CHAPTER III

EXPERIMENTAL PROCEDURES

3.1 Raw materials

Raw materials used in this research are listed in the following:

- Hydrometallurgical zinc waste (Padaeng Industry Public Co., Ltd.)
- Traditional tile body (Thai Ceramic Co., Ltd.)
- Transparent frit; FP-921 (Ferro (Thailand) Co., Ltd.)
- Transparent frit; FP-936 (Ferro (Thailand) Co., Ltd.)
- Opaque (zircon) frit; FP-436 (Ferro (Thailand) Co., Ltd.)
- Lead silicate frit; UC-7822 (Unicer Co., Ltd.)
- ZnO (Toblight Co., Ltd.)
- Zirconium silicate (Industric Bitossi s.p.a.)
- Boric acid (Fisher Scientific UK Limited.)
- $MgCO_3$ (HiMedia Laboratories Put.Ltd.)
- Silica sand (Sibelco Minerals (Thailand) Co., Ltd)
- Kaolin (Ranong clay)
- Na-feldspar (Sibelco Minerals (Thailand) Co., Ltd)
- K-feldspar (Sibelco Minerals (Thailand) Co., Ltd)
- Fe_2O_3
- Limestone
- Soda ash
- Dolomite

3.2 Characterization of zinc waste

Hydrometallurgical zinc waste from the plant of Padaeng Industry Public Co., Ltd., was characterized by using various techniques as follows:

- Phase composition was analyzed by X-ray diffractometer (Bruker D8 Advance), with K_α Cu radiation, $10^\circ<2\theta<70^\circ$, step size 0.02 degree, 40 KV and 40mA.
- Chemical composition was examined by X-ray Fluorescence spectroscopy (Phillips Pw-2400).
- Particle size distribution was measured by Master sizer (Malvern, Masterrrizer Ver 2.19).

3.3 Experimental procedure

3.3.1 Preparation of tile bodies

Batch compositions of tile bodies were formulated using the mixtures of traditional tile body and zinc waste in different proportions. All of batch compositions are shown in Table3.1. Their chemical compositions, which were calculated from the chemical composition of zinc waste and traditional tile body based on the proportions, are shown in Table 3.2.

Table 3.1 Batch composition of tile bodies

Formula	Zn-waste (wt %)	Traditional tile body (wt %)
T1	0	100
T2	10	90
T3	20	80
T4	30	70
T5	40	60
T6	50	50
T7	60	40
T8	70	30
T9	80	20
T10	90	10
T11	100	0

Each batch composition of tile was prepared by wet milling in a high speed ball mill for different times to obtain a residue of 3 wt% on a sieve of #230 mesh (63 μm). After that, the slurry was dried at 110°C and ground to powder. The moisture content of dried powder was adjusted to a moisture content of 5 wt%, aged for 24 h in closed container and then was sieved through of a sieve #35 mesh (500 μm) for granulation purpose. The granulated powder was pressed by uniaxial pressing under pressure of 270 Kg/cm^2. The specimens were dried at 110°C and fired at temperatures between 1075°C and 1175°C. The firing schedule comprised heating at rate of 5°C/min and soaking at maximum temperature for 20 minutes in an electric furnace.

Table 3.2 Chemical compositions of tile bodies

Oxides	Formula (wt%)										
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11
SiO_2	71.50	70.06	68.61	67.17	65.73	64.29	62.85	61.41	59.97	58.53	57.09
Al_2O_3	19.66	18.11	16.55	14.99	13.44	11.88	10.32	8.76	7.21	5.65	4.09
Na_2O	4.37	3.93	3.50	3.06	2.63	2.19	1.75	1.32	0.88	0.45	0.01
MgO	0.52	0.58	0.65	0.72	0.79	0.86	0.92	0.99	1.06	1.13	1.19
K_2O	1.82	1.73	1.63	1.53	1.43	1.33	1.23	1.13	1.03	0.93	0.83
CaO	1.01	1.94	2.86	3.78	4.71	5.63	6.56	7.48	8.40	9.33	10.25
Fe_2O_3	0.53	1.23	1.94	2.64	3.34	4.04	4.74	5.44	6.14	6.84	7.55
ZnO	-	0.954	1.91	2.86	3.81	4.77	5.72	6.67	7.62	8.58	9.53
SO_3	-	0.48	0.96	1.44	1.92	2.41	2.89	3.37	3.85	4.33	4.81
PbO	0.01	0.13	0.25	0.37	0.50	0.62	0.74	0.86	0.99	1.11	1.23
TiO_2	0.35	0.34	0.32	0.30	0.29	0.27	0.26	0.24	0.22	0.29	0.19
P_2O_5	0.19	0.18	0.17	0.16	0.15	0.14	0.14	0.13	0.12	0.11	0.10
MnO	-	0.054	0.11	0.16	0.21	0.27	0.32	0.38	0.43	0.48	0.54
ZrO_2	1.59	1.43	1.27	1.11	0.95	0.79	0.64	0.48	0.32	0.16	-
CuO	-	0.02	0.03	0.05	0.07	0.09	0.10	0.12	0.14	0.15	0.17
BaO	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	-	0.02	-
L.O.I.	-	-	-	-	0.02	0.41	0.81	1.21	1.62	1.92	2.42

3.3.2 Preparation of glaze for stoneware

To investigate the possibility of using zinc waste as color stain of glaze for stoneware tile, zinc waste was mixed with other raw materials of glaze. The batch compositions are shown Table 3.3 and Table 3. 5. Their chemical compositions, in form of oxides are also calculated and presented in Table 3.4 and Table 3.6.

Raw materials were precisely weighed. The glaze slip then was mixed in a high speed ball mill for various times, to obtain a residue of less than 3% on sieve

#325 mesh. The density of slip was adjusted to 1.6 g/cm^3 density. After that, slip was glazed on green tiles and dried in air for 24 h. The tiles were fired at 1230°C for 20 min with a heating rate of 3°C/min.

Table 3.3 Batch compositions of glossy glaze

Raw materials	Formula			
	GG1	GG2	GG3	GG4
Na-feldspar (g)	45	45	45	45
Silica sand (g)	30	30	30	30
ZnO (g)	10	10	10	10
Limestone (g)	15	15	15	15
Kaolin (g)	5	5	5	5
Zirconium silicate (g)	5	5	5	5
Zinc-waste (%)	-	5	10	15
Water (cc)	50	50	50	50

Table 3.4 Chemical compositions of glossy glaze

Oxides	Formula (wt%)			
	GG1	GG2	GG3	GG4
SiO_2	65.00	67.85	70.71	73.56
Al_2O_3	10.57	10.77	10.98	11.18
CaO	8.41	8.92	9.43	9.95
Na_2O	5.33	5.33	5.33	5.33
K_2O	0.10	0.14	0.18	0.22
ZrO_2	3.36	3.36	3.36	3.36
ZnO	10	10.48	10.95	11.43
Fe_2O_3	-	0.38	0.75	1.13
MgO	-	0.06	0.12	0.18
PbO	-	0.06	0.12	0.18
SO_3	-	0.241	0.48	0.72

Table 3.5 Batch compositions of for matt glaze

Raw materials	Formula			
	MG1	MG2	MG3	MG4
K-feldspar (g)	40	40	40	40
Silica sand (g)	25	25	25	25
Al_2O_3 (g)	10	10	10	10
Limestone (g)	20	20	20	20
Kaolin (g)	10	10	10	10
Zirconium silicate (g)	5	5	5	5
Zinc-waste (%)	-	5	10	15
Water (cc)	50	50	50	50

Table 3.6 Chemical compositions of matt glaze

Oxides	Formula (wt%)			
	GG1	GG2	GG3	GG4
SiO_2	57.40	60.26	63.11	65.96
Al_2O_3	20.97	21.17	21.38	21.58
CaO	11.22	11.74	12.25	12.76
Na_2O	0.02	0.02	0.02	0.02
K_2O	6.97	7.01	7.05	7.10
ZrO_2	3.36	3.36	3.36	3.36
ZnO	-	0.48	0.95	1.14
Fe_2O_3	-	0.38	0.75	1.13
MgO	-	0.06	0.12	0.18
PbO	-	0.06	0.12	0.18
SO_3	-	0.241	0.48	0.72

3.3.3 Preparation of glaze for floor tiles

Similar to glaze for stoneware tile, zinc waste was added to common glaze for floor tile. Their batch compositions are shown in Table 3.7. Four different kinds

of frit were used as basic glaze for floor tile glazes. Each batch of glaze was ground by high speed pot mill to attain a residue of 3 wt% on sieve #325 mesh. Then, adjusting the slip density to 1.6 g/cm^3 and glazed on engobed tiles. After that, glazed tiles were dried in air for 24 h and fried at 1150°C for 15 min with a heating rate of 3°C/min. The composition of engobe is shown in Table 3.8.

Table 3.7 Batch composition of glaze for floor tiles

Raw materials	Formula			
	TG1	TG2	TG3	TG4
Transparent frit (FP-921) (g)	90	-	-	-
Transparent frit (FP-936) (g)	-	90	-	-
Opaque (zircon) frit (FP-436) (g)	-	-	90	-
Lead silicate frit (UC-7822) (g)	-	-	-	90
Kaolin (g)	10	10	10	10
Zinc-waste (%)	10	10	10	10
Water (cc)	50	50	50	50

Table 3.8 Batch composition of engobe for floor tiles

Raw materials	Wt %
Opaque (zircon) frit (FP-436)	20
Na-feldspar	15
Clay	34.7
Zirconium silicate	20
Al_2O_3 (A-21)	10
CMC	0.3
Water	50
Density 1.6 g/cm^3	

3.3.4 Preparation of frit from zinc waste

Table 3.9 show the chemical composition of zinc waste (100% waste), analyzed by XRF. This indicated that the waste composed of various oxides such as

SiO_2, CaO, Al_2O_3, Fe_2O_3 and ZnO which are probable to use as raw material to make ceramic frit. This designed frit compositions are shown in Table 3.10. Compare this designed composition with zinc waste composition, it was found that the waste contains more amount of SiO_2, Al_2O_3, Fe2O3 and ZnO and less CaO, Na_2O, B_2O and MgO than the designed composition, This problem have been solved by reducing percent of zinc waste to 30% and adding other raw materials to produce suitable percent of oxides in each formula in Table 3.10.

Table 3.9 Calculation of suitable percent oxide of zinc waste as raw material.

Oxides	100% Zn waste	30% Zn waste
SiO_2	57.09	17.13
Al_2O_3	4.09	1.23
Na_2O	0.01	-
CaO	10.25	3.08
Fe_2O_3	7.55	2.26
ZnO	9.53	2.86
B_2O_3	-	-
MgO	1.19	0.36
PbO	1.23	0.37

Table 3.10 Chemical composition of frit

Oxides (wt %)	Formula			
	F1	F2	F3	F4
SiO_2	62	52	49	60
Al_2O_3	3	3	3	3
Na_2O	10	10	5	10
CaO	15	15	15	15
Fe_2O_3	7	7	5	5
ZnO	3	3	3	3
B_2O_3	-	10	10	4
MgO	-	-	10	-

Table 3.11 Raw materials used for frit melting.

Raw materials	Formula (wt%)			
	F1	F2	F3	F4
Silica sand	44.87	34.87	31.87	42.87
Al_2O_3	1.77	1.77	1.77	1.77
Soda ash	17.10	17.10	8.56	17.10
Limestone	21.28	21.28	-	21.28
Fe_2O_3	4.74	4.74	2.74	2.74
ZnO	0.14	0.14	0.14	0.14
Boric acid	-	17.76	17.76	7.11
$MgCO_3$	-	-	1.07	-
Dolomite	-	-	39.21	-
Zinc-waste	30	30	30	30

Zinc waste and other raw materials in Table 3.11 were weighed mixed and ground, then sieved through a sieve #100 mesh. The mixture was loaded into zircon-alumina crucible and melted in an electric furnace at 1450°C for 45 min. The melted glass was quenched by pouring into water to obtain glassy frit.

3.3.5 Preparation of glaze based on frit from zinc waste for floor tile

The preparation of glaze for floor tile based on frit from zinc waste that compositions are shown in Table 3.12, is same as the process described in section 3.3.3

Table 3.12 Raw materials used as glaze base on frit from zinc waste for floor tile

Raw materials	Formula			
	TF1	TF2	TF3	TF4
F1 (g)	90	-	-	-
F2 (g)	-	90	-	-
F3 (g)	-	-	90	-
F4 (g)	-	-	-	90
Kaolin (g)	10	10	10	10
Water (cc)	50	50	50	50

3.4 Characterization of tile bodies and glazes

3.4.1 Characterization of tile bodies

3.4.1.1 Physical properties

- Visual observation

Visual observations of fired specimens such as surface, texture and color were investigated.

- Linear shrinkage

The lengths of specimens were measured before and after firing. Linear shrinkage were shown in equation (eq.3.1)

$$\% \text{ Linear shrinkage} = \left[\frac{(l_1 - l_2)}{l_1}\right] \times 100 \quad \ldots \text{(eq.3.1)}$$

where

l_1 = length of green specimen

l_2 = length of fired specimen

- Bulk density, water absorption and apparent porosity

Bulk density (B.D.), percent of water absorption (W.A.) and percent of apparent porosity (A.P) of fired specimens were measured according to the procedure described in ASTM C373 [26]. The calculated equations are as follows:

$$B.D = \left[\frac{W_1}{(W_3 - W_2)}\right] \times \text{Density of water} \quad \text{... (eq.3.2)}$$

$$W.A. = \left[\frac{(W_3 - W_1)}{W_1}\right] \times 100 \quad \text{..... (eq.3.3)}$$

$$A.P. = \left[\frac{(W_3 - W_1)}{(W_3 - W_2)}\right] \times 100 \quad \text{..... (eq.3.4)}$$

where

W_1 = dry weight of specimen

W_2 = weight of specimen in water

W_3 = water filled weight

3.4.1.2 Microstructure

The fired specimens were cross-sectioned and mounted in resin then polished by using SiC paper started from #400, #800 and down to #1200. Finally, the morphology of specimens was investigated by Optical Microscope (OM: Olympus BX60MF5).

3.4.1.3 Phase formation analysis

Phase formation of fired specimens was analyzed by X-ray diffractometer (Bruker D8 Advance). The operating condition is: $10^{\circ}<2\theta<70^{\circ}$, step size of 0.02 degree, 40 KV and 40 mA.

3.4.1.4 Bending strength

Bending strength of fired specimens was measured by 3-point bending method. Specimens were formed in rectangular shape with size of 50x10x5 mm^3. Five specimens of each formula were tested by using universal testing machine (LLOYD500, Intro enterprise Co., Ltd). The cross head speed was constant at 100 mm/min and length of support span is 45 mm.

3.4.1.5 Abrasive resistance

Abrasive resistance of fired specimens was tested according to standard of ISO 10545-6 [27]. The equations for calculate abrasive resistances are as follows:

$$V = \left[\frac{\pi\alpha}{180} - \sin\alpha\right]\frac{hd^2}{8} \quad \text{..... (eq.3.5)}$$

With

$$\sin(0.5\alpha) = \frac{l}{d} \quad \text{..... (eq.3.6)}$$

Where

α = the angle, in degrees, subtended at the center of the rotating disc by the chord(see fig3.1)

h = the thickness, in millimeters, of rotating disc

d = the diameter, in millimeters, of the chord

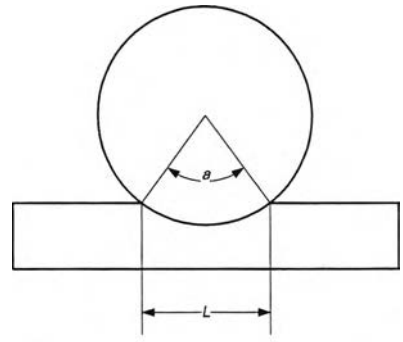


Fig3.1 Definition of the chord

3.4.1.6 Chemical resistance

Chemical resistance was tested according to ASTM C650 [28]. The test specimens were contacted with hydrochloric acid solution 3 %(v/v) and potassium hydroxide solution 30g/l for 24 h. and then cleaned with acetone and dried. After drying, several lines were draw on the surface of tested specimens using HB grade pencil, then remove these pencil lines. Thel effect of hydrochloric acid solution, potassium hydroxide solution and pencil were visually investigated.

3.4.1.7 Toxic leaching

Since zinc waste contained significant amount of lead (Pb), it was very important to examine the Pb leaching. Pb leaching of fired specimens was tested by following toxicity characteristic leaching procedure (TCLP) method 1311, [29].

The sizes of specimens were ground to the size less than 9.5 mm. Specimens were then added in distilled water and stirred. The pH was then measured for determination of extraction fluid. After that, specimens were mixed in appropriate extraction fluid which the solid:liquid ratio was determined to be 1:15. These were transferred to agitator with 30 rpm for 18 h. The liquid was separated by filtration. Pb release was analyzed from the filtrated liquid using atomic absorption spectrometry (AAS).

Fig 3.2 and Fig 3.3 show the agitator and flow chart of toxicity characteristic leaching procedure (TCLP), respectively.

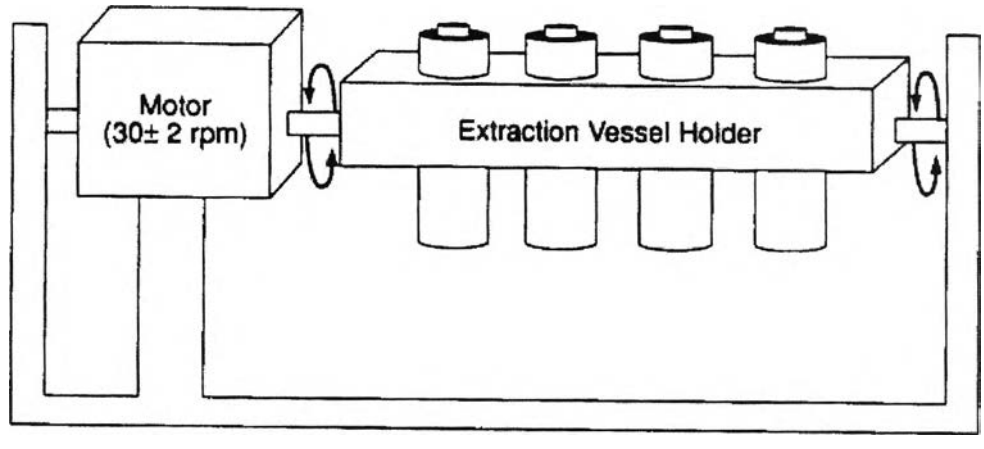


Fig 3.2 The agitator of toxicity characteristic leaching procedure (TCLP)

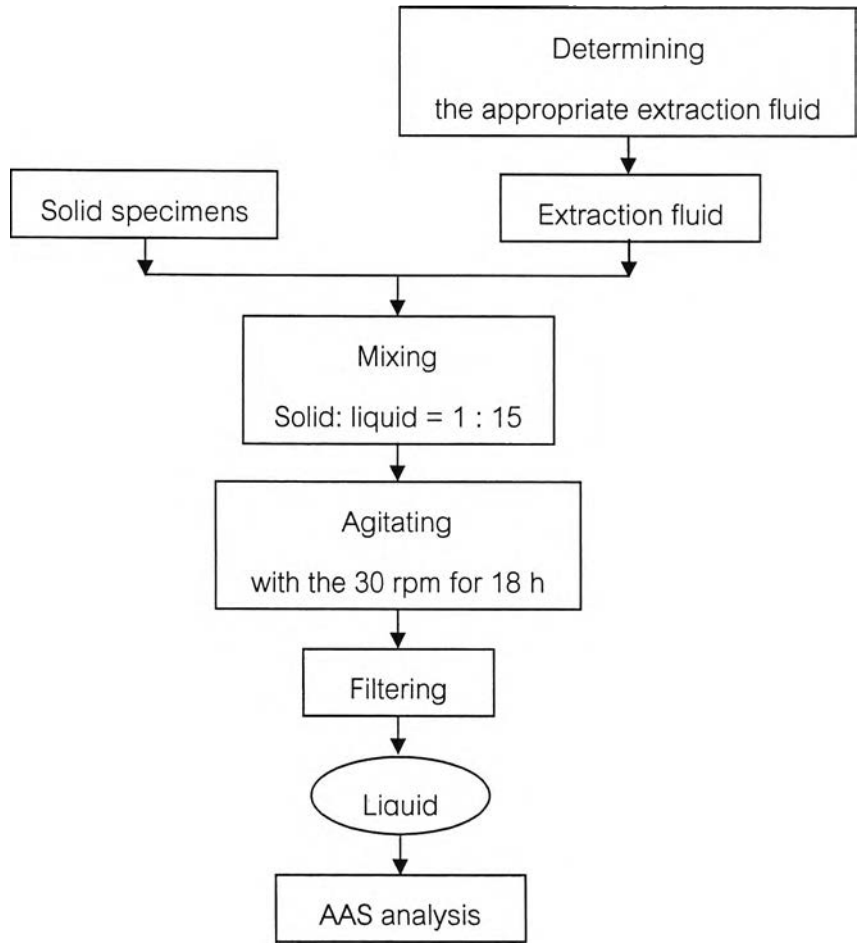


Fig 3.3 Flow chart of toxicity characteristic leaching procedure (TCLP).

3.4.2 Characterization of glaze

3.4.2.1 Characterization of glaze using zinc waste as color stain

- Visual observation

Physical properties such as color, glossy appearance of glaze for stoneware tiles and floor tiles were visually observed.

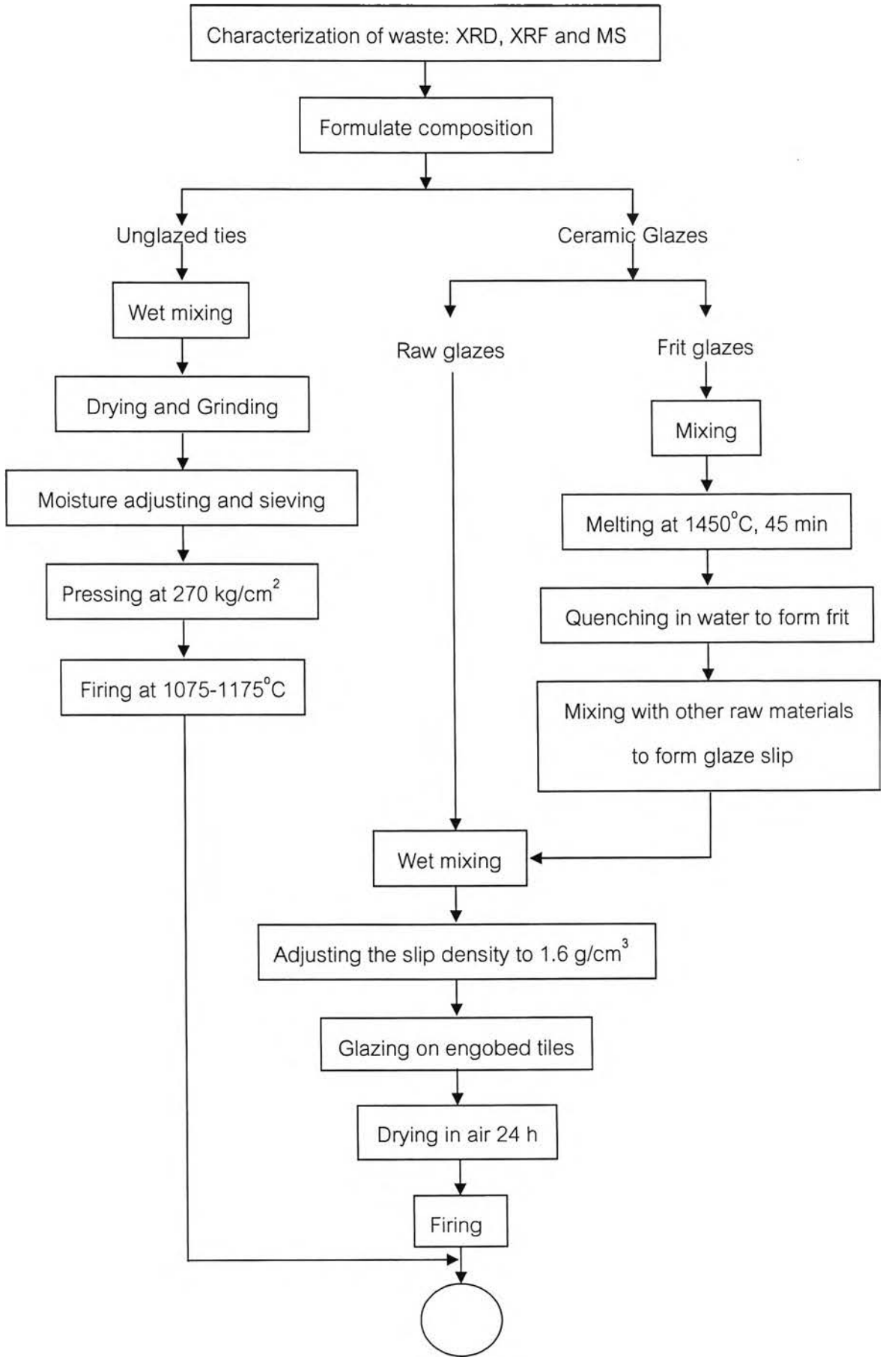
3.4.2.2 Characterization of glaze base on frit from zinc waste

- Visual observation

Physical properties such as color, glossy appearance of glaze base on frit from zinc waste were investigated as same as glaze stain.

- Chemical resistance

Chemical resistance of glazed was also determined by using a method following ASTM C650.


Characterization of waste: XRD, XRF and MS
Formulate composition
Unglazed ties
Ceramic Glazes
Wet mixing
Raw glazes
Frit glazes
Drying and Grinding
Mixing
Moisture adjusting and sieving
Melting at 1450°C, 45 min
Pressing at 270 kg/cm2
Quenching in water to form frit
Firing at 1075-1175°C
Mixing with other raw materials to form glaze slip
Wet mixing
Adjusting the slip density to 1.6 g/cm3
Glazing on engobed tiles
Drying in air 24 h
Firing

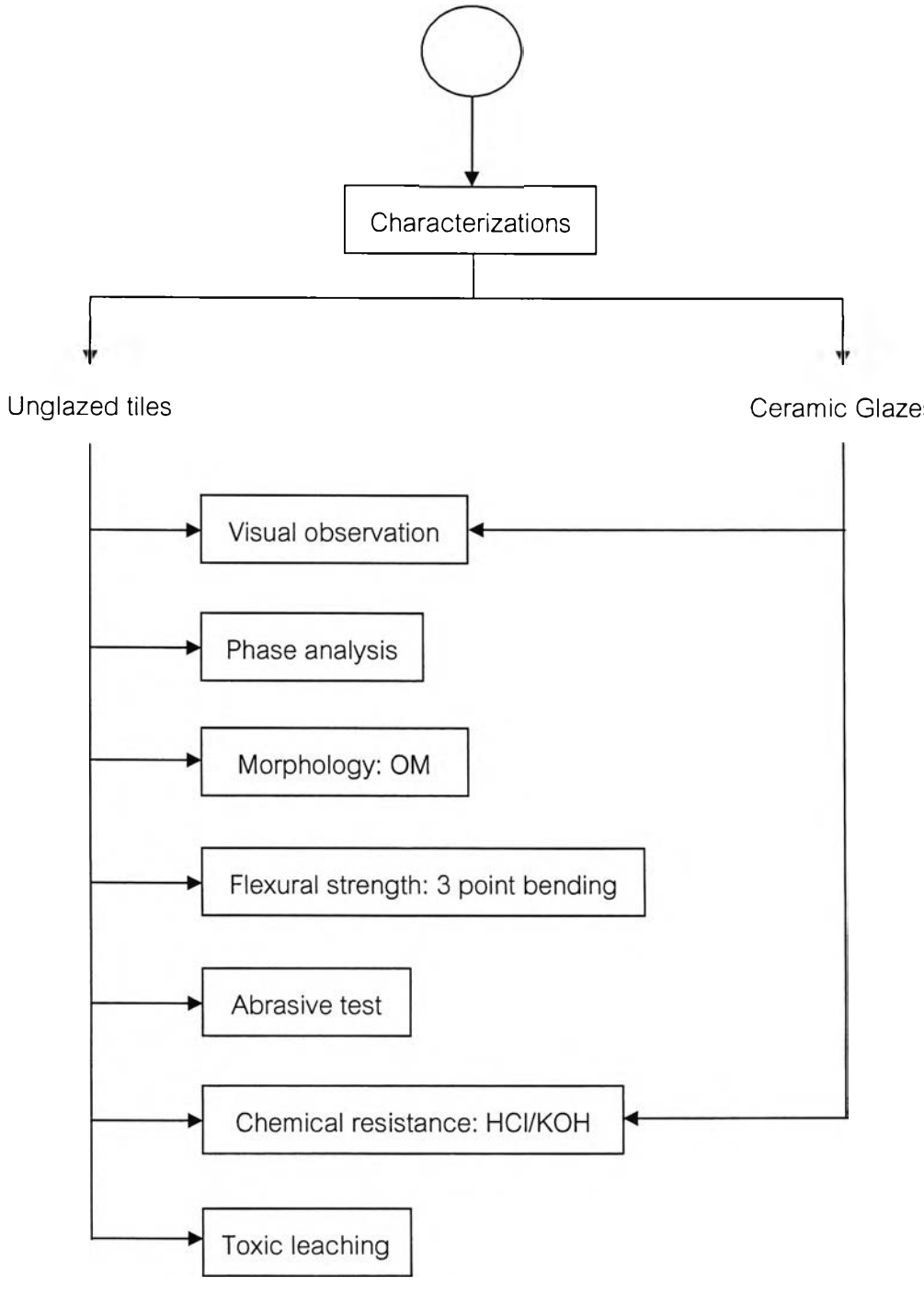


Fig 3.4 Flow chart of the experimental procedure