Chapter III

Experiment Procedure.

Before starting the experiment, the appropriate grinding time of both in the laboratory and in the production should be set for the same result. These could be done by using rapid pot mill with 800 gm. raw materials capacity and ball mill with 80kg. raw materials capacity respectively.

From pot mill grinding, the samples after grinding times 25,45,65,and 85 min. were picked up.

For ball mill grinding, the samples after grinding times 24,36,48,60,72,and 84 hr. were picked up.

All these samples were characterized for the most suitable finess within the same result. After choosing the appropriate grinding time, the batch compositions were set up, then further experiments were continued.

[The grinding results were shown in appendix 1.]

The experiments were divided into two parts ;

Part 1. Preparation of specimens by casting.

This part provided for choosing the most suitable composition and sintering temperature before starting production. The specimens of different compositions would be determined by comparison the physical properties after sintering.

Part 2. Production of liners by extrusion forming method.

The suitable alumina body, chosen from the experiment in part 1., would be extruded in the desired shape and after drying, they would be sintered at the same sintering temperature as defined from part 1.

3.1 Equipment.

   3.1.1 Equipments for Experiment and Production.
      - Electrical balance
      - High alumina pot mill and balls
      - Hot air dryer
      - Experimental gas kiln
        [maximum temperature 1700 c.]
      - Plaster mould [rod shape with 18 mm.diameter
        and 200 mm. long.]
      - Ball mill with high alumina liners and balls.
      - Sieve no. 150 and 400 mesh
      - Magnetic ferro filter
      - De-airing extruder
      - Filter press

   3.1.2 Equipments for characterization.
      - Centrifugal particle size analyzer
        [Shimadzu, model: SA-CP 2]
      - Scanning electron microscope
        [Jeol, model: JSM-35 CF]
      - X-Ray diffractometer [XRD]
        [Phillips, no. DY 1023 Type: PW 1730/10]
      - Energy dispersive spectrometer [EDS.]
        [NORAN series 5502]
      - 3-points bending testing machine
      - Dilatometer
        [Orton Dilatometer, model 1000.]
      - Impact strength testing machine
        [model JB.300]
      - Hardness testing machine
        [model HRU. 45]
      - Olympus Microscope

3.1.3 Raw material and chemical used in this
investigation

1. <u>Calcined alumina</u>

A-11   standard grade from Nippon Light Metal Company, Japan.

A-12   standard grade from Showa Company, Japan.

A-21   medium grade from Sumitomo Company, Japan.

    2. <u>Bentonite</u>
       from Siam Fine Clay Company, Thailand.

    3. <u>Ball clay</u>
       from Compound Clay Company, Thailand.

    4. <u>Wallastonite</u>
       from Ceramic ´R Us Company, Thailand.

    5. <u>Talcum</u>
       from MC Company, Thailand.

    6. <u>Dispex</u>
       from Loxley Company, Thailand.

The raw materials characterizations were presented in clause 4.1

3.2 Part 1. Preparation of Specimens.
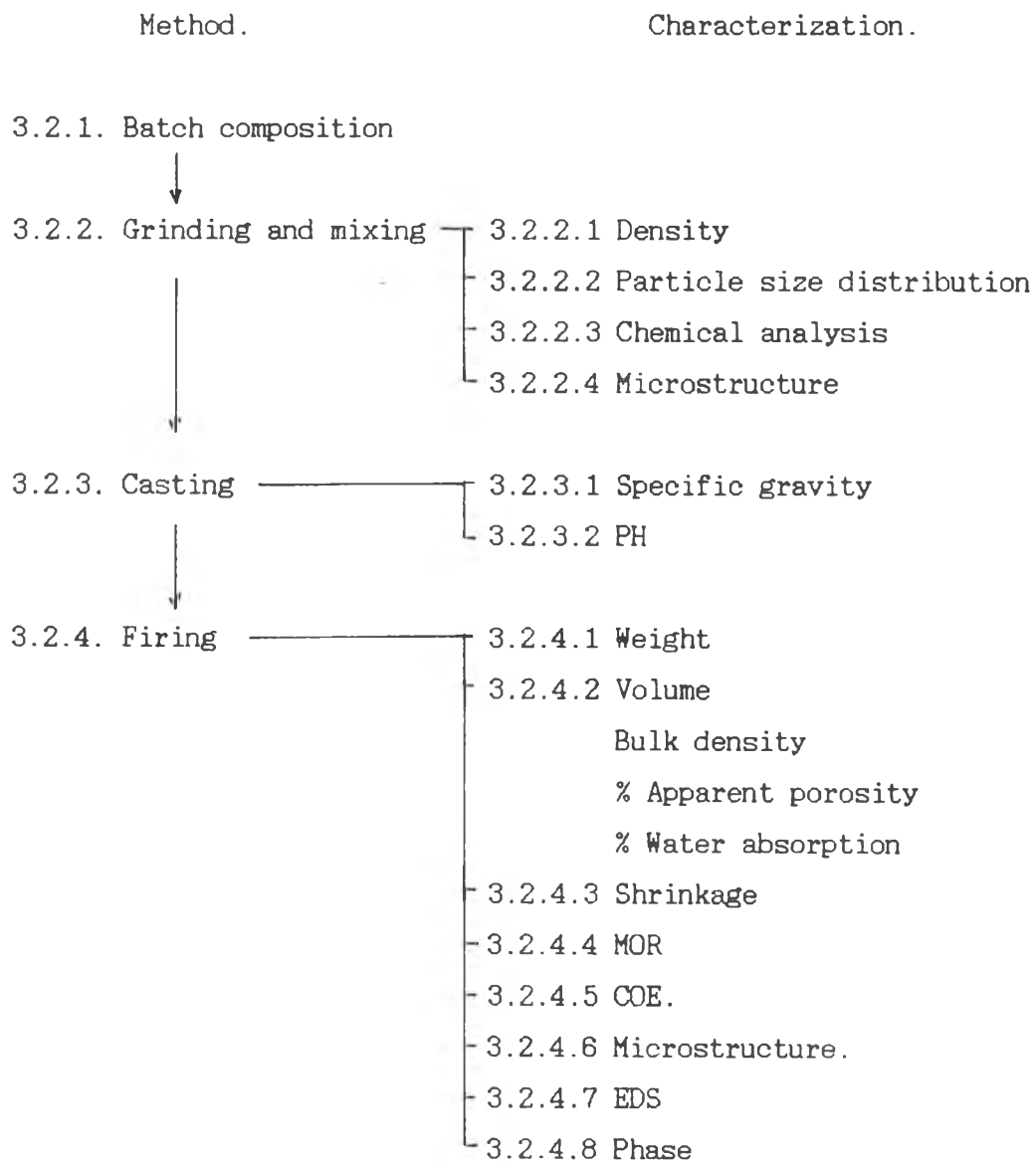
Determination of the starting composition.

From the literature survey no. II and according to the fact that the higher the % Al_2O_3, the higher the mechanical properties, this could be gained with proper sintering aids to provide good sintering in the desired firing schedules and proper plasticity for extrusion forming method which were the main purposes of this experiment.

The five compositions with various ranges in % Al_2O_3, % sintering aids (talc and wallastonite), and % plasticity (ball clay and bentonite) were defined as followed ; Table 2. Five starting compositions.

Material	LI-16	LI-19	LI-22	LI-23	LI-24
Calcined alumina	82.40	84.00	88.00	90.00	92.50
Ball clay [MC]	5.40	5.00	3.00	2.00	2.00
Bentonite	5.40	4.00	3.50	3.00	3.00
Talcum	3.40	4.50	4.00	4.25	2.15
Wallastonite	3.40	2.50	1.50	0.75	0.35

After this first trial experiment (see appendix 2.), only LI-22 and LI-23 compositions were continued by the following process flow chart.

Process Flow Chart of Specimens Preparation.

Method.   Characterization.

3.2.1. Batch composition

3.2.2. Grinding and mixing ── 3.2.2.1 Density

3.2.2.2 Particle size distribution

3.2.2.3 Chemical analysis

3.2.2.4 Microstructure

3.2.3. Casting ──────── 3.2.3.1 Specific gravity

3.2.3.2 PH

3.2.4. Firing ──────── 3.2.4.1 Weight

3.2.4.2 Volume

Bulk density

% Apparent porosity

% Water absorption

3.2.4.3 Shrinkage

3.2.4.4 MOR

3.2.4.5 COE.

3.2.4.6 Microstructure.

3.2.4.7 EDS

3.2.4.8 Phase

3.2.1 Batch Composition.

The 2 batch compositions were prepared as followed ;

Table 3. Batch composition

Material [gm.]	LI-22	LI-23
Calcined Al_2O_3	704.0	720.0
Ball clay	24.0	16.0
Ca-bentonite	28.0	24.0
Talcum	32.0	34.0
Wallastonite	12.0	6.0
Total	800.0	800.0

3.2.2 Grinding and Mixing.

Pot mill of mill volume 1000 cc. was filled with 900 gm. of balls (diameter 1.5-2.0 cm.), the 800 gm. batch composition as shown in table 3, 560 cc. water and (0.2 gm./cc.) Dispex N40 = 8 cc.

The sample after grinding time 85 min. were picked up, dried and sieving through 150 mesh then characterized by SEM and particle size analyzer.

The results were shown in Table 13 and Fig.17

Characterizations.

3.2.2.1 Chemical analysis

From the chemical analysis of the raw material used, the chemical analysis of the LI-22 and LI-23 composition could be calculated as presented in Table 11.

3.2.2.2 Density ; by using pycnometer.

$$D = \frac{[R-P]}{[R-P] - [S-Q]}$$

Where; P = weight of pycnometer bottle [gm.]
        Q = weight of pycnometer bottle + water [gm.]
        R = weight of pycnometer bottle + powder [gm.]
        S = weight of pycnometer bottle + powder + water [gm.]

Table 4. Density data of composition
Data ; For LI-22 composition.

	P	Q	R	S
1.	30.39	80.30	32.58	81.88
2.	30.24	80.24	32.22	81.65
3.	30.23	80.24	32.26	81.69
4.	30.38	80.33	32.58	81.89

For LI-23 composition.

	P	Q	R	S
1.	30.38	80.33	32.47	81.83
2.	30.38	80.28	32.68	81.95
3.	30.22	80.27	32.36	81.81
4.	30.38	80.30	32.34	81.33

The results were shown in Table 12.

3.2.2.3 Particle Size Distribution.

By using the particle size analyzer and
the average density of powder calculated in Table 12 , the
particle size distribution curves and results were shown in Fig.17
and Table 13 .

3.2.2.4 Morphology.

By using the scanning electron
microscope, the morphology of LI-22 and LI-23 powder
compositions could be observed. The SEM micrographs and results
were shown in Fig.18.

3.2.3 Casting

Slip means liquid clay mixture and also means suspension of powder in aqueous medium for non-clay ceramic.

In slip casting of high alumina body, the slip should be in a deflocculated state which was obtained with acids, chiefly hydrochloric acid and the addition of the proper amount of water and deflocculant. The viscosity of slurry was affected by the charged different. The basic factors with making slip-casting possible were ion exchange capacity and the presence of some portion of colloids which behaved like true molecules. If the powder was too fine, slip-casting became impossible as there would be no proper build-up on the mould surface and the cast would badly crack during drying. It was important to avoid uniform finess, the reasonable slip properties were obtained with powders consisting of not more than 30 % of crystals below 1μm.[including the colloidal fraction] and 25-30% above 10 μm.to provided suitable packing. The maximum specific gravity obtained by the appearence of dilatancy in the system.

The LI-22 and LI-23 slurries, their pH were adjusted by adding hydrochloric acid [dil.] , the deflocculant used was Dispex N 40 [sodium salt of polycarboxylic acid, pH 7.5] for appropriate viscosities, and aging for 10 days.

Before casting, the slurries were determined for specific gravity and pH. values.

3.2.3.1 Specific Gravity ; by using pycnometer.

$$S = \frac{W_1 - W}{W_2 - W}$$

Where ; W = weight of pycnometer bottle [gm.]

W_1 = weight of pycnometer + slurry [gm.]

W_2 = weight of pycnometer + water [gm.]

Table 5. specific gravity data of composition

Data ;

Slurry	W	W_1	W_2
LI-22	30.56	122.66	80.17
LI-23	30.23	126.95	79.83

The results were shown in Table 14.

3.2.3.2 pH. of LI-22 and LI-23 slurries.

By using the pH. paper indicator ,the results were shown in page 89.
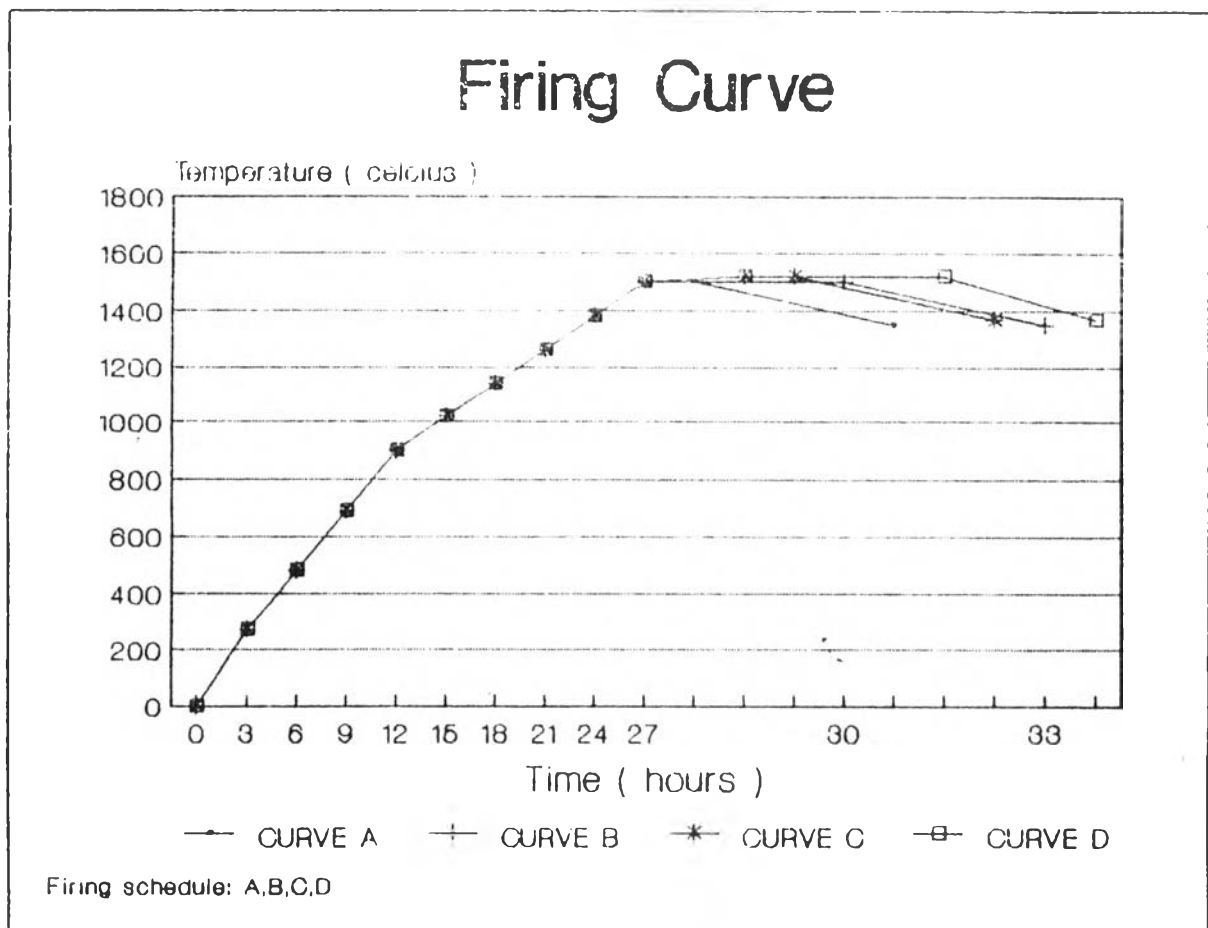
3.2.4 Firing.

After casting, the specimens were aired dry and prepared for firing. The firing schedules were shown in Fig.5 and Table 6.

Table 6. Firing schedule

Curve no.	Firing time [hours]	Maximum temperature [°C.]	Soaking time [hours]
A.	27	1500	1/4
B.	27	1500	3
C.	27	1520	1/4
D.	27	1520	3

Fig. 5 Firing schedule.

Firing schedule: A,B,C,D

After firing,the specimens were characterized as followed.

3.2.4.1 Weight (according to ASTM designation no. C373) by using electrical balance, suitable to weight accurately to 0.01 gm.

The specimens were dried by heating in an oven at 150 °C., followed by cooling in a desicator, then determined the dry mass "W" to the nearest 0.1 gm.

The specimens were placed in a pan of water and boiled for 5 hours, in which all the specimens were covered with water. After the 5-hr. boil,the specimens were allowed to soak for an additional 24 hours.

After impregnation, weighing the suspened mass "S" by placing the specimen in a basket which immerse in water,then blotted each specimen lightly with a cotten cloth to remove all excess water from the surface and determine the saturated mass "M" to the nearest 0.01 gm. also.

The results of "W", "S", and "M" of the LI-22 and LI-23 specimens were shown in Table 15.

3.2.4.2 <u>Shrinkage</u> ; the total linear shrinkage of specimens after drying and firing were calculated as a percentage as followed ;

$$S_1 = \frac{[L_P - L_f] \times 100}{L_P}$$

where; S_1 = % total linear shrinkage after drying and firing,

L_P = plastic length of test specimen, mm.,

L_f = fired length of test specimen, mm.

Table 7. Shrinkage data of specimen

no.	LI-22		LI-23	
	L_P	L_f	L_P	L_f
1.	95.7	74.8	96.3	75.4
2.	93.5	73.7	97.4	77.6
3.	93.5	74.3	97.4	76.5
4.	92.4	73.7	97.9	75.9
5.	95.2	73.7	96.8	74.7
6.	93.5	73.2	96.3	75.4
7.	94.1	72.6	97.4	75.9
8.	94.1	73.7	96.3	76.5
9.	93.5	73.7	96.3	77.0
10.	94.1	73.7	95.7	76.5

[The results were shown in Fig.19]

3.2.4.3 Calculations :

The volume "V", bulk density "D",
% apparent porosity "P", and % water absorption "A" were calculated
by using these formulas ;

$$V = M - S$$

$$D = W / V$$

$$P = \frac{[M - W] \times 100}{V}$$

$$A = \frac{[M - W] \times 100}{W}$$

[The results were shown in Fig.20]

3.2.4.4. Modulus of Rupture. [MOR.]

The prepared specimens [rod shape] were fired at different temperatures and soaking times. After firing, determined the modulus of rupture of these specimens by measuring the transverse strength [by three-points bending] of them and the MOR. could be calculated from ;

$$MOR. = \frac{8WL}{\pi D^3}$$

where ; W = load applied, [kg.]

L = span length, [cm.]

D = diameter of specimen, [cm.]

The datas of testing were shown as followed ;

Table 8. The breaking load of specimens

Curve A. 1500° c. + 1/4 hour soaking

The breaking load [Kgs.] of specimens were ;

	LI-22	LI-23
1.	236.375	241.750
2.	192.000	235.500
3.	222.125	276.250
4.	211.125	276.000
5.	200.625	210.250
6.	250.625	251.500
7.	217.625	210.500
8.	226.500	283.000
9.	205.625	-
10.	241.875	-
ave. diameter[cm.]	1.37	1.43

Curve B.   1500 c. + 3 hours soaking.

The breaking load [Kgs.] of specimens were ;

no.	LI-22	LI-23
1.	244.500	330.750
2.	251.000	271.250
3.	236.250	257.500
4.	254.250	296.500
5.	246.250	248.500
6.	227.750	259.750
7.	219.500	285.750
8.	284.500	272.750
9.	219.500	250.000
10.	242.75	–
ave. diameter[cm.]	1.37	1.44

Curve C.   1520°c. + 1/4 hour soaking.

The breaking load [Kgs.] of specimens were ;

no.	LI-22	LI-23
1.	245.500	230.000
2.	211.250	236.750
3.	218.500	241.750
4.	265.500	223.250
5.	217.250	253.000
6.	210.500	270.000
7.	212.250	259.250
8.	281.750	201.250
9.	268.000	269.250
10.	230.000	-
ave. diameter[cm.]	1.36	1.40

Curve D. 1520 c. + 3 hours soaking.

The breaking load [Kgs.] of specimens were ;

no.	LI-22	LI-23
1.	255.500	252.750
2.	219.750	260.000
3.	215.000	235.750
4.	219.000	224.000
5.	232.750	287.0C0
6.	301.000	290.500
7.	236.750	309.500
8.	249.500	263.000
9.	227.250	255.500
10.	238.750	–
11.	301.000	–
ave. diameter[cm.]	1.35	1.38

The MOR. results were shown in Fig.21   and appendix 3.

3.2.4.5. <u>Coefficient of Linear Thermal Expansion</u>

The test specimens were subjected to the firing curve D.[1520° C. + 3 hour soaking] ,the length of specimens after firing must be 1.00 inch. $\pm$ 0.1 % with flat ground ends and perpendicular to the axis of the specimen. Insert the test specimen into the furnace of the dilatometer at room temperature. Apply power to the furnace and make adjustments from time to time to give a heating rate of not more than 3° c./ min., take temperature and expansion readings at no greater interval than 25° c.

Calculate the percentage expansion by plotting directly with automatic recording apparatus, the COE. could be calculated at any temperature range, T_1 to T_2, with in the limits of the test, as followed ;

$$P = \frac{[L \times 100]}{L_0} + A$$

$$\alpha = \frac{0.01\ P}{T_2 - T_1}$$

where ; P = percent linear thermal expansion from temperature T_1 to T_2.

L_0 = sample length at T_0 [between 20° and 30° c.]

L_1 = sample length at T_1

L_2 = sample length at T_2

A = instrument correction.

The results were shown in Fig.22

3.2.4.6 Microstructure :

The specimens of LI-22 and LI-23 were broken and the fracture surface were determined by using scanning electron microscope[SEM]. The SEM micrographs were shown in Fig.23

3.2.4.7 EDS analysis :

The emission spectroscopy based on arc and spark source, the energy supplied was enough to stimulate various elements in the sample to be in the excited state and emit radiation, by continuous line spectrum.

Line spectra caused by the returning of exited state to ground state of the external valence electron of element showed particular characteristic of those elements. From this principle, we could determine the elements composed in the sample.

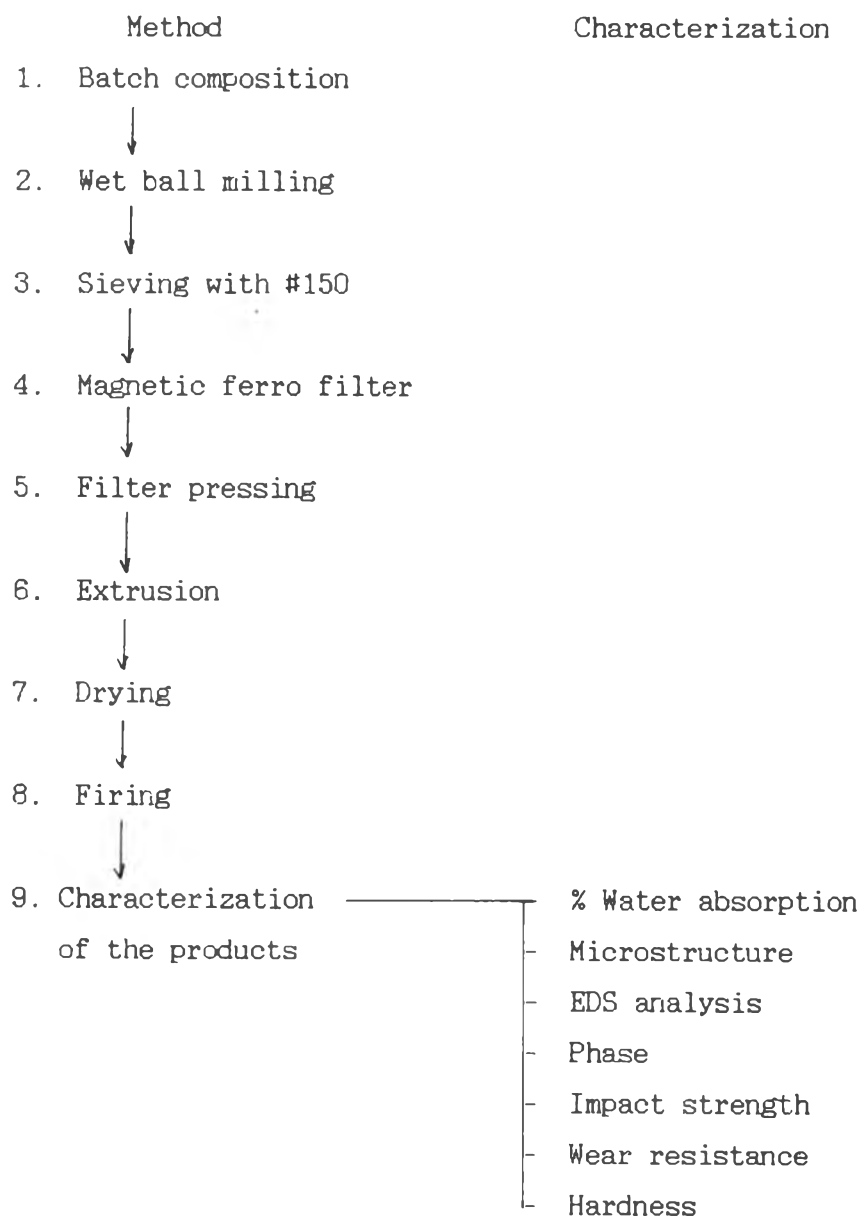The results of EDS analysis were shown in Table 17.

3.2.4.8 Phase analysis :

The powder of LI-22 and LI-23 specimens sintered from firing schedules A,B,C,and D were prepared for XRD analysis. The phases presented in all these samples were shown in XRD patterns in 4.4.8

3.3 Production of Liners by Extrusion Forming Method

By extrusion experiment, the LI-23 had good appearace and shown no defects and cracks after drying,together with the results of specimens experiment we could conclude that LI-23 composition was suitable for large scale production.

The liner-production flow chart was set up according to the production process, as followed ;

Process flow chart of the liner production

Method   Characterization

1. Batch composition
   ↓
2. Wet ball milling
   ↓
3. Sieving with #150
   ↓
4. Magnetic ferro filter
   ↓
5. Filter pressing
   ↓
6. Extrusion
   ↓
7. Drying
   ↓
8. Firing
   ↓
9. Characterization ──────────┬── % Water absorption
   of the products   ├─ Microstructure
                              ├─ EDS analysis
                              ├─ Phase
                              ├─ Impact strength
                              ├─ Wear resistance
                              └─ Hardness

Batch composition LI-23

Calcined Al_2O_3 (Kg.)	72.0
Ball clay MC	1.6
Ca- bentonite	2.4
Talcum	3.4
Wallastonite	0.6
Total	80.0 kg.
Water	56.0 kg.

After grinding and mixing, the powder of composition was prepared for chemical analysis, by EDS.

The result was presented in Table 11b .

Filter Pressing and Extrusion

The 22 % moisture content of the filter cake exhibitted surface crack to the extruded column, small cracks entered at the edge and the crack arose from the greater friction at the corner of the die than on the faces. When the moisture content was decreased to 20 % , the extruded column could be done with in the certain shape and without crack.

Firing

After extrusion, the green bodies were dried and fired in the shuttle kiln with the firing curve D.

Characterization

- _% Water absorption_ : According to ASTM
  designation C373, the results were shown in Table16

- SEM and EDS analysis ;
  The product was broken and some of the fracture
  pieces were prepared for SEM and EDS analysis.
  The results were shown in Fig.24,25,26 and Table 18.

- Phase analysis :
  The product was broken and ground into powder form
  and determined the phases by XRD analysis.
  The XRD pattern was presented in Fig. 27.

- Impact Strength. ;

  The liner[before firing] was cut into 5 pieces [bar
shape],with the size about 12.5 mm.x12.5 mm.x68.5 mm. and then
fired by using firing curve D. After firing, the surfaces of these
specimens were ground for accuracy measurement to the size
10.0 mm.x 10.0 mm.x 55.0 mm. for impact strength testing
[Chrapy Impact Test.] according to ASTM designation E23.The results
were shown in Fig.29.

- Wear Resistance [Abrasion test].

  The ability to resist fracture of liners could be
measured by ball milling. This experiment was set up by using
laboratory pot mill in such the same way of preparation as the
test specimens. The pot mills were prepared by casting the
LI-23 composition and after drying, they were fired in
laboratory shuttle kiln, using firing curves A,B,C and D.

After firing, weight of pot mill was recorded and then 900 gm. of ball, 800 gm. of tabular alumina and 560 cc. of water were put into the pot mill. The grinding time was fixed at 48 min./cycle. After grinding the slurry was taken off. The pot mill was cleaned with water and put into the 150 c. dryer for 1 hour. After drying, the weight of pot mill was recorded again. The experiments were done again until the weight loss of pot mill was nearly stable.

[according to appendix. 5]

The results were shown in Fig. 28 and Table 19-20.

- Hardness :

The liner was broken and some fractures were mounted into bekelite and polised, then the hardness was examined by the Rockwell 45 N system.[ASTM. E.18]

The results were shown in clause 4.4.9