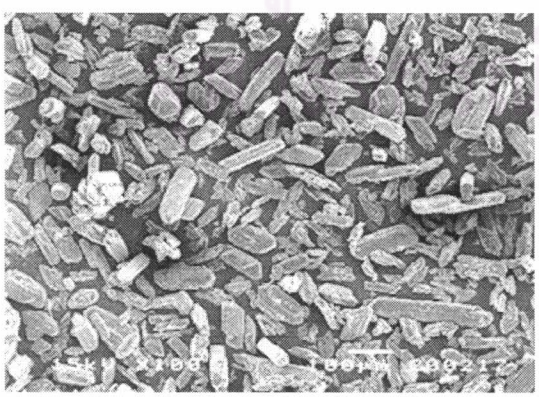


Fig. 3.1 XRD patterns of starting raw materials for the synthesis of α-HH.

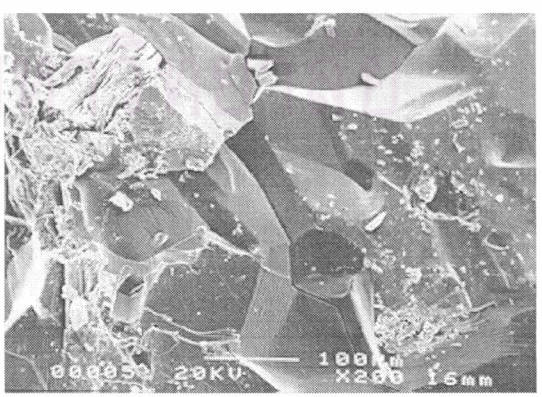


Mae Moh FGD gypsum (as-received)

Mae Moh FGD gypsum (precleaned)



Lippendorf FGD gypsum (as-received)



Natural gypsum

Fig. 3.2 SEM micrographs of starting raw materials for the synthesis of α-HH.

3.2 Materials preparation

3.2.1 Precleaning of Mae Moh FGD gypsum

Due to the high content of colored inclusions, i.e. lignite fly ash, kaolinite, quartz and etc., in the Mae Moh FGD gypsum, it had to be cleaned [1,2] prior to calcining process. Before the stage of cleaning, the FGD gypsum was air dried and sieved through 200 mesh to get rid of coarse impurities. After that, FGD gypsum was mixed with water at water to solid ratio of 0.60. The suspension was fed into the hydrocyclone classifier (Mozley, orifice diameter 2 inch), passed through the magnetic separator (Magneto, MP673), and ultrasonicated to separate the remaining impurities, then the suspension was filtrated and dried at 40°C. The detail of precleaning is schematically presented in Fig. 3.3.

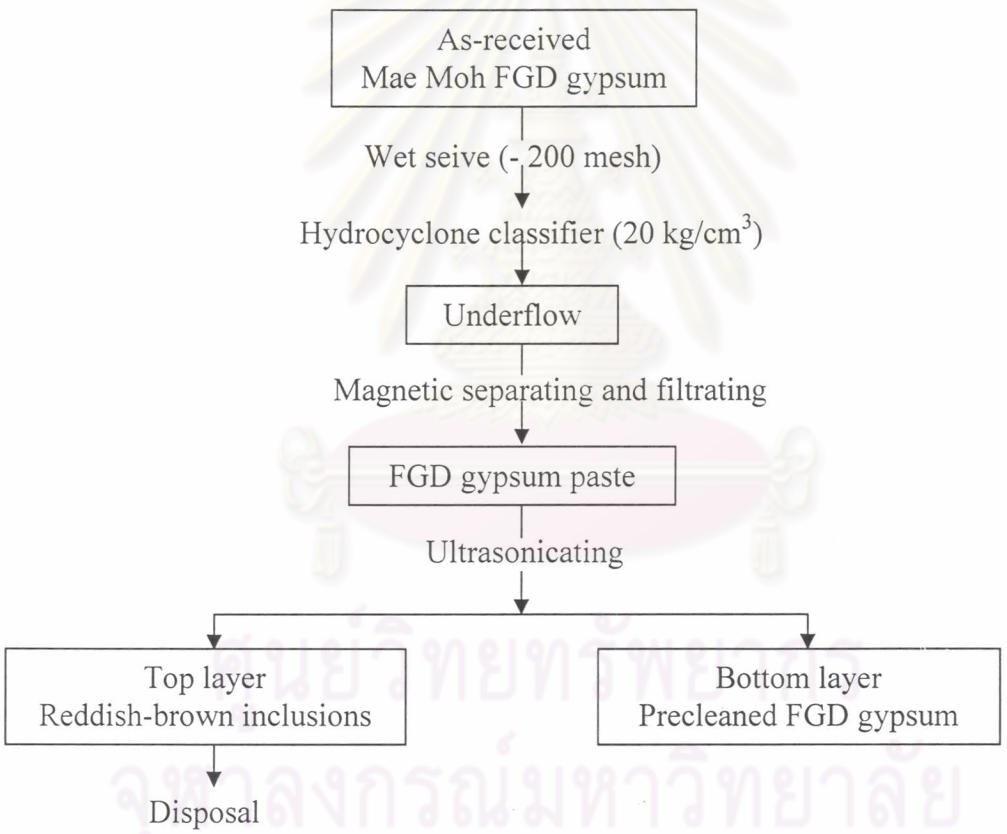


Fig. 3.3 Flow chart for the precleaning of Mae Moh FGD gypsum.

3.2.2 Preparation of FGD gypsum briquette[1]

FGD gypsum had to be dried first. Then, several grams of the dry FGD gypsum were compacted in dry state without additives by a hydraulic press with a compaction pressure of 200 bars to produce 50x50x10 mm. briquette (apparent density ~ 2.1 g/cm^3).

3.2.3 Preparation of natural gypsum lumps

Gypsum rock was crushed in a jaw crusher, sieved through 100 mm. screen and dried at 40°C for 24 hours.

3.3 Method for the synthesis of α–HH

3.3.1 Experimental heating curve

The FGD gypsum briquettes and natural gypsum lumps were used as the starting materials to synthesis α–HH. Each of them was calcined in a laboratory autoclave (CMC Machine Z.I.B.P. 33 84 800) at temperatures of 130 to 163°C and pressure 2 to 6 bars for 1 to 2 hours. After calcining the products were dried immediately at 100°C for 1 hour, ground (Lab grinding machine, FRITSCH Speed Mill Pulverisette 14) into fine powder, and investigated for phase composition by infrared moisture determination balance (A&D Company Limited AD-4712, AD-4713) and wet chemical analysis. The method was as described in Fig. 3.4.

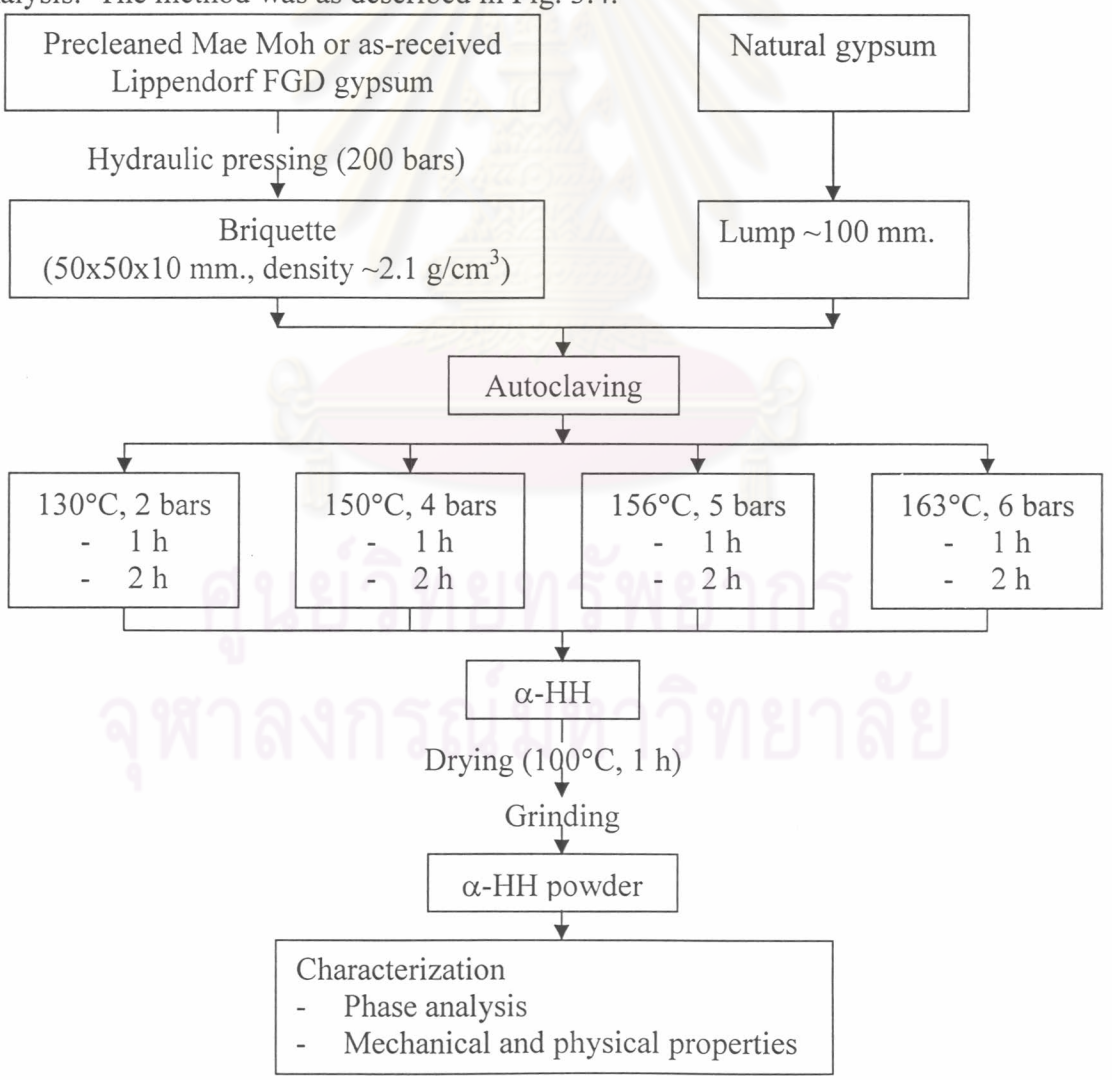


Fig. 3.4 Flow chart for the synthesis of α-HH.

3.4 Effect of additives on the physical and mechanical properties of α-HH

Additives : additives employed in the synthesis of α-HH were

- Sodium succinate [$(CH_2COONa)_2$, Merck, AR grade)]
- Succinic acid [$(CH_2COOH)_2$, Merck, AR grade)]
- Magnesium nitrate [$Mg(NO_3)_2$, Merck, AR grade)]
- Mixture of sodium succinate and magnesium nitrate (1:1)

3.4.1 Method for the calcining of the gypsum with additives

The additives was dissolved in the distilled water first with the fixed concentration at 10 wt% additive solution. FGD gypsum briquettes and natural gypsum lumps were dipped in the solution at dipping time 0 to 15 min (Fig. 3.5). Each of them was calcined in an autoclave at 163°C, 6 bars, 1 hour for FGD gypsum briquettes and at 163°C, 6 bars, 2 hour for natural gypsum. After calcining the products were dried immediately at 100°C for 1 hour, ground with the lab-grinding machine for 10 min (FRITSCH Rotor Speed Mill Pulverisette 14) and determined for phase composition, and particle size distribution (PSD) in absolute ethanol using laser scattering method (CILAS Granulometre 715 No. T024).

3.4.2 Method for the fabrication of test specimens of α-HH plasters

The synthesized α-HH at selected condition was mixed with distilled water to form slurry having water to plaster ratio (W/P) of 0.37 (Fig. 3.5), stirred to homogeneous mixture and poured into a brass mold of 160x40x40 mm (DIN 1164 part 7)[64], then it was placed in a desiccator and vacuumed to remove air bubbles out of the slurry. After the gypsum specimens had set, they were taken out of the mold and cured in the humid air (65% RH) at 20°C for 7 days (DIN 1168 part 2)[65].

Following the flexural strength measurement, portions of the crushed pieces of specimens were detected for morphology by the scanning electron microscope (SEM, JSM T 220 A, supplied by JEOL, Japan). The effect of additives on the setting time of gypsum specimens was investigated by knife cutting method (DIN 1168 part 2)[65].

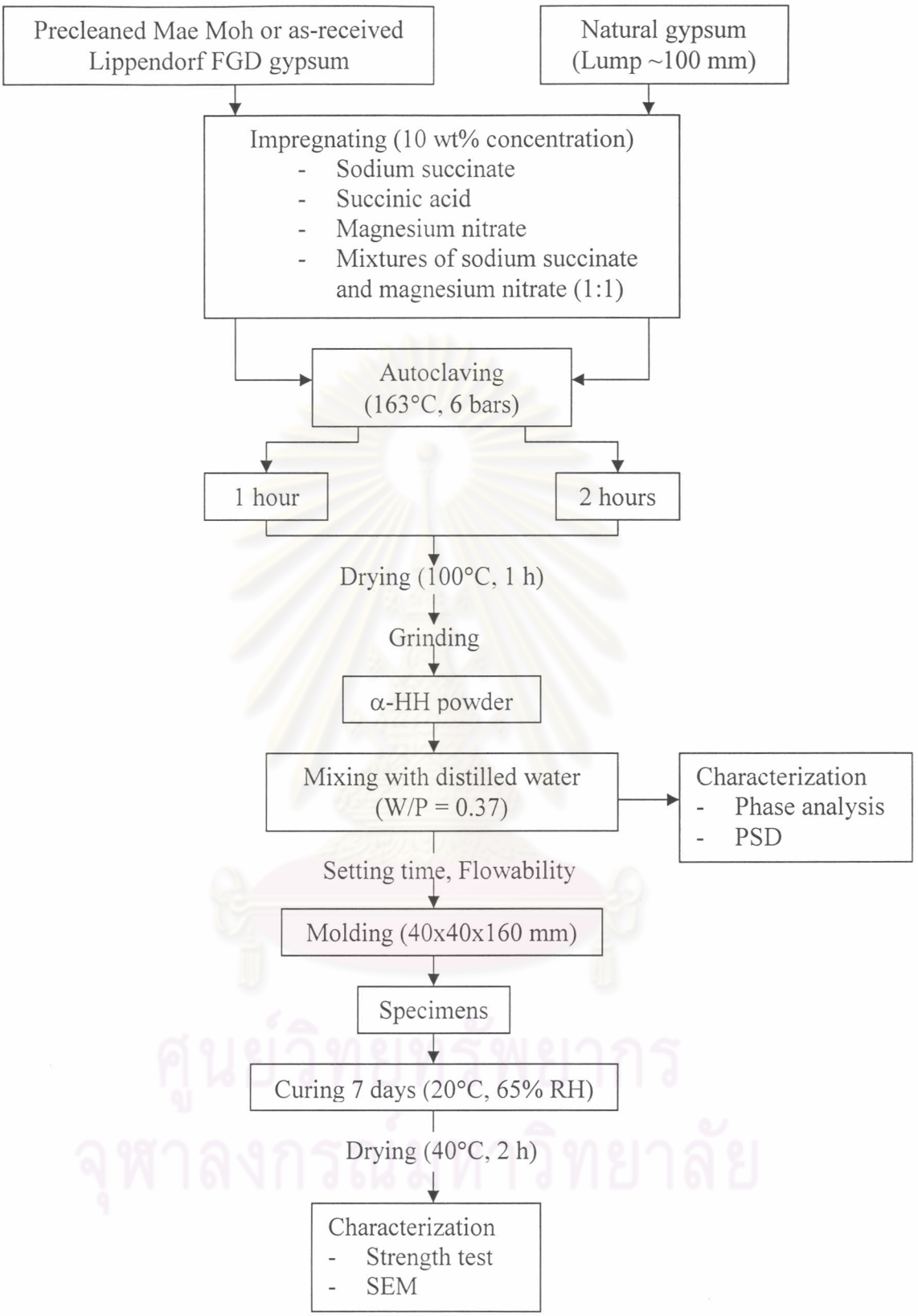


Fig. 3.5 Flow chart for the fabrication of α-HH test specimens.

3.4.3 Method for the improvement of flowability of α-HH products

Materials :α-HH from FGD gypsum synthesized by either dipping in sodium succinate for 15 min or in succinic acid for 7 min.

Method : In order to adjust the particle size distribution of the fine α-plasters (α-HH) synthesized according to Fig. 3.5, a portion of coarse particles was added to each of them. The selected range of coarse size is 10 to 200 μm. This coarse-size was made by crushing the corresponding products and sieving through 70 mesh screen (210 μm), then it was added to the fine products (Fig. 3.6) in the ratio of 10, 20, and 30%, respectively. Then the adjusted products were investigated for PSD, flowability, and flexural strength.

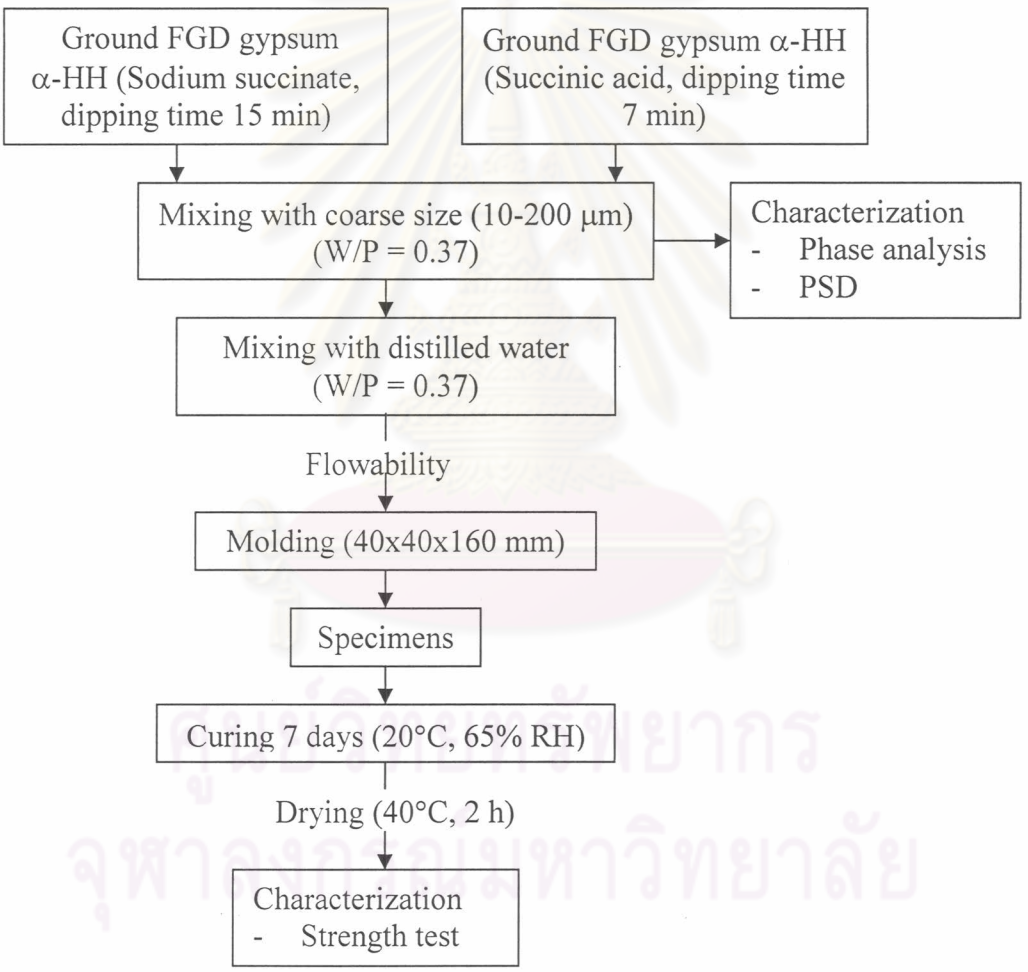


Fig. 3.6 Flow chart for the improvement of flowability of α-HH products.

3.4.4 Study on the recycling of dipping solution

FGD gypsum briquettes and natural gypsum lumps were each dipped in either 10 wt% of sodium succinate or 10 wt% of succinic acid solution before

calcining. Dipping times were selected from the optimized results of HH content, and setting time and are shown as the following :

- dipping time 10 and 14 min for sodium succinate
- dipping time 3 and 7 min for succinic acid

Physical and mechanical properties, and microstructure of α-HH synthesized from reused dipping solutions (0 to 8 cycles) were examined.

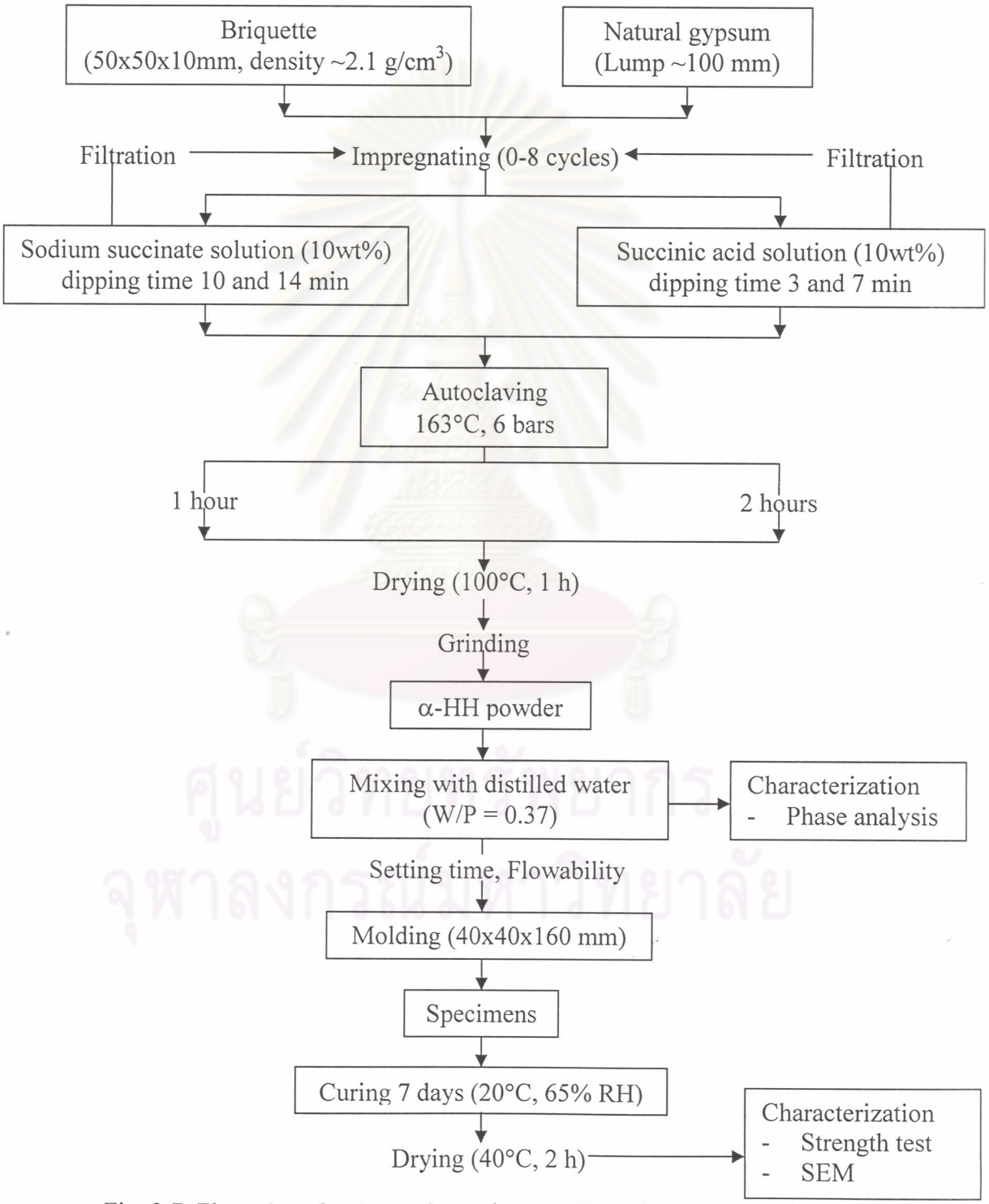


Fig. 3.7 Flow chart for the study on the recycling of dipping solution.

B. Preparation of FGD gypsum-fly ash-lime composite materials

Materials :

- FGD gypsum (from the Mae Moh power plant, Thailand)
- Fly ash (from the Mae Moh power plant, Thailand)
- Lime (Calcium hydroxide, $Ca(OH)_2$, Fluka, AR grade)

Physical properties, chemical composition (X-ray fluorescence), and phase analysis (X-ray diffraction, Philips PW 1050/80) of the raw materials are presented in Table 3.2, Table 3.3, and Fig. 3.8, respectively.

Table 3.2 Physical properties of the raw materials.

Characteristic	FGD gypsum (Hydrocyclone)	Fly ash	Lime
Free water content (%)	7.23	0.15	-
Density (g/cm^3) (Archimedes method)	2.35	2.47	2.24
Mean particle size (μm) (Laser light scattering)	20.35	5.63	-
Particle size distribution (Sieve analysis, % finer than)	200 mesh (75 μm) 100.00 230 mesh (63 μm) 80.67 325 mesh (45 μm) 65.30 400 mesh (38 μm) 27.22	100.00 96.24 85.09 74.38	100.00 100.00 97.30 90.75
Specific surface area (m^2/g) (BET)	4.91	10.83	14.56
Mineralogical composition (XRD)	Gypsum, Anhydrite	Anhydrite, Hematite, Quartz, Mullite, Magnetite	Portlandite

Table 3.3 Chemical composition of starting raw materials.

Composition (%)	FGD gypsum (Hydrocyclone)	Fly ash	Lime
SiO_2	1.43	44.80	-
TiO_2	0.01	0.39	-
Al_2O_3	0.45	26.85	-
Fe_2O_3	0.20	7.35	<0.05
MnO	<0.01	0.08	-
MgO	0.13	3.79	-
CaO	33.15	10.81	75.00
SO_3	46.36	2.46	-
Na_2O	0.09	1.14	<0.01
K_2O	0.02	2.23	<0.02
P_2O_5	-	0.10	-
Free lime	-	0.60	-

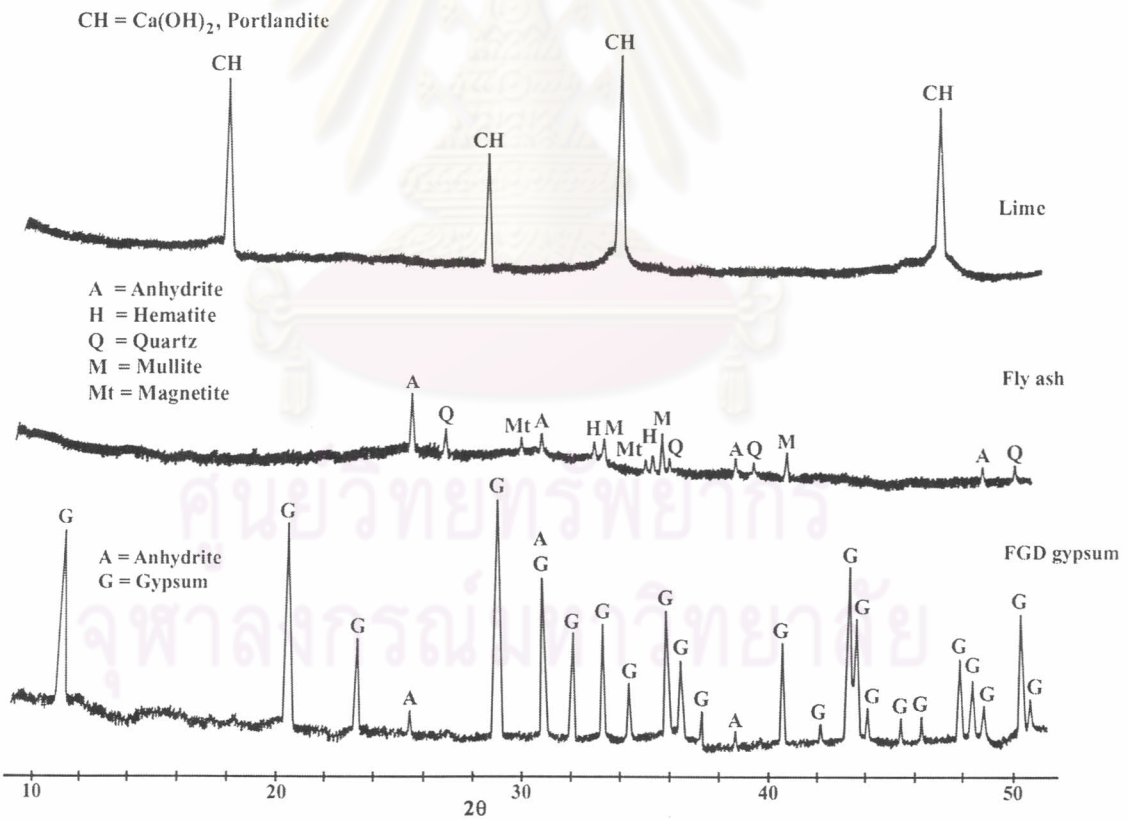


Fig. 3.8 XRD patterns of starting raw materials for the synthesis of composite materials.

3.5 Formulation of FGD gypsum-fly ash-lime

3.5.1 Method for the preparation of test specimens

The test specimens were produced by casting process. Accordingly, FGD gypsum had to be converted to β-HH by calcining at 130°C for 3 hours[1]. The mixtures of β-HH, fly ash, and lime in different propotions were prepared (Table 3.4) into specimens with water to solid ratio (W/S) of 0.50. The paste was mixed by mechanical stirrer for 3 min, cast into 50 mm diameter and 50 mm height metal moulds, then mechanically vibrated for 2 min, and placed in humid air, >98% relative humidity (RH) chamber, at 20°C for curing. These cylindrical specimens were demoulded quickly when they showed a certain strength, and then put back into the curing chamber and cured until testing ages were attained. The experimental procedure is illustrated in Fig. 3.9.

Table 3.4 The propotion of the mixtures of FGD gypsum-fly ash-lime (wt%).

No.	FGD gypsum (β-HH)	Fly ash	Lime	Lime/Fly ash
1	30	58	12	0.21
2	40	48	12	0.25
3	60	28	12	0.43
4	30	54	16	0.29
5	40	44	16	0.36
6	60	24	16	0.66
7	30	50	20	0.40
8	40	40	20	0.50
9	60	20	20	1.00

3.5.2 Characterization of FGD gypsum-fly ash-lime specimens

- Compressive strength test.

Strengths of specimens were tested in compression at the ages of 1 to 28 days. At every testing age, four specimens were taken out from the curing room. The ends of these specimens were polished to make the two bearing surfaces flat and parallel. The strength results reported are an average of the three specimens. The coefficient of variation of these results is less than 10%.

- Bulk density and Total porosity (Σ).

Bulk density of specimens was performed following the ASTM C472-93[66]. The total porosity[67] (Σ) can be determined by using the relation :

$$\Sigma = Wd_g/d_W$$

Where ; W = weight loss on drying at 40°C until a constant weight

d_g = the dry density of specimen

d_W = the density of water

- X-ray diffraction (XRD) analysis and SEM observation.

The specimens were crushed into small fragments, put into the absolute ethanol to arrest the hydration, and dried at 40°C to remove evaporable water. The dried fragments were stored in a sealed container and used for SEM observation and X-ray diffraction analysis.

- Determination of free lime content.

The progress of pozzolanic reaction among lime, fly ash, and FGD gypsum can be monitored by measuring free $Ca(OH)_2$ in the mixtures at different ages. The free lime content was determined using the above dried fragment. The weight loss due to the dehydration of $Ca(OH)_2$ was graphically calculated on recorded thermogravimetric curves (Du Pont 1090 Thermal analyzer). Then free $Ca(OH)_2$ content was back-calculated based on the weight loss.

- Kinetic analysis

Kondo et al.[68] have classified a reaction process based on the reaction grade (N) using a modified Jader's equation (eq 1) :

$$\left(1-\sqrt[3]{1-\alpha}\right)^N = Kt \qquad (1)$$

where α is the reaction degree ; K is the reaction constant ; t is the reaction time ; and N is the reaction grade.

1. If the reaction is controlled by the reaction occurring on the surface grains, or by the dissolution of the reactants or the precipitation of reaction products, then $N \leq 1$.

2. If the reaction is controlled by the diffusion of reactants through a layer of porous reaction products, then $1 < N \leq 2$.

3. If the total reaction is controlled by the diffusion of reactants through a layer of dense reaction products, then $N > 2$.

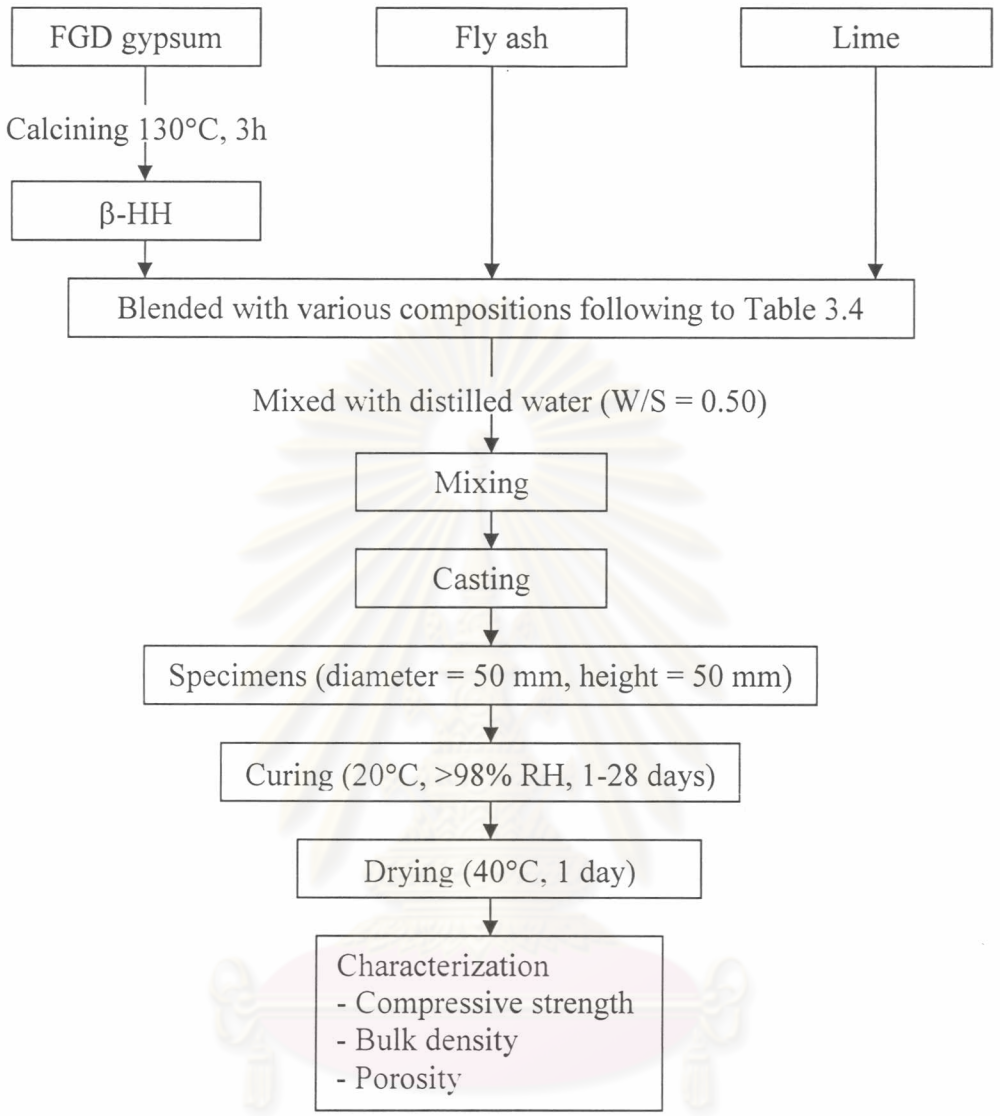


Fig. 3.9 Flow chart for the formulation of FGD gypsum-fly ash-lime test specimens.

3.6 Improvement of the physical and mechanical properties of FGD gypsum -fly ash-lime specimens

Materials : The chosen composition was the mixtures of 30 wt% FGD gypsum-54 wt% fly ash-16 wt% lime (lime/fly ash ratio of 0.29).

3.6.1 Thermally accelerating method

The test samples were made with W/S ratio of 0.50, cast into 50 mm diameter and 50 mm height moulds, then mechanically vibrated for 2 min, and placed in the humid air (>98% RH) chamber at 20, 40, 50, and 65°C for curing, respectively (Fig. 3.10). These specimens were demoulded as soon as they showed a certain strength, and then put back into the curing chamber and cured until testing ages were attained. The strength, bulk density, porosity, and volume variance of specimens were determined at the scheduled ages.

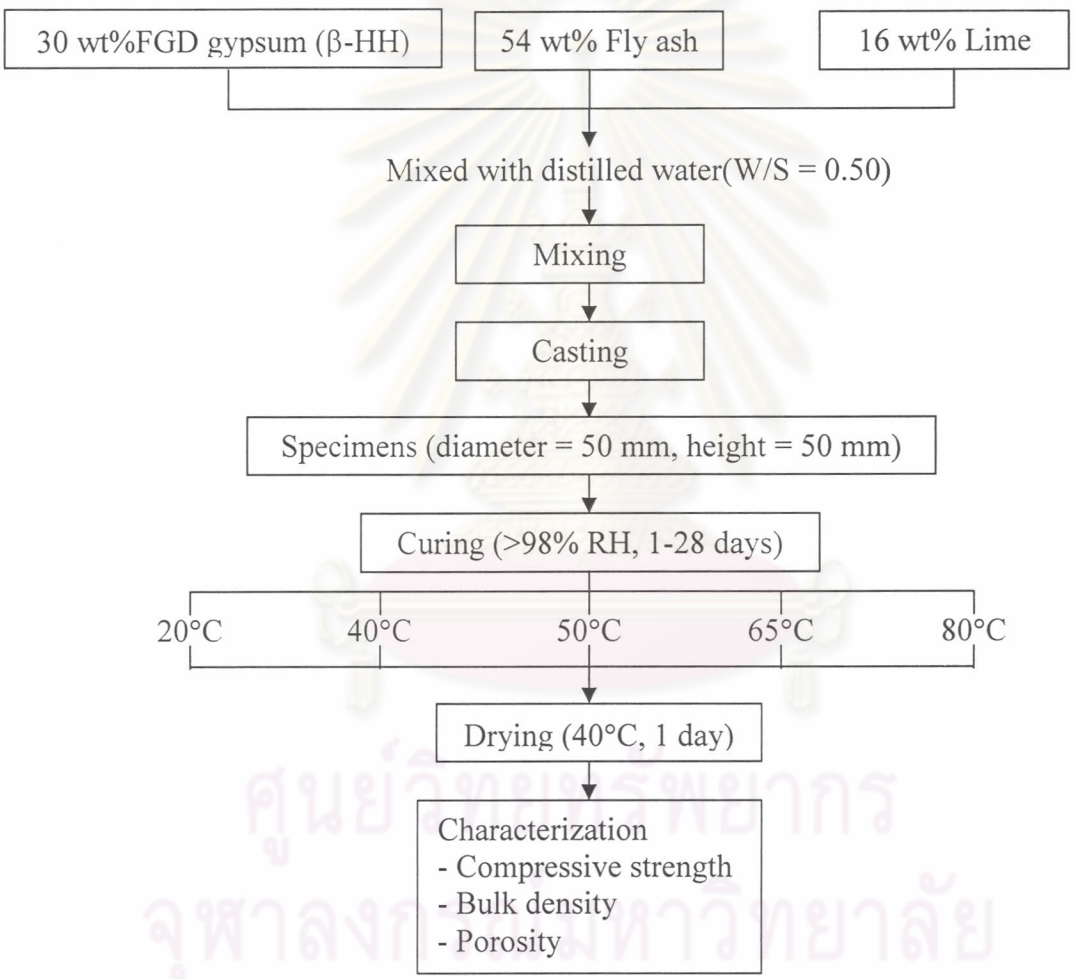


Fig. 3.10 Flow chart for the properties improvement of specimens by thermally accelerating method.

3.6.2 Physically accelerating method

The test samples were prepared by casting method (water to solid ratio of 0.50, cylinder of 50 mm diameter and 50 mm height). The lime/fly ash weight

ratio (0.29) was kept constant at 0.29. β-HH was added to the blended lime and fly ash at 30,40,50,60, and 70 wt% (Fig. 3.11). The flowability was adjusted according to Fig. 3.5 before the forming method. The specimens were cured in the humid air (>98% RH) chamber at 20°C and 50°C, respectively. After curing, the phase composition, microstructure, compressive strength, bulk density, porosity, and volume variance of specimens were determined at the testing ages.

The performance of the prepared specimens under water was also studied. The 28-day specimens were immersed in water (20°C) for various periods of time. The physical properties of specimens under water were characterized at different ages. The flow chart for this improvement is shown in Fig. 3.11.

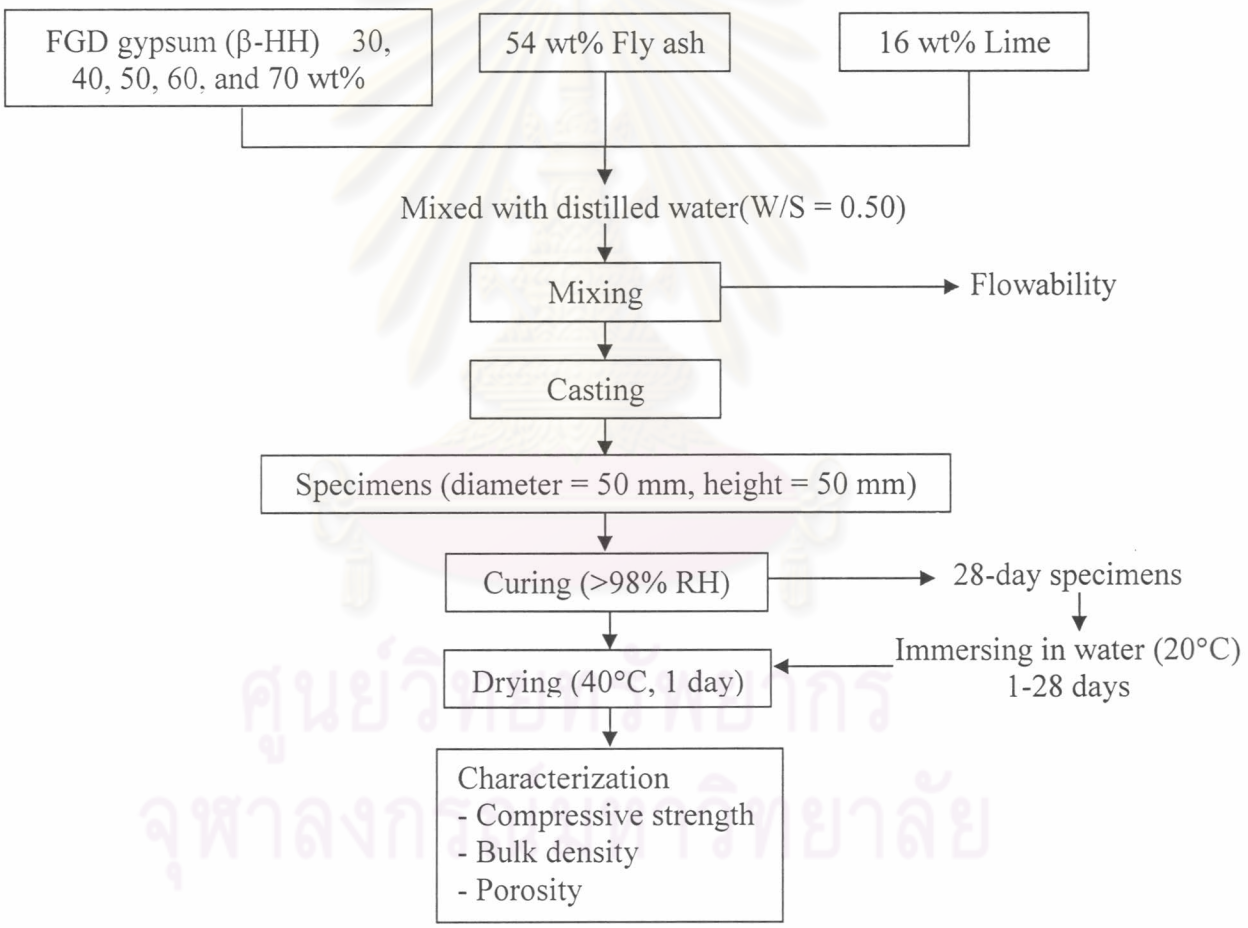


Fig. 3.11 Flow chart for the properties improvement of specimens by physically accelerating method.

3.6.3 Chemically accelerating method

Additives :

- Sodium carbonate (Na_2CO_3, AR grade, MERCK).
- Calcium chloride ($CaCl_2$, AR grade, MERCK).

The test samples were prepared by casting (water to solid ratio of 0.50, cylinder of 50 mm in diameter and 50 mm in height). The additive, 0-4 wt%, was firstly dissolved in the mixing water, then mixed with the composite materials. The specimens were cured in the humid air (>98% RH) chamber at 20°C. The phase composition, microstructure, compressive strength, bulk density, porosity, and volume variance of specimens were determined at the testing ages (Fig. 3.12).

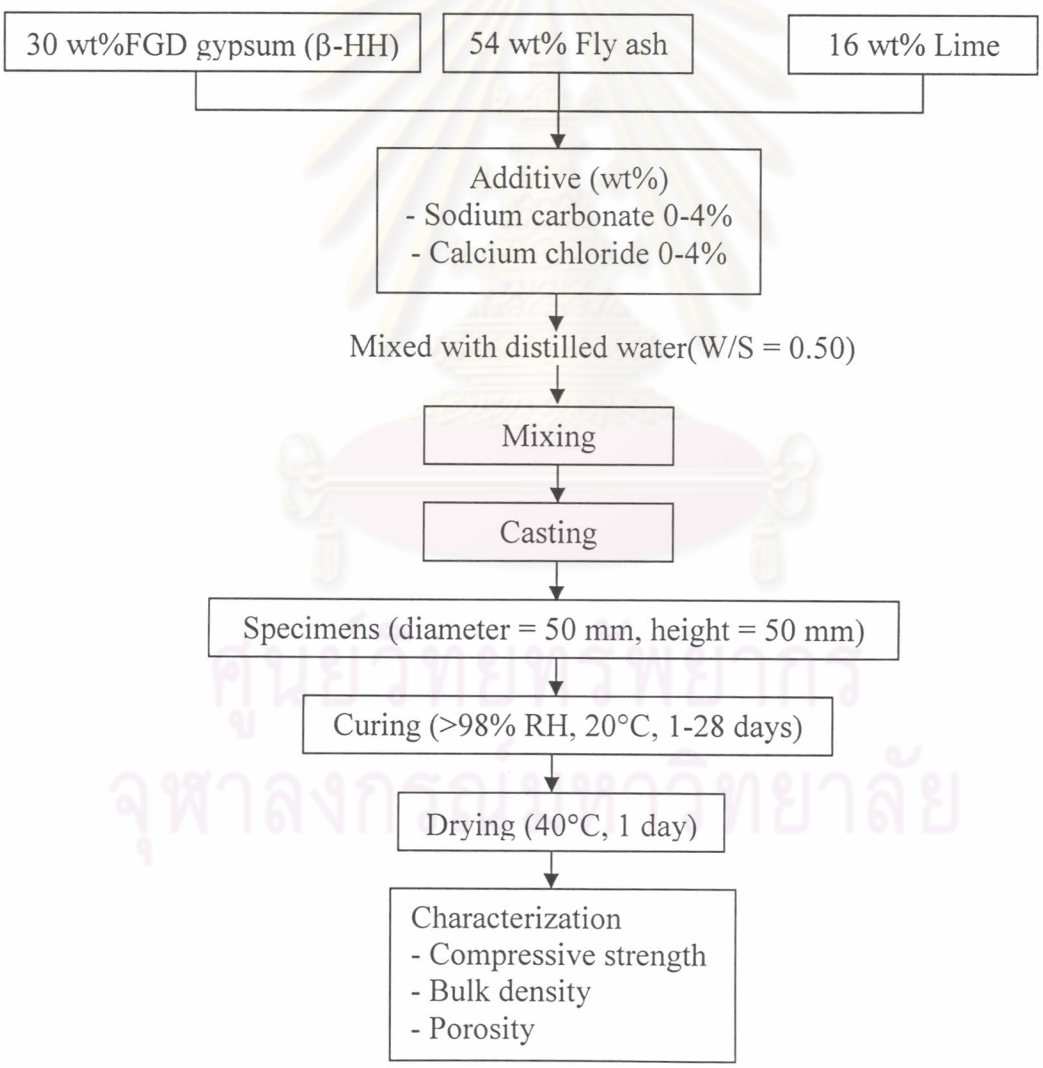


Fig. 3.12 Flow chart for the properties improvement of specimens by chemically accelerating method.

3.6.4 Mechanically accelerating method

Material : Granules of the Mixture of 30 wt% FGD gypsum - 54 wt% fly ash-16 wt% lime (lime/fly ash ratio of 0.29) (Fig. 3.13).

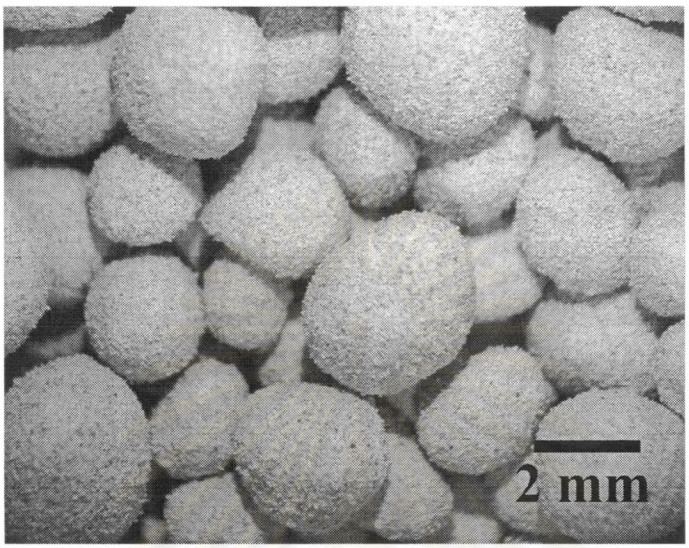


Fig. 3.13 FGD gypsum-fly ash-lime granule.

Granulation technique was used to prepare the mixture of raw materials before the pressing process. The granules were manaully produced by sieving, using 10 wt% of water (total water content including the moisture contents of the individual components) (Fig. 3.13). The size distribution of granule was controlled in range of 1-4 mm. The test specimens in the form of cylinder (diameter 30 mm, height 30 mm) were prepared by pressing a quantity of the moist granules into a metallic mould at a preesure of 20 MPa (Fig. 3.14). The demoulded specimens were cured in the humid air (>98% RH) chamber at 50°C. The strength, bulk density, porosity, and volume variance of specimens were determined at the scheduled ages. The experiment was run in parallel with specimens prepared by casting methods.

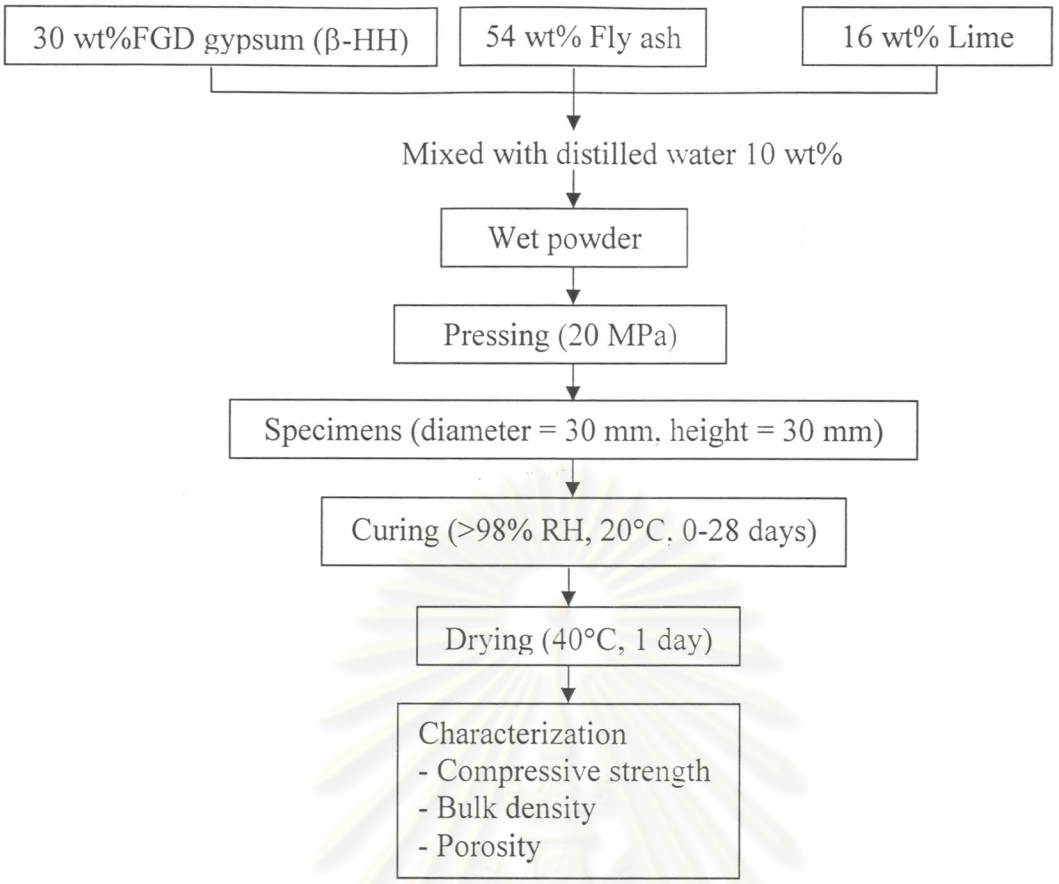


Fig. 3.14 Flow chart for the properties improvement of specimens by mechanically accelerating method.

3.6.5 Combination of accelerating methods

After the test described in Fig. 3.10 and Fig. 3.12, the composite materials prepared from thermally accelerating method, curing at 50°C, and from the chemically accelerating method, mixed of 3 wt% Na_2CO_3 or 4 wt% $CaCl_2$, were selected because they showed higher optimum physical properties than the others. The further details of experiment are demonstrated in Fig. 3.15.

The specimens prepared from the mechanically accelerating method showed superior strength. However, the hydrated product content was lower than those from the casting. Therefore, the performance of the specimens obtained by the mechanically accelerating method might be improved by thermally and chemically accelerating means. The sequences of the improvement are also illustrated in Fig. 3.15.

3.6.6 Dimensional stability under wetting/drying cyclic storage

Following the curing, the 28-day hardened specimens were deliberately left exposed to the extreme condition. The following wetting and drying cycle was used :

- 8-hour immersing under water at 20°C.
- 16-hour drying at 40°C.

The wetting/drying was carried out for 10, 20, 30, 50, and 100 cycles. The physical properties of specimens, i.e. compressive strength, bulk density, and linear change, were measured.

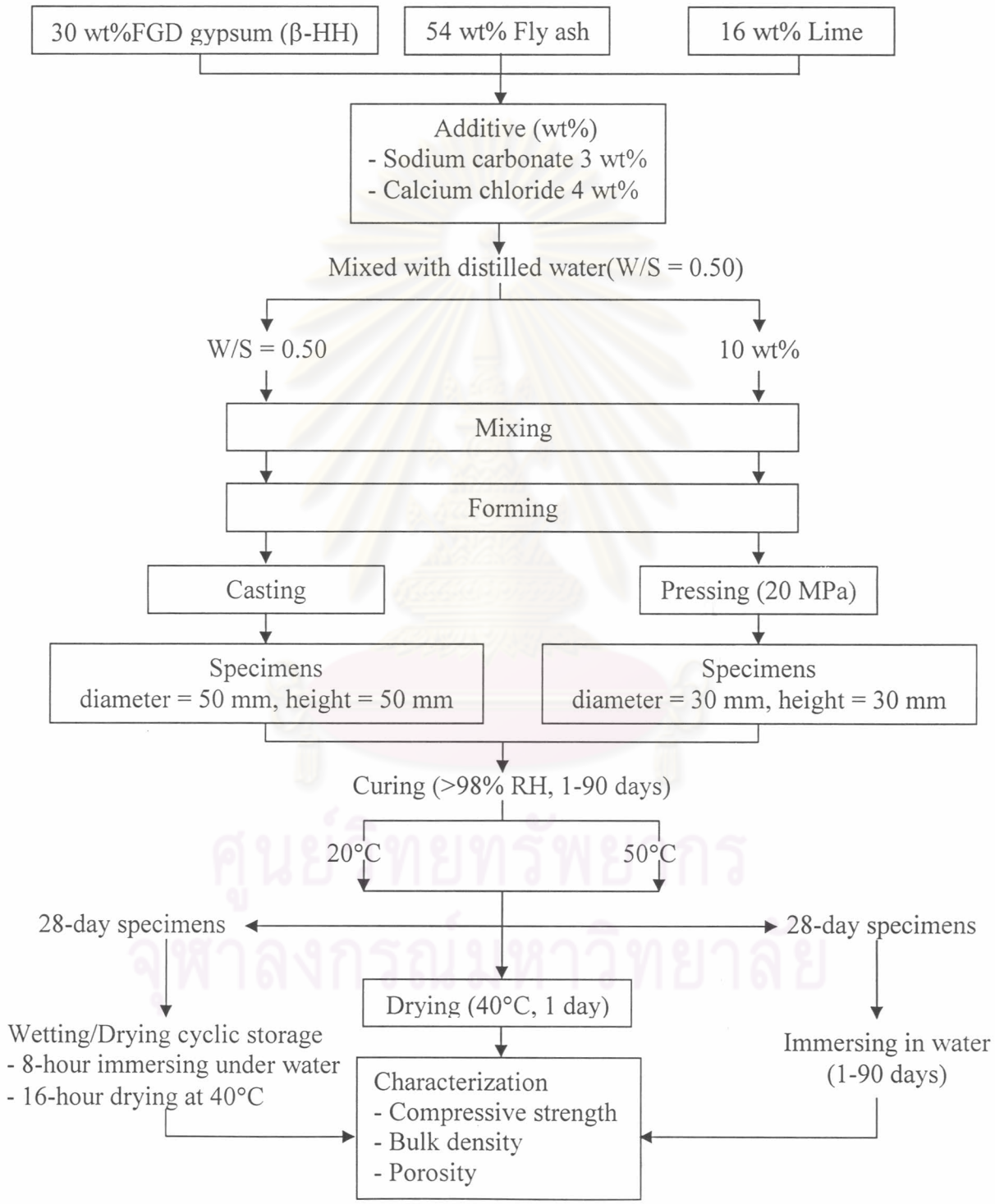


Fig. 3.15 Flow chart for the properties improvement of specimens by the combination of accelerating methods.

3.7 Formulation of FGD gypsum-fly ash-lime-lime containing materials

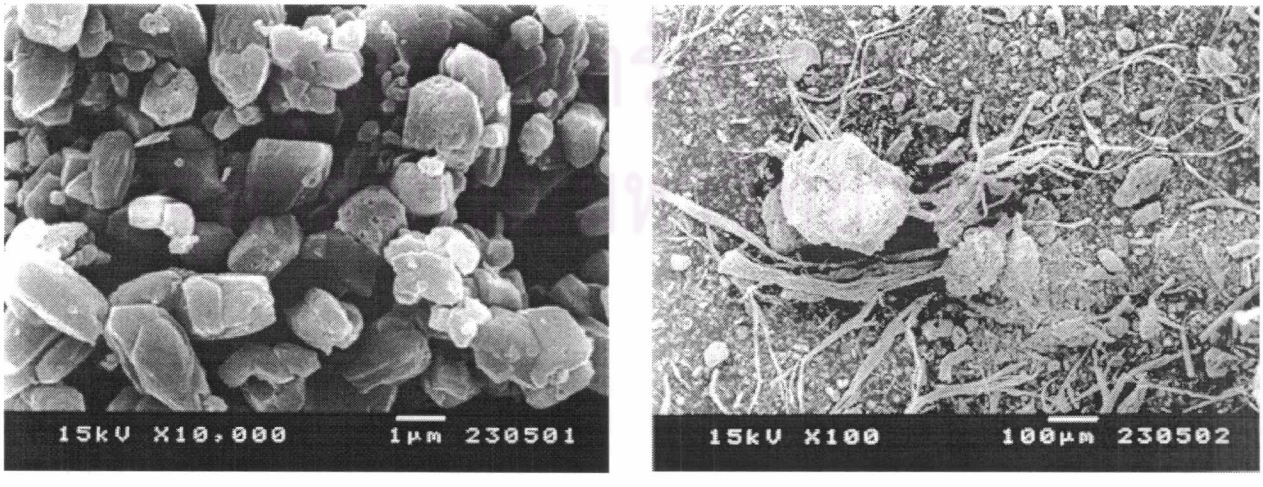
Materials :

- Lime mud (from the Siam cellulose Co. Ltd.)
- Sludge waste (from the Siam cement roofing tile Co. Ltd.)

The physical properties, chemical composition (X-ray fluorescence), morphology (Scanning electron microscope, JEOL JDX 3530), and phase analysis (X-ray diffraction) of lime mud and sludge waste are presented in Table 3.5, Table 3.6, Fig. 3.16, and Fig. 3.17, respectively.

Table 3.5 Physical properties of lime mud and sludge waste.

Characteristic	Lime mud	Sludge waste
Free water content (%)	14.38	64.28
Density (g/cm^3) (Archimedes method)	2.54	1.85
Mean particle size (μm) (Laser light scattering)	2.37	-
Specific surface area (m^2/g) (BET)	20.57	8.96
Mineralogical composition (XRD)	Calcite, Portlandite	Calcite, Chrysotile, Portlandite



Lime mud Sludge waste

Fig. 3.16 SEM micrographs of lime-containing materials.

Table 3.6 Chemical composition of lime mud and sludge waste.

Composition (%)	Lime mud	Sludge waste
SiO_2	20.5	19.8
TiO_2	-	0.18
Al_2O_3	0.03	6.28
Fe_2O_3	0.01	3.32
MnO	0.02	0.06
MgO	0.71	4.54
CaO	76.12	35.3
SO_3	-	-
Na_2O	1.57	0.48
K_2O	0.13	0.88
P_2O_5	0.02	-
Free lime	7.50	7.10

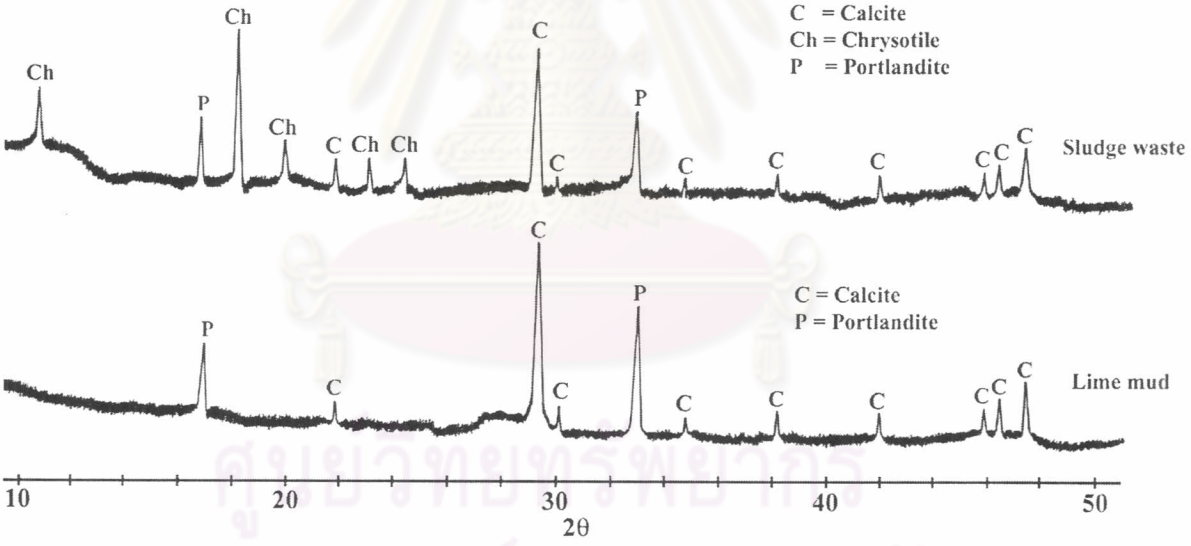


Fig. 3.17 XRD patterns of lime mud and sludge waste.

3.7.1 Method for the formulation of testing specimens

The test specimens at composition of 30 wt% FGD gypsum (β-HH)-54 wt% fly ash-16 wt% lime were produced as standard specimens by casting method. Lime in the composition is replaced by lime mud or sludge waste (Fig. 3.18) at 0, 10, 30, 50, 70, and 100 wt%. The casting procedure and curing condition of specimens were the same as in Experiment 3.2. Physical and mechanical properties of specimens were determined at the testing ages.

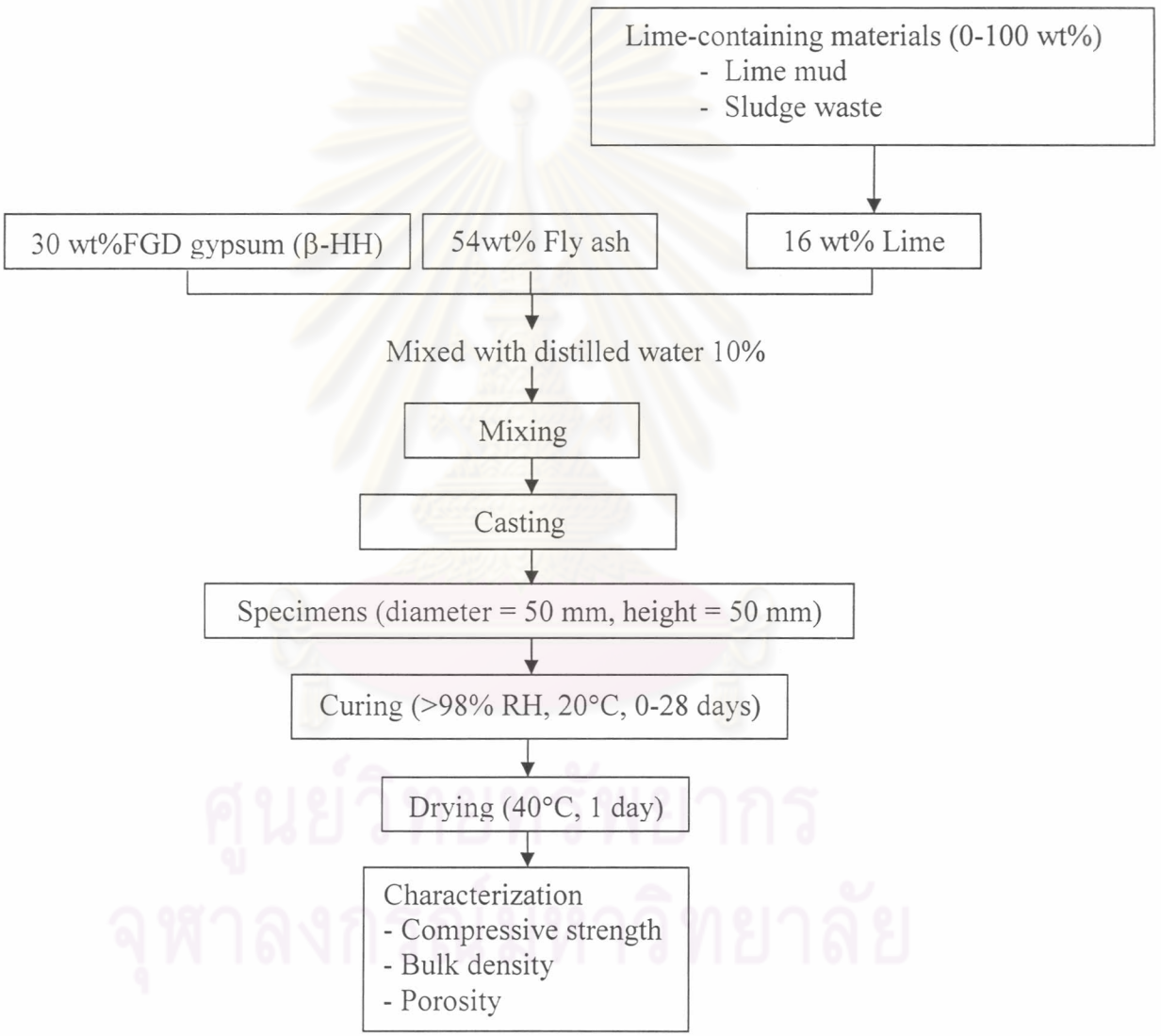


Fig. 3.18 Flow chart for the formulation of FGD gypsum-fly ash-lime-lime containing composite materials.

3.8 Improvement of the physical and mechanical properties of FGD gypsum-fly ash-lime-lime containing materials specimens

3.8.1 Combination of accelerating methods

Materials :

- Mixtures of 30 wt% FGD gypsum (β-HH)-54 wt% fly ash-16 wt% lime with lime/fly ash ratio 0.29.
- Lime-containing materials 50 wt% and 30 wt% from lime mud and sludge waste, respectively, of lime in the mixtures.

Additives :

- 3 wt% Na_2CO_3
- 4 wt% $CaCl_2$

The lime-containing materials testing specimens were also formed by combination of the accelerating methods described in Fig. 3.15. The additive, 3 wt% Na_2CO_3 or 4 wt% $CaCl_2$, was dissolved in the mixing water first then mixed with the blended materials. The specimens were cured in the humid air (>98% RH) chamber at 20 and 50°C, respectively. The phase composition, microstructure, compressive strength, bulk density, porosity, and volume variance of specimens were determined at the schedule ages.

Following the curing state, the 28-day hardened specimens were exposed to the wetting/drying cyclic storage for 10, 20, 30, 50, and 100 cycles. The properties of specimens, i.e. compressive strength, bulk density, and linear change, were investigated. The further details are illustrated in Fig. 3.19.

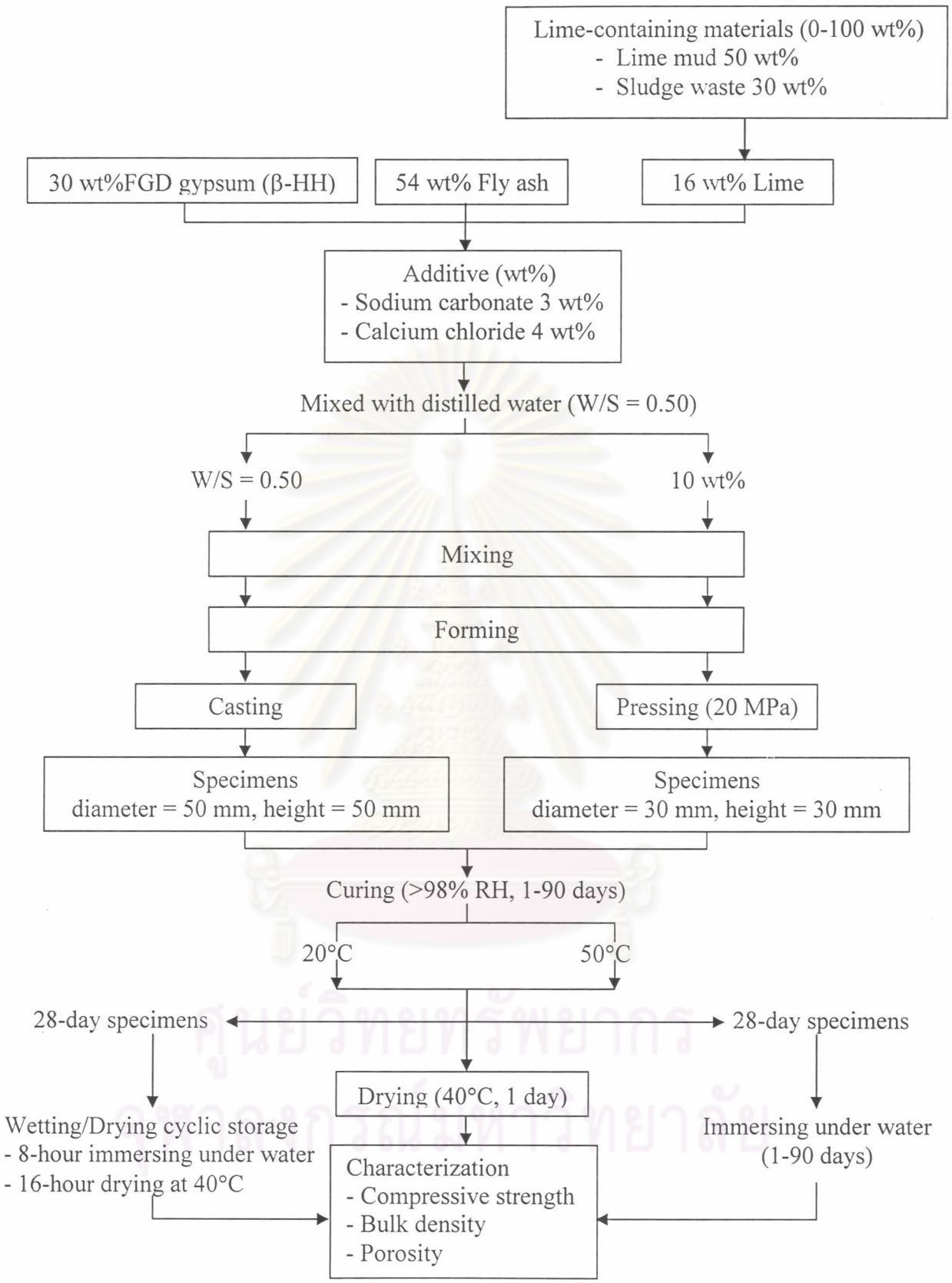


Fig. 3.19 Flow chart for the properties improvement of FGD gypsum-fly ash-lime-lime-containing composite materials by the combination of accelerating methods.