CHAPTER IV

RESULTS AND DISCUSSION

4.1 The physical and chemical characteristics of raw meal

4.1.1 The appearance of raw meal

The raw meal involved the blending of raw materials such as limestone, shale, high alumina clay, laterite and gypsum. Generally, the particle size of the raw meal was approximately 74 μm and its color was reddish or brownish.

4.1.2 Moisture content and Loss on Ignition (LOI)

According to the ASTM C114-05, the moisture content was 0.0073 %. The value was very low. It indicated that the raw meal was a good storage.

From the raw meal being burnt at 750 °C for a period of 30 minutes, loss on ignition (LOI) was 0.11 percent. The standard value is usually less than 3%. Thus, this raw meal was lower than standard. If the raw meal has a high LOI value, it will cause a low compressive strength in the concrete (Ruangchuay, 2005).

4.1.2 The bulk chemical composition

The bulk chemical compositions refer to the total chemical compositions of raw meal. Mostly, the X-ray fluorescence (XRF) spectrometry was used to measure the quantities and the results were reported in oxide forms including SiO_2, CaO, Al_2O_3, and Fe_2O_3. The bulk chemical composition of raw meal is shown in Table 4.1. The interesting compounds to note were SiO_2, CaO, Al_2O_3, and Fe_2O_3 because these compounds were important for the clinkerization process and C_2S, C_3S, C_3A, and C_4AF formation. Typically, the main compositions of raw meal were kept at the following percentages: CaO around 60-70%, SiO_2 around 18-22%, Fe_2O_3 around 2-4%, and Al_2O_3 around 3-6%.

Table 4.1 Chemical compositions of the raw meal

Constituents	Quantity (wt %)
Na_2O	0.09
MgO	1.60
Al_2O_3	3.91
SiO_2	14.54
P_2O_5	0.08
SO_3	0.11
K_2O	0.34
CaO	74.12
TiO_2	0.28
NiO	0.01
ZnO	0.07
Cr_2O_3	0.03
MnO	0.07
Fe_2O_3	4.53
Co_2O_3	0.04
CuO	0.07
LOI	0.11
Total	100.00

4.1.3 Heavy metals

In this research, the meaning of heavy metal or trace element generally refers to less than 100 ppm of the concentration. Many of the analyses defined below exceed this limit for individual elements. The digested raw meal was measured by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The concentrations of heavy metal from the raw meal are displayed in Table 4.2.

Table 4.2 Concentration of heavy metals in the raw meal

Heavy metal	Concentration (mg/kg)
Mn	180.91
Zn	119.61
Tl	116.67
Cu	108.97
Cr	42.33
Pb	27.59
Ni	13.23
Ga	8.78
Co	4.86
Cd	1.29
Bi	1.24
Ag	1.08

4.2 The physical and chemical characteristics of the petroleum sludge

Table 4.3 The physical and chemical analysis of the petroleum sludge

Parameter	Result
Heating Value	3,914.5 cal/g
pH	8.5
Flash point	42°C
Cl,%	0.78%
SO_4,%	2.31%

4.2.1 Heating value

The heating value was an important parameter for classification between alternative fuels (AF) and alternative raw materials (AR). If the heating value is higher than 2,000 cal/g, it will be classified as an alternative fuel (AF) (Holcim, 2006).

The heating value of the petroleum sludge was 3,914.5 cal/g. Therefore, it can be used as an alternative fuel in the co-processing of cement production.

4.2.2 Chloride and sulfur value

The amount of chloride was 0.78% and sulfur was 2.31%. The limited amounts of chloride and sulfur in the waste for co-processing in the cement industry were 2.5% and 10%, respectively (Holcim, 2006). The high amount of chloride could damage and clog the refractory inside the rotary kiln. Chloride and sulfur form acid gas in the burning process. In addition, workers should avoid any skin exposure to or inhalation of chloride and sulfur.

4.2.3 pH

The pH value of the petroleum sludge was 8.5, a weak base. By default, pH is one of the important parameter used for choosing basic personal protective equipment for workers.

4.2.4 Flash point

Flash point means the lowest temperature at which it can form an ignitable mixture in air. The flash point is often used as an explanation of characteristic of alternative fuel. To be accepted as an AF, flash point in a waste is set at the minimum of 29°C (Holcim, 2006). This petroleum sludge, with the flash point of 42 °C, can be kept in room temperature because the flash point of the petroleum sludge is higher than the limit value.

4.2.5 Heavy metals

The petroleum sludge was digested using a microwave digester according to US EPA SW-846 Method 3052 and the concentrations of heavy metals were measured by ICP-OES. The concentrations of heavy metals were called total heavy metal. The total heavy metal results compared with Total Threshold Limit Concentration (TTLC) set in the Notification of Ministry of Industry B.E. 2548 and the results were presented in Table 4.4. It was found that concentration of Zn and Pb exceeded the standard values. Therefore, this petroleum sludge was classified as hazardous waste. The heavy metals of interest in this research were Zn, Ni, Pb, and Cr because of their high concentrations and potential adverse effects on the cement properties.

Table 4.4 Total heavy metals in petroleum sludge compared with TTLC of the Notification of MOI B.E. 2548

Heavy metal	Concentration (mg/kg)	TTLC (mg/kg) MOI B.E. 2548
Zn	23,170.33	5,000
Mn	7,302.67	-
Ni	1,558.43	2,000
Pb	1,182.97	1,000
Cr	892.58	500*, 2,500**
Ga	250.47	-
Bi	69.45	-
Co	36.00	8,000
Cd	33.55	100
Tl	21.47	700
Ag	21.46	500
V	4.49	2,400
In	4.42	-

Note: *Cr^{6+}, **Cr^{3+}

4.3 The physical and chemical characteristics of the clinker

In order to investigate the effects of the heavy metals on the synthetic clinker and to use the obtained information to illustrate the leaching of heavy metal from the real clinker, the synthetic clinker should be made with similar manner compared with the real clinker. In this study the clinker was burnt at 1,450 °C for a period of 90 minutes.

4.3.1 Moisture content and Loss on Ignition (LOI)

The moisture content in the synthetic clinker was very low. Therefore, it was classified as a non-significant parameter. While the LOI value of all samples varied from 0.775 to 1.462 %, the maximum acceptable the LOI value was 3 % (Shovishian, 2001). The results were presented in Table 4.5.

4.3.2 The bulk chemical composition

The bulk chemical composition of the synthetic clinkers were calculated in both the Bogue and Modulus equations and presented in Table 4.5. Since petroleum sludge was used as an alternative fuel in the cement production, the chemical composition of the raw mix was considered important. Typically, the composition parameters of the synthetic clinkers were controlled at SR values of around 2.0-3.0, AR values of around 1.0-4.0, LSF value of around 92-98, free lime value of around 0.5-1.0, C_3S of around 45-55%, C_2S of around 15-35%, C_3A of around 7-15%, and C_4AF of around 5-10%.

In this research, it was found to be feasible to use heavy metal-containing sludge as an alternative fuel in the cement production. By controlling the compositional parameters (the lime saturation factor, silica ratio, alumina ratio, C_3S, C_2S, C_3A, and C_4AF) in the modern cement, the replacement could be exchanged with up to 20% of petroleum sludge. These values were acceptable after comparing them with the limitation value of both the Bogue and Modulus equations. As a result of the petroleum sludge replacement in the cement production, the C_3S and C_2S fluctuated. While increasing the percentage of the petroleum sludge replacement, the C_3A decreased but the C_4AF increased.

Table 4.5 Chemical composition analysis and modulus of the clinker

Chemical Composition (%)	0%	5%	10%	15%	20%
Na_2O	0.12	0.17	0.2	0.26	0.31
MgO	1.99	1.98	1.94	1.92	1.99
Al_2O_3	5.33	5.44	5.15	5.68	5.33
SiO_2	22.51	22.06	21.29	20	20.32
P_2O_5	0.09	0.18	0.28	0.38	0.51
SO_3	0.09	0.14	0.35	0.77	1.13
K_2O	0.09	0.16	0.21	0.23	0.15
CaO	65.13	64.36	63.81	62.37	61.37
TiO_2	0.25	0.28	0.3	0.35	0.39
MnO	0.07	0.08	0.08	0.09	0.09
Fe_2O_3	3.56	4.35	5.13	6.59	6.96
LOI	0.78	0.8	1.25	1.37	1.46
Moisture content	0.002	0.002	0.002	0.003	0.003
Total	100	100	100	100	100
Bogue Equations					
C_3S	53.15	51.58	55.96	54.38	49.67
C_2S	24.45	24.34	18.83	16.3	20.78
C_3A	8.09	7.04	4.97	3.9	2.35
C_4AF	10.83	13.24	15.6	20.03	21.15
Modulus Equations					
LSF	90.91	90.62	92.42	93.13	90.65
SR	2.53	2.25	2.07	1.63	1.65
AR	1.49	1.25	1	0.86	0.77
Free lime (%)	0.85	0.78	1.11	1.01	1.4

4.3.3 Heavy metals

The content of heavy metals in the clinker was determined and shown in Table 4.6. The results also showed the total concentrations of heavy metals in the clinkers. While the percentage of the petroleum sludge replacement increased, the concentration of heavy metals also increased. The Total Heavy Metal results were compared with the Total Threshold Limit Concentration (TTLC) in the Notification of the Ministry of Industry B.E. 2548 were shown in Table 4.6. It was found that the total amount of heavy metals in the synthetic clinkers did not exceed the standard value; however, the waste could not yet be classified as a non-hazardous material. Therefore, the Waste Extraction Test (WET) was used for further testing of the waste to determine whether it should be classified as hazardous or non-hazardous.

Table 4.6 Concentrations of heavy metals in clinkers at different % of petroleum sludge replacement

Heavy metal	Concentration (mg/kg)					TTLC (mg/kg) MOI B.E. 2548
	0%	5%	10%	15%	20%	
Mn	3,412.60	2,912.20	3,330.80	4,007.93	4,222.93	-
Zn	944.32	1,258.91	1,521.59	1,918.77	2,428.20	5,000
Cr	672.69	722.94	734.58	806.25	894.04	500*, 2,500**
Ni	212.21	301.23	323.77	391.67	436.96	2,000
Ga	100.83	116.98	122.82	149.96	152.40	-
Co	74.88	77.54	88.69	89.64	97.00	8,000
Pb	27.59	32.10	43.55	64.45	73.13	1,000
Cd	6.45	6.95	7.37	9.96	9.17	100
Bi	0.89	3.79	4.73	39.99	43.35	-
Ag	0.75	0.88	0.89	0.93	1.70	500

Note: *Cr^{6+}, **Cr^{3+}

4.3.4 Mineralogical compositions

The information on bulk chemical compositions only gives a rough idea as to how much each element is found in the materials. But information on the compounds those elements constitute is really important for the prediction of chemical reactions.

The X-ray Diffraction (XRD) is used for clinker's structure analysis. The results of the X-ray Diffraction (XRD) showed the phases C_3S, C_2S, C_3A, and C_4AF of the clinkers. The XRD pattern was also used to compare the clinker characteristics between the obtained and the real clinker. In this research, the temperature and time for clinker synthesis in the laboratory was 1,450 ^{o}C for a period of 90 minutes.

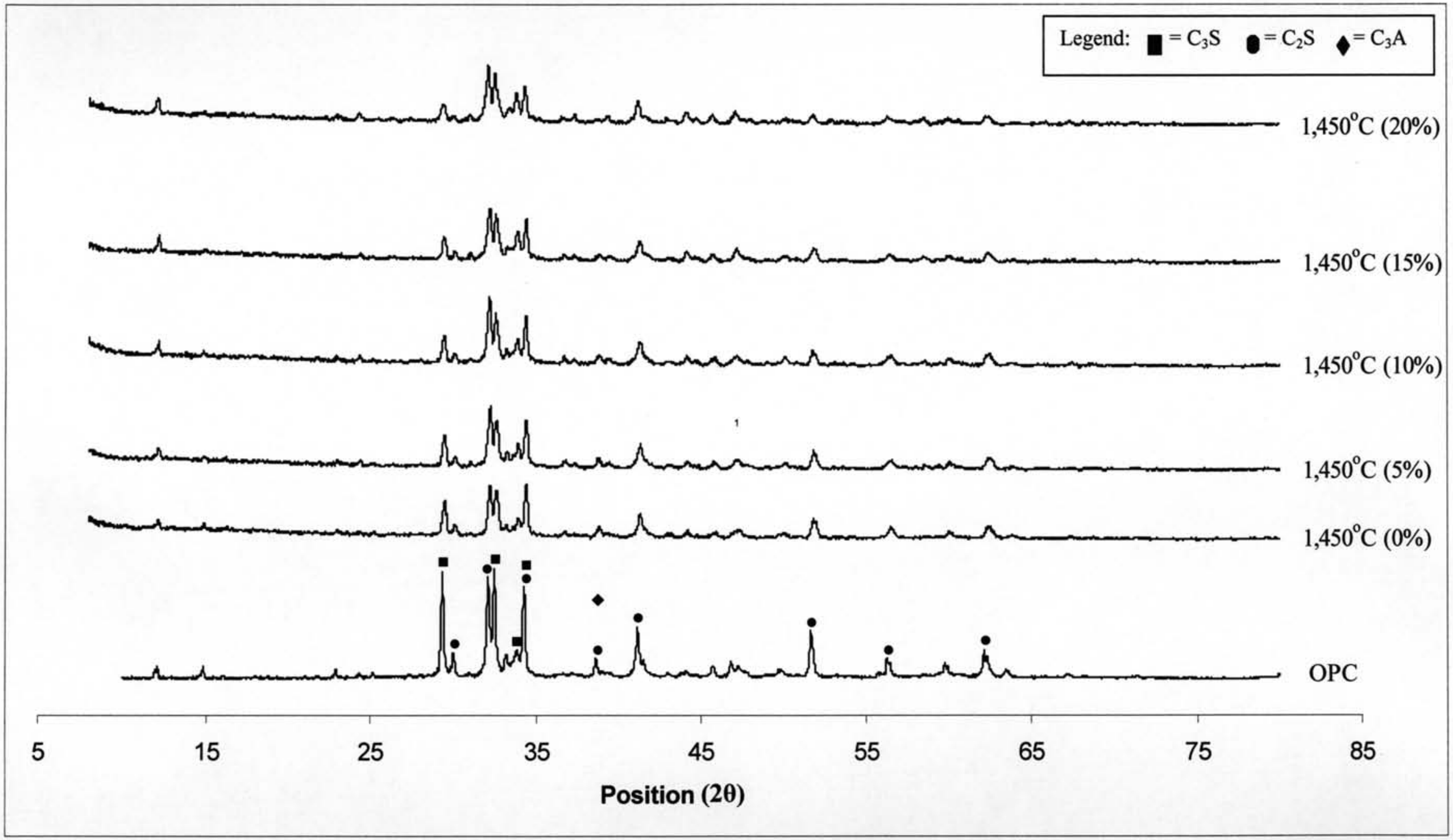


Figure 4.1 XRD patterns of the clinker at 1,450 °C with 90 min.

Figure 4.1 showed the XRD patterns at the different percentages of petroleum sludge addition. The prominent peaks in the clinker from industry were those of tricalcium silicate (C_3S) at 2θ of 29.5°, 32.6°, 33.8°, and 34.5°, dicalcium silicate (C_2S) at 2θ of 32.3°, 51.7°, 56.5°, and 62.2°, and aluminite (C_3A) at 2θ of 38.8°. The patterns obtained from the synthetic clinker at the different percentages of the petroleum sludge addition exhibited a similar pattern as compared with the spectrum of the real clinker.

4.3.5 Morphology

The microstructure of the synthetic clinker was studied through a Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS). Results demonstrated evidence to support the similarity of synthesis with the real clinkers. Figure 4.2 (a) and (b) showed the micrograph of the synthetic clinker at 0% of petroleum sludge replacement that was analyzed at a magnification multiplied by 1,000 and 5,000, respectively. It can be seen in the crystalline phase with the C_3S in crystal shape.

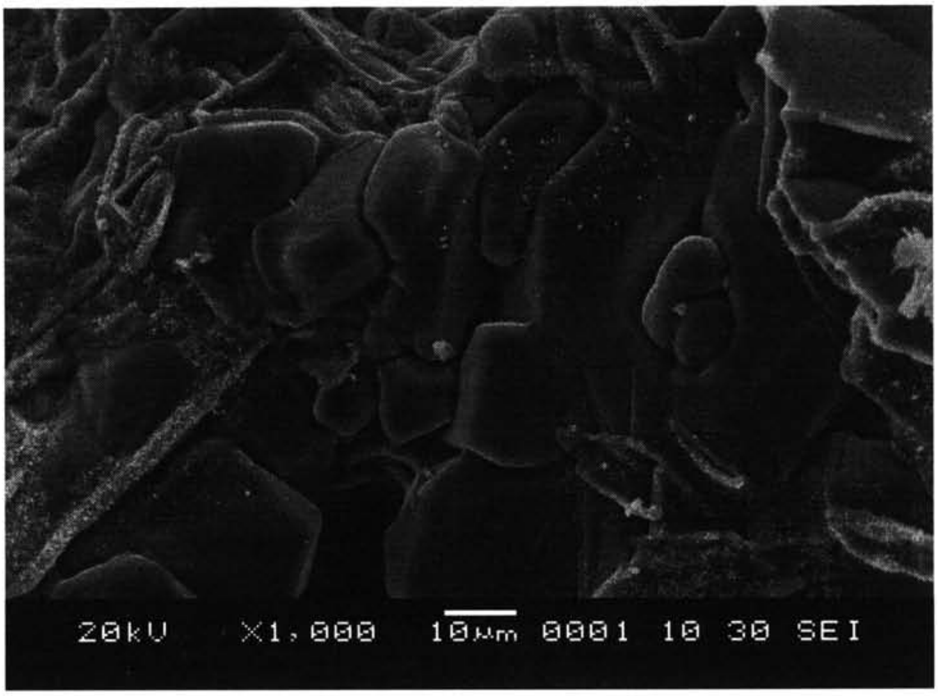
Figure 4.3 (a) and (b) showed the micrograph of the synthetic clinker at 5% of petroleum sludge replacement analyzed at a magnification multiplied by 300 and 5,000, respectively. It can be seen in the crystalline phase with the C_3S in a pseudohexagonal shape and the C_2S in spherical form. It was noted that the C_3S was larger in size than the C_2S.

Figure 4.4 showed the micrograph of the synthetic clinker at 10% of petroleum sludge replacement analyzed at a magnification multiplied by 5,000. It can be seen in the crystalline phase with the C_3A in bar shape.

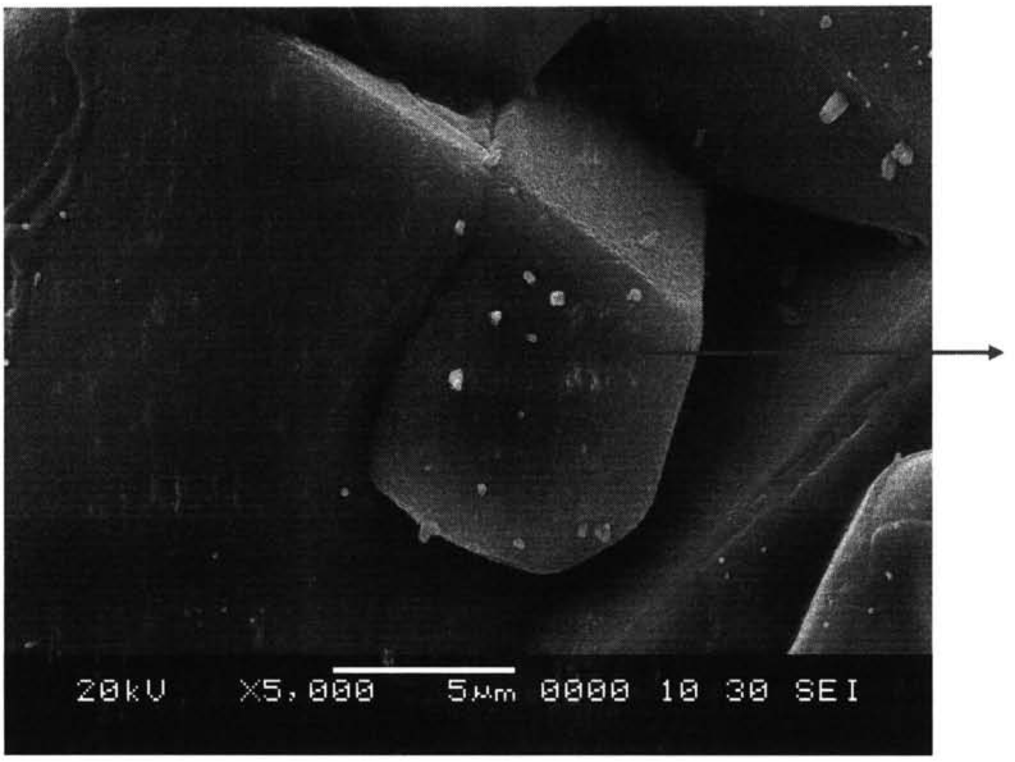
Figure 4.5 (a) and (b) showed the micrograph of the synthetic clinker at 15% of petroleum sludge replacement analyzed at a magnification multiplied by 2,000 and 10,000, respectively. It can be seen in the crystalline phase with the C_3S in crystal shape and in a larger size.

Figure 4.6 (a) and (b) showed the micrograph of the synthetic clinker at 20% of petroleum sludge replacement analyzed at a magnification multiplied by 5,000. It can be seen in the crystalline phase with the C_3A in bar shape.

Due to the small amount of C_4AF, the form was not found in this study. In the SEM results the distribution of heavy metal in the clinker phase was not found because of the low concentration of heavy metals.

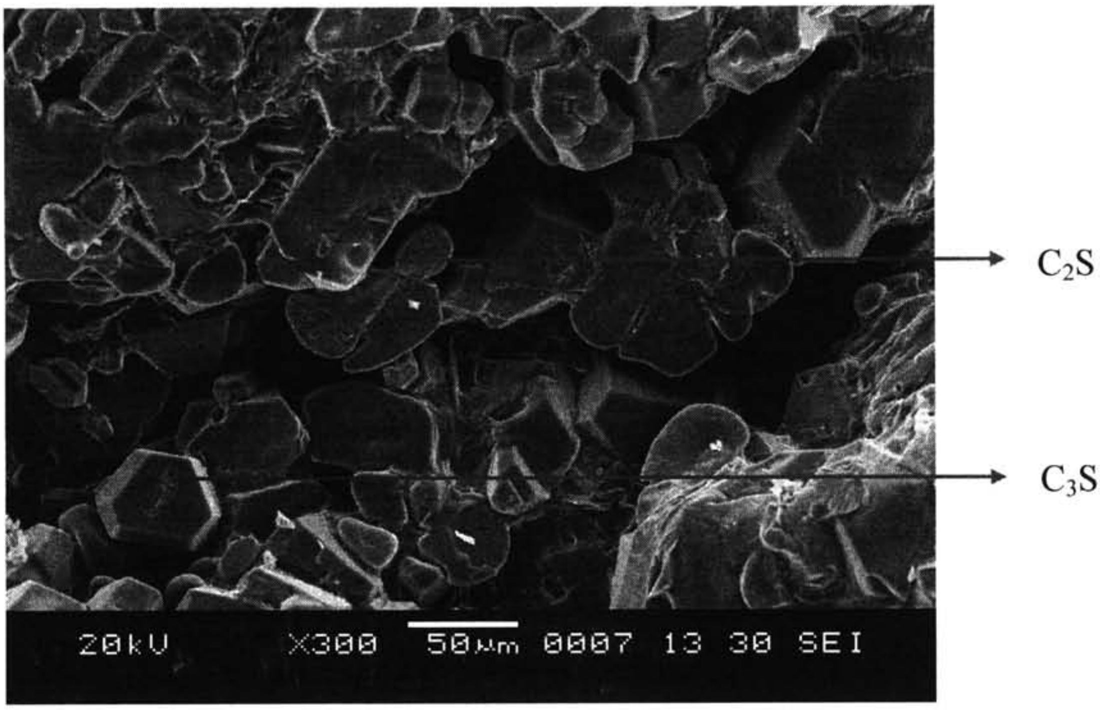


(a)

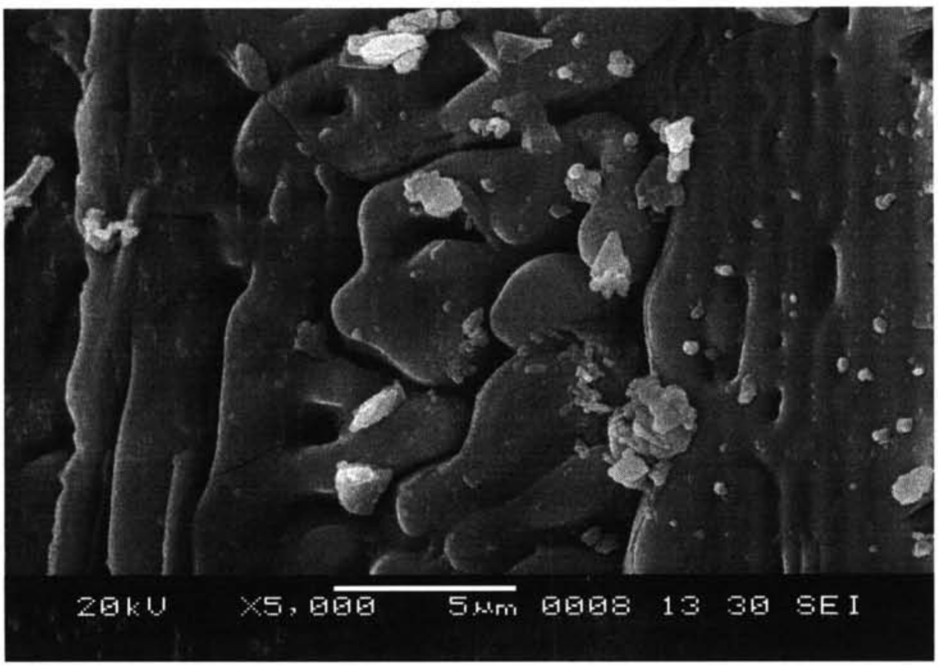


(b)

Figure 4.2 Scanning Electron Micrograph of the synthetic clinker at 0% replacement (a) The synthetic clinker at 1,000x and (b) C_3S in the synthetic clinker at 5,000x



(a)



(b)

Figure 4.3 Scanning Electron Micrograph of the synthetic clinker at 5% replacement (a) C_2S and C_3S in the synthetic clinker at 300x and (b) The synthetic clinker at 5,000x

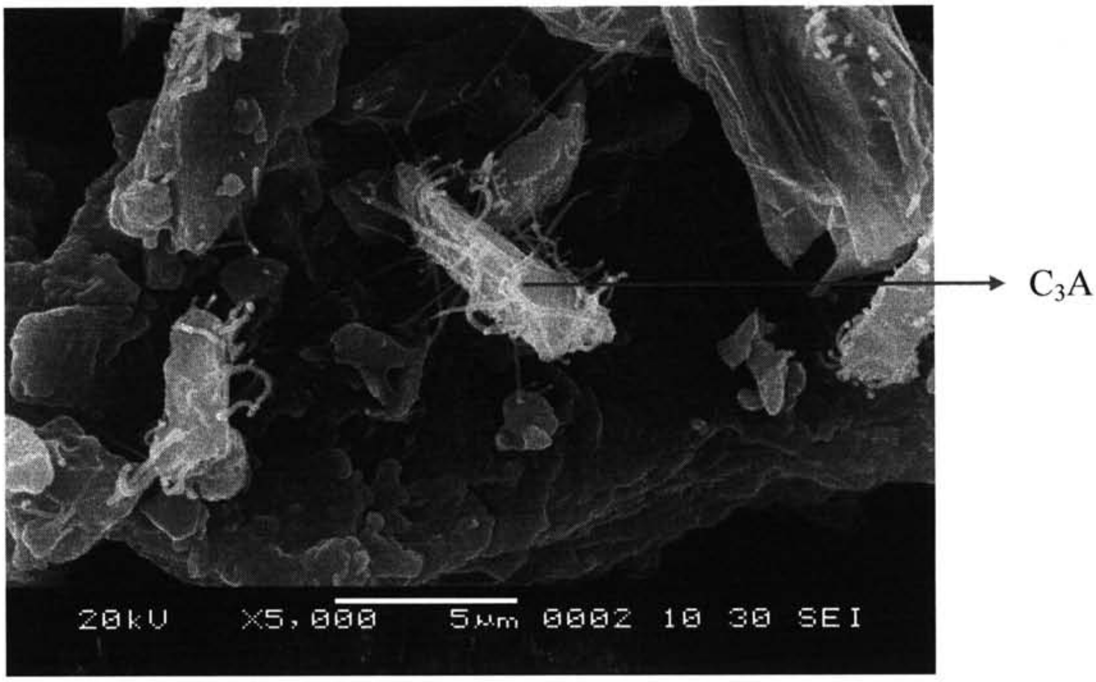
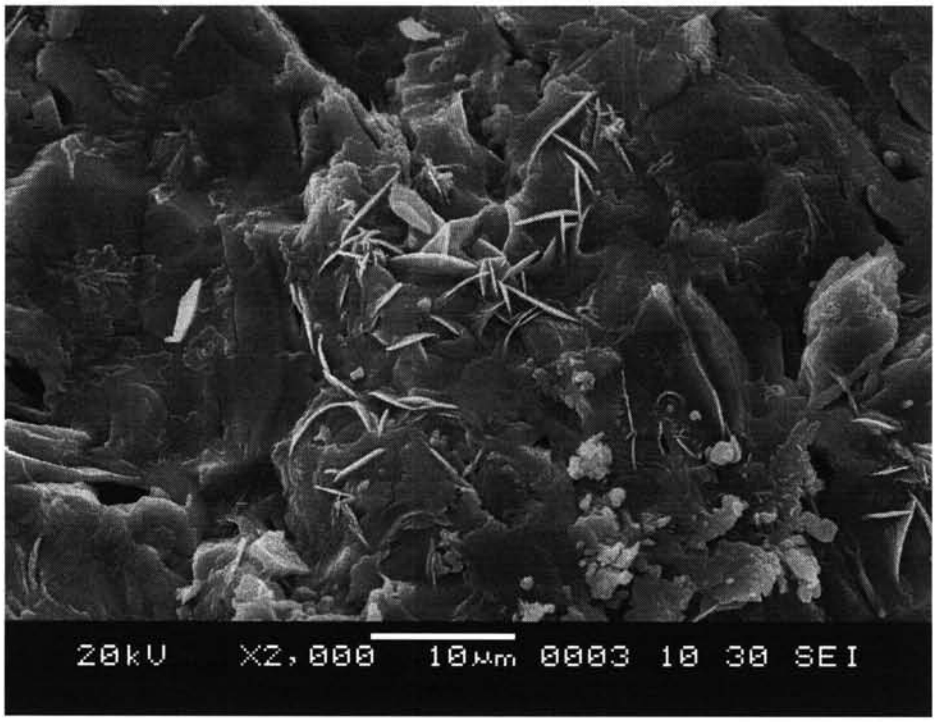
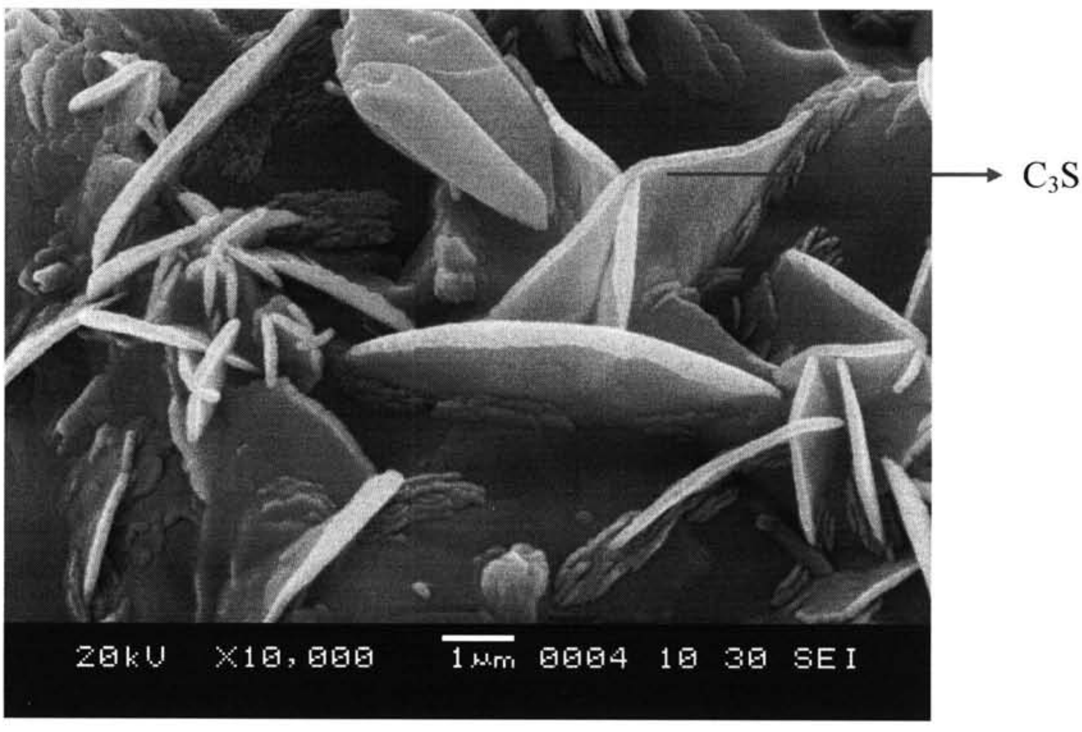


Figure 4.4 Scanning Electron Micrograph 5,000x of the synthetic clinker at 10% replacement

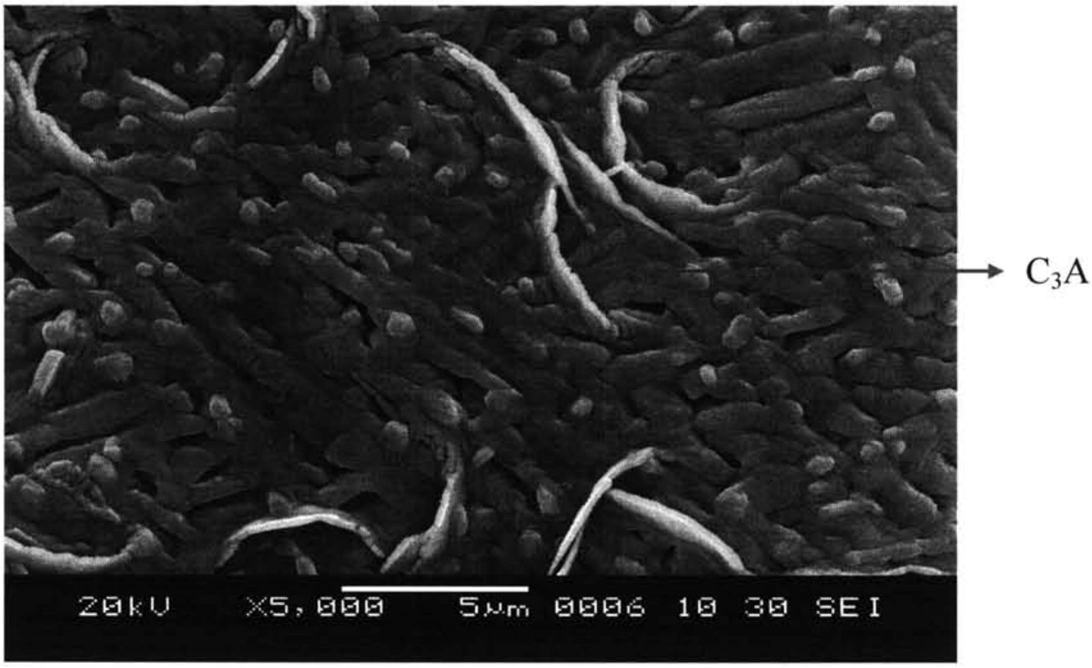


(a)

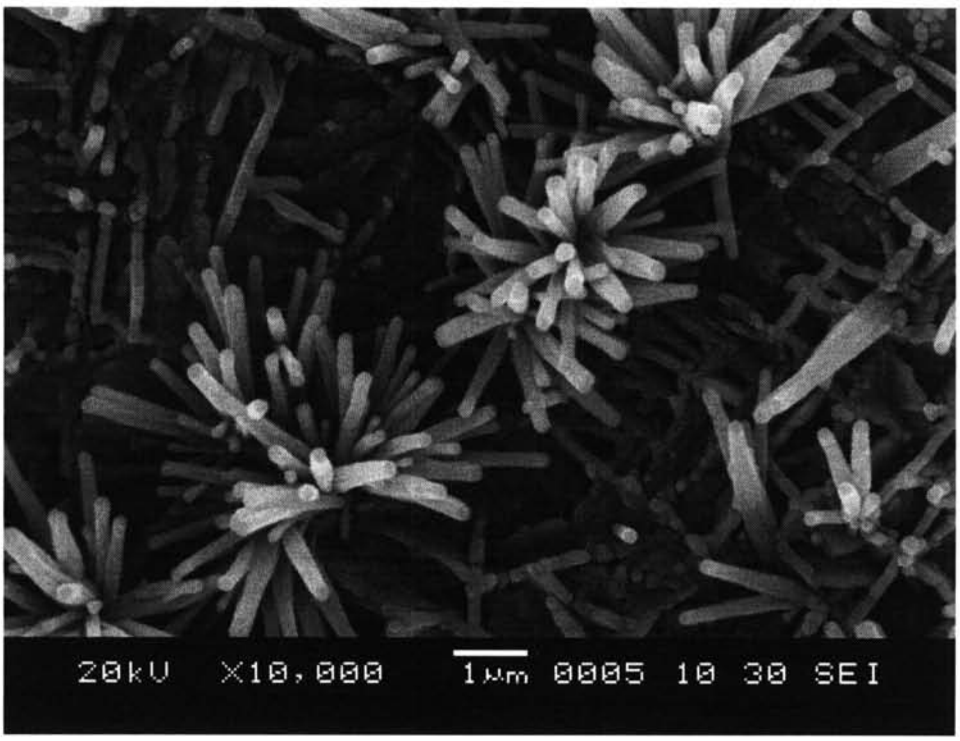


(b)

Figure 4.5 Scanning Electron Micrograph of the synthetic clinker at 15% replacement (a) The synthetic clinker at 2,000x and (b) C_3S in the synthetic clinker at 10,000x



(a)



(b)

Figure 4.6 Scanning Electron Micrograph of the synthetic clinker at 20% replacement (a) C_3A in the synthetic clinker at 5,000x and (b) The synthetic clinker at 10,000x

4.4 The compressive strength

The compressive strength results were satisfactory according to the ASTM C109/C109M–95. The results were presented in ksc (kg/cm^2) with the standard value was 245 kg/cm^2 at 28 curing days according to the ASTM.

Figure 4.7 showed compressive strengths of the synthetic cement with the percentages of petroleum sludge addition. It was found that when the weight from the percentage of the petroleum sludge addition increased the compressive strengths did not show a significant change. That is, the addition of the heavy metals petroleum sludge did not have an adverse effect on the compressive strength. Additionally, the sludge addition of up to 20 percentage by weight still produced acceptable 28-day strength, according to the ASTM standard value.

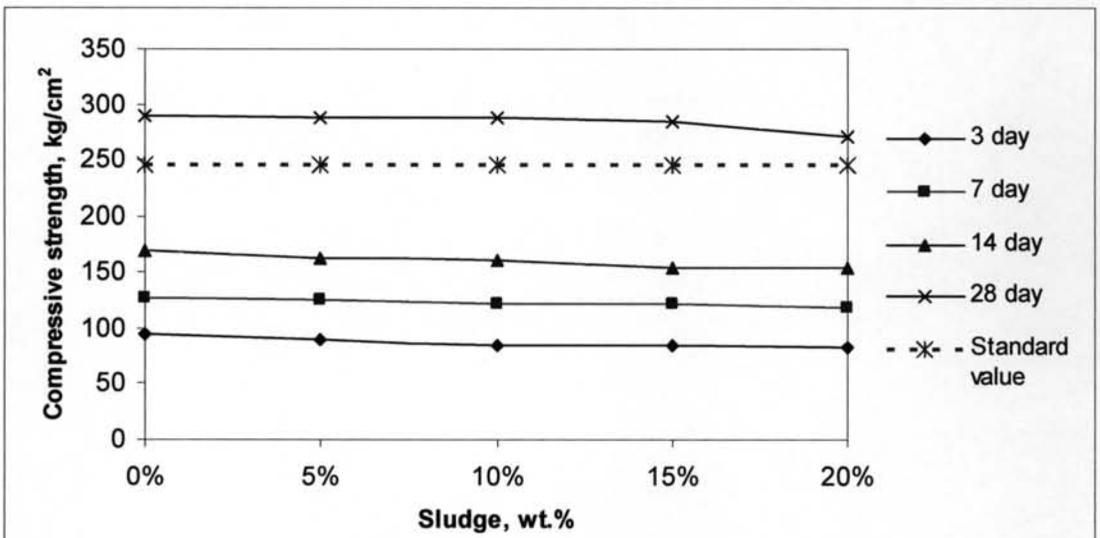


Figure 4.7 The compressive strength of synthesized cement with the percentages of petroleum sludge additions

4.5 Leaching tests

The leaching study focuses on concentrations of Cr, Ni, Pb and Zn that leached from the mortar samples at the 28th day of the curing period.

4.5.1 Leaching of Chromium (Cr)

After burning raw material containing chromium, it was discovered that most of the chromium remained in the clinker. When considering this clinker to be used for cement production, it was understood that this cement might actually be classified as hazardous waste. Thus, the Notification of the Ministry of Industry No.6 B.E. 2540, the Notification of the Ministry of Industry B.E. 2548 and the United States regulations, 40 CFR 261.24 (TCLP), were employed in order to identify whether this cement chould be classified as hazardous waste. The TCLP was proposed by the U.S. EPA.

Figure 4.8 showed the results obtained from the leaching procedure of the Notification of the Ministry of Industry No.6. B.E. 2540. After 18 hours of leaching, the amounts of chromium were detected at additions of 0, 5, 10, 15, and 20 wt% of petroleum sludge of which the concentrations of chromium were measured at 0.020, 0.024, 0.036, 0.041 and 0.052 mg/L, respectively. According to the Notification of the Ministry of Industry No.6 B.E. 2540, the allowable value for chromium in the leachate must be less than 5 mg/L. From the results, it was noted that the chromium in the extraction fluid was lower than the allowable value. Therefore, the raw mix of cement with an addition of up to 20 wt% of petroleum sludge could be labeled as non-hazardous and can be used as a product.

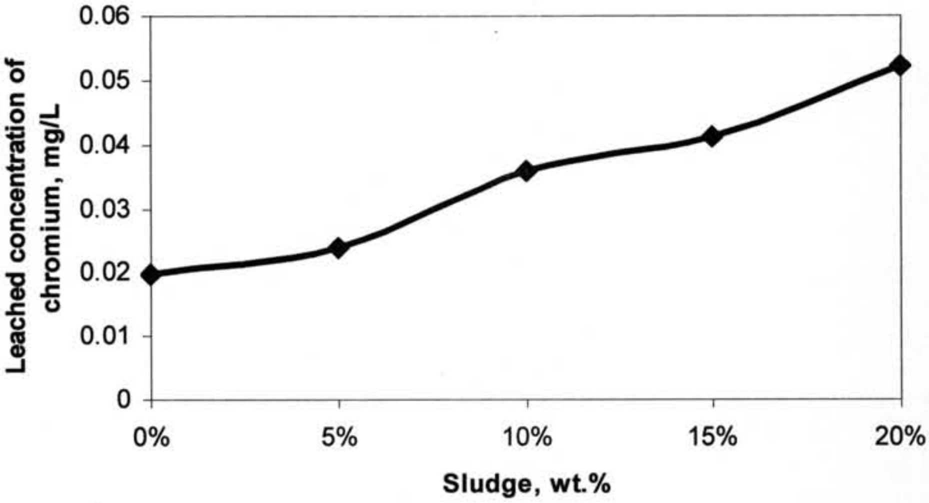


Figure 4.8 The average leached concentration of chromium from the Notification of the Ministry of Industry No.6. B.E. 2540

Figure 4.9 showed the results obtained from the TCLP. After 18 hours of leaching, amounts of chromium were detected at additions of 0, 5, 10, 15, and 20 wt% of petroleum sludge in which the concentrations of chromium were measured at 0.024, 0.027, 0.035, 0.050 and 0.052 mg/L, respectively. According to the U.S. EPA, the allowable value of chromium in the leachate should be less than 5 mg/L. The results showed that the chromium in the extraction fluid was lower than the allowable value. Therefore, the raw mix of cement with an addition of up to 20 wt% of petroleum sludge could be labeled as non-hazardous and can be used as a product.

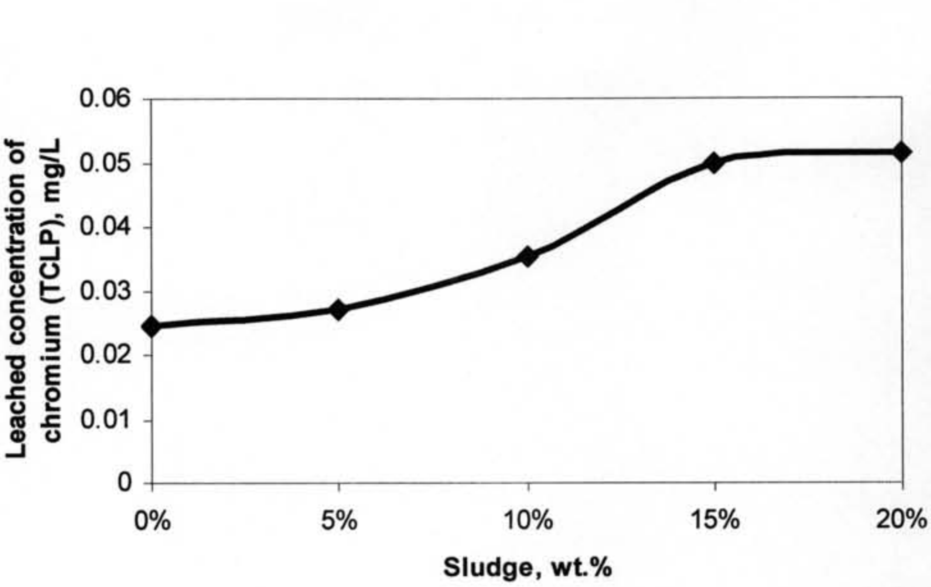


Figure 4.9 The average leached concentration of chromium from the TCLP

Figure 4.10 showed the results obtained from the leaching procedure the Notification of the Ministry of Industry B.E. 2548. After 48 hours of leaching, amounts of chromium were detected at additions of 0, 5, 10, 15, and 20 wt. % of petroleum sludge in which the concentrations of chromium were measured at 0.40, 0.55, 0.68, 0.72 and 0.76 mg/L, respectively. According to the Notification of the Ministry of Industry B.E. 2548, the allowable value of chromium in the leachate must be less than 5 mg/L. Since chromium in the extraction fluid was lower than the allowable value, the raw mix of cement with an addition of up to 20 wt% of petroleum sludge could be identified as non-hazardous and can be used as a product.

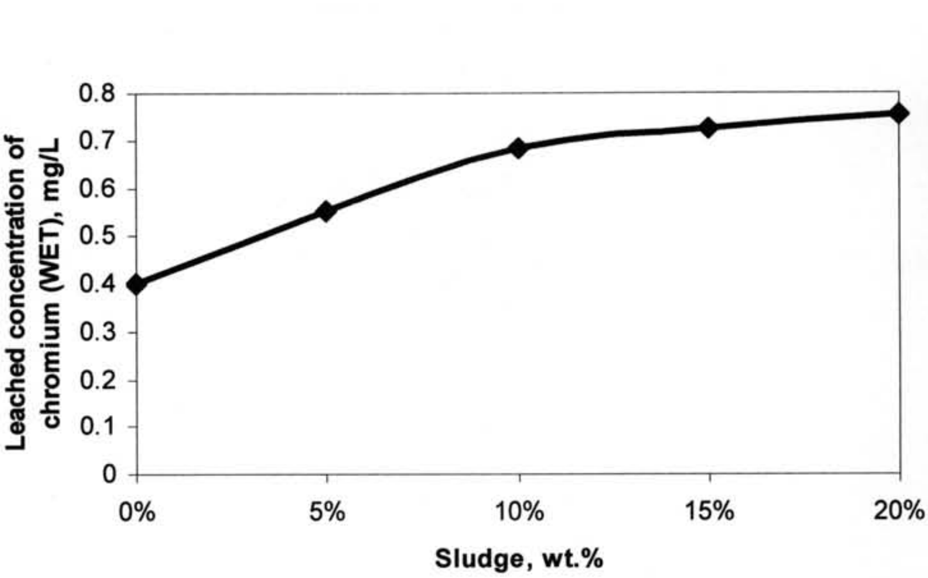


Figure 4.10 The average leached concentration of chromium from the WET by the Notification of the Ministry of Industry B.E. 2548

4.5.2 Leaching of Nickel (Ni)

After burning raw material containing nickel, it was discovered that most of the nickel remained in the clinker. When considering the use of this clinker for cement production, it was understood that this cement might be classified as a hazardous waste. According to the leaching procedures described in the Notification of the Ministry of Industry No.6 B.E. 2540 and the U.S. regulatory leaching procedure (TCLP), the allowable value nickel concentration in the leachate was not regulated. However, in an attempt to quantify the hazard, the U.S. EPA established the guideline that if metal concentrations in the extracts do not exceed 100 times the maximum contaminant levels (MCLs), the waste would not be considered hazardous waste (Hardaway et al., 1999). The MCL of nickel is 0.1 mg/L. Thus, nickel would be considered as hazardous, if the concentrations of nickel in the extraction fluid exceeded 10 mg/L. Moreover, there wasn't any nickel leached from either method. The leached concentrations from both methods were lower than the specified criteria. Hence, it is likely that this cement would be classified as non-hazardous waste.

Figure 4.11 showed the results obtained from the Notification of the Ministry of Industry B.E.2548. The results showed the maximum concentrations of nickel to be leached out at the extreme environmental conditions for different initial concentrations. From the graph, it was shown that the maximum concentration of nickel is a function of the initial concentration of nickel. As the initial concentration of petroleum sludge was added, the maximum concentrations of nickel to be leached out at extreme environmental conditions increased. The amounts of nickel were detected at additions of 0, 5, 10, 15, and 20 wt% of petroleum sludge in which the concentrations of nickel were measured at 0.063, 0.070, 0.089, 0.118 and 0.136 mg/L, respectively. According to the Notification of the Ministry of Industry B.E. 2548, the allowable value of nickel in the leachate should be less than 20 mg/L. From the results, it has been noted that the nickel in the extraction fluid was lower than the allowable value. Therefore, the raw mix of cement with an addition of up to 20 wt% of petroleum sludge could be labeled as non-hazardous and can be used as a product.

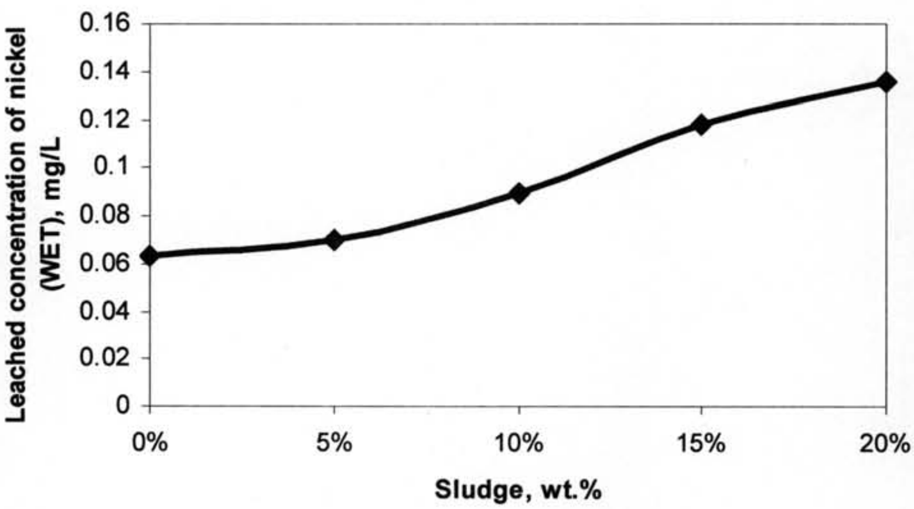


Figure 4.11 The average leached concentration of nickel from the WET by the Notification of the Ministry of Industry B.E. 2548

4.5.3 Leaching of Zinc (Zn)

According to the Notification of the Ministry of Industry No.6 B.E. 2540 and U.S. regulatory leaching procedure (TCLP), the allowable concentration of zinc in the leachate is not regulated. However, in an attempt to quantify the hazard, the U.S. EPA established the guideline that if metal concentrations in the extracts do not exceed 100 times the maximum contaminant levels (MCLs), the waste would not be considered hazardous waste (Hardaway et al., 1999). The MCL of zinc is 5 mg/L. Thus, zinc would be considered as hazardous waste, if the concentrations of zinc in the extraction fluid exceeded 500 mg/L.

Figure 4.12 showed the results obtained from the Notification of the Ministry of Industry No.6 B.E. 2540. After 18 hours of leaching, the amounts of zinc were detected at additions of 0, 5, 10, 15, and 20 wt.% of petroleum sludge in which the concentrations of zinc were measured at 0.023, 0.031, 0.041, 0.063 and 0.074 mg/L, respectively. The leached concentrations of zinc were lower than 500 mg/L. Thus, it is likely that this cement would be classified as non-hazardous waste. In addition, the lowest concentration of metals which are regulated for the Notification of the Ministry of Industry No.6 B.E. 2540 was also applied to identify the cement as hazardous or non-hazardous. The lowest concentration of metals is 0.2 mg/L which is regulated for mercury. When the lowest concentration of metals and leached concentrations from the Notification of the Ministry of Industry No.6 B.E. 2540 were compared, the leached concentration of zinc was lower than the allowable value. Thus, the cement was likely to be classified as non-hazardous waste.

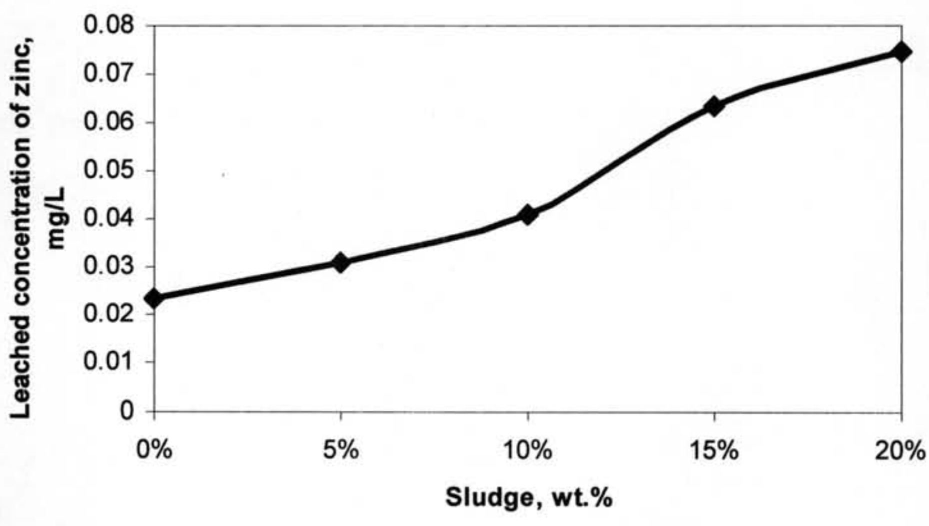


Figure 4.12 The average leached concentration of zinc from the Notification of the Ministry of Industry No.6 B.E. 2540

Figure 4.13 showed the results obtained from the TCLP. After 18 hours of leaching, amounts of zinc were detected at additions of 0, 5, 10, 15, and 20 wt% of petroleum sludge in which the concentrations of zinc were measured at 0.015, 0.026, 0.036, 0.058 and 0.078 mg/L, respectively. The leached concentrations of zinc were lower than 500 mg/L. Thus, it is likely that this cement would be classified as non-hazardous waste. In addition, the lowest concentration of metals which is regulated for the TCLP was also applied to identify the cement as hazardous or non-hazardous waste. The lowest concentration of metals is 0.2 mg/L which is regulated for mercury. When the lowest concentration of metals and leached concentrations from the TCLP were compared, the leached concentration of zinc was found to be lower than the allowable value. Thus, the cement was likely to be classified as non-hazardous. Therefore, the raw mix of cement with an addition of up to 20 wt% of petroleum sludge could be labeled as non-hazardous and can used as a product.

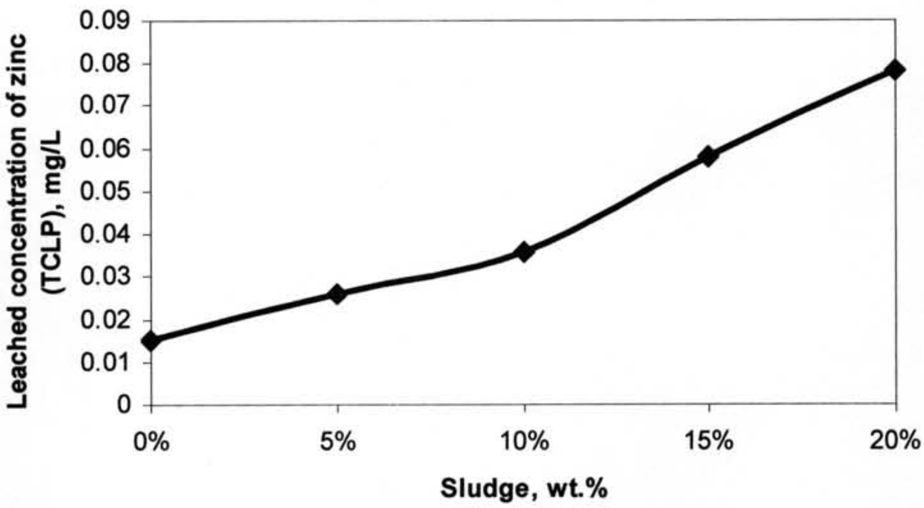


Figure 4.13 The average leached concentration of zinc from the TCLP

Figure 4.14 showed the results obtained from the leaching procedures described in the Notification of the Ministry of Industry B.E. 2548. After 48 hours of leaching, amounts of zinc detected from 0, 5, 10, 15, and 20 wt% of petroleum sludge addition were 0.078, 0.080, 0.131, 0.159 and 0.211 mg/L, respectively. According to the Notification of the Ministry of Industry B.E. 2548, the allowable value of zinc in the leachate should be less than 250 mg/L.

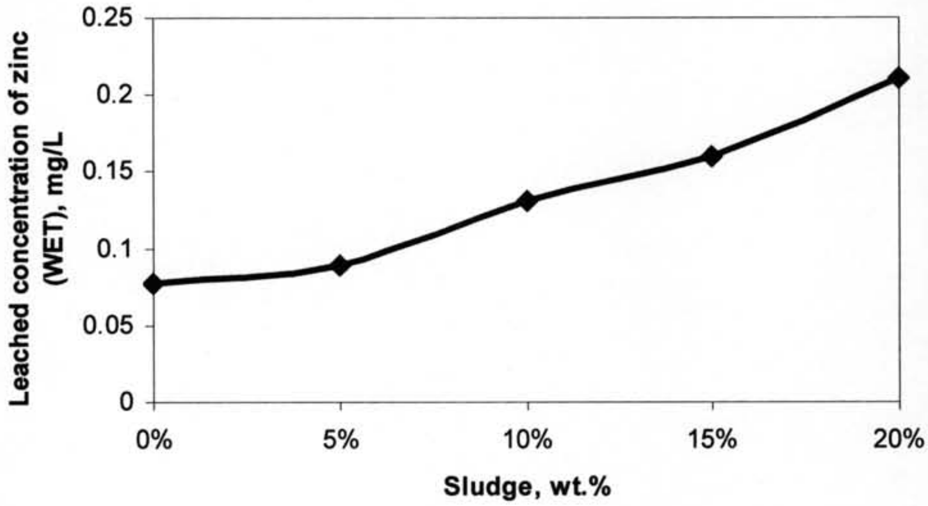


Figure 4.14 The average leached concentration of zinc from the WET by the Notification of the Ministry of Industry B.E. 2548

From the results, it has been noted that the zinc in the extraction fluid was lower than the allowable value. Therefore, the raw mix of cement with an addition of up to 20 wt% of petroleum sludge could be labeled as non-hazardous and used as a product.

4.5.4 Leaching of Lead (Pb)

According to the procedures described in the Notification of Ministry of Industry No.6 B.E. 2540, U.S. regulations, and the Notification of Ministry of Industry B.E. 2548, the allowable of concentration of lead in the leachate should less than 5 mg/L. From the results, there was no lead detected in the leachates from these methods. The initial concentration of lead was very low. The leached concentrations from these methods were lower than these criteria. It could be indicated that this cement was likely to be classified as non-hazardous waste

Therefore, the raw mix of cement with addition up to 20 wt% of petroleum sludge could be identified as non-hazardous waste that can be use as a product.

The results of leaching test showed that Cr, Ni, and Zn were leached via WET of the Notification of Ministry of Industry B.E. 2548 more easily than the TCLP and the Notification of Ministry of Industry No. 6 B.E. 2540 (Table 4.7) which may be the result from that the samples in WET were placed in contact with a different leaching fluid, a longer mixing period, and a lower solid to liquid ratio. The WET extraction fluid contains citric acid, which is a strong chelating agent. Because of this, the WET test usually extracts higher quantities of most metal than the TCLP test (Hooper, 1998).

Table 4.7 Concentrations of Cr, Ni, Zn, and Pb in leachate using three leaching methods

Heavy metal	Leached concentration (mg/L)				
	TCLP				
	0%	5%	10%	15%	20%
Cr	0.024	0.027	0.035	0.050	0.052
Ni	nd	nd	nd	nd	nd
Zn	0.015	0.026	0.036	0.058	0.078
Pb	nd	nd	nd	nd	nd
Heavy metal	Leached concentration (mg/L)				
	MOI No. 6 B.E. 2540				
	0%	5%	10%	15%	20%
Cr	0.020	0.024	0.036	0.041	0.052
Ni	nd	nd	nd	nd	nd
Zn	0.023	0.031	0.041	0.063	0.074
Pb	nd	nd	nd	nd	nd
Heavy metal	Leached concentration (mg/L)				
	MOI B.E. 2548 (WET)				
	0%	5%	10%	15%	20%
Cr	0.399	0.552	0.682	0.723	0.755
Ni	0.063	0.070	0.089	0.118	0.136
Zn	0.078	0.089	0.131	0.159	0.211
Pb	nd	nd	nd	nd	nd

4.6 The Sequential Extraction Test

The sequential extraction test was developed from that of Tessier et al. (1979). This research focuses on concentrations of Cr, Ni, Pb and Zn that can be removed from the cement at each extraction step. The sum of the concentrations from the five steps was compared with the total concentrations. The accuracy of the sequential extraction methods is much more difficult to estimate than that of a total metal determination due to the many extraction steps involved (Li et al, 1995).

4.6.1 The Sequential Extraction of Chromium (Cr)

Figure 4.15 showed the sequential chemical extraction results (Tessier's method) of the cement. They indicated that at various additional percentages of petroleum sludge, chromium was detected from about 0.6% to 1.4% in fraction 1, 42% to 45% in fraction 3 and 54% to 57% in fraction 5. With every added percentage of petroleum sludge, no extracted concentrations of chromium were detected in fraction 2 or fraction 4. The results can be observed that the chromium was bound to iron, and the manganese oxides (fraction 3) and chromium mainly distributed in fraction 5 which was more stronger bound.

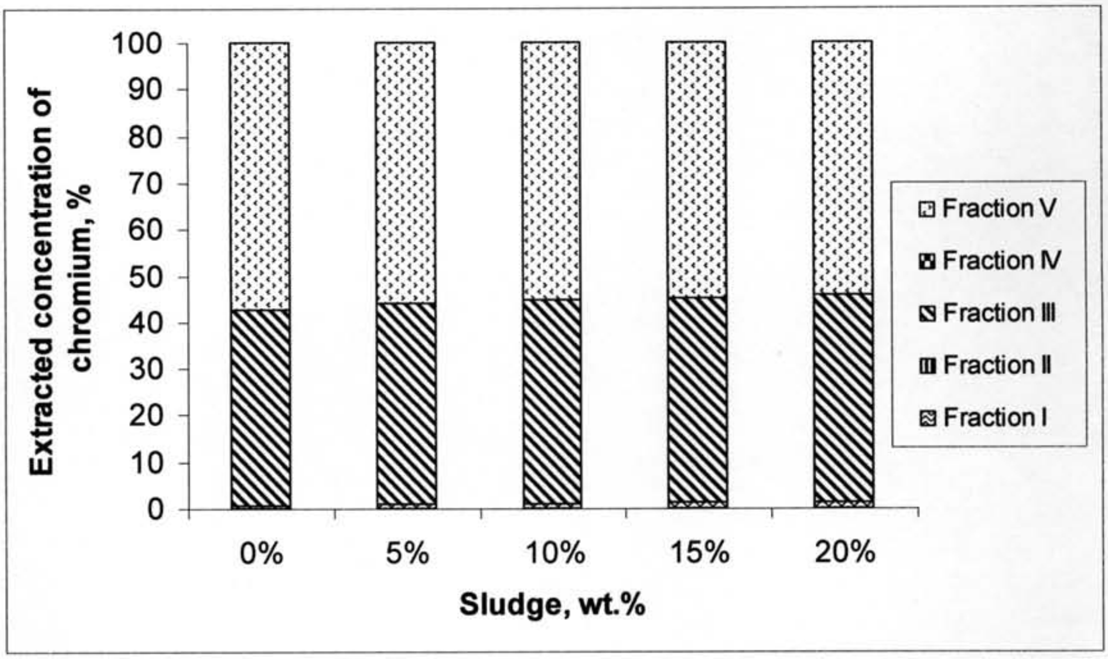


Figure 4.15 The average extracted concentration of chromium from the sequential extraction test

4.6.2 The Sequential Extraction of Nickel (Ni)

Figure 4.16 showed the sequential chemical extraction results of the cement which indicated that at various additional percentages of petroleum sludge, nickel was extracted from about 6% to7% in fraction 1, 5% to13% in fraction 3, 0.2% to 3% in fraction 4 and 81% to 83% in fraction 5. With every added percentage of petroleum sludge, no extracted concentrations of nickel were detected in fraction 2. Apparently, the majority of nickel was bound to iron, and the manganese (fraction 3) and nickel mainly distributed in fraction 5 which was more stable.

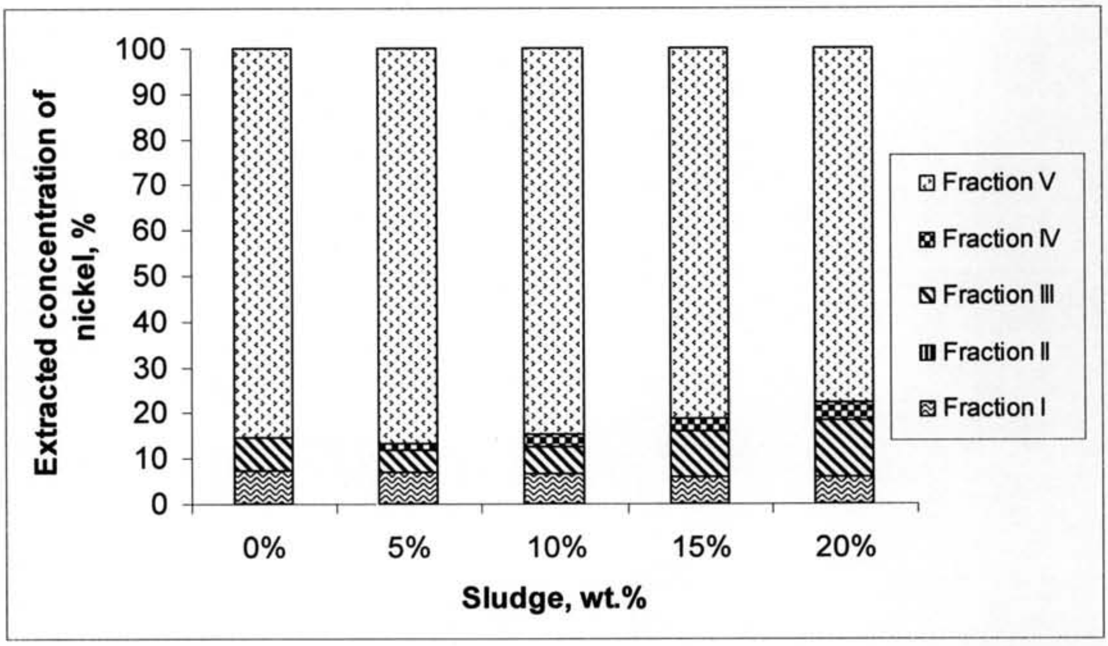


Figure 4.16 The average extracted concentrations of nickel from the sequential extraction test

4.6.3 The Sequential Extraction of Zinc (Zn)

Figure 4.17 showed the sequential chemical extraction results of the cement which indicated that at various additional percentages of petroleum sludge, less than 1% of zinc was extracted in fraction 1, 14% to19% in fraction 3, 0.2% to 3% in fraction 4 and 81% to 83% in fraction 5. With every added percentage of petroleum sludge, no extracted concentrations of zinc were detected in fraction 2. The results, it can be observed that the zinc was bound to iron, and the manganese (fraction 3) and zinc was mainly distributed in fraction 5 which was more stable,

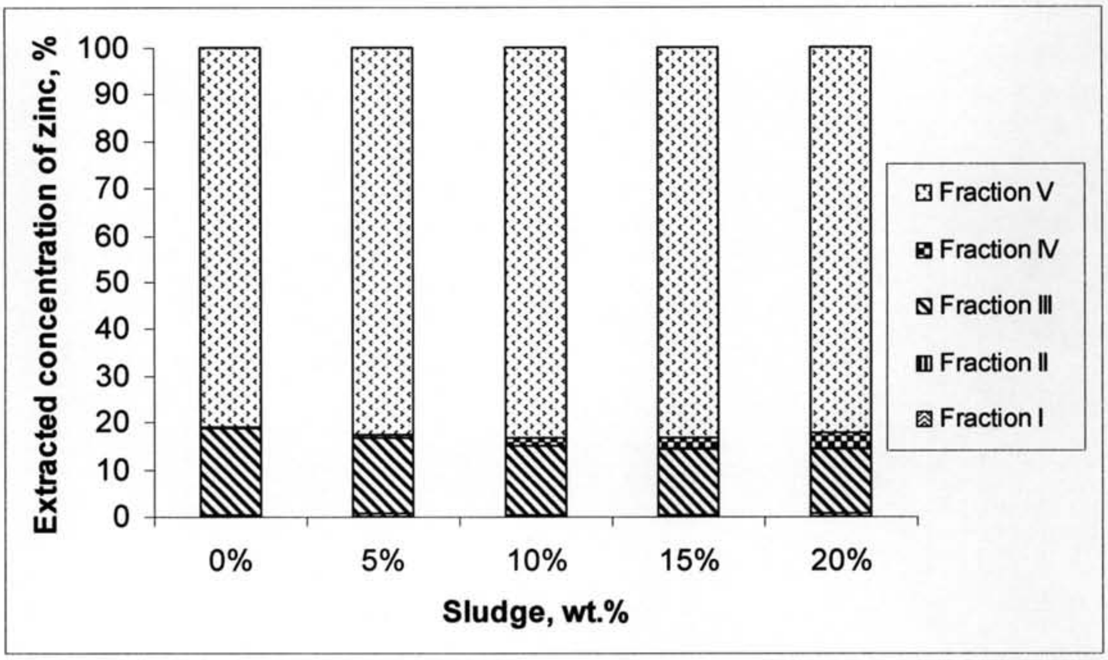


Figure 4.17 The average extracted concentration of zinc from the sequential extraction test

4.6.4 The Sequential Extraction of Lead (Pb)

Lead was not detected in all extract fractions from the sequential extraction procedures. Some possible explanation can be that in the sequential extraction results of Tessier's original method, some possible overlap could exist between Fraction 2 and 3 due to the high pH of the sample matrix, which could limit the reagent's strength to dissolve the metals in Fraction 2. It was difficult to dissolve any heavy metals in carbonate or hydroxide forms from the S/S matrix. This might be the main reason why metal concentrations were low or not leached in fraction 2. The chemical speciation of heavy metals was strongly dependent on their chemical behaviors during the cement hydration process and the potential binding mechanisms within the cementitious matrix (Li et al, 2001).

The results of the sequential extraction study showed that major proportions of the heavy metals (Cr, Ni, Zn, and Pb), remained in fraction 5 (residual fraction). It means that the heavy metals may be leached to the environment with great difficulty. However, low concentrations of heavy metals were extracted in fractions 3, 4, and 1. The metal-binding fraction that implies the most easily leached fraction in the environment is, of course, the exchangeable fraction, or fraction 1. The sequential extraction results demonstrated that in fraction 1 nickel was found in higher amount than those of zinc and chromium. Therefore, if a concrete structure containing these heavy metals were in contact with surface water, these metals can be easily leached in to the environment. They may produce adverse impacts on human health and the aquatic lives. Then, the extracted concentration of heavy metals from the sequential extraction test should be compared with the surface water quality standards. Table 4.8 showed the extracted concentrations of chromium, nickel, zinc, and lead in fraction 1 compared with the surface water quality standards of the Notification of the Ministry of Environment No. 8 B.E. 2537 (1994). It was found that the extracted concentrations of chromium in fraction 1 with 0%, 5%, 10%, 15%, and 20% of petroleum sludge addition were measured at 0.003, 0.005, 0.007, 0.010, and 0.010 mg/L, respectively which were considerably lower than the standard value of 0.05 mg/L. Likewise, the extracted concentrations of nickel and zinc in fraction 1 of all petroleum sludge additions were much lower than standard values of 0.1 mg/L and 1.0 mg/L, respectively.

Table 4.8 The extracted concentration of heavy metals at fraction 1 compared with the standard value of surface water quality criterion

Heavy metals	Fraction	Extracted concentration					Standard* value
		0%	5%	10%	15%	20%	
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Cr	1	0.003	0.005	0.007	0.010	0.010	0.05
Ni	1	0.013	0.019	0.021	0.023	0.025	0.1
Zn	1	0.002	0.006	0.007	0.008	0.009	1
Pb	1	nd	nd	nd	nd	nd	0.05

Source: *the Notification of the Ministry of Environment No. 8 B.E. 2537 (1994)