

## CHAPTER III

### METHODOLOGY

#### 3.1 Chemical and materials

1. Synthetic fly ash composition
2. Ethanol
3. Distilled Water
4. Mixing of LiOH and LiCl solution
5. Multichannel Pump
6. Twin Timer

#### 3.2 Preparation of Material

Since fly ash mineralogy is homogeneous in nature, it is difficult to separate the real fly ash into different phases. Fly ash used in this research was prepared with a specific ratio of  $\text{CaO}/\text{Na}_2\text{O}+\text{K}_2\text{O}$ . As mentioned in theory, fly ash is composed of both the glassy phase and crystalline phase. Only the glassy phase in fly ash was studied here since it can contribute constituents for pozzolanic action.

The glass used in this experiment is a mixture of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$ . The ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  was determined by taking the average of various fly ash sources as shown in Table 3.1 and Table 3.2. The oxides were mixed in different compositions with a fixed ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  at 5:2.5:1. The ratio of  $\text{CaO}/\text{Na}_2\text{O}+\text{K}_2\text{O}$  were varied at 1:3, 1:1, and 3:1 for class F and at 1:3, 1:1, 3:1, 1:10, and 10:1 for class C with the equal part of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . The mixture compositions of synthetic fly ash were plotted in the ternary diagram as shown in Figure 3.1 and their mixture compositions are shown in Table 3.3. The mixed oxides were melted in a platinum crucible at 1450 °C (Jiricka and Helebrant, 1998). The soak time was 2 hours in order to ensure the completion of the homogeneous melting. Then they were quenched immediately to create the glassy form of the fly ash.

**Table 3-1:** Fly ash composition from various sources (Class F)  
(Committee of Civil Engineering Department, 2000) CaO <10 %

Fly ash	Chemical composition (%)						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
FA-4	58.5	19.9	5.6	1.7	6.7	1.5	1.3
FA-5	60.1	27.8	3.8	1.0	0.7	0.3	2.8
FA-7	56.0	25.7	8.3	1.1	1.7	0.3	2.8
FA-8	49.0	21.8	17.9	1.0	2.4	0.4	2.7
FA-13	45.0	19.6	23.9	0.9	1.7	0.4	2.3
FA-14	47.7	29.5	9.7	0.7	1.9	0.3	1.9
FA-15	52.7	28.6	5.8	1.0	1.3	0.3	2.4
FA-16	50.6	27.6	8.2	1.0	1.6	0.4	2.5
FA-17	49.8	21.6	7.0	1.7	7.5	2.8	0.7
FA-18	43.6	26.0	16.6	0.9	2.2	0.3	1.9
Average	51.3	24.81	10.68	1.1	2.77	0.7	2.13

**Table 3-2:** Fly ash composition from various sources (Class C)  
(Committee of Civil Engineering Department, 2000) CaO >10 %

Fly ash	Chemical composition (%)						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
FA-1	36.3	17.7	6.7	4.6	25.5	1.6	0.6
FA-2(a)	38.8	13.4	12.5	1.5	15.5	0.5	1.9
FA-9(a)	50.5	17.7	6.6	3.4	11.6	3.5	1.2
FA-10(a)	35.9	17.1	5.6	5.1	28.2	1.8	0.5
FA-11(a)	51.4	16.9	5.8	3.5	16.9	0.6	0.8
Average	42.58	16.56	7.44	3.62	19.54	1.6	1

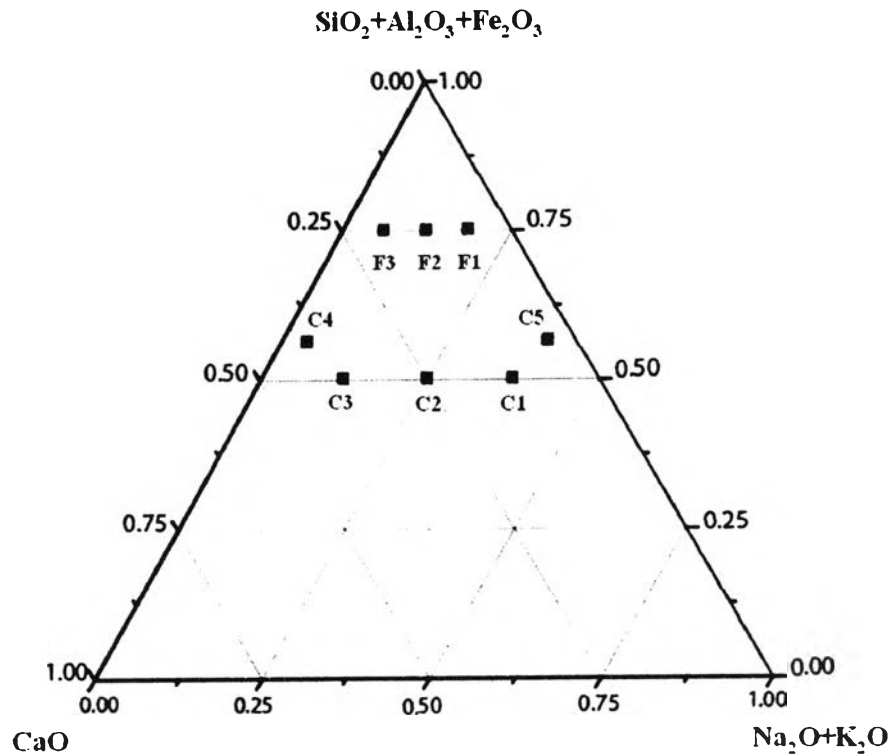


Figure 3.1: Ternary diagram of synthetic fly ash

Table 3-3: Mixture composition of fly ash (% by weight)

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
F1	41.9	23.6	8.5	1.7	6.0	9.2	9.1
F2	41.9	23.6	8.5	1.7	12.2	6.0	6.1
F3	41.9	23.6	8.5	1.7	18.3	3.0	3.0
C1	28.5	15.0	5.9	1.7	12.3	18.4	18.2
C2	28.5	15.0	5.9	1.7	24.5	12.3	12.1
C3	28.5	15.0	5.9	1.7	36.7	6.1	6.1
C4	31.5	17.7	6.4	1.7	38.9	1.9	1.9
C5	31.5	17.7	6.4	1.7	3.9	19.4	19.3

After cooling, a few pieces of synthetic glass were set aside for further experiments. Another portion was broken up manually into small fragments and was then crushed in the disc mill, which was made of tungsten carbide, to obtain the powdered form. To obtain fly ash with a close particle size range, the fly ash was sieved with sieve number 200-325 mesh, which yielded the required size of 45-75 micron.

### **3.3 Characterization of synthetic glass**

After the synthetic processes, a determination of synthetic fly ash's characteristics should be done to confirm whether they are totally in the glassy phase as well as to assure that the factors that affect leaching were controlled. The seven methods used for investigating the physical and chemical characteristic of fly ash are discussed below.

#### **3.3.1 Appearance of synthetic fly ash**

The appearance of two types of synthetic fly ash, class C and class F, were compared after melting. Color differences, homogeneity, and the melting behavior in general were observed.

#### **3.3.2 X-Ray Diffractometer (XRD)**

X-ray diffractometer (XRD) is used to identify the proportions of the different minerals present, as well as the degree of crystalline of the minerals present. Each mineral type is defined by the characteristic crystal of each structure, with a unique x-ray diffraction pattern, allowing for the rapid identification of the minerals present within the material. The fly ash was ground to a fine powder (less than 45 microns). An angle from 10 to 70 degrees with a scan speed of 5° per min was used. The software used was DQUANT. In this research, the XRD was used to determine the presence of the crystalline and amorphous phases in synthetic fly ash.

#### **3.3.3 X-Ray Fluorescence Spectrometer (XRF)**

The chemical compositions of prepared materials were determined since there might be some loss of substances during the melting. Thus, determinations of the chemical compositions after melting were done. The synthetic fly ash was analyzed by an XRF spectrometer to measure the bulk chemical composition of the materials. The synthetic fly ash had been ground to the fine powder, less than 45 micron. The 0.5 grams of sample was mixed with 4.5 grams of boric acid. The mixtures were pressed in aluminum cups at 150 kN for 1 minute before the tests. The XRF model, Bruker AXS/ SRS 3400 was used to determine the bulk chemical compositions.

### 3.3.4 Porosimeter

Surface area is an essential factor affecting the leaching rate of synthetic fly ash. Thus the surface area of the powdered sample was measured using a Porosimeter, with nitrogen gas as the absorbate. Nitrogen gas was adsorbed by a sample at the boiling point of nitrogen to determine the surface area. The analysis model was SA 3100 Analyzer, The Compact Coulter™.

### 3.3.5 Particle Size Analyzer

Particle size is other parameter controlling leaching behavior. A particle size analyzer was used to consider the particle size distribution. The glass powder was investigated by a wet system with the RI equal to 1.5. The analysis model is the single narrow mode, Mastersizer 2000 Ver.4.

### 3.3.6 Density

The density of the glasses will be measured by following the ASTM B311-93 (2002), which is the test method for the density determination of powder metallurgy materials. This method is based on Archimedes' principle. It can be assessed by following the following formula:

$$\rho_{\text{sample}} = [M_{\text{dry}} / (M_{\text{dry}} - M_{\text{suspended}})] \times \rho_{\text{water}} \dots \dots \dots (1)$$

Where  $\rho_{\text{sample}}$  is the glass density ( $\text{g}/\text{m}^3$ ),  $M_{\text{dry}}$  is the dry weight of the glass sample (g),  $M_{\text{suspended}}$  is the suspended weight of the glass sample which is submerged in water (g), and  $\rho_{\text{fluid}}$  is the density of the immersion water.

### 3.3.7 Refractive Index

The refractive index of a glass is directly related to its chemical composition. Thus it could be used to characterize the reactivity of a particle. The small piece of glass ( $\sim 5\text{mm} \times 5\text{mm} \times 2\text{mm}$ ) was touched the RI standard solution and then was put on the prism of the refractometer. The refractive index was directly read from the scale.

### 3.4 Modified Single Pass Flow Through (SPFT) method

In this experiment, the single pass flow through (SPFT) method (McGrail et al., 2000) was selected to test glass leachability. The process was modified as the fly ash particle was very fine. The process is described as follows.

#### 3.4.1 Sample Preparation

The powdered sample was washed in deionized water (DIW) and rinsed in ethanol to remove any adhering particles. The sample was dried in a 90 °C oven for an hour and kept in the desiccators for later laboratory work.

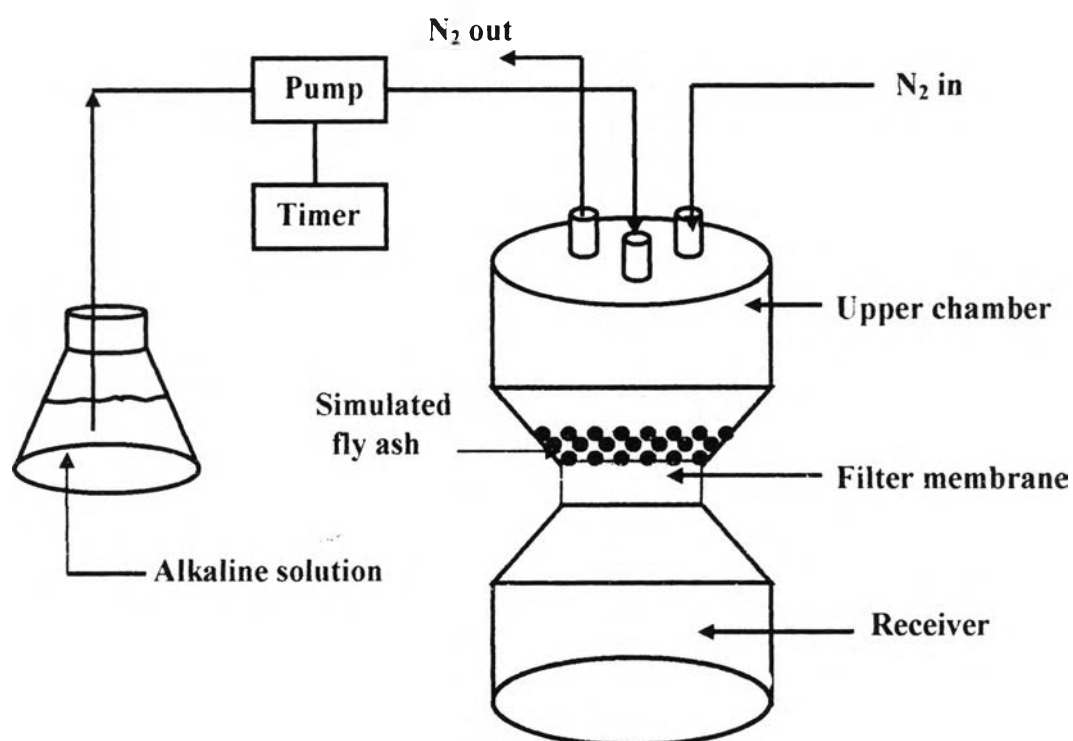
#### 3.4.2 Method

The SPFT tests were conducted in a filter holder reactor with a total height of 18 cm. This reactor is composed of 3 pieces screwed together: 250 ml in the upper chamber, an 11.25 cm<sup>2</sup> filter area, and a 250 ml receiver. At the top of the upper chamber, there are 3 ports that allow for vacuum lines or syringes.

The powdered fly ash was put at the upper part of the reactor with a leachant volume of 10 cc/gram of sample mass. Nitrogen gas was allowed to flow continuously through the reactor to prevent CO<sub>2</sub> interference in the system. Also, the buffer leaching solution was put into the upper chamber with a very small flow rate at 20 ml/day. In this experiment, a multichannel pump and twin timer were used to achieve this flow rate. The multichannel pump was adjusted to 0.5 ml/min. The twin timer was connected to this pump to control the pump operation. It was set to switch on the pump for about 20 seconds and to switch it off for about 12 minutes. This condition was repeated along with the experiment.

The pH used was 11.5, 12, and 12.5, as these values are within the typical range for concrete pore water. Furthermore, above a pH of 11, silica solubility increases and the Ca(OH)<sup>+</sup> species begin to dominate Ca<sup>2+</sup>. Both of these effects could

be significant factors in fly ash leaching rates. The alkaline solution was prepared from LiCl and LiOH. The effluent from the leachability test was passed through the filter area and was collected by the receiver at the bottom. The pH of the solutions was checked to ensure that it is maintained constant throughout the experiment. The schematic diagram of the SPFT experiment set up is shown in the following figure.



**Figure 3.2:** Schematic diagram of the SPFT experiment set up

Blank solutions were analyzed for the background concentration. The first collection of each experiment was at the beginning and the holding time for each sampling was 24 hours. General information on the materials used and the conditions for each experiment are shown in Table 3.4

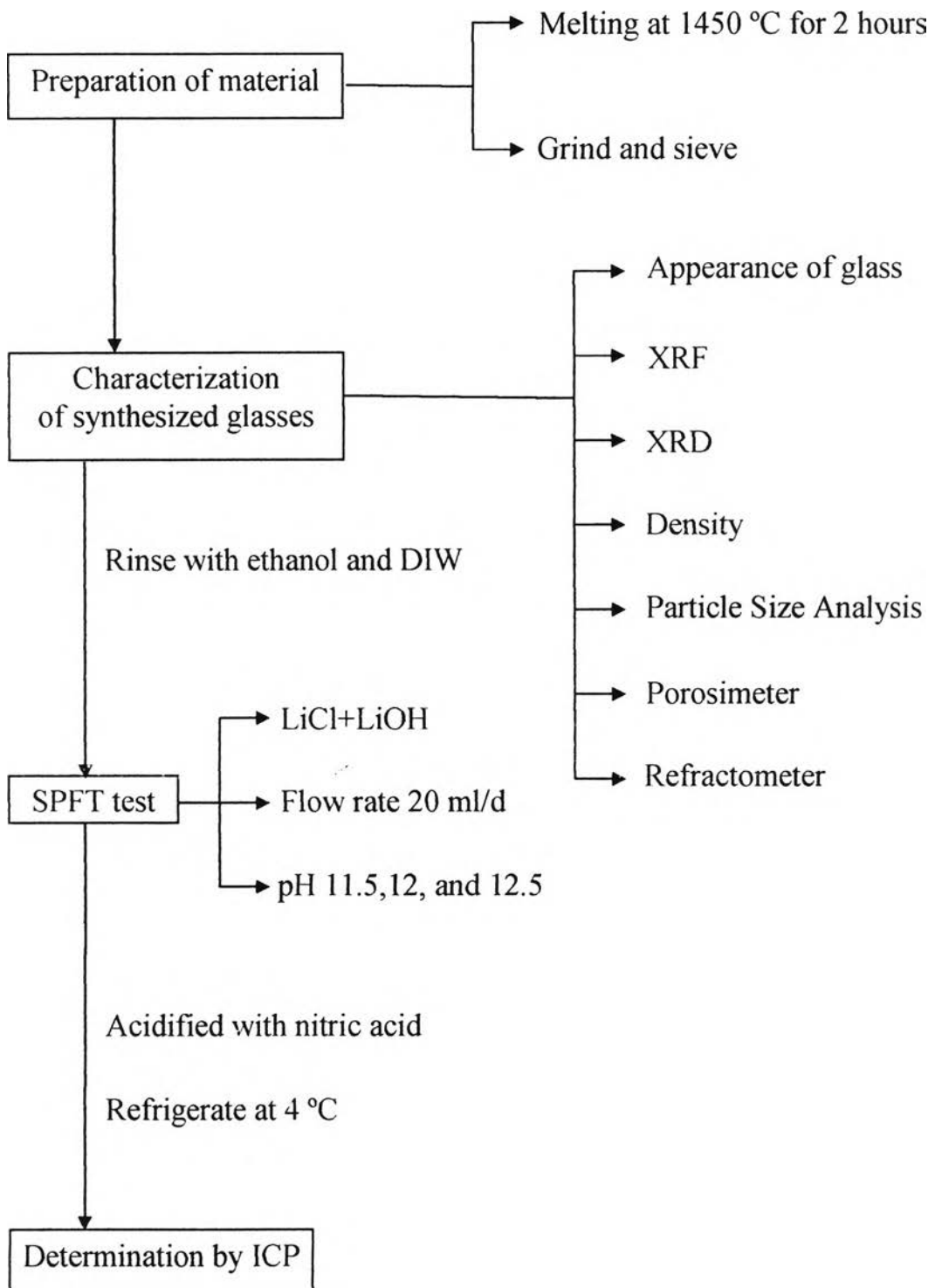
**Table 3.4:** General information on the materials used and the conditions for each experiment

Materials used and condition	Setting parameters
Powder fly ash	1 g
Holding time for each sampling	1 day
Holding time for each experiment	28 day
Alkaline solution flow	20 ml/day
Nitrogen gas flow	100 ml/day

After sampling, the reactor was rinsed with 20 ml of deionized water to remove the components that might be attached inside the reactor or on the glass-powder surface. Since the sample solution was a strong base and had a high alkaline content, the rinsed water was then used for the dilution of the sample.

The inductively coupled plasma (ICP) method was used to analyze the leachate. The ICP model used was the VISTA-MXP/ CCD Simultaneous ICP-OES and the software used was the ICP Expert. Following the sample collection, the output solutions were acidified immediately with concentrated nitric acid to a pH<2 (usually 1.5 ml conc. HNO<sub>3</sub>/L sample) to preservation the aqueous metal sampling follow the standard methods for the examination of water and wastewater, 1995. After acidification, they were refrigerated at 4 °C and subsequently analyzed by the ICP. Only the silica oxide released was of concern because it can represent as the leaching rate since the rate-limiting reaction of glass is the hydrolysis of siloxane bonds (Abraitis et al., 2000). However, the other released oxides were measured for more accurate result interpretations. The flow chart of this experiment is shown as follows:





**Figure 3.3:** Experimental flow chart