

# **CHAPTER III**

## **METHODOLOGY**

### **3.1 Materials and chemicals**

#### **3.1.1 Raw meal**

Raw meal was taken from Siam City Cement Public Company Limited (SCCC) in Saraburi province. It was collected and preserved in a suitable container (clean and dry with a lid) to prevent extraneous contamination.

#### **3.1.2 Petroleum sludge**

Petroleum sludge was obtained from General Environmental Conservation Public Company Limited (GENCO) in Rayong province; it contained heavy metals. The petroleum sludge was collected in a suitable container (clean and dry, with a lid) to prevent extraneous contamination.

#### **3.1.3 Sand**

The river sand used for making the specimens conformed to the requirements for graded sand as specified by ASTM C778-92.

#### **3.1.4 Water**

Ordinary tap water was used for all mixtures.

### 3.1.5 Chemicals

- Hydrochloric acid (HCl)
- Boric acid ( $H_3BO_3$ )
- Nitric acid ( $HNO_3$ )
- Sulfuric acid ( $H_2SO_4$ )
- Hydrofluoric acid (HF)
- Magnesium chloride ( $MgCl_2$ )
- Sodium acetate (NaOAc)
- Hydroxylamine hydrochloride ( $NH_2OH \cdot HCl$ )
- Ammonium acetate ( $NH_4OAc$ )
- Hydrogen peroxide ( $H_2O_2$ )

## 3.2 Experimental programs

### 3.2.1 The physical and chemical analysis of the raw meal and petroleum sludge

The physical and chemical properties of the raw meal and petroleum sludge affect to physical and chemical of the synthetic clinker and leaching of heavy metals. The physical and chemical analysis of the raw meal and petroleum sludge show in Table 3.1 and Table 3.2, respectively.

**Table 3.1 The physical and chemical analysis of the raw meal**

Parameter	Method/Analysis instrument
1. Moisture content, %	ASTM C311-96 and ASTM C114-94
2. Loss on ignition	ASTM C311-96 and ASTM C114-94
3. Heavy metals	SW 846 Method 3052 and ICP-OES
4. Chemical composition	X-ray fluorescence (XRF)

**Table 3.2 The physical and chemical analysis of the petroleum sludge**

Parameter	Method/Analysis instrument
1. Heating Value	Bomb calorimeter
2. Heavy metals	Acid digestion and ICP-OES
3. Chloride	Chloride Potentiometer Titration (ASTM C1152)
4. Sulfur	ASTM D1266
5. pH	pH meter
6. Flash point	ASTM D93-96

### 3.2.2 The clinker synthesis

#### 3.2.2.1 Raw mix preparation and mix ratios

The petroleum sludge was mixed with raw meal at various ratios using a laboratory mill for 1 hour. The proportions of the petroleum sludge were varied at 0%, 5%, 10%, 15% and 20% with raw meal as show in Table 3.3. Raw mix was prepared for 10 kg for each composition.

**Table 3.3 Mixture ratios of the petroleum sludge and raw meal (% w/w)**

Sample Symbol	Raw meal,%	Petroleum sludge,%
M0	100.0	0.0
M5	95.0	5.0
M10	90.0	10.0
M15	85.0	15.0
M20	80.0	20.0

#### 3.2.2.2 Burning process

The raw mix was preheated at 900 °C for 30 minutes and burned at 1,450 °C for 90 minutes at a high temperature in the furnace for clinker synthesis.

### 3.2.3 The physical and chemical analysis for the clinker

After the clinker samples were prepared, several physical and chemical properties were determined. The physical and chemical analysis of the clinker show in Table 3.4.

**Table 3.4 The physical and chemical analysis for the clinker**

Parameter	Method/analysis instrument
1. Moisture Content,%	ASTM C311-96 and ASTM C114-94
2. Loss on ignition	ASTM C311-96 and ASTM C114-94
3. Heavy metals	SW 846 Method 3052 and ICP-OES
4. Chemical composition	X-ray fluorescence (XRF)
5. Crystalline phase	X-ray power diffraction (XRD)
6. Microstructure	Scanning Electron Microscopy (SEM)

### 3.2.4 Compressive strength test

The clinker was ground and mixed with 4.5 % wt. of gypsum which helps to retard the setting time of the cement. It was then molded by mixing it with sand and water (1:2.75:0.485) following ASTM C109 and it was cured at 3, 7, 14, and 28 days. After that, the mortar was tested for its compressive strength.

### 3.2.5 Leaching tests

Leaching test were performed using 28 days curing mortar. The mortar was ground to < 125  $\mu\text{m}$  and tested with leaching test method of U.S.EPA, the Notification of the Ministry of Industry B.E. 2548 (2005), the Notification of the Ministry of Industry B.E. 2540 (1997), and sequential extraction test.

### **3.3 Experimental procedures**

#### **3.3.1 Moisture content and Loss on ignition (LOI)**

Moisture content is free water, it was determined by the weight loss of raw meal and clinker in an oven at  $105 \pm 10$  °C after 24 hours. The technique that was used to determine the moisture content is described in ASTM C311. Approximately 5 grams of sample was dried in a ceramic cup in the oven at a temperature of 105-110°C for 24 hours. After that, it was cooled at room temperature in the desiccators to prevent moisture absorption from the atmosphere. The weight loss was assumed to be the absorbed water.

Loss on Ignition (LOI) is typically defined as the carbon content in raw meal and clinker. According to ASTM C311 and ASTM C114, LOI can be determined by igniting 5 grams of the sample, the residue from moisture content determination, in the porcelain crucible to a constant weight in a muffle furnace at  $750 \pm 50$  °C for 15 minutes. The weight loss after ignition was assumed to be the carbon content in the material or sample. LOI can be used as an indicator of the degree of burnout in material or the combustion efficiency.

#### **3.3.2 Heavy metals**

The method for determining heavy metals in raw meal, petroleum sludge and clinker is described by U.S. EPA SW-846 Method 3052. This method utilizes microwaves to promote the acid digestion and is conducted to analyze the concentration of heavy metals, i.e., chromium (Cr), nickel (Ni), zinc (Zn), lead (Pb) etc. by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). It is design to supply accelerated multi-element acid leach digestion prior to analysis. The need for leaching tests of a waste.

For microwave assisted acid digestion of siliceous and organically based matrices (U.S. EPA SW-846 Method 3052), approximately 0.5 grams of sample was weighted into vessel. Approximately 9 ml. of concentrated HNO<sub>3</sub> and 3 ml. concentrations of HF were added. After that, the vessels were put into a microwave

digestion unit. The digestion temperature and time were set as follow: first, the temperature reached 180°C in 5.5 minutes. Then, it was held at 180°C for 9.5 minutes. After cooling, the solution was filtered with filter paper before being analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

### **3.3.3 The bulk chemical composition**

X-ray fluorescence (XRF) spectroscopy is carried out to measure the bulk chemical compositions of raw meal and clinker. The Philips XRF Spectrometer Model 2400 was used in this study. Bulk chemical composition analysis is a test that determines the qualitative and quantitative elemental compositions of the material. The sample was initially ground in a steel mortar to a homogenous fine powder below 45 microns because the X-ray only penetrates up to a few millimeters from the surface of a sample. After that, 1.5 grams of H<sub>3</sub>BO<sub>3</sub> (2.5% by weight) binder was added to approximately 4.5 grams of ground sample. Then, the mix of the sample and binder was pressed into a pellet for convenient handling and measurement. The pilled sample was put in a sample cup before running and loading it on a feeder tray of the XRF instrument. It took 30 minutes for the instrument to detect the characteristic X-rays of elements emitted from each sample.

### **3.3.4 Mineralogical composition**

X-ray diffraction examines the crystal structure of clinker. X-rays are scattered and diffracted by a lattice structure of crystals, yielding patterns characteristic to various crystals based on the lattice spacing. In this study, a powder X-ray diffraction (XRD) spectrometer, Bruker D8, was used to identify the crystalline phases of the samples. XRD patterns were obtained with a computer controlled diffractometer equipped with a copper X-ray tube and a scintillation detector. A graphite monochromator was used to produce diffracted lines according to a single X-ray wavelength with low background. Each sample was pulverized in a steel mortar until homogeneous with particle size of below 45 microns. All samples were analyze at a 40 kV accelerating voltage, 40 mA current and 5° to 75° 2θ scanning range.



### **3.3.5 Morphology**

Scanning Electron Microscopy (SEM) is a technique for examining the surfaces of solid materials. The microstructure of clinker was observed by a JEOL JSM-6400 scanning electron microscope (SEM). SEM can be used to understand the particle shape, surface texture or morphology of the sample. Magnification of the SEM can be varied from 5x to 1,000,000x, almost 300 times higher than optical instruments, yielding resolutions of approximately 5 nm. The samples were initially glued on an aluminum stub and coated with gold palladium alloy. Each sample was taken at different magnifications and different locations in order to obtain the representative image.

### **3.3.6 The clinker synthesis**

Various proportions of petroleum sludge were mixed with raw meal using a laboratory mill for 1 hour. The proportions of the petroleum sludge were varied at 0%, 5%, 10%, 15% and 20% by raw mix weight. Approximately 150 g of raw mix was burned in crucibles in a high temperature furnace. The temperature was preheated at 900°C for 30 minutes and heated up to the designed temperature which was 1,450°C for 90 minutes. After burning, the samples were taken out from the furnace immediately for rapid cooling by air. When they reached room temperature, they were ground into smaller size particles before analyzing their physical and chemical properties.

### **3.3.7 The compressive strength test**

Compressive strength is the most important commonly concerned property of hardened concrete/mortar; this is because the other properties such as bonding or durability are related to compressive strength. The compressive strength was tested according to ASTM C109-95 for measuring the compressive strength of hydraulic cement mortars. For the test, the clinker was ground and mixed with 4.5 wt.% of gypsum to make cement, and it was molded by mixing it with sand and water

(1:2.75:0.485) with mixer. The cement was added to the sand and water simultaneously in the mixer. After mixing, it was used to consolidate the mortar into 5x5x5 cm<sup>3</sup> cubic molds. After 24 hours, all of the specimens were demoulded and cured for 3, 7, 14, and 28 days. After that mortar was tested for its compressive strength by a 30-ton compressive strength test machine.

### **3.3.8 Leaching tests**

This experiment is a laboratory method for evaluating the concentrations of chromium (Cr), nickel (Ni), zinc (Zn), and lead (Pb). For this research, the mortar was cured for 28 days for the leaching test. Leaching test was employed to identify the distribution of heavy metals in cement made from co-processed industrial sludge and determine whether the cement was hazardous or not. U.S. EPA SW 846 method 1311, the Toxicity Characteristic Leaching Procedure (TCLP) determined the mobility of both organic and inorganic matter present in the liquid, solid and multiphase wastes within a landfill condition; the Notification of the Ministry of Industry No.6 B.E. 2540 (1997) was used to determine the toxicity of the leachate; and the Waste Extraction Test (WET) of the Notification of the Ministry of Industry B.E. 2548 (2005) was used to classify hazardous wastes. Sequential extraction methods were also used to study the speciation and possible associations between the metals and cement components.

#### **3.3.8.1 The Sequential Extraction Test**

In this research, the sequential extraction presented by Tessier et al. (1979) which was widely used in soil, sediment and cement studies which could affect the differentiation of metals between various physical and chemical forms in modified cement was used. The chemical partitioning of metals is operationally defined according to the reagents used and the matrix of the samples.

Fraction 1 – exchangeable, the sample was extracted with 0.5M MgCl<sub>2</sub> at pH 7.0 at a solid to solution ratio of 1:8, with continuous agitation for 5 hours at room temperature;



Fraction 2 – bound to carbonates/specifically adsorbed. The residual from (1) was extracted with 1M NaOAc (adjusted to pH 5.0 with HAc) at a solid to solution ratio of 1:8. Continuous agitation was maintained for 5 hours at room temperature;

Fraction 3 – bound to iron and manganese oxides. The residual from (2) was extracted with 0.04M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% (v/v) HAc (pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 hours at  $96^\circ\text{C}$ ;

Fraction 4 – bound to organic matter/sulfide. The residue from (3) was extracted with 30%  $\text{H}_2\text{O}_2$  (pH 2.0 and a solid to solution ratio of 1: 2) with occasional for 6 hours at  $85^\circ\text{C}$  and then extracted with 3.2 M  $\text{NH}_4\text{OAc}$  in 20% (v/v) agitation  $\text{HNO}_3$  with continuous agitation for 30 minutes;

Fraction 5 – residual fraction. The residue from (4) is digested with concentrated  $\text{HNO}_3$ , HF and  $\text{HClO}_4$  acids at  $90\text{-}190^\circ\text{C}$  for 18 hours.

### **3.3.8.2 The U.S. EPA method 1311: The Toxicity Characteristic Leaching Procedure (TCLP)**

The TCLP was employed in this study in accordance with the standard procedures described by the U.S. EPA. The sample was crushed to a particle size smaller 9.5 mm. About 100 g samples were weighted into polypropylene bottles. The TCLP No. 2 leachant (0.1M HAc, pH  $2.88 \pm 0.1$ ) was added. This condition was selected to mimic the conditions of a landfill. The liquid-to-solid weight ratio was 20:1 for 2000 ml of extraction fluid. The bottles were tumbled at  $29 \pm 1$  rpm in a rotary agitator at room temperature for 18 hours. At the end of the extraction, the leachate was filtered with a 0.6 to 0.8  $\mu\text{m}$  Whatman GF/C 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 by ICP-OES.

### **3.3.8.3 The Notification of the Ministry of Industry No.6 B.E. 2540 (1997)**

The experiment prescribed by Notification of the Ministry of Industry No. 6 B.E 2540 (1997) was employed to analyze the mobility of both the organic and inorganic matter that was found in the liquid, solid and multiphase wastes. In this test, the particle size of the waste was reduced to be smaller than 9.5 mm. Approximately 100 g of the sample was weighted into polypropylene bottles. The extraction fluid made with sulfuric acid (80%) and nitric acid (20%) in deionized (DI) water at a pH of 5.0 was used because it mimicked the conditions in a synthetic precipitation. The crushed sample was mixed with the extraction fluid to liquid-to-solid weight ratio of 20:1, which was based upon the alkalinity of the waste. The extraction vessel was rotated at  $29 \pm 1$  rpm for 18 hours at room temperature by a rotary agitator. The sample was filtered through a 0.6 to 0.8  $\mu\text{m}$  glass fiber filter. The samples were analyzed for their heavy metal concentrations by ICP-OES.

### **3.3.8.4 The Notification of the Ministry of Industry B.E 2548 (2005)**

The leachate extraction procedure described in the Notification of the Ministry of Industry B.E 2548 (2005) was used to determine toxicity of the leachate under landfill conditions. The waste extraction test (WET) was used to classify the waste as hazardous or non-hazardous when the total concentration of heavy metals in the waste is less than the Total Threshold Limit Concentration (TTLC). After leaching test with the waste extraction test, if heavy metals concentration is equal or higher than the Soluble Threshold Limit Concentration (STLC), waste should be classified as hazardous waste if heavy metals concentration is less than the Soluble Threshold Limit Concentration (STLC), waste should be non-hazardous. Table 3.5 shown the maximum values of heavy metals in waste (mg/kg) and leachate (mg/L) according the Notification of the Ministry of Industry B.E 2548 (2005).

Then, the sample was crushed to a particle size smaller than 2 mm. Approximately 50 g portions of the sample were placed into polypropylene bottles. The extraction fluid was 0.2 M of sodium citrate at a pH of  $5.0 \pm 0.1$ . The crushed sample was mixed with the extraction fluid at liquid-to-solid weight ratio of 10:1 or 500 ml of extraction fluid. The extraction vessel was rotated at  $29 \pm 1$  rpm for 48 hours by a rotary agitator. The sample was filtered through a  $0.45 \mu\text{m}$  membrane filter. The sample was analyzed for heavy metal concentrations by ICP-OES.

**Table 3.5 Maximum standard value of heavy metals in waste (mg/kg) and leachate (mg/L) of the Notification of MOI B.E. 2548**

Heavy metals	MOI B.E. 2548	
	TTLIC (mg/kg)	STLC (mg/L)
Ag	500	5
As	500	5
Ba	10,000	100
Be	75	0.75
Cd	100	1
Co	8,000	80
Cr	500*, 2,500**	5
Cu	2,500	25
Hg	20	0.2
Mo	3,500	350
Ni	2,000	20
Se	100	1
Tl	700	7
V	2,400	24
Pb	1,000	5
Zn	5,000	250

Source: the Notification of the Ministry of Industry B.E. 2548

Note: \*Cr<sup>6+</sup>, \*\*Cr<sup>3+</sup>