CHAPTER III

TREATMENT PROCESSES

3.1 Materials

3.1.1 Chemicals

3.1.1.1 Types of inorganic ion-exchangers

Material	Particle Size
Titanium dioxide	0.001 mm.
Kaolinite	0.001 mm.
Zeolite	<0.001 mm.
Hydrated Antimony Pentoxide (HAP)	0.01 mm.
Antimony Pentoxide	0.1 mm.
Bentonite	0.001 mm.
Sand	0.01 mm.
Sandy Soil	0.01 mm.

3.1.1.2 Tracer Solutions

A radioactive Technetium (^{99}Tc) stock solution was prepared by diluting sodium pertechnetate ($Na^{99}TcO_4$) having an activity level of 2.6259 μCi/25 ml with de-ionized water to 100 ml. The Tc-99 was obtained from the Isotope Production Division of OAEP.

The radioactive Cesium (^{137}Cs) stock solution was prepared by dilution of a 0.049 μCi/ml standard Cesium-137 solution with de-ionized water to 100 ml.

3.1.1.3 Liquid Scintillation Cocktail

3.1.1.4 De-ionized Water

3.1.1.5 Nitric acid

3.1.1.6 Sodium hydroxide

3.1.1.7 Portland Cement

3.1.2 Glassware and Plasticware

3.1.2.1 Cylinders: 50 ml, 25 ml, 10 ml

3.1.2.2 Beaker, 10 ml

3.1.2.3 Volumetric flask, 100 ml

3.1.2.4 Glass bottle, 1 litre

3.1.2.5 Plastic bottle, 5 ml

3.1.2.6 Polyethylene centrifuge tube

3.1.2.7 Polyethylene container for cement mixing

3.1.2.8 Plastic vials, No.2 diameter, 3.8 cm and height 5.5 cm

3.1.2.9 Plastic vials, No.5 diameter, 1.8 cm and height 4.2 cm

3.2 Apparatus

3.2.1 The MSE Centrifuge, Model MINOR

3.2.2 pH meter, Model Sp-33 digital

3.2.3 Magnetic stirrer

3.2.4 Oven

3.2.5 Balance

3.2.6 Auto-pipette

3.2.7 Machanical Shaker, Model G-2 Scientific

3.2.8 Mixer

3.2.9 Compressive Strenght Tester

3.2.10 Counting equipment

The detection systems consist of the following components:

3.2.10.1 A Rack Beta Liquid Scintillation Counter (LSC) Model 1209-005 with 230 Volt supply and 50 Hz. frequency setting. A Printout device: PC Computer and a Printer Epson LX-800.

3.2.10.2 A Nucleus Personal Computer Analyzer (PCA-II) Card Multichannel Analyzer with 100 MHz Wilkinson ANALOG TO DIGITAL CONVERTER (ADC). The Nucleus Ge detecter with a Nucleus Model 5020 Spectroscopy Amplifier and 2000 voltages supply.

3.2.10.3 OAEP Portable Survey Meter model 1205. A GM counter detector.

3.3 Procedure

3.3.1. Experiments on Sorption Characteristics

3.3.1.1 Investigation of the effect of pH and residual contact time

3.3.1.1.1 Sorption of Cesium-137

Sorption of radioactive Cesium-137 (^{137}Cs) were determined by the batch method using an inorganic ion-exchanger to water ratio of 1:10 (3 g. of ion-exchanger : 30 g. of de-ionized water). The optimum pH and contact time were determined as follows:

Three grams of each inorganic ion-exchanger was weighed in polyethylene centrifuge bottles. The pH of the simulated liquid wastes, prepared with de-ionized water and radioactive ^{137}Cs tracer, were adjusted by using HNO_3 and NaOH. The solutions were adjusted to pH of 1, 3, 5, 7, 9, 11 and 13. Each sample, consisting of 29 ml aqueous solution and 1 ml radioactive tracer was added to the polyethylene bottles containing the ion-exchangers. Mixture was then agitated by using a mechanical shaker (300 rpm) at room temperature (25°C), as shown in Figure 3.1. Following the shaking periods, the samples were centrifuged (2000 rpm) and 1 ml aliquot of the clear supernatant solution were collected with a micropipette. After a contact time of 5 min, 10 min, 20 min, 30 min, 1 hr, 2 hrs, 4 hrs and 24 hrs.repectively, the radioactivity in each of the clear supernatant solutions were counted with a Nucleus Personal Computer Analyzer (PCA-II) Card Multichannel Analyzer. The detector consisted of a Ge(Li) combined with a Nucleus Model 5020 Spectroscopy Amplifier and a 2000 volt supply. The counting system is shown in Figure 3.2.

3.3.1.1.2 Sorption of Technetium-99

The sorption of radioactive ^{99}Tc was determined using the same method as for ^{137}Cs above. However, the residual contact times were as follows : 1 hour, 1 day, 5 days and 10 days. The activity levels of the clear supernatant solutions were counted with a Rack Beta Liquid Scintillation Counter(LSC), Model 1209-005, having a 230 Volt supply at a 50 Hz. frequency setting. The data were obtained using an Epson LX-800 Printer. The counting system used is shown in Figure 3.3.

3.3.1.2 Investigation of the Effect of Temperature

The samples were prepared similar to those described in 3.3.1.1.1 and 3.3.1.1.2, at the optimum pH and residual time. The various temperatures used were as follows: 30 °C, 40 °C, and 50 °C.

3.3.1.3 Calculation of the Percentage of Sorption Efficiency

The percentage of sorption efficiency were calculated by comparing the activity of the sample with the standard solution as follows.

$$\% \text{ Sorption Efficiency} = \frac{(\text{initial activity} - \text{final activity})}{\text{initial activity}} \times 100$$

3.3.1.4 Determination of the Optimum Weight Ratio

The weights of ion-exchangers used were 0.3, 1, and 3 g. These amounts were used to determine the optimum ratio of ion-exchanger to solution, by comparing the sorption efficiency of each ratio.

3.3.2. Cementation Process Experiment

In the cementation process experiment, the following selected exchangers were used: TiO_2, Zeolite, Bentonite, Kaolinite and Sand.

3.3.2.1 Density Measurements for Inorganic Ion-exchanger and Portland Cement

Each sample was packed in a pre-weighed no.2 vial (volume 62.38 cm^3). These samples were then weighed and computed for density.

3.3.2.2 Calculation of Material Ratios by Weight

The ratio of exchanger : cement used in this study were as follows: 25 : 75, 30 : 70, 35 : 65, 40 : 60, 45 : 55, and 50 : 50 percent by weight. (See Appendic B)

3.3.2.3 Cement Mixing

Each exchanger was mixed with Portland cement to obtain exchanger to cement ratios as stated above in section 3.3.2.2.

The appropriate amount of de-ionized water, required to hydrate the cement, was added to the mixtures which were then agitated by a mixer at a speed of 300 rpm for 10 minutes (Figure 3.4). The homogeneous mixtures were then transfered to the molds, being careful to avoid entrapped air bubbles and after 2 hrs., the exposed specimen surfaces were leveled off in preparation for compressive testing. The specimens were cured for 28 days, after which time, the molds were removed and the specimens were labelled, as shown in Figure 3.5.

3.3.2.4 Basic Properties of Cement Waste Forms

3.3.2.4.1 Physical and Mechanical Property Tests

3.3.2.4.1.1 Homogeneity

The specimens were checked by visual observation. Any discoloration on the waste form would be an indication of non-homogeneity either through segregation or by incomplete mixing.

3.3.2.4.1.2 Percentage of Weight-loss and Density

During the curing time, the specimens were weighed, measured, and calculated for density. The amount of weight losses observed during and after curing can be attributed to loss of water by vaporization.

3.3.2.4.1.3 Compressive Strengths Test

The compressive strengths were tested after 28 days of curing time at ambient room temperature by using the mechanical compressive strength tester, as shown in Figure 3.6.

3.3.2.4.1.4 Exchanger/Cement Ratio

Since the exchanger/cement ratios are related to compressive strengths (normally, the higher the ratio, the lower the strength), the results obtained from the compressive strength tests were used to determine the optimum ratio of materials required to give a satisfactory waste form.

3.3.2.4.2 Leaching Test

The leaching test was based on BNL'S Accelerated Leach Test (Fuhrmann, 1990). The specimens were prepared by mixing ^{137}Cs adsorbed-exchanger (Kaolinite was used in this study) with Portland cement and water, in proportions used to obtain the optimum ratio as determined in 3.3.2.4.1. The leach test was performed as follows:

Twenty-six specimens were prepared using the ratio of 24 % Kaolinite : 76 % Cement by weight. Vials no.5(diameter = 1.8 cm,

hight = 4.2 cm) were used as molds. After curing for 28 days, the specimens were weighed and placed into glass containers. 500 ml of de-ionized water was added into glass containers. Then, specimens were separated into two groups. The leaching test for the first group was performed at room-temperature (25°C) and the second group was performed at 50 °C (Figure 3.7)

Leaching time was studied for 13 time intervals as follows: 2 hrs, 7 hrs, 1 , 2 , 3 , 4 , 5 , 6 , 7 , 8 , 9 ,10 and 11 days. After this period of time, the specimens were removed and the 200 ml leachant was counted for radioactivity by a "Nucleus" Multichannel Analyzer with Ge detector. The results were reported and calculated for the leach rate. (see in Appendix B)

From the results of the leaching test, comparisons of the incremental fraction leached, cumulative fraction leached, and prediction of leach rates for 200 days can be obtained.

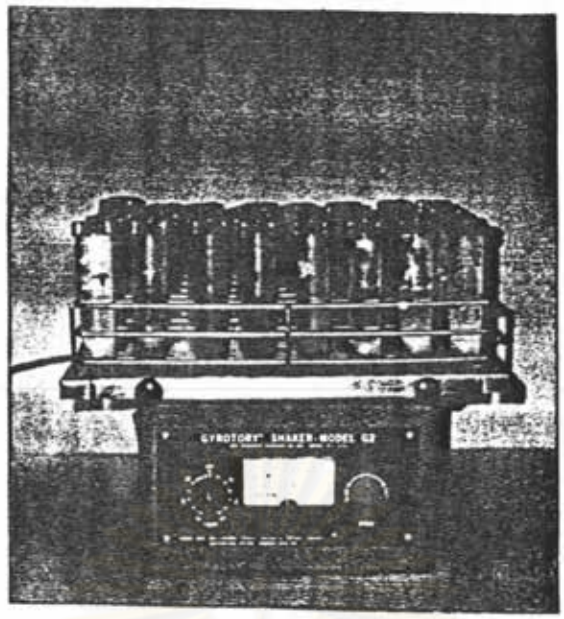


Figure 3.1 Machanical Shaker.

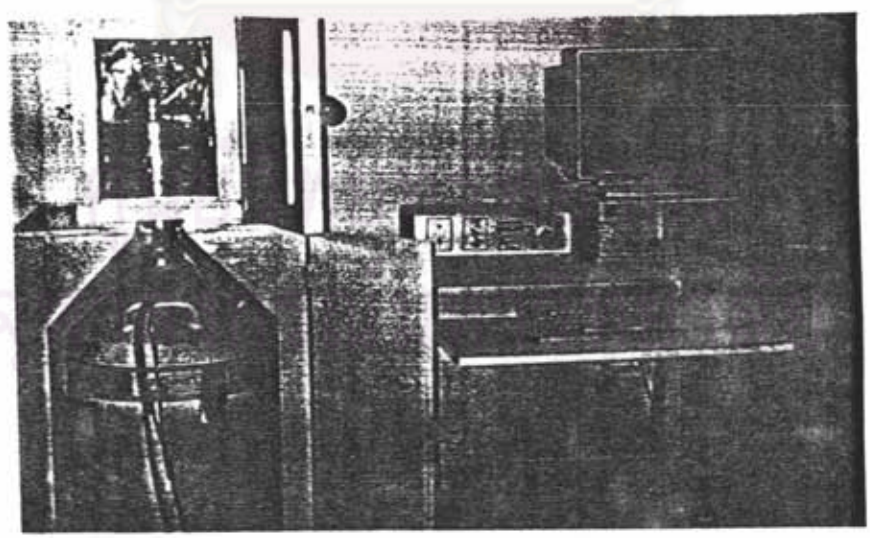


Figure 3.2 Nucleus Personal Computer Analyzer (PCA-II) Card Multi-channel Analyzer.

Figure 3.3 Beta Liquid Scintilation Counter.

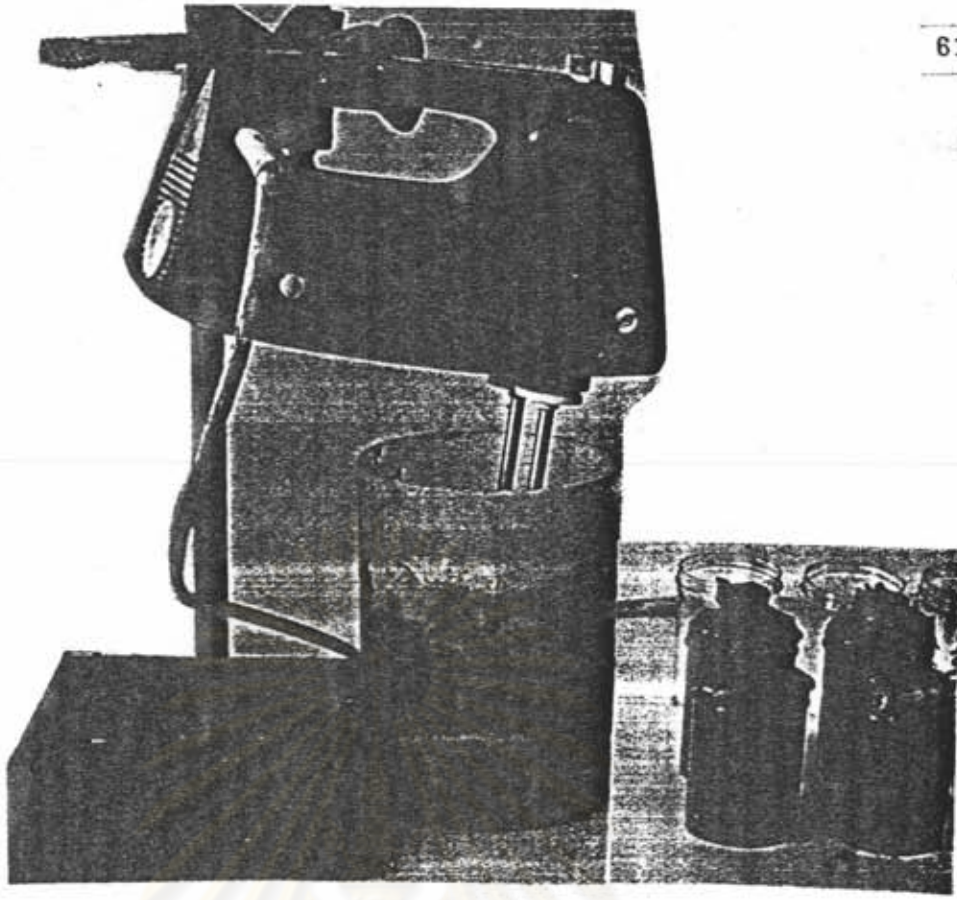


Figure 3.4 Cement Mixer.

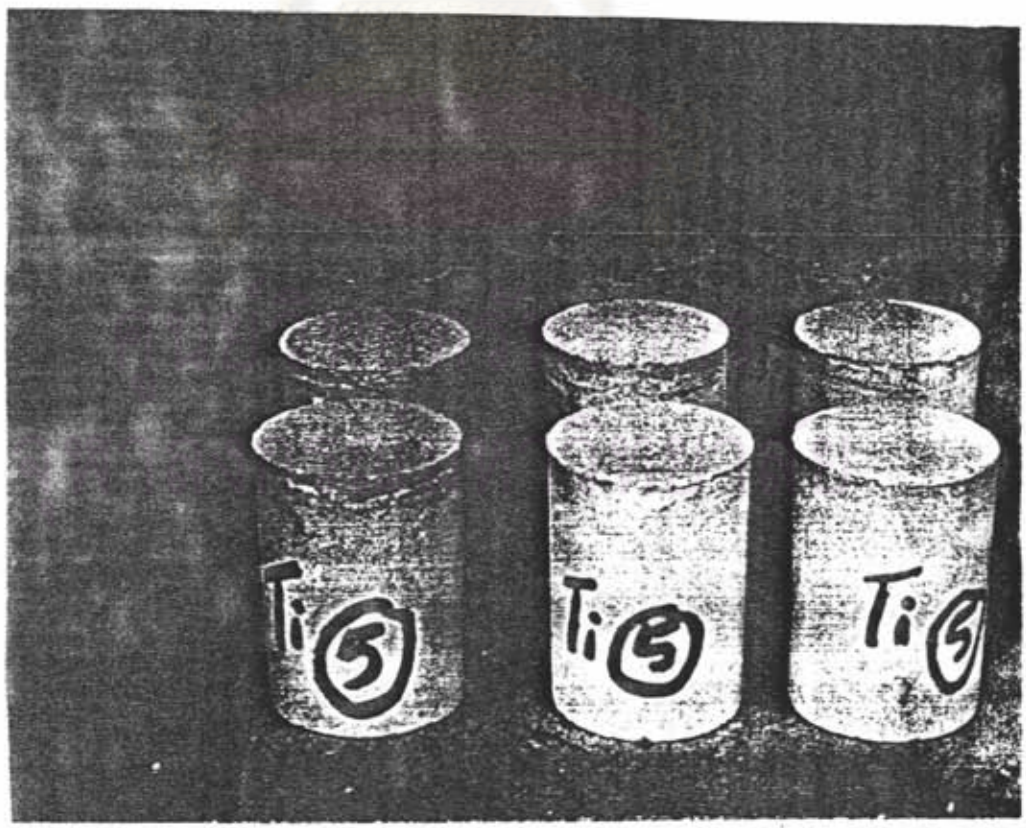


Figure 3.5 Conditioned Specimens.

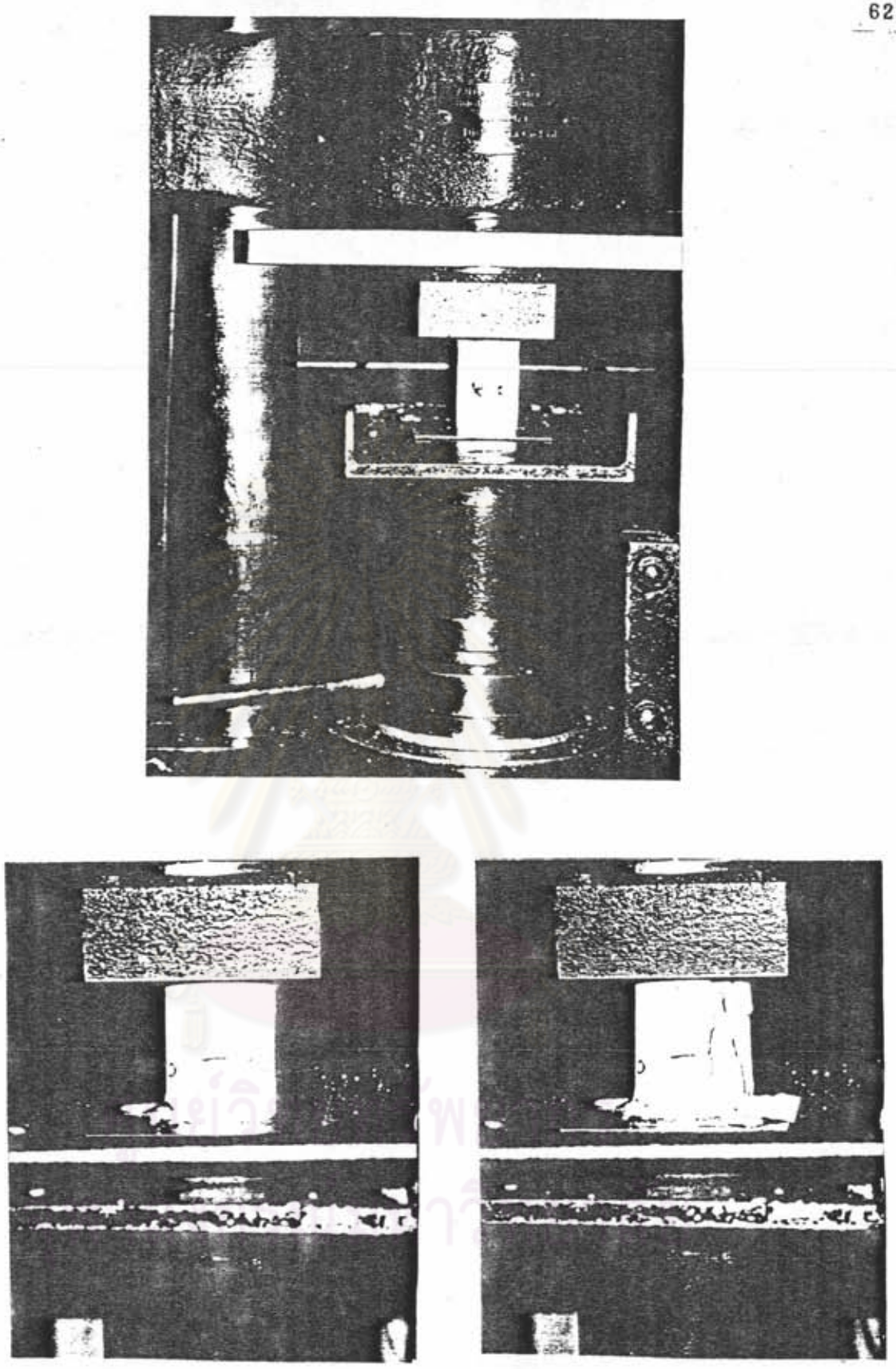
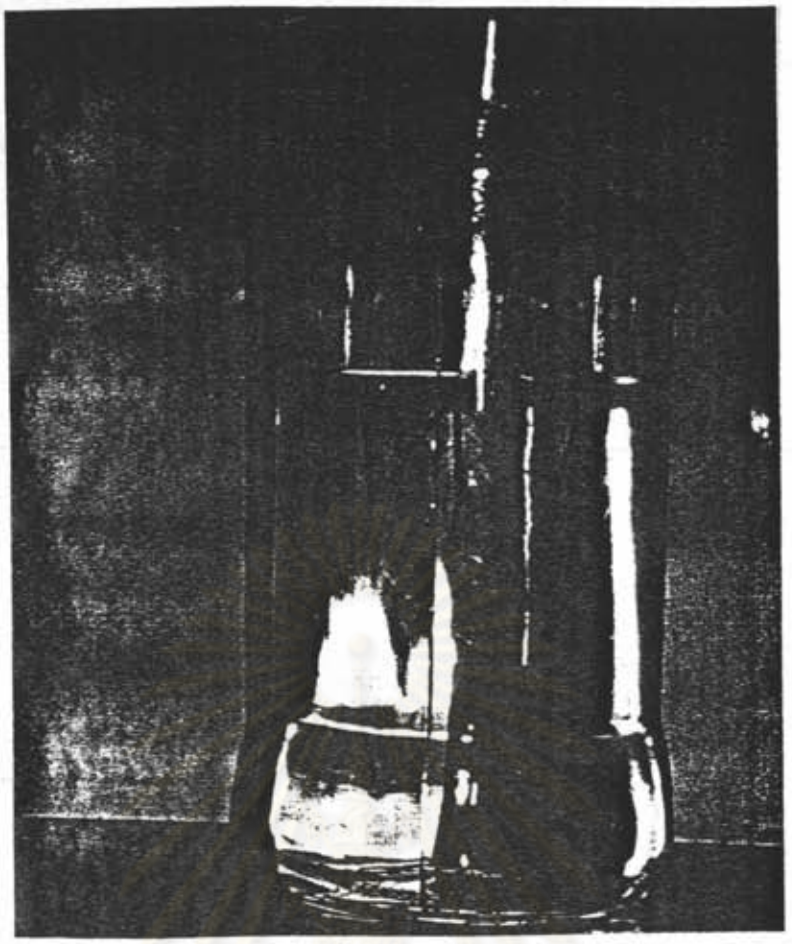
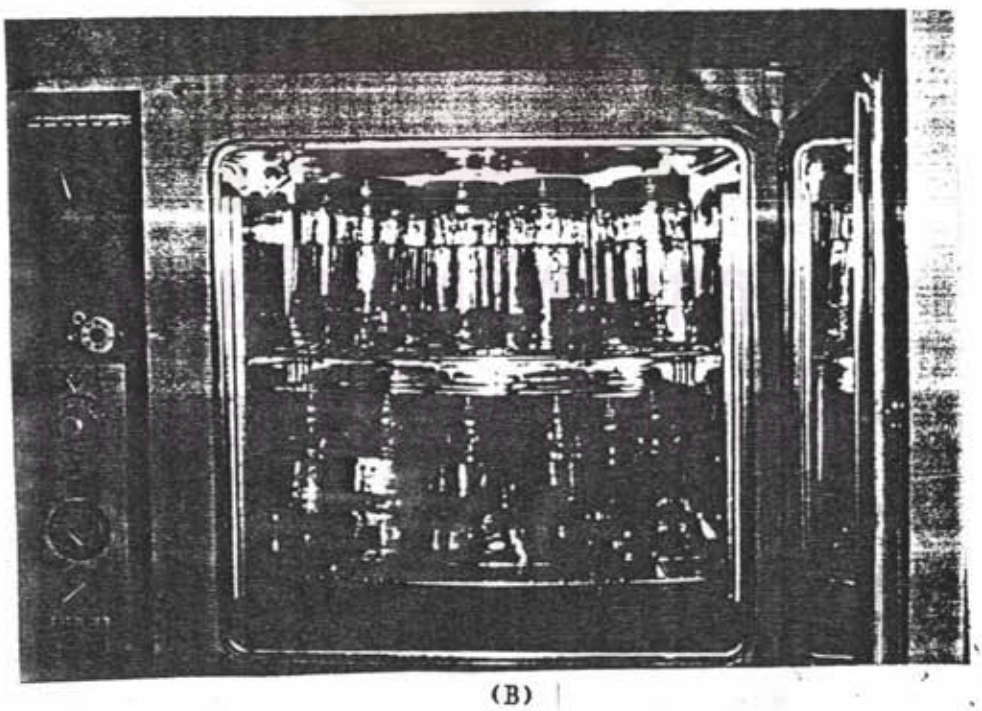


Figure 3.6 Compressive Strength Test.



(A)



(B)

Figure 3.7 Accelarated Leaching Test.

A) at 25°C

B) at 50°C