CHAPTER 3

MATERIALS AND METHODS

Materials

The main materials in the experiments were Mae Moh flue-gas gypsum (FG) and natural gypsum (NG).

3. Properties and material preparation

3.1 Properties of FG and NG

Mae Moh FG was chosen as the starting material and the experiment run in parallel with NG. Properties of these gypsums are shown in Table 3.1.

Table 3.1 Properties of experimental materials.

Characteristic	FG (as received)		NG
Free water content (dried at 40°C)	5.14%		–
Density (Archimedes methods)	2.58 g/cm^3		2.35 g/cm^3
Mean particle size (Laser light scattering)	66.92 μm		–
Particle size distribution (sieve analysis, % finer than)	45 mesh (335 μm)	94.55%	–
	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)	45.23%	–
	400 mesh (38 μm)	11.31%	–
Specific surface area (BET)	4.84±0.15 m^2/g		–
Mineral phases (XRD)	Gypsum + fly ash + other impurities		Gypsum + dolomite
Mineral composition (Calculation)	93.33% Gypsum 4.57% Fly ash 2.10% Other impurities		80.07% Gypsum 19.93% Dolomite
Color	Brown		White

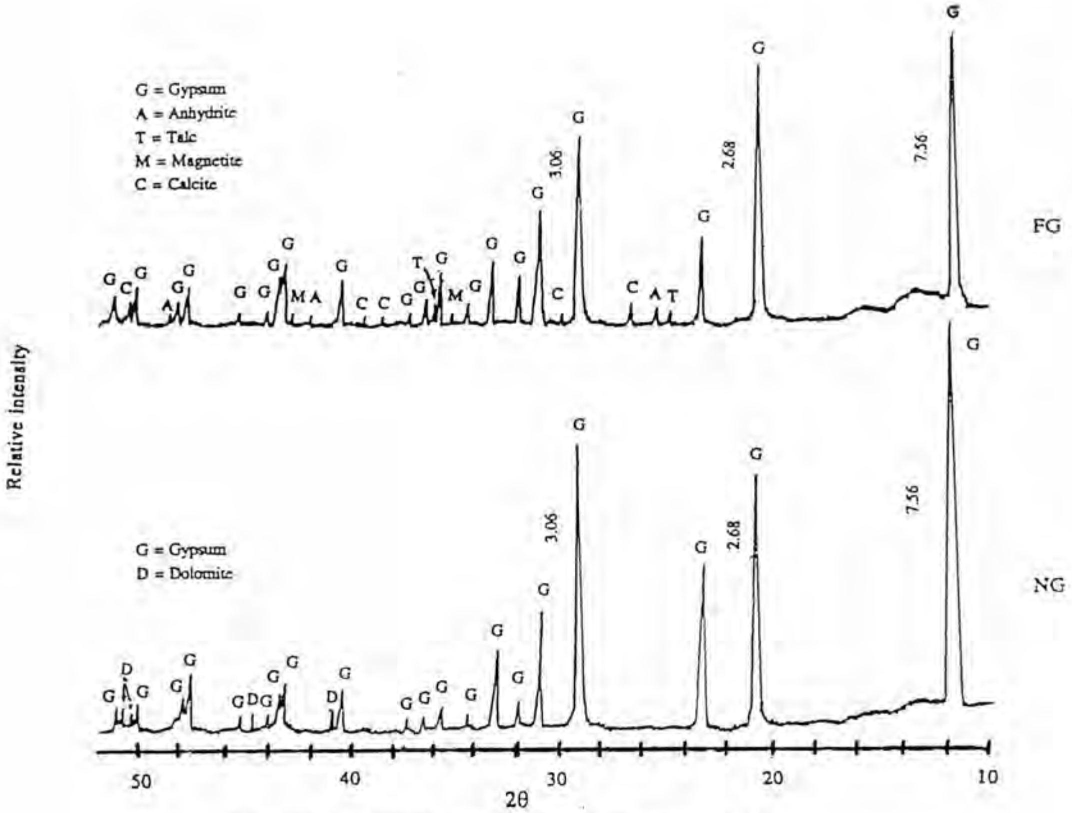
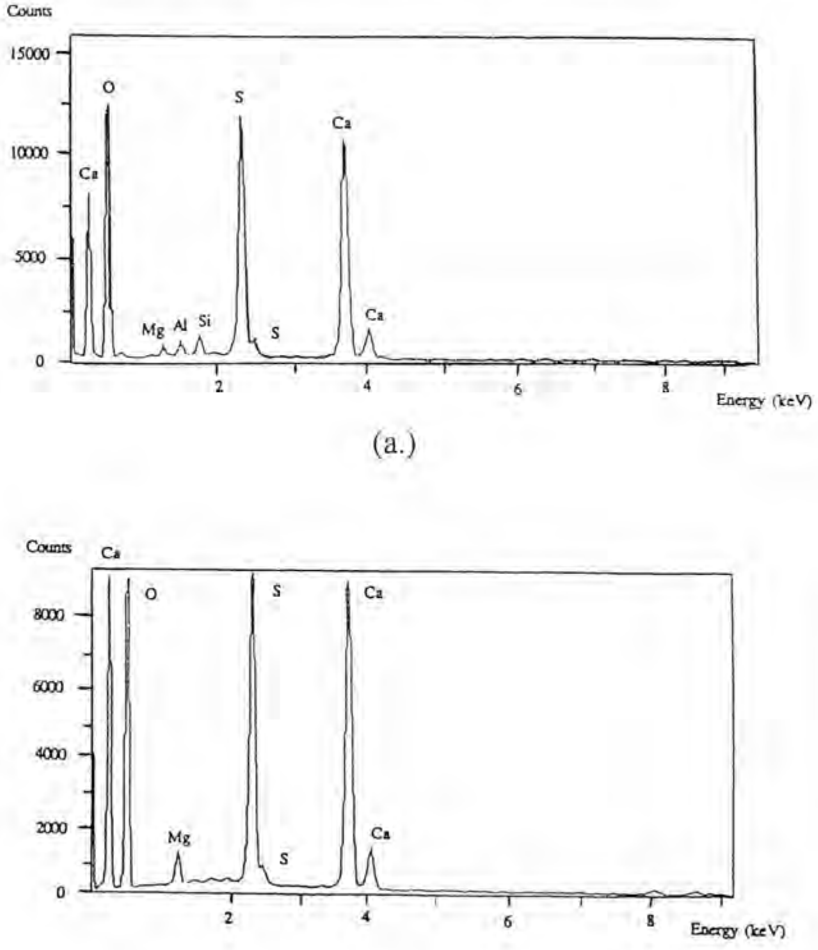


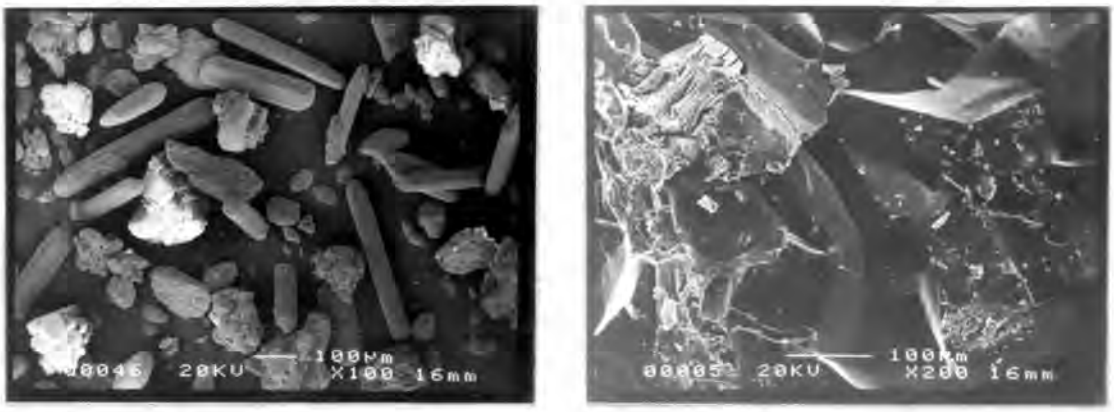
Fig. 3.1 XRD patterns of FG and NG.



(a.)

(b.)

Fig. 3.2 EDS of a.) FG and b.) NG.



(a.) (b.)

Fig. 3.3 SEM micrographs of a.) FG and b.) NG.

3.2 Preparation of FG

3.2.1 Methods for the washing of FG

Due to the color of impurities contaminating in the FG, the as received FG had to be washed prior to calcining process. Before the stage of washing, the FG was air dried and sieved through 200 and 325 mesh to get rid of coarse impurities. After that, several grams of FG were mixed with distilled water and various amounts of diluted sulfuric acid[*] or hydrogen peroxide[+]. Then, the first set of the suspensions were stirred at room temperature and the other at 100°C. Each suspension was filtered and dried at 40°C. The washed FG powder was investigated for mineral phases by means of XRD and calculation methods. The elements present were detected by EDS and morphology was observed by SEM. The detail of the preparation is illustrated in Fig. 3.4.

[*] Sulfuric acid (AR grade, EEC 231-639-5).

[+] Hydrogen peroxide (AR grade, J.T. Baker 8016-52).

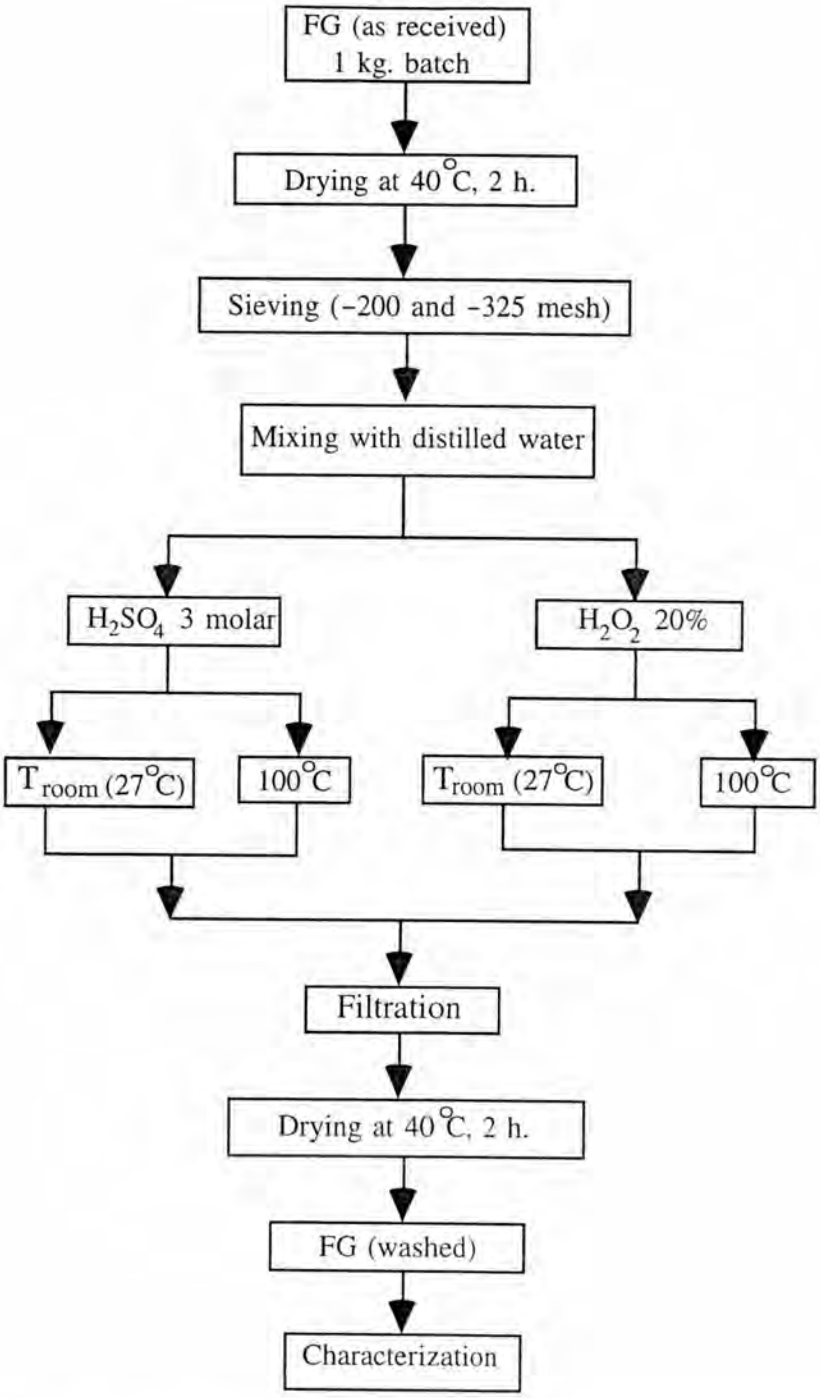


Fig. 3.4 Flow chart for the preparation of FG.

3.3 Preparation of NG

Gypsum rock was crushed in a jaw crusher and ground in a disc mill, then, sieved through 200 mesh screen and dried at 40°C for 2 hours. The obtained NG powder was used as a control for all the experiments with FG.

3.4 Syntheses of β–HH and anhydrites (A)

3.4.1 Method for the synthesis of β–HH

The FG and NG obtained from the preparation were each used as the starting materials to synthesize β–HH by the method reported by Jinawath, Pinidkar and Taweekoon (1995). The detail of the procedure is illustrated in Fig. 3.5.

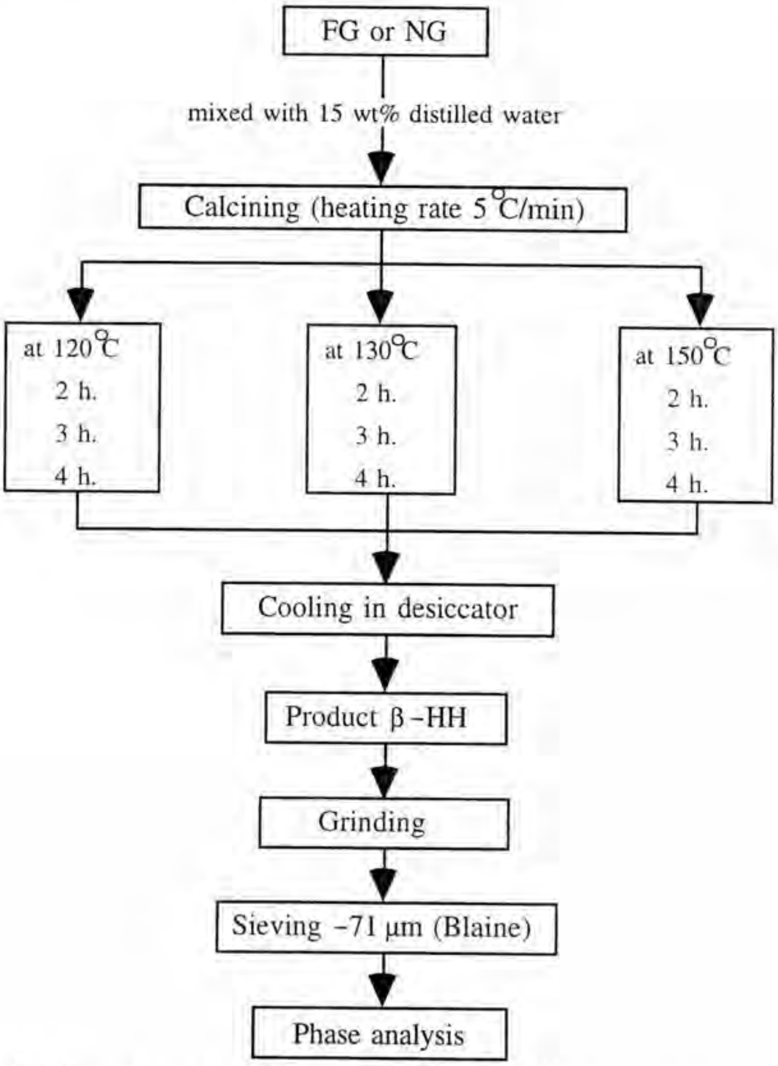


Fig. 3.5 Flow chart for the synthesis of β–HH from FG and NG.

3.4.2 Method for the synthesis of anhydrites (A)

Following the method described by Jinawath et al. (1995), several grams of gypsum were mixed with distilled water 15% by weight of gypsum, placed in a clay crucible, heated to 400-600°C. The further detail is illustarted in Fig. 3.6.

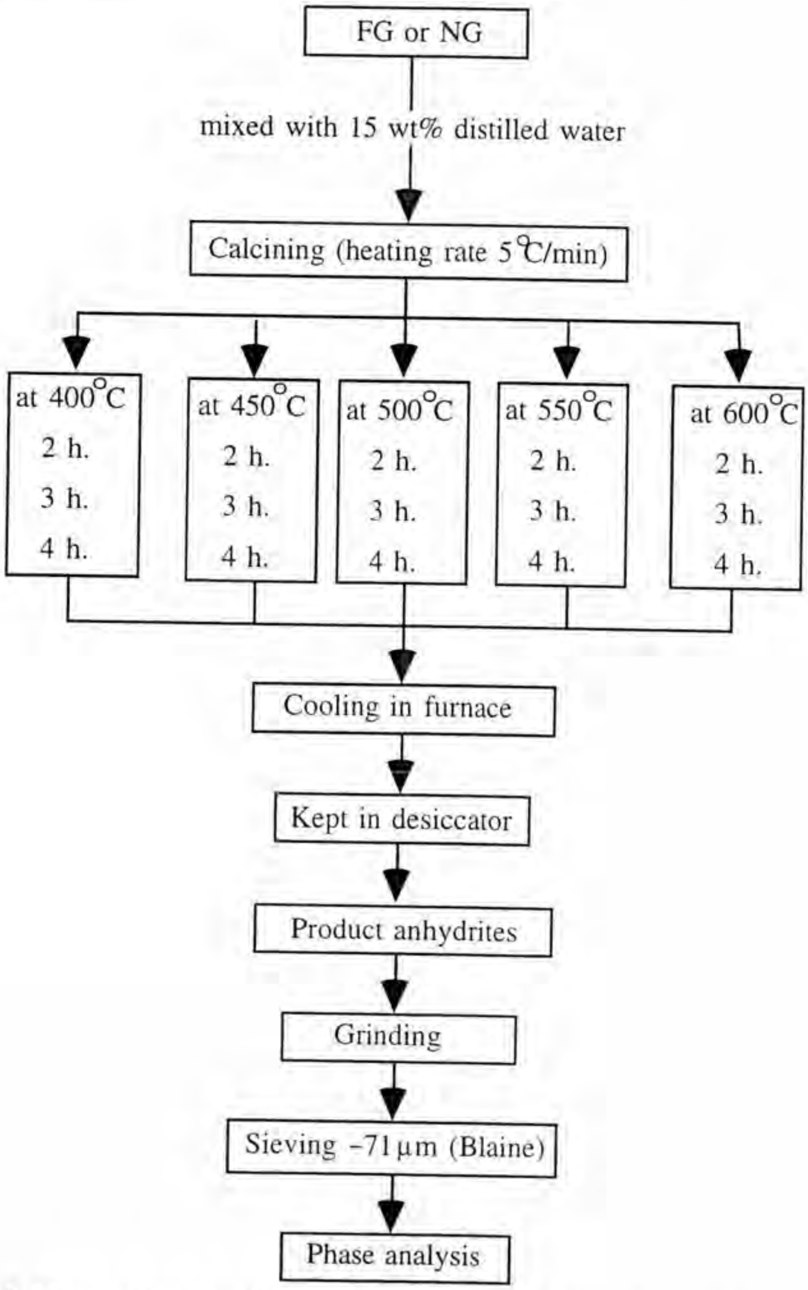


Fig. 3.6 Flow chart for the synthesis of anhydrites from FG and NG.

3.5 Aridization of β-HH and anhydrites (Hoggatt, 1934)

3.5.1 Materials :

- β-HH (obtained by calcining FG or NG at 130°C for 4 hours).
- Anhydrites (obtained by calcining FG at 600°C for 2 hours and NG at 550°C for 4 hours).
- $CaCl_2$ (AR grade), calcium chloride (97%, mol. wt. 110.98) supplied by Merck (dried at 100°C for 2 hours).

3.5.2 Method for the aridization of β-HH and anhydrites

Several grams of the synthesized β-HH or anhydrite were mixed with various amounts of $CaCl_2$, ranging from 0.1 to 0.5 wt% and left exposing to air for 1 hour, 1 day and 3 days. The products were investigated for phase analysis by x-ray diffraction and calculation.

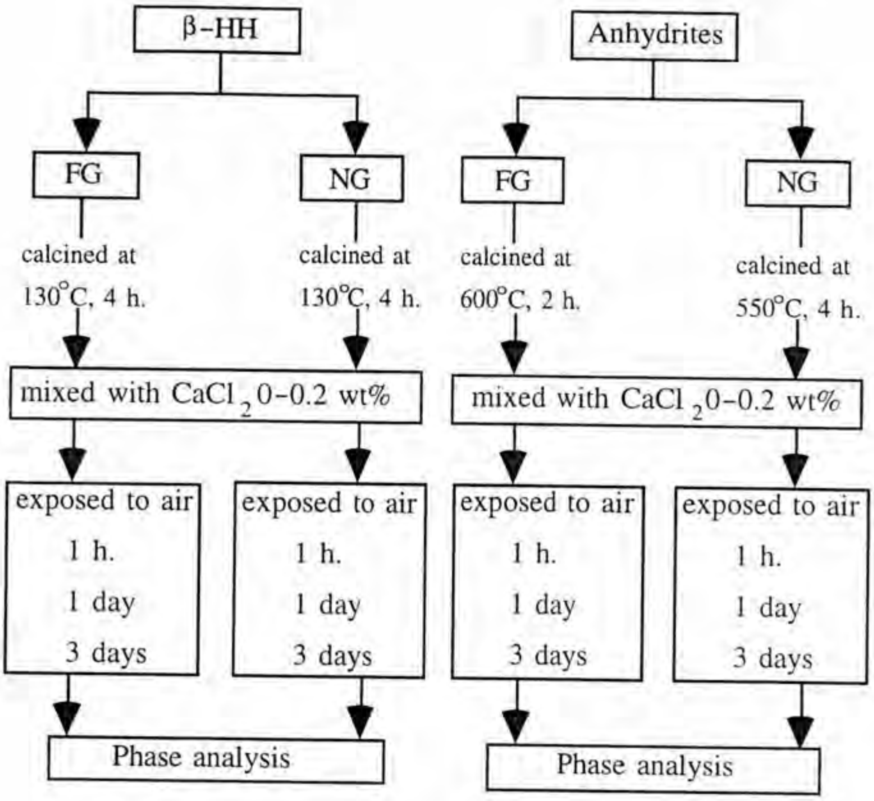


Fig. 3.7 Flow chart for the aridization of β-HH and anhydrites.

3.6 Preparation of multiphase plaster (MP)

3.6.1 Materials and material agglomeration :

a.) As a bulk form

- Briquet (B) obtained by compacting FG in dry state.
- Pellet (P) obtained by compacting mixtures of FG, β-HH and distilled water.
- NG obtained from grinding and sieving the gypsum rock to obtain the particle sizes of 3.35-4.36 mm. and 4.75-5.60 mm.

Preparation of briquet (Fig. 3.8)

FG had to be dried first. Then, several grams of the dry FG were compacted in dry state without additives by a hydraulic press with a compaction pressure of 50-200 bars to produce briquets. The results from SEM micrographs are shown in Fig. 4.17.

Preparation of pellet (Fig. 3.8)

25% β-HH and 8% of distilled water were added to the moist FG (<10 wt% moisture) as bonding agents. Several grams of the mixture were compacted with a compaction pressure of 50-200 bars by a hydraulic press to produce pellets. The results from SEM micrographs are shown in Fig. 4.18.

b.) As a ready mix powder having a composition of MP

- 45 wt% β-HH powder from FG or NG (Fig. 3.5).
- 5 wt% Anhydrite III (AIII) from FG or NG (Fig. 3.6).
- 50 wt% Anhydrite II (AII) from briquet or NG (Fig. 3.9).

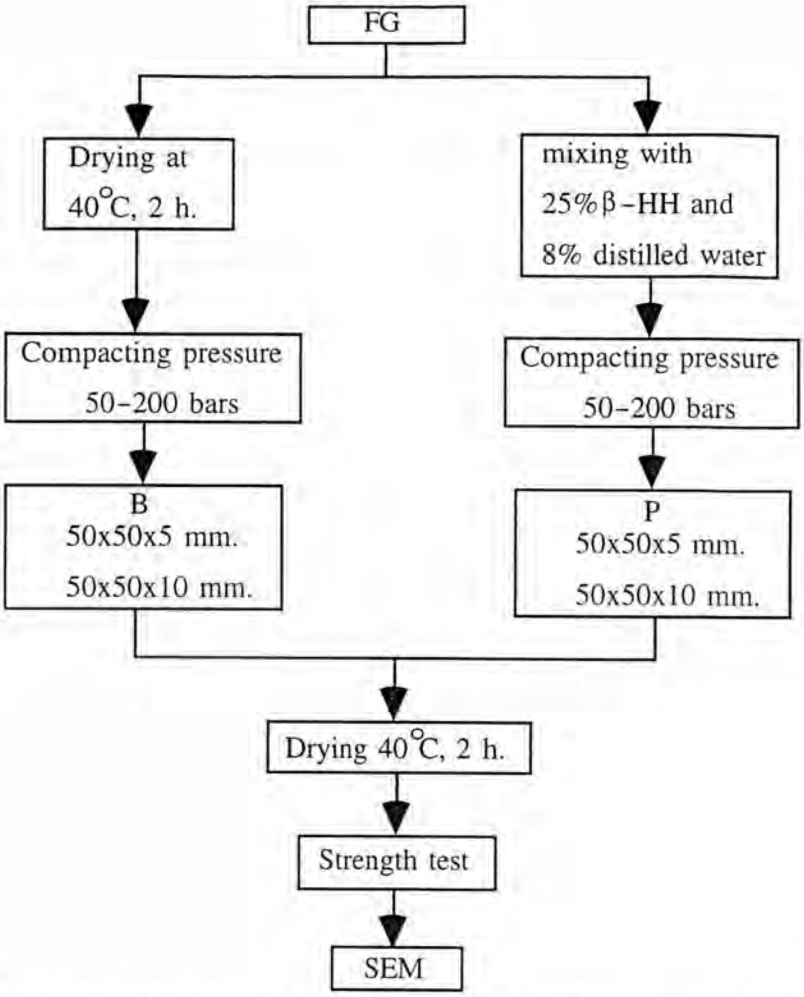


Fig. 3.8 Flow chart for the agglomeration of the FG in forms of B and P.

3.6.2 Methods for the preparation of MP

a.) Preparation from bulk material (direct method).

B, P, and NG were used as starting materials to prepare MP directly. Each of them was calcined in an electric furnace at temperatures 300 to 600 °C for 1, 2 and 3 hours. The products were cooled inside the furnace and investigated for phase analysis by x-ray diffraction.

b.) Preparation from a ready mix powder (indirect method).

The method was as described in Fig. 3.9.

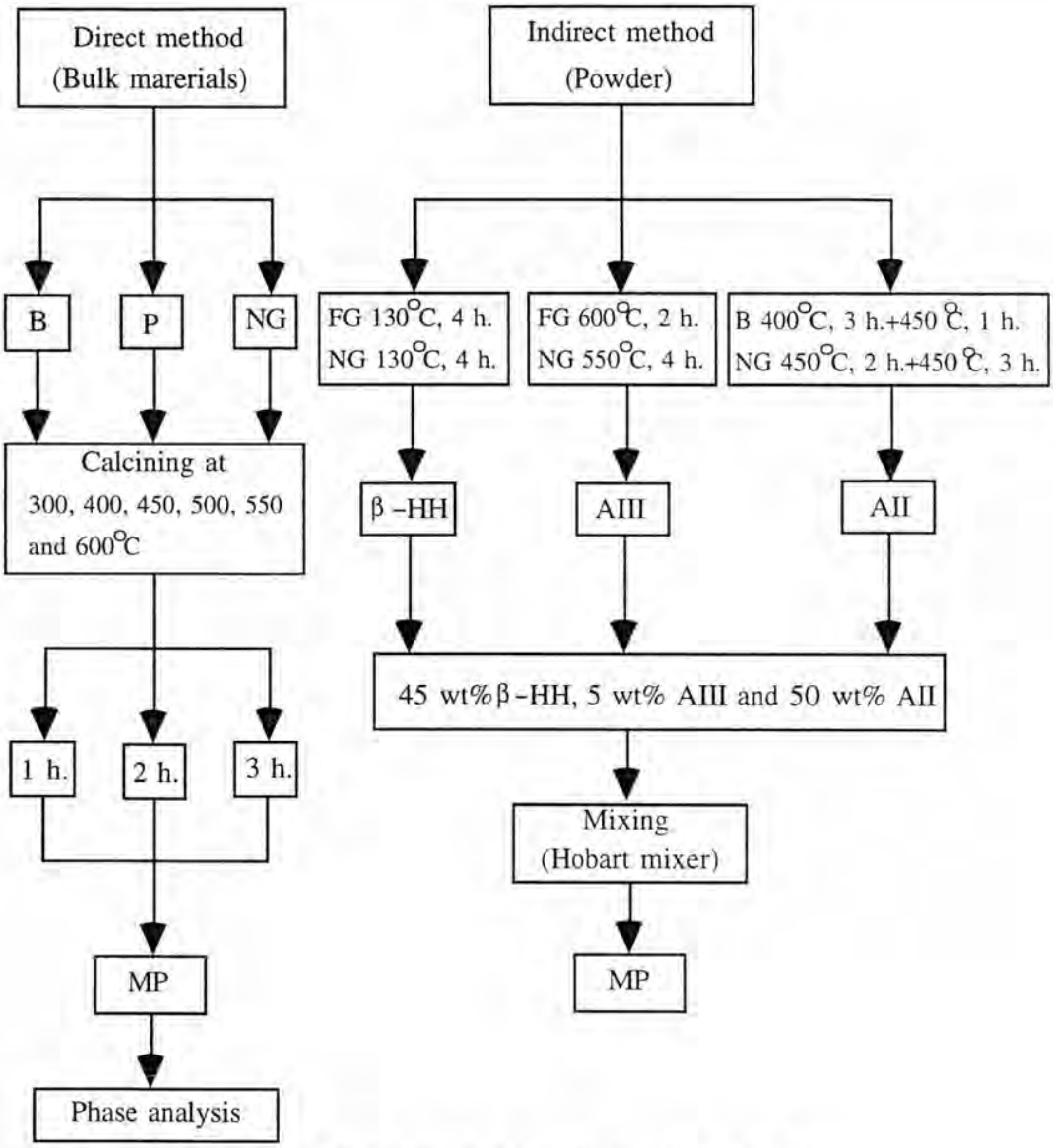


Fig. 3.9 Flow chart for the preparation of MP.

3.6.3 Characterization of β–HH, anhydrites and MP

- Phase present (XRD, calculation).
- Thermal behavior (DTA).
- Particle size (Airjet screening, Blaine calculation).
- Morphology (SEM).

1. Phase analysis

Phases of gypsum plasters were determined by an x-ray diffractometer (Philips, PW 1730/70) with CuK$_\alpha$ radiation and Ni filter at 30 mA 40 kV. A time constant of 1 s. and a scanning speed of 2°/min were used. 2θ was run from 14° to 52° to identify the phases of gypsum plasters and the amount of phase that contained in each of gypsum plaster was calcalated from their mole ratio. The test was according to the method described by Conradt and Ritheravee (1994).

Fig. 3.10 Philips diffractometer (PW 1730/70).

2. Thermal analysis

Thermal behavior of gypsum plaster powder was determined by DTA (Netzsch model Nr 1.303003). The powder was dried at 40°C for 2 hours before proceeding the experiment. The heating rate used in the determination was 10°C/min.

Fig. 3.11 Netzsch thermal analyser (Nr 1.303003).

3. Particle size analysis

a.) Particle size distribution

The test was performed according to the test method described in DIN standards 1975 No. 1168 part 2. In this method, particle size distribution of gypsum plaster powder was determined by using a set of air jet sieve (Alpine 200 LS-N).

Fig. 3.12 Alpine air jet sieve (200 LS-N).

b.) Specific surface area

Average particle size of gypsum plaster was also calculated from its specific surface area measured by air permeability apparatus (Blaine, model 7201).

$$\bar{a} = \frac{\psi_A/\psi_V}{SD}$$

where, $\bar{a}$ = average grain size, μm.

ψ_A/ψ_V = shape factor, 6 (assumed as spherical particle)

D = density, g/cm^3.

S = specific surface area, m^2/g.

Fig. 3.13 Air permeability apparatus (Blaine, model 7201).

4. Morphology of particles

Fine gypsum plaster powder was dispersed in absolute ethanol, mounted on an aluminium stub and coated with gold. The SEM (model JSM T 220A, supplied by JEOL, Japan) examination was performed on the specimens to observe morphology of particles.

Fig. 3.14 Scanning electron microscope (JSM T 220A, supplied by JEOL).

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* Absolute ethanol GR 99.9% (AR grade, Merck).

3.7 Preparation of gypsum board from β-HH and MP

3.7.1 Materials :

1. β-HH from the calcining of FG and NG at 130°C, 4 hours (Fig. 3.5).
2. MP from the calcining of various bulk materials (Fig. 3.9).

In order to achieve the MP with designed composition (45 wt% β-HH, 5 wt% AIII and 50 wt% AII), the products from two calcining temperatures of each material had to be mixed in the weight ratio of 1:1.

- B (at 400°C, 3 hours and mixed with 450°C, 1 hour).
- P (400°C, 1 hour and mixed with 400°C, 2 hours).
- NG (450°C, 2 hours and mixed with 450°C, 3 hours).

3. Additives. :

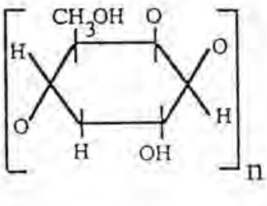
● Retarder.

- $C_6H_8O_7$ (AR grade), citric acid (99.5%, d. 1.542 and mol. wt. 192.12) supplied by Merck, D-6100.

- CH_3COOH (AR grade), acetic acid (97%, d. 1.053 and mol. wt. 60.05) supplied by Fluka, 71600.

- $Na_2B_4O_7$ (AR grade), sodium borate (99%, d. 1.730 and mol. wt. 201.27) supplied by Merck, I-11364.

- $KAl(SO_4)_2 \cdot 12H_2O$ (AR grade), potassium aluminium sulfate dodecahydrate or potassium alum (99.5% and d. 1.725) supplied by Fluka, 60060.

- 

methylcellulose (d. 0986) supplied by Premier Co.

● Accelerator.

- $CaSO_4 \cdot 2H_2O$ obtained from grinding and sieving NG through 325 mesh screen.

- K_2SO_4 (AR grade), potassium sulfate (99%, d. 2.66 and mol. wt. 174.26) supplied by BDH, 30231.
- H_2SO_4 (AR grade), sulfuric acid (98% and sp. gr. 1.84) supplied by BDH, 10276.

3.7.2 Methods for the fabrication of the gypsum board test specimens

β-HH or MP was mixed with various additives (Fig. 3.15) and distilled water to form slurry having water to plaster ratio (W/P) of 0.9, stirred to homogeneous mixture and poured into a plastic mold (150x50x5 mm.) that placed in a desiccator and vacuumed to remove any air bubble out of the slurry. Then, after the gypsum specimens had set, they were taken out of the plastic mold and covered on each side with kraft paper.

Following the flexural strength measurement, portions of the crushed pieces of the specimens were ground to fine powder for morphology investigation by SEM. The effect of additives on the setting time of gypsum specimens was investigated by vicat needle apparatus (DIN standards 1975, No. 1168 part 2).

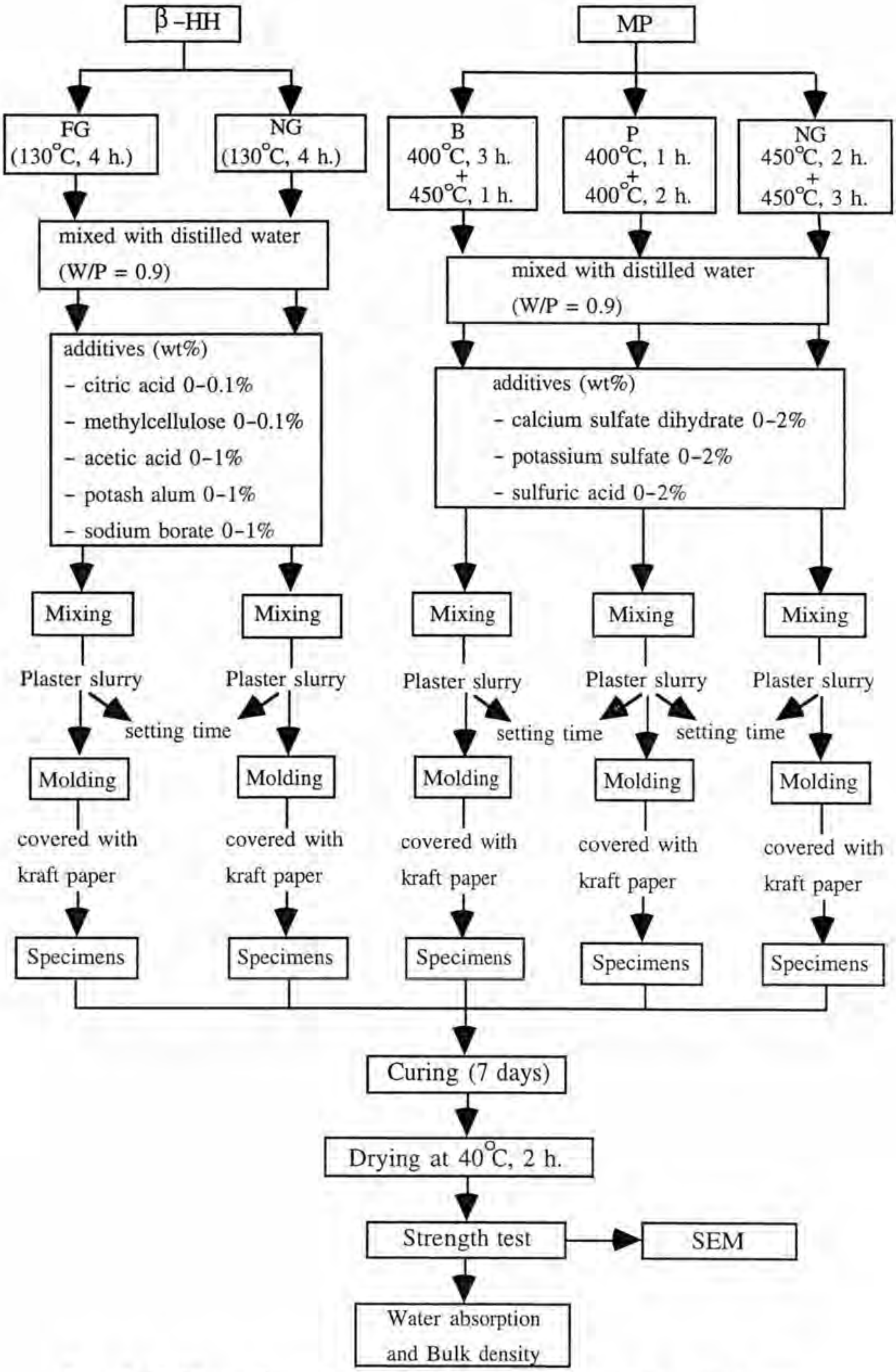


Fig. 3.15 Flow chart for the fabrication of gypsum board test specimens from β-HH and MP.

3.7.3 Test for physical property of gypsum plaster specimens

1. Setting time of the gypsum plaster paste

The test was performed according to method described in DIN 1168 part 2.

Fig. 3.16 Vicat apparatus with needle.

2. Flexural strength (N/mm^2)

The test was performed according to the method described in ASTM C. 472-73.

More specifically, the specimens were cured at room temperature for 7 days. After curing the specimen was pressed at a cross head speed of 1 mm/min by an Instron testing machine (series IX automated materials testing system 7.26.00) until failure.

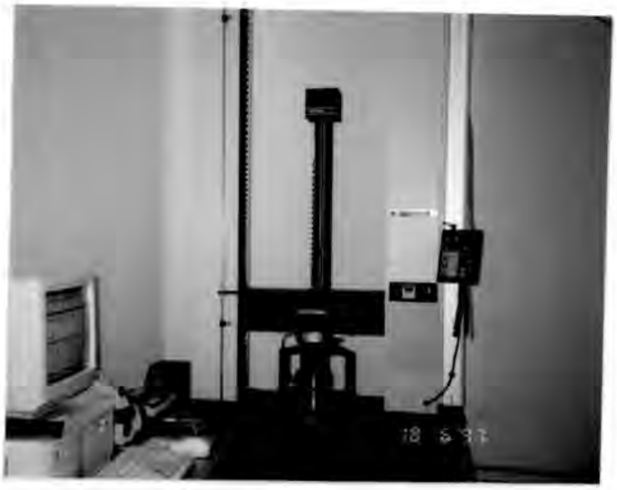


Fig. 3.17 Material testing machine, Instron corporation (series IX automated materials testing system 7.26.00).

3. Water absorption

% water absorption of the test specimens was determined by the method in ASTM C.373-72.

4. Bulk density

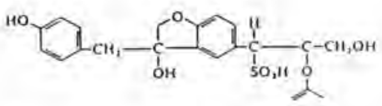
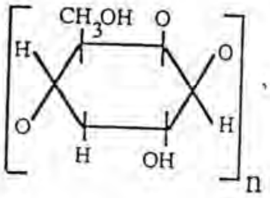
The bulk density of the test specimens was determined by the Archimedes method which described in ASTM C.472-73.

3.8 Preparation of projection plaster from MP

3.8.1 Materials for projection plaster test specimens :

1. MP obtained from the direct method (bulk materials).
2. MP obtained from the indirect method (ready mix powder).

3. Additives supplied by SCC.

- , Sodium lignosulfonate (d. 1.053).
- , Methylcellulose (Tylose, d. 1.342).
- $C_4H_6O_2$, Vinyl acetate (mol. wt. 86.09).

The materials used for projection plaster must have all of particles below 20 µm in size. For this reason, both MP plasters were crushed to pass 14 mesh sieve and ground to fine powder by a high speed mill with various grinding times, ranging from 0–20 min. Particle sizes were calculated from the specific surface areas which were investigated by air permeability apparatus (Blaine).

3.8.2 Methods for the fabrication of projection plaster test specimens from MP

To study the effect of methylcellulose on physical properties of the projection plaster, the test specimens were fabricated as to be described.

Both MPs were each well mixed with distilled water (W/P 0.6) and various amounts of methylcellulose, ranging from 0–0.1% (Fig. 3.18). It was chosen as an additive because of its combined action as both retarder and binder. The mixtures were mixed and poured into a brass mold (160x40x40 mm.). Then, after setting the specimens were taken out of the brass mold, cured and characterized for physical properties. The effect of methylcellulose on the rate of setting of the MP was investigated by a vicat needle apparatus.

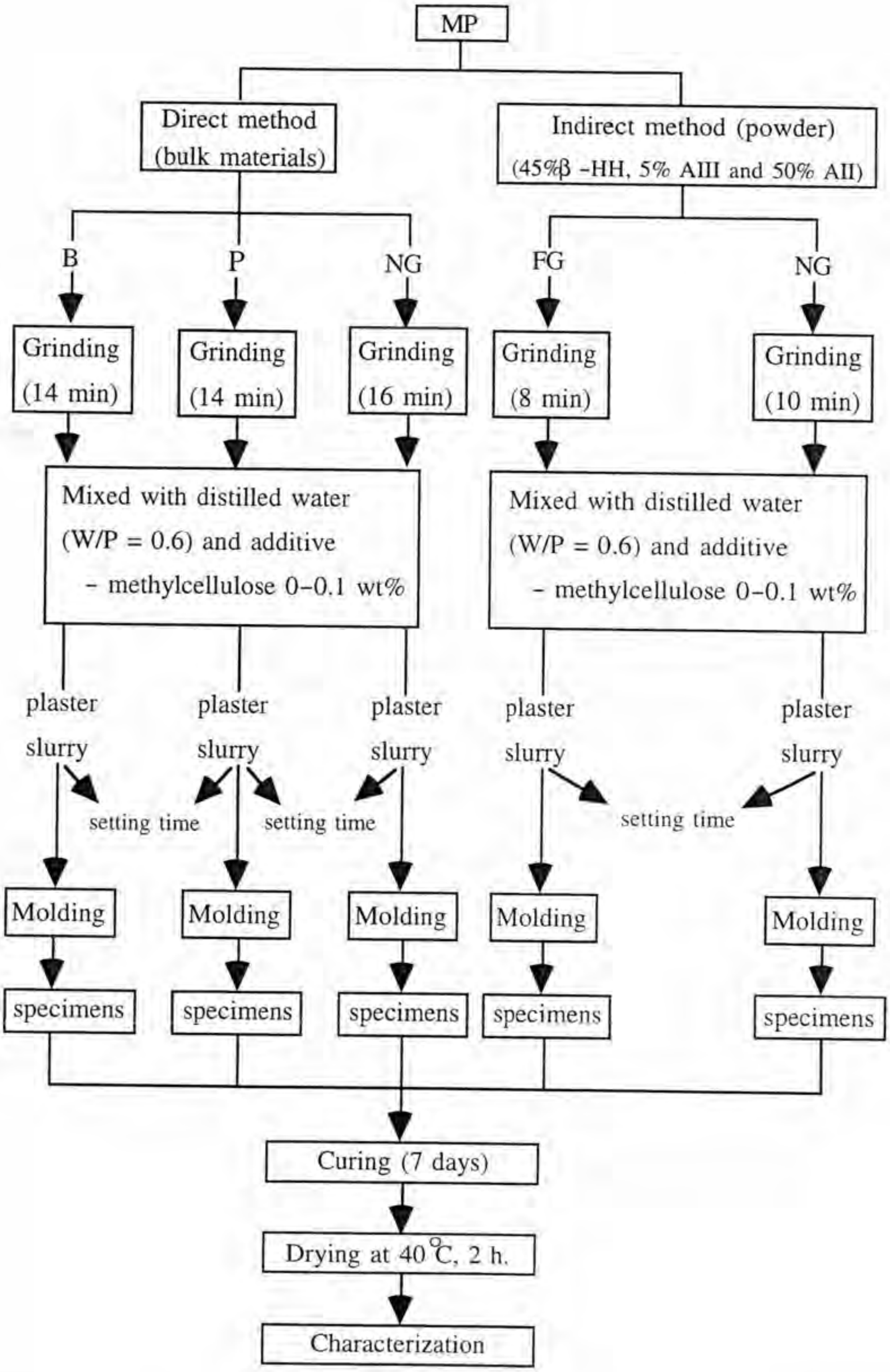


Fig. 3.18 Flow chart for the fabrication of projection plaster test specimens.

3.8.3 Formulation of projection plaster

After the tests described in Fig. 3.18., only MP prepared from calcining the bulk materials was used in the formulation because they had more suitable grain morphology than that obtained from indirect method. B, P and NG ground for 14, 14 and 16 min, respectively, were chosen because they contained all of particle sizes below 20 μm. Projection plaster was prepared by dissolving MP in distilled water with W/P of 0.6. Various amounts of sodium lignosulfonate and methylcellulose, ranging from 0–1% and 0–0.5%, respectively, were added to the mixture (Fig. 3.19). They acted as dispersing agent and binder, respectively. Vigorously stirring by an electric mixer should be done to make a homogeneous projection plaster slurry. Viscosity of the slurry was measured by a Brookfield viscometer. Then, it was manually applied on a cement wallboard and also molded to test specimens.

The projection plaster prepared as described had low strength. So, the addition with various amounts of vinyl acetate, ranging from 0–1% to the slurry was needed as a surface hardener. The sequence of preparation is illustrated in Fig. 3.19.

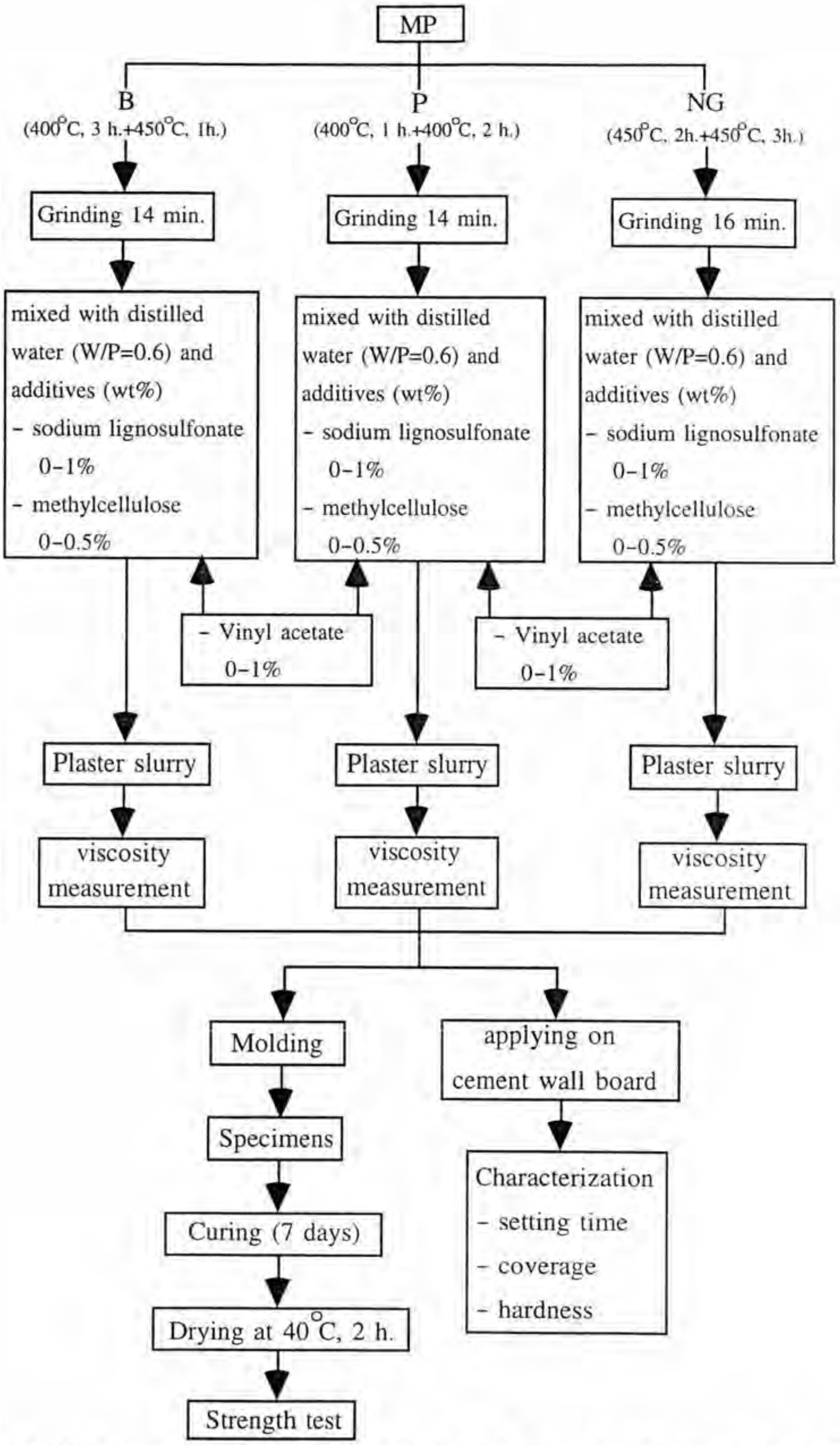


Fig. 3.19 Flow chart for the formulation of projection plaster from MP.

3.8.4 Characterization of projection plaster

1. Setting time

The setting time was tested according to DIN standard (DIN 1168 part 2) using the specimens prepared as described in Fig. 3.19.

2. Rheological property

Rheological property of the projection plaster was carried out following the ASTM designation : D 2196-86 (reapproached 1991). The measurement was performed with a rotational Brookfield viscometer model RVTD AO 4184.

Fig. 3.20 Brookfield viscometer.

3. Hardness of projection plaster

The hardness of projection plaster was determined by pencil test method (ASTM D 3363-92a) using a set of wood pencil as the scale of hardness.

Scale of hardness can be assigned as follow :

6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H

Softer Harder