

CHAPTER III

MATERIAL AND METHODS



3.1 Raw materials

Raw meal which is not mixed with heavy metal was taken from Siam City Cement, Co., Ltd. The compositions of raw meal are shown in Table 3.1. Heavy metal compounds were chromic oxide, nickel monoxide and, zinc oxide. All heavy metal oxides were purchased from Carlo Erba Company. All reagents used in this study were at least reagent grade.

Table 3.1 Compositions of raw material

Components	Quantity (% by weight)
SiO ₂	14.33
Al ₂ O ₃	3.26
Fe ₂ O ₃	2.17
CaO	43.13
MgO	1.14
K ₂ O	0.47
Na ₂ O	0.03
SO ₃	0.17
LOI*	35.31
Total	100.00

* LOI = Loss on ignition

3.2 Experimental Procedures

The experiment procedures were separated into 2 parts; cement preparation and leaching tests.

3.2.1 Cement preparation

3.2.1.1 Investigation of burning temperature for clinker synthesis in the laboratory

Approximately 150 g of raw meal was burned in crucibles in a tube furnace. The temperature was heated up to the designed temperature which were 1,300, 1,400, and 1,450°C. Raw meal was burned at these temperatures for 60 minutes. After burning the samples were taken out from furnace immediately for rapid cooling by air. After reach the room temperature, it was ground to smaller size before analyzing for the residual free lime in the clinker, which should be in the range of 1.2–1.5 wt. %. This value used to tell the burnability of clinker. The analysis methods including X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), were used to analyze the cement matrix phase of the synthetic clinker in comparison with that of real clinker from the cement manufacturing process. The analysis settings of XRD were shown in Table 3.2. The appropriate burning condition was obtained from the synthetic clinker analysis that gives the cement matrix phase most comparable with the manufacturing one. The steps of this experiment are shown in Figure 3.1.

Table 3.2 Analysis settings of XRD

Parameters	Settings
2 θ	5-80 degree
Step size	0.1 degree.
Step time	1 second
Voltage	30 kV
Electric current	30 mA
Temperature	25°C

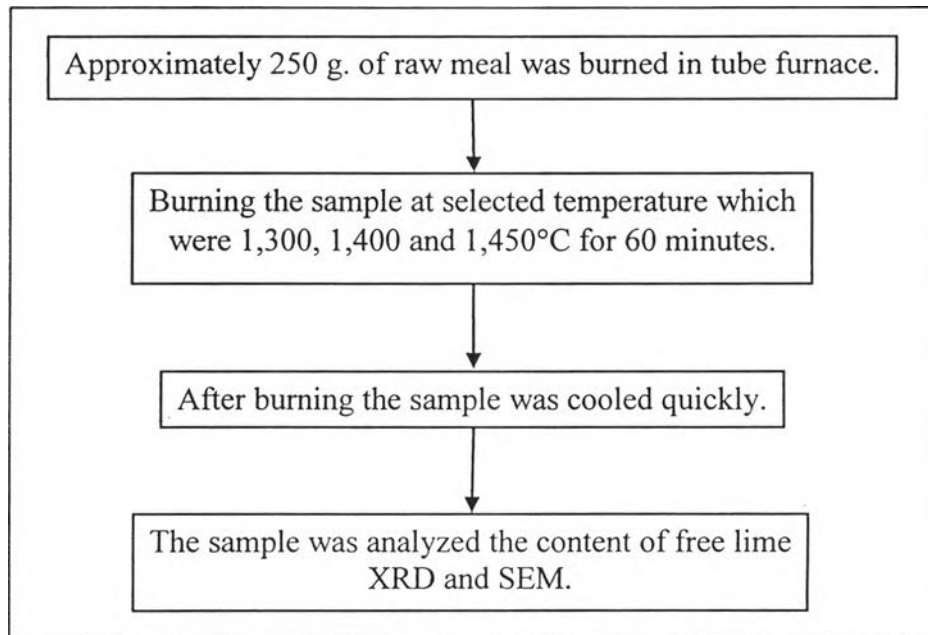


Figure 3.1 Steps of finding the suitable burning temperature.

3.2.1.2 Investigation of burning time for clinker synthesis in laboratory

Approximately 150 g of raw meal was burned in crucibles in a tube furnace. The burning temperature was brought from the first part of experiment. In this experimental set, material was burned at the optimum temperature for 30, 60, and 90 minutes, respectively. After burning the sample was taken out from furnace immediately for rapid cooling by air. Then, it was ground to smaller size before analyzing the residual free lime in the clinker, which should be in the range of 1.2 – 1.5 wt. %. The analysis methods, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), were used to analyze the cement matrix phase of the synthetic clinker in comparison with that of real clinker from the cement manufacturing process. The appropriate burning condition was obtained from the analysis of synthetic clinker that gives the cement matrix phase most comparable with the real one. The XRD result of obtained clinker should match with XRD result of clinker from industrial as shown in Figure 3.3. The steps of this experiment are shown in Figure 3.2.

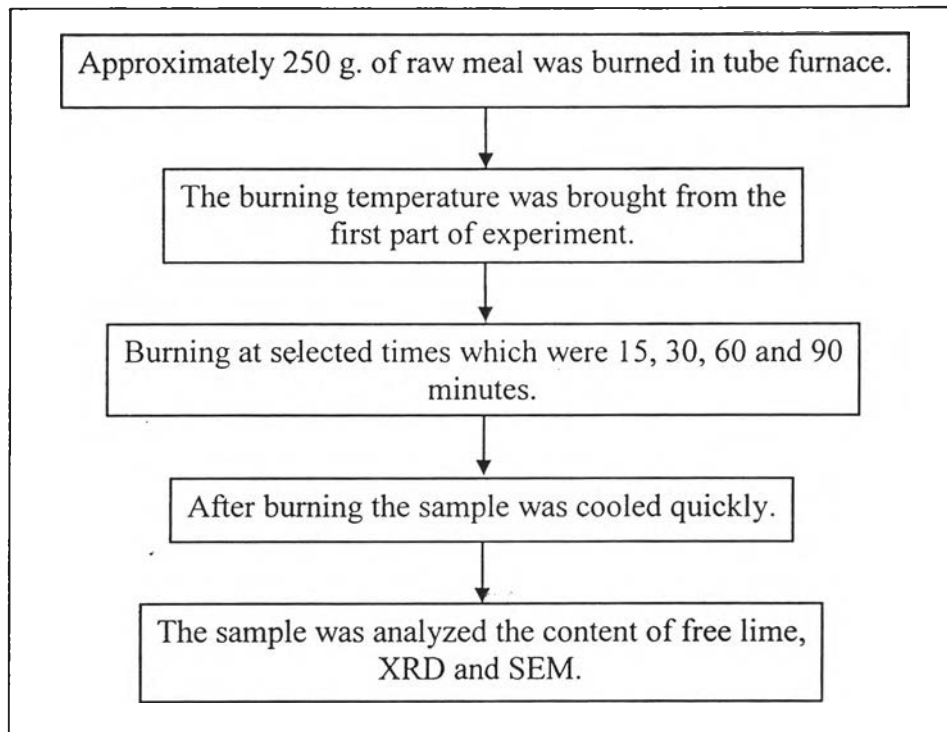


Figure 3.2 Steps of finding suitable burning time.

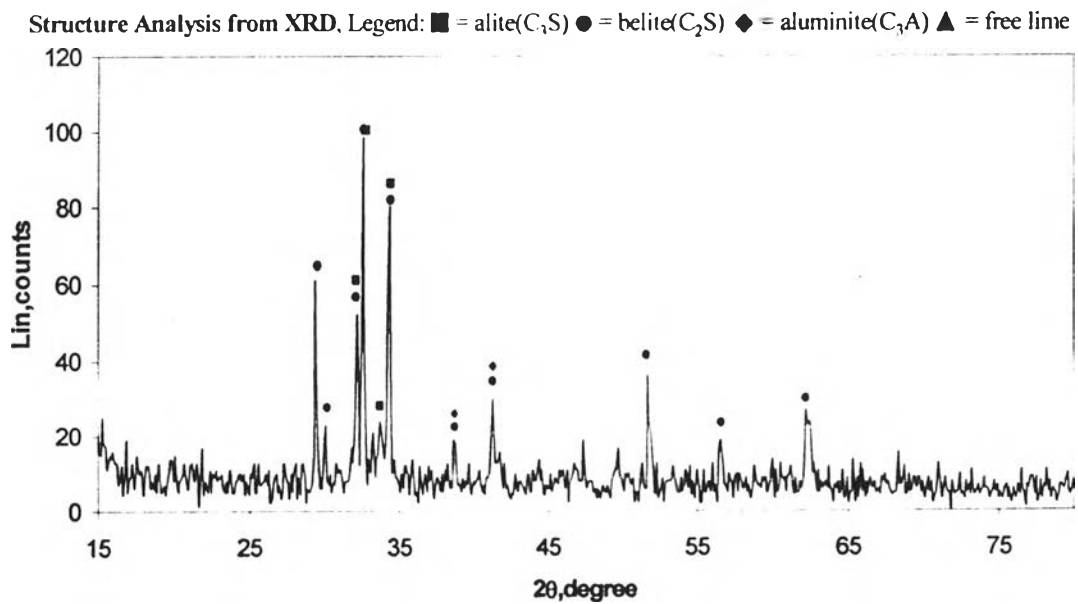


Figure 3.3 Structure analyses from XRD of clinker from cement industry

3.2.1.3 Effect of heavy metals on clinker

Approximately 150 g of raw meal was mixed with the heavy metal oxides to give concentrations of approximately 0.1, 0.5, 1, 2 wt. %. The raw meal was burned in a crucible in a tube furnace. The burning condition was brought from the first and second part of experiment. After burning, the clinker was taken out from furnace immediately for rapid cooling by air. After cooling, it was ground by a disc mill. Then, the clinker was homogeneously mixed with 4.5 wt. % of gypsum. This compound is called cement. According to the ASTM C109, the cement was molded by mixing with sand and water. The ratio of cement, sand, and water was determined as 1: 2.75: 0.485. The size of mold was $5 \times 5 \times 5 \text{ cm}^3$ as shown in Figure 3.5 (a). After 24 hours, the cement mortars were taken off from the mold as shown in Figure 3.5 (b). Then, the cement mortars were cured in water for 28 days. After that, the cement mortars were ground to $< 125 \mu\text{m}$ before use in the leaching tests. The steps of this experiment are shown in Figure 3.4.

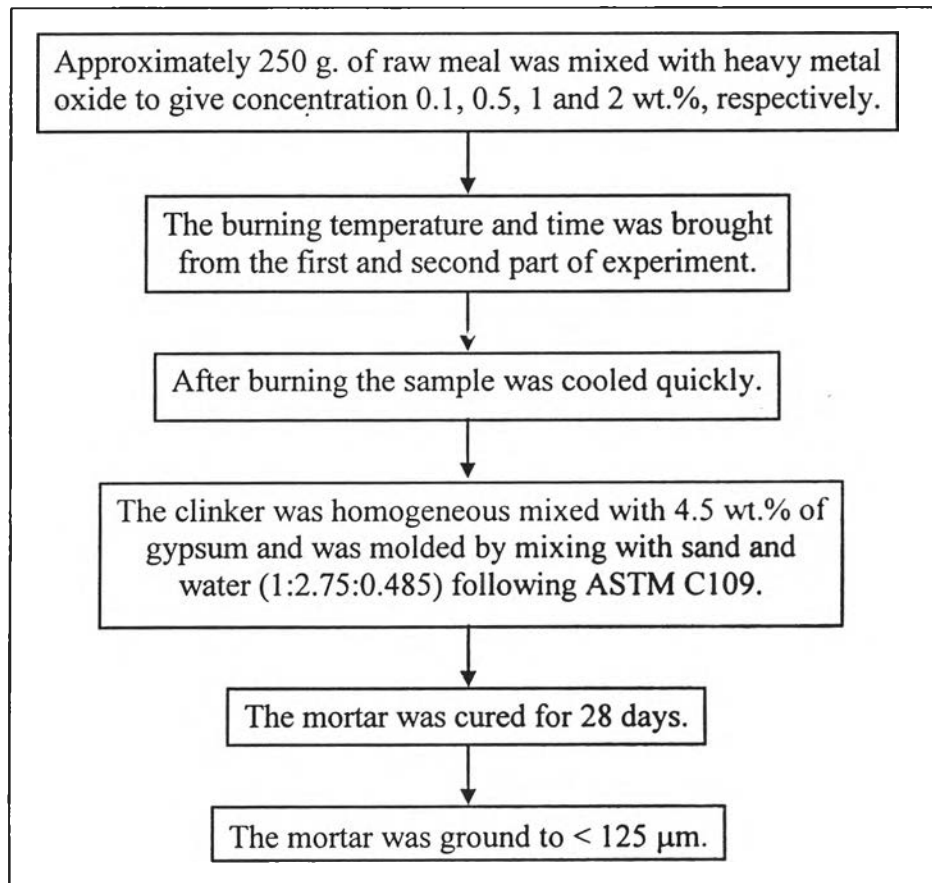


Figure 3.4 Steps of preparation clinker with heavy metal.

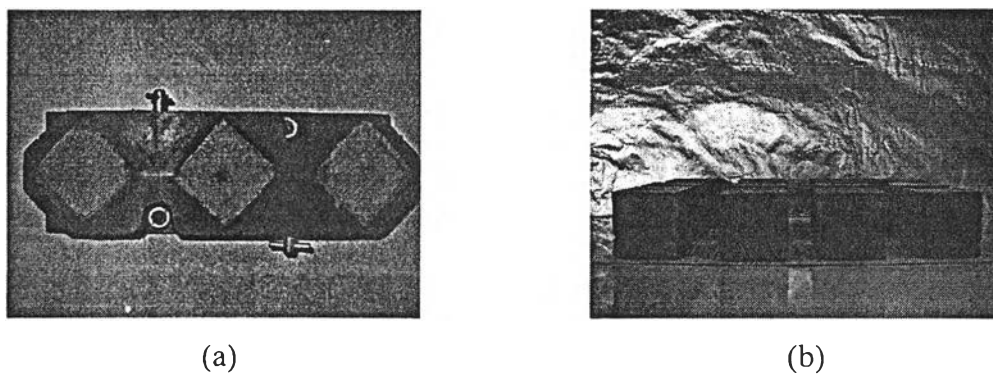


Figure 3.5 Cement mortars (a) before take off (b) after take off

3.2.2 Leaching Tests

The leaching tests in this study consisted of 5 methods. Microwave-assisted leach method 3051 A was used to study total extracted concentration of heavy metal without heavy metal in siliceous matrices in the samples. The toxicity characteristic leaching procedure and Notification of Ministry of Industry No.6 B.E. 2540 (1997) were used to classify wastes as hazardous or non-hazardous. The availability leaching test was used to determine the maximum leachability of heavy metals. The pH static leach test was used to find the leachability of heavy metals at various pH. Microwave assisted acid digestion of siliceous and organically based matrices (U.S. EPA method 3052) was used to study total heavy metal in the sample. The details of the methods are described below.

3.2.2.1 Microwave assisted acid digestion of siliceous and organically based matrices (U.S. EPA method 3052)

Approximately 0.5 g of sample was weight into advanced composite vessel. Approximately 9 ml. of concentrated HNO_3 and 3 ml. concentrated HF were added. After that, the vessels were put into a microwave. The digestion temperature and time were set as follow: First, the temperature was reached to 180°C in 5.5 min. Then, it was held at 180°C for 9.5 min. After cooling, the solution was filtered with filter paper before being analyzed. The procedures are shown in Figure 3.6.

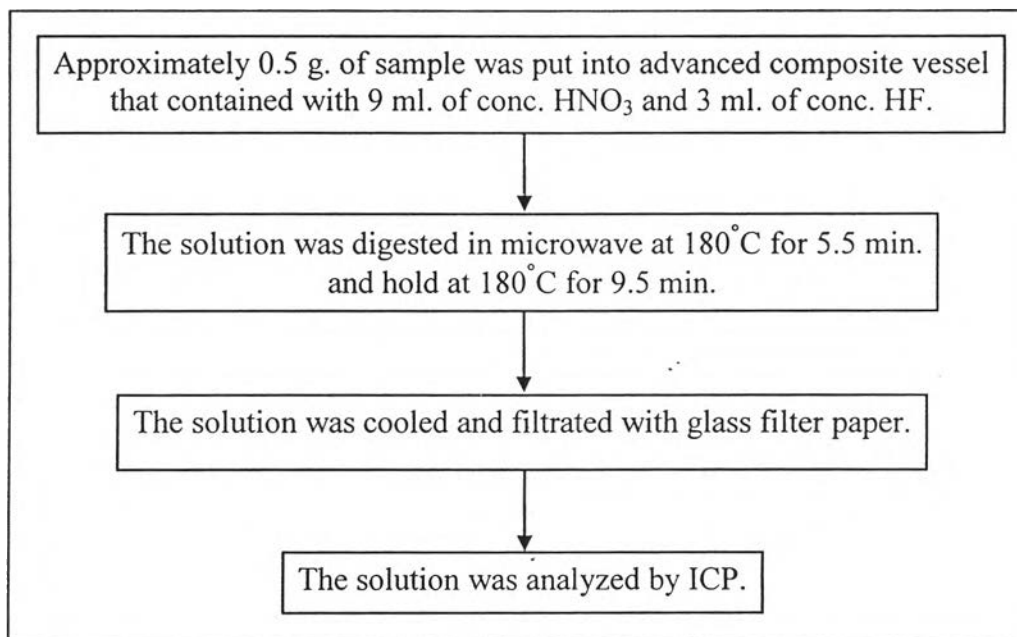


Figure 3.6 Microwave assisted acid digestion of siliceous and organically based matrices extraction procedure.

3.2.2.2 Microwave-assisted leach method 3051 A

Approximately 0.5 g. of sample was weight into advanced composite vessel. Approximately 10 ml. of concentrated HNO₃ was added. After that, the vessels were put into a microwave. The digestion temperature and time were set as follow: First, the temperature was reached to 175 °C in 5.5 minutes. Then, it was held at 175°C for 4.5 min. After cooling, the solution was filtered with glass fiber filter paper before being analyzed. The procedures are shown in Figure 3.7.

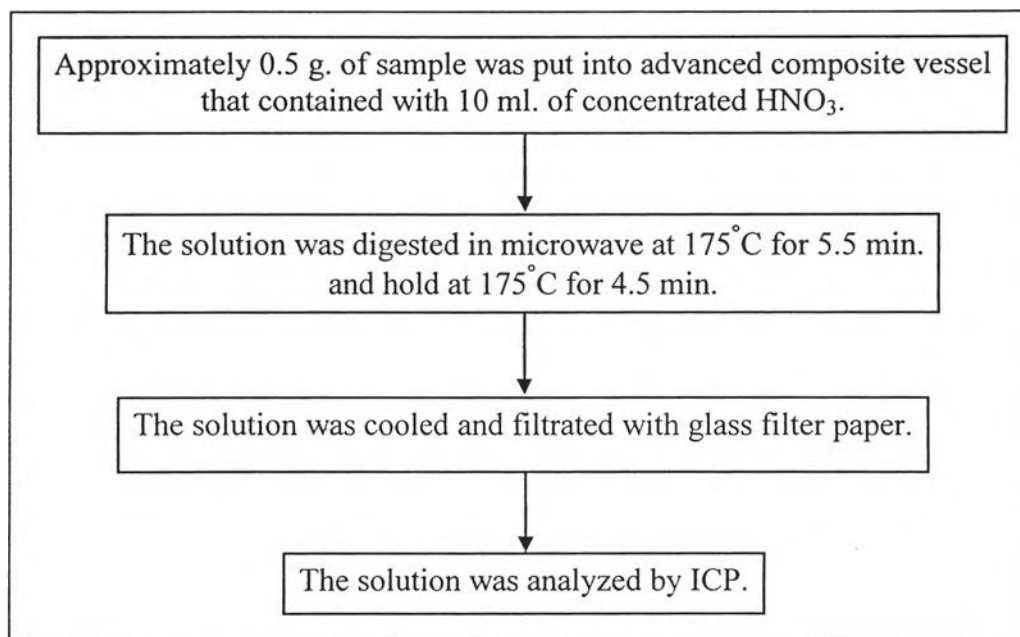


Figure 3.7 Microwave-assisted leach method 3051A extraction procedure

3.2.2.3 Toxicity characteristic leaching procedure (TCLP)

Approximately 10 g. of sample was weighted into polypropylene bottles along with a 20:1 ratio of extracted liquid to sample. About 200 ml. of the TCLP extraction fluid No. 2 was added. This solution was 0.1 M acetic acid and was tested to ensure the pH is 2.88 ± 0.1 . The bottles were tumbled at 30 rpm in a rotary extractor at room temperature for 18 h. At the end of the extraction, the leachate was filtered with glass fiber filter paper. The pH of the filtrate was measured and the leachate was acidified by a small amount of concentrated nitric acid to $\text{pH} < 2$ before being analyzed. The procedures are shown in Figure 3.8.

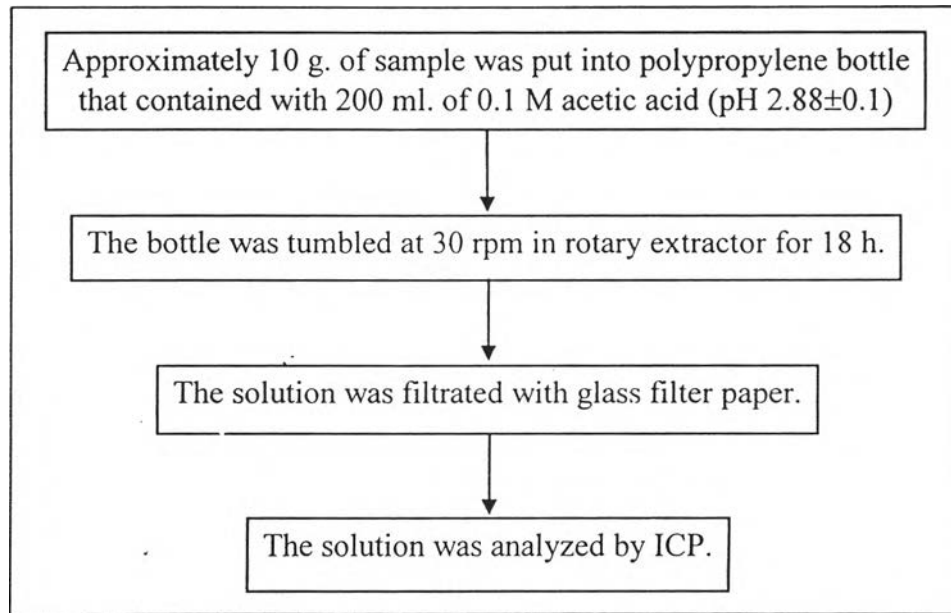


Figure 3.8 Toxicity characteristic leaching procedure

3.2.2.4 Notification of Ministry of Industry No.6 B.E. 2540(1997)

Approximately 10 g. of sample was weighted into polypropylene bottles along with a 20:1 ratio of extracted liquid to sample. About 200 ml. of the extraction fluid was added. This solution was 80:20 ratio of nitric acid to sulfuric acid and was tested to ensure the pH was 5. The bottles were tumbled at 30 rpm in a rotary extractor at room temperature for 18 h. At the end of the extraction, the leachate was filtered with glass fiber filter paper. The pH of the filtrate was measured and the leachate was acidified by a small amount of concentrated nitric acid to pH < 2 before being analyzed. The procedures are shown in Figure 3.9

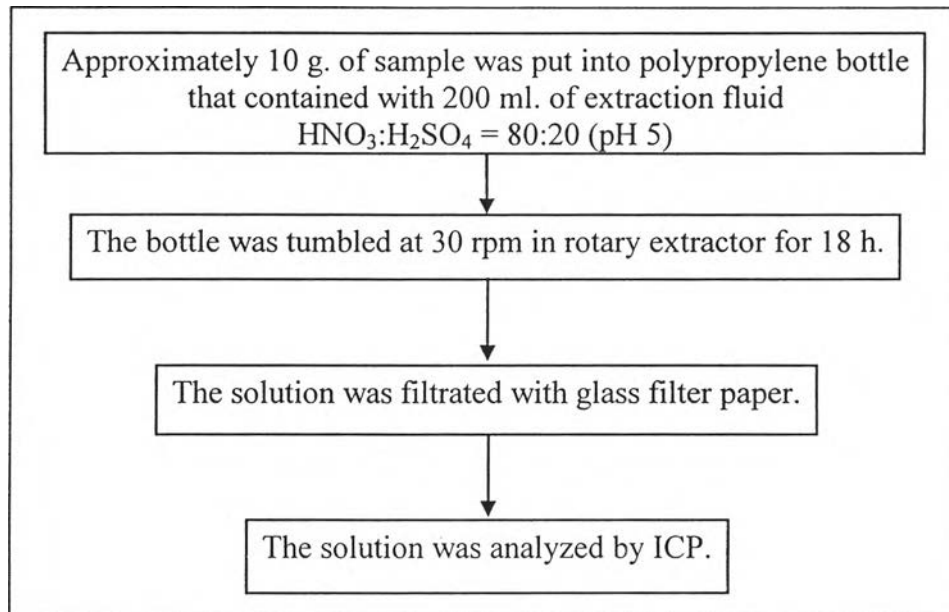


Figure 3.9 Notification of Ministry of Industry No.6 leaching test procedure

3.2.2.5 Availability Leaching Test

A sample mass equivalent to 10 g. was weight into bigger that contained with 500 ml. DI water. First, the sample was extracted at a pH value of 7 ± 0.2 for 3 h. The solution was mixed with a magnetic stirrer and solution pH was maintained by the addition of 0.5 N nitric acid or sodium hydroxide via a pH controller. At the end of the first extraction, the sample was filtered through glass fiber filter paper. The solid was returned to extract with 500 ml. DI water. For the second extraction, the sample was extracted at a pH of 4 ± 0.2 for 3 h. The solution was mixed with a magnetic stirrer and solution pH was maintained by the addition of 0.5 N nitric acid or sodium hydroxide via a pH controller. At the end of the second extraction, the solution was filtered through glass fiber filter paper. The solution from the first and second extraction was mixed together. The solution was acidified by a small amount of concentrated nitric acid to $\text{pH} < 2$ before being analyzed. The procedures are shown in Figure 3.10.

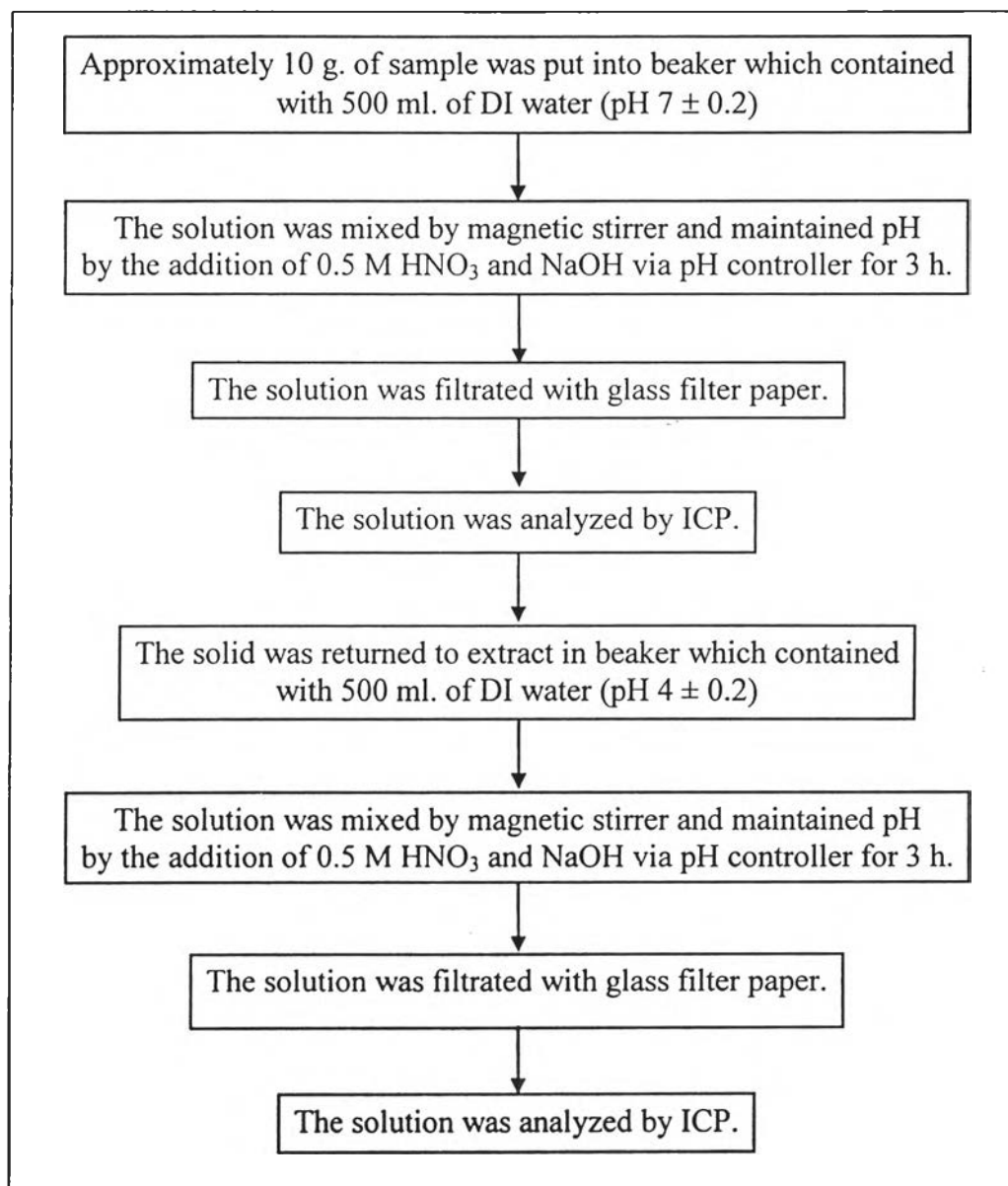


Figure 3.10 Availability leaching test procedure

3.2.2.6 pH Static Leach Test

Approximately 30 g. of sample was extracted in DI water at L/S ratio of 10 ml/g under static pH conditions. The sample was extracted at the following pH values 4-12. The solution was kept open to the atmosphere at 20°C and was stirred continuously during 24 h. The solution pH was automatically adjusted by addition of 1 M HNO₃ or NaOH via a pH controller when the measured pH deviates by more than a preset value from setpoint. After that, the solution was filtered by glass fiber filter

3.3. Chemical Analysis

3.3.1 Analysis of Free lime

Approximately 0.5 g. of sample was weight into flask which contained with 15 ml. of ethylene glycol and 7.5 ml. of methanol. This solution was boiled and equipped with reflux condenser. During boiling, the solution was mixed with stirrer for 30 minutes. After that, this solution was cooled by air. After cooling, the solution was filtrated by number 40 filter paper. Then, the obtained solution was added a few indicator. The indicator was 0.005 g. of methyl red and 0.5 g. of bromocresol green in 100 ml. methanols. The solution was titrated with 0.1 N HCl. An amount of free lime was calculated by the following equation:

$$\% \text{ free lime} = \text{ml. of 0.1 N HCl} \times 0.56$$

3.3.2 Analysis of Heavy metal concentrations

All heavy metal in this study was analyzed by Inductive Couple Plasma (ICP). Before analyze, the solutions were diluted to ensure that their concentration were over the standardization. The dilution factor depended on each tests. For Microwave assisted acid digestion of siliceous and organically based matrices (U.S. EPA method 3052) and, Microwave-assisted leach method 3051A, the solution was diluted by 100 times. For the Availability leaching test (NEN 7341), the solution was diluted by 50 times. For the others method, the solution was diluted by 10 times.

3.3.3 pH measurement

The pH controller (Prominent D1C type D) was used to control the pH. The pH value was determined by pH meter (Sartorius).