CHAPTER 4

EXPERIMENT

4.1 Experiment

The experiment is carried out in five sections.

- The first section is raw material characterization that consists of identification of raw materials such as chemical analysis by x-ray fluorescence (Philips PW 1404 and PW 1480), mineral composition analysis by x-ray diffraction (Jeol JDX 3530, Philips PW 1730/10 x-ray diffractometer ; CuK_α radiation, $\lambda = 1.5405$ A°) and thermal properties by differential thermal analysis (Perkin Elmer DTA 7 differential thermal analyzer; heating rate $10^\circ C/min$) and thermal gravitational analysis (Perkin Elmer TGA 7 differential thermal analyzer ; heating rate $10^\circ C/min$). Particle size distribution is investigated by particle size analyzer (Shimadzu SA-CP2) and SEM (Jeol JSM-S410LV scanning electron microscope) for microstructure, shape and size.

Raw materials and additives used in this experiment consist of

1. BCW : the southern ball clay from Nakornsrithammarat, which has high plasticity. BCW is mixed with water, classified to separate the coarse fractions, screened by 200# and de-watered before use.

2. K325 : the Ranong kaolin in form of washed kaolin which has low plasticity but has whiter color before and after firing.

3. B85 : the another Ranong kaolin clay in form of noodle - washed kaolin that has the best color both before and after firing . B85 has physical properties as the same of K325 but whiter and less impurties.

4. Hypure Vector® : spray dried granules from ECC International Ltd. are used to be the reference.

5. Deflocculant : Na_2SiO_3 – density 1.43-1.44 g/cm^3 – from MC Industrial Chemical Co.,Ltd. is the commercial deflocculant used in this work.

6. Binder : Polyacrylic binder (Duramax™ B-1000), supplied by Rohm and Haas company, is employed to control the rheology of slip.

- The second section is formulation and characterization of refined ball clay slip and physical properties of selected formulas. They are formulated by applying triaxial technique to investigate interesting formulas which are mostly nearby commercial refined ball clays. In this step, impurities such as Fe_2O_3 and TiO_2 are regarded as main factors to consider especially less than or closer to Hypure Vector® prototype. Other main oxides of concern are Al_2O_3 and SiO_2 contents. Each chosen formula was made into slip of 50 wt% solid for rheological behavior study on deflocculant demand and cast for both green strength testing (MOR) and fired property testing at 1150°C, 1200°C and 1245°C. Besides, particle size distribution of these formulas was investigated.

- The third section is the slip characterization. Only two interesting formulas were studied in detail on slip properties. Effects of solid content and binder on flow behavior were investigated by Brookfield viscometer, and green strength by a universal testing machine. The refined clay slips were prepared for spray drying under the optimal condition chosen from the experiment.

- The fourth section is spray drying. Spray dryer L8 (Ohkawara Kakohki Co., Ltd.) with a rotary atomizer and co-current flow, is selected for our study. By means of spray drying, the moisture of products is consistent at lower than 3% and easy to use both in mixing and grinding. As-mined ball clay is very sticky when it has high moisture, very hard when it is dried and moisture distribution of the fine particles after pressing is not consistent. The spraying conditions used were atomizer speed at No. 5-50 Hz, equivalent to 32,500 rpm. from the instruction manual, feed rate at 50 ml. per min, inlet and exhaust air temperature at 250°C and 125-140°C, respectively. Condition in spray drying is the important parameter to control size of granules and granule defects simultaneously with slip controlling.

- The last section, the granule characterization is proceeded in two stages. Stage one is general granule characterization such as; moisture content, size and shape of granule by sieve analysis and stereomicroscope examination, apparent density, flow ability of granule and tap density by the flowmeter apparatus and tapping device. Other stage is the workability test of refined spray dried granule. Granule was pressed at various pressures and studied on deformation of granule by using scanning electron microscope (SEM). Physical properties both before and after firing were detected and compared with commercial spray dried ball clay, Hypure Vector®. Furthermore, the modulus of rupture or the green strength of the clay before and after spray drying was also evaluated. The flow chart of all the experiment steps is presented in Fig. 4.1

4.2 Formulation

In this experiment, we try to find out the most suitable composition from the trivial diagram that has good properties both before and after firing compared with Hypure Vector®. Chemical composition from raw materials is the priority to consider by using triaxial technique and calculating the chemical composition as shown in Fig. 5.10 and Table 5.3. Main chemicals, Al_2O_3, SiO_2 including Fe_2O_3 and TiO_2 contents, must be close to Hypure Vector® in the limit $\pm$2% of Al_2O_3 and SiO_2 while the oxides of impurities should be less in this study. Five formulas consist of RC6, RC9, RC10, RC11 and RC12 are chosen because these formulas follow the range of acceptance. Besides, RC formulas should have good rheological property for spray drying. Deflocculant used in this study is Na_2SiO_3 because of its low cost and wide use in ceramic manufacture. Slip preparation at 50 wt% solid (Appendix A) is investigated on deflocculant demand and fully dispersed condition is chosen to prepare specimens for testing of green strength and fired properties at 1150°C, 1200°C and 1245°C.

4.3 Slip characterization

RC9 and RC11 are chosen to study slip properties and flow behavior by varying the solid and binder contents. RC9 contains the solid content in the range of 50 to 60 wt% and the binder (solution) at 0-1 wt% based on dry clay while those of RC11 is in the range of 40-50 wt% and at 1 wt% binder addition. The difference in the solid range is because RC11 has higher ball clay content. The flow of its slip is difficult to process by screening, magnetic separation and by hydrocyclone classifier at low solid content (approximately 30%). The higher ball clay content in the formula, the lower solid content adjustment. Each RC slip is reported for its deflocculant demand by using Brookfield viscometer LV with spindle No.2 at a fixed revolution, 60 rpm. RC slips in fully dispersed condition are chosen for the investigation of flow behavior (Table 4.1) using Brookfield small sample DVII+. The curve between shear stress (τ) and shear rate ($\mathring{\gamma}$) is plotted and the empirical power law equation[23] is employed.

$$\tau = K\mathring{\gamma}^{n} \qquad (4.1)$$

where

τ = Shear stress ($dyne/cm^2$)

K = The consistency index

$\mathring{\gamma}$ = Shear rate (sec^{-1})

n = Empirical constant or flow rate index

$$n = \frac{d(\log \tau)}{d(\log \mathring{\gamma})} \qquad (4.2)$$

where

n = 1 ; Newtonian flow

n < 1 ; Shear thinning constant or pseudoplastic flow

n > 1 ; Shear thickening constant or dilatant flow

Furthermore, slips are characterized for particle size distribution and green strength, especially RC9 which has lower strength than Vector before adding the binder. Only 50%RC9 with 1%Binder is tested in partially dispersed condition by using lower percentage of Na_2SiO_3 to decrease the viscosity and investigated the effect of change on spray drying result.

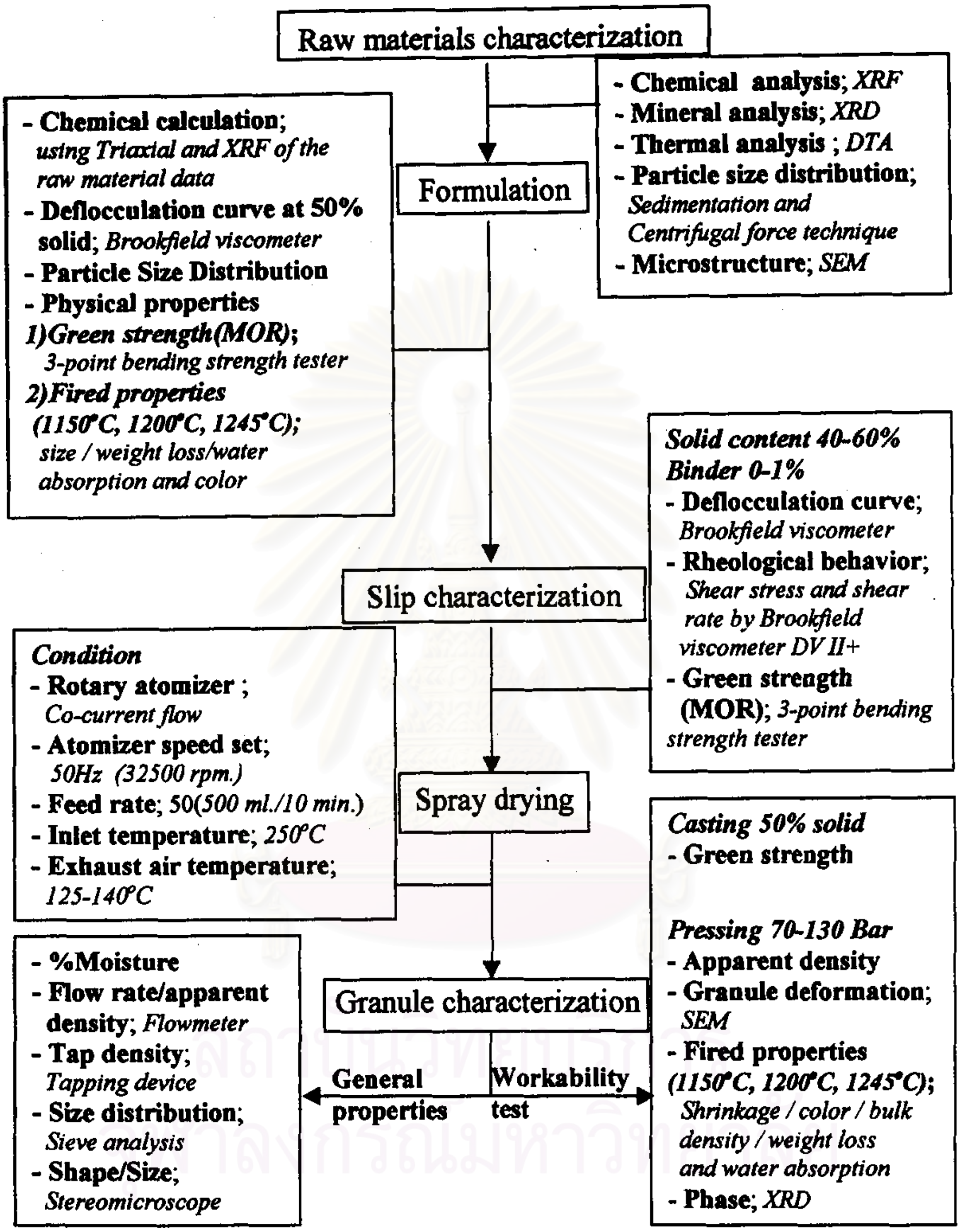

Fig.4.1 Flow chart of experiment

4.4 Spray drying

In this step, RC11 at 46-50% solid were used to test for the condition of spray drying, first by varying the atomizer speed at 21,250-32,500 rpm. (Table 5.7) to observe the atomizer speed effect on size of granules. Unfortunately, at the lower speed of atomizer we found the clogging problem in the atomizer, but the granule size was larger than other conditions. After that the atomizer speed is fixed at 32,500 rpm. and other conditions are in the same patterns as in the flow chart, Fig. 4.1 and the samples used are in Table 5.7 and 5.8.

4.5 Granule characterization

Granule characterization is separated in two parts. The first part is general characterization of granules by mostly referring ASTM test methods. The second part is workability test on dry pressing and green strength after spray drying.

General characterization of granules consists of;

a) % moisture by using 50 g of granule dried in oven at 110°C 24 h. and kept in desiccator before weighing.

$$\% \text{ Moisture} = \frac{50\text{-dry weight}}{50} \times 100 \qquad (4.3)$$

b) Flow rate of granule (ASTM B213)
c) Apparent density (ASTM B212)
d) Tap density (ASTM B527)
e) Size distribution by sieve analysis (ASTM B214). The series of

sieves are 80# (180μm), 120# (125μm), 140# (106μm), 200# (75μm), and 325# (45μm).

f) Shape and size of granules by stereomicroscopic examination. (Zeiss Stereomicroscope Model MC 100 SPOT)

Workability test of granules consists of;

a) Green strength after spray drying.

Slip is prepared at 50% solid with 0.1wt% Na_2SiO_3 addition, stirred with the motor stirrer at the speed of 700 rpm. for 10 min, screened past 40# and casted in cylindrical plaster moulds (1.2 cm diameter and 18 cm in length). After demoulding, test pieces are dried at 110°C for 24 h. at least and kept in a desiccator before breaking with the 3-point bending tester (Hungta Instrument). The green strength (Modulus of Rupture) is calculated from the equation ;

$$MOR = \frac{8PL}{\pi D^3} \qquad (4.4)$$

P = Load at rupture, kg

L = Distance between supports, cm (12.7 cm)

D = Diameter of rupture, cm

MOR = Modulus of rupture, kg/cm^2

(For unit conversion : 1 kg/cm^2 = 0.0980665 MN/m^2 = 0.0980665 MPa)

b) Workability of dry pressing specimen

About 25 g. of granule is pressed in a lubricated metal mold (5.5 cm x 5.5 cm) by a hydraulic press with applied pressures of 7 MPa (70 bar) , 9 MPa (90 bar) and 11 MPa (110 bar).

1. Green density: The pressed specimen is dried at 110°C, 12 h. and kept in a desiccator. Then it is weighed and measured the size.

$$\text{Green density (g/cm}^3) = \frac{\text{Weight of dry specimen}}{\text{Volume of dry specimen}} \quad (4.5)$$

2. SEM: Granule deformation is detected in the planes normal and parallel to the pressure load.

3. Firing shrinkage: The specimens are fired at 1150°C, 1200°C and 1245°C and measured the length of specimen size.

$$\text{\% Firing shrinkage (Dry-Fired)} = \frac{D-F}{D} \times 100 \quad (4.6)$$

D = Length of dry specimen

F = Length of fired specimen

4. % Weight loss : Calculate from weight before and after firing.

$$\text{\% Weight loss} = \frac{\text{Dry weight-Fired weight}}{\text{Dry weight}} \times 100 \quad (4.7)$$

5. %Water absorption and bulk density: following ASTM C373.

6. Color after firing is investigated by Minolta Chromameter CR300.

L = Brightness variable

a = Chromaticity variable where – is green and + is red

b = Chromaticity variable where – is blue and + is yellow

7. XRD: The phase occurred after firing from interesting formula was investigated by an x-ray diffractometer.