CHAPTER 4 SOLIDIFICATION & STABILIZATION

4.1 MATERIAL & METHOD

In this study, the reduction potential and/or treatability of the electronic waste was investigated. This is the first step to evaluate the waste's suitability for treatment by S/S and identifying the optimum amount, types of binder and additive to be applied (Hebapuria & Arafat, 1999). Ordinary Portland Cement (OPC) and white cement, with and without activated carbon were utilized in this study.

The solidified/treated waste should conform to certain standards to ensure the treated waste posed the minimum impact to the environment. The properties of concern in the standards guidance for the solidified waste form are summarized in Table 4.1.

4.1.1 Collection of samples

The waste was obtained from QT Optoelectronics (M) Sdn. Bhd. It was collected from the store in the manufacturing plant. The waste is in a gel form and white in colour. It is used to cover the diode and the circuit to provide a total reflective optical transmission medium. The waste is transferred to the drum 3 times per day. So waste was collected at different time and composite samples used for analysis.

Table 4.1
Standards guidance for solidified waste form

Properties	Test Methods	Criteria
Leachability	ANS 16.1	Leachability Index ≥ 6
Compressive Strength	ASTM C 39 or D 1074	414 kPa (60 psi)
Radiation Stability	See 1983 TP[a]	414 kPa compressive strength after 10E + 8 rads
Biodegradation	ASTM G 21 and G 22	No growth[b] and compressive strength > 414 kPa
Immersion	See 1983 TP[a]	414 kPa compressive strength after 90 days
Thermal Cycling	ASTM B 553	414 kPa compressive strength after 30 cycles
Free Liquid	ASTM 55.1	0.5 %

Sources : Morgan and Bostick, 1992; Stegemann and Cote, 1992.

[a] The 1983 Branch Technical Position (TP) paper calls a minimum compressive strength of 345 kPa (50 psi). this has been raised to 414 kPa (60 psi) to accomadate an increased maximum burial depth at Hanford of 55 ft (from 45 ft) as defined by the U.S. Nuclear Regulatory Commission publication.

[b] The 1983 Branch (TP) paper calls for a multistep procedure for biodegradation testing : if observed culture growth rated ">1" is observed following a repeated ASTM G 21 test, or any growth is observed following a repeated test of ASTM G 22 test, longer term testing for (at least six months) is called for using the Bartha-Pramer Method. From this test, a total weight loss extrapolated foe full size waste forms to 300 years should produce less than a 10% loss of total carbon in the sample.

4.1.2 Material

For S/S studies, Ordinary Portland Cement (OPC) and white cement were used, with and without activated carbon.

Table 4.2
Typical chemical composition of the OPC and white cement used in this project

Chemical Compounds	OPC (wt.%)	White cement (wt. %)
CaO	63.22	68.34
SiO_2	20.80	24.30
Al_2O_3	4.62	1.94
Fe_2O_3	2.57	0.37
MgO	4.15	0.59
Na_2O	0.16	0.13
K_2O	0.51	0.02
SO_3	2.70	2.01

Source : Sora, *et al.*, 2002.

4.1.3 Preparation of Apparatus

The apparatus used in the experiment included weighing balance, steel moulds (50 mm x 50 mm x 50 mm), cylindrical plastic containers, incubation shakers (New Brunswick), filtration devices, Hanna Instrument Membrane pH meter, magnetic stirrer (Hanna Instrument, H1300N), glassware and plastic bottles (100 ml) and ELGASTAT® UHQPS to process ultra pure water. All the apparatus were cleaned thoroughly prior to use. The glassware and plastic bottles used in the leaching test were pre-soaked in detergent (to remove any organics), and then in dilute nitric acid (to remove bound metals), and finally soaked in ultra pure water for 24 hours.

4.1.4 Preparation of Sample Specimens

Trial Mix

OPC or white cement was mixed with the waste at various ratios as indicated in Table 4.3.. Another set of samples were prepared for both cement types with activated carbon additive . Activated carbon has chemical properties for sorption and decreased porosity (Barth, 1990). It is believed that some sort of bonding between waste material and the sorbent will eventually be achieved with sorbent in the waste mixture (Conner, 1990).Water was not added because the waste itself was in a semi-liquid form. The resulting mixture was then transferred to steel-moulds and cured for 24 hours to ascertain their solidibility within the period. The ratios are summarized in Table 4.3.

Table 4.3
Test run conditions for cement-based solidification

Binding agent		Waste	Number of samples		
Type	Amount (wt %)	Amount (wt %)	TCLP	ANS 16.1	Comp. Strength
OPC or white cement	50	50	2	1	4
	40	60	2	1	4
	30	70	2	1	4
	20	80	2	1	4
	10	90	2	1	4
	0	100	2	1	4
AC : OPC or white cement	3:47	50	2	1	4
	4:36	60	2	1	4
	5:25	70	2	1	4
	6:14	80	2	1	4
	7:03	90	2	1	4

AC : Activated Carbon

Mixing, Casting and Curing

The waste and cement was mixed in a blender for 1 minute . Water was not added because the waste was in a semi-gel form. The mixture was mixed at high speed for 3-4 minutes. These procedures were necessary to ensure a homogeneous mixture is obtained prior to casting. After mixing, the resulting waste loaded grout paste was quickly transferred to the specified moulds. The size of the mould is 5cm x 5cm x 5cm The moulds were covered by plastic bags or Perspex and left undisturbed for 24 hours at room temperature (range 27 - 34°C) and 92% relative humidity. At the end of this period, the specimens were removed from the mould and further cured for 27 days under 30°C and humidity 98% to simulate the curing condition as normally encountered in landfill situation.

4.2 LEACHING TEST

4.2.1 Toxicity Characteristics Leaching Procedure (TCLP)

The TCLP protocol (US EPA method 1311, 1992) was performed using the solidified samples which were manually cut to a particle size smaller than 9.5 mm. This can be done because he samples are elastic and rubbery. Prior to the performance of this protocol, a test was carried out to determine the appropriate extraction fluid for the extraction procedure. The extraction fluid is a buffer of acetic acid acid and sodium hydroxide adjusted to a pH of 4.93 ± 0.05.

The leaching procedure involved mixing a single batch of material with extraction fluid at a liquid-to-solid ratio of 20:1. The flasks were covered with parafilm, capped with aluminium foil and then mechanically shaken for 18 hours continuously at 300 rpm and at the temperature of 25 ± 2°C in an incubation shaker (News Brunswick) to allow full reaction.

At the end of the 18 hour contact time, the leachates were then filtered through a 0.8μm pore size borosilicate glass fibre filter, to separate the solid and liquid phase. The filtered liquid is termed as TCLP extract. Measurement of pH of the extract was taken by using Hanna Instrument Membrane pH meter, equipped with a standard glass electrode. The extract was collected into 100 ml polyethylene bottles or glass bottles, acidified with 1 ml of nitric acid and stored in refrigerator at 4°C until metal analysis was carried out. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), model 2000 BAIRD was used to analyze the heavy metals in the leachate.

The results of this extraction test were expressed in terms of the percentage of leachable fraction, *f*, for each element (Brodersen, *et al.*, 1992). The leachable fraction is defined as the amount of a particular heavy metal extracted relative to the amount in untreated waste. This fraction, or the corresponding leachable amounts, can be regarded as a measure of the availability of various metals for leaching from that particular material over a period of time.

4.2.2 American Nuclear Society ANSI / ANS 16.1 (Modified)

In addition to TCLP, ANS 16.1 (ANS, 1986) was selected because it gives substantially more information about the rate at which hazardous constituents leach from the solidified waste. The leaching procedure used in this study is modification of that proposed by the American Nuclear Society for solidified low-level radioactive waste in standard ANSI / ANS 16.1, which is conducted for a total of 90 days.

The modified ANS 16.1 static leaching procedure involved the following steps : the solidified specimens prepared were cylindrical with thickness-to-diameter ratio of 0.3.

During the test, the specimens were suspended in the leachant by using nylon fishing line. The leaching of all samples was carried out in plastic containers, which are made of non-reactive polypropylene. Neither the containers nor the fishing line contributed to the concentration of heavy metals in the leachate. The leachant is not stirred/agitated during the leaching interval. The specimens were suspended in beakers.

The ratio of the leachant volume and the external geometric surface area of the solid specimens is maintained at about 10 ± 0.2 during the leaching interval. This is sufficient to minimize leachant composition changes during reasonably short leaching intervals, while providing sufficient concentration of leached elements for analysis (ANS, 1986). Ultra pure water of resistivity = 18 Mohm-cm (processed by ELGASTAT® UHQPS) was used as the leachant in this test. At this purity level , the water is very aggressive and can extract ions even from metals, causing pitting corrosion (Biyani and Fort, 1997).

The leaching of samples were monitored over a period of 28 days (sampling at the 1st., 7th., 14th. and 28th. Days) when the specimens were removed and placed into fresh leachant at the end of each leaching interval. The pH measurement for the leachant was taken at the end of each interval. Standard buffer solution at pH 4.00 and 7.00 was used to calibrate the pH meter. The leachate was collected into plastic or glass bottles, acidified with nitric acid and stored in refrigerator until metal analysis was carried out. ICP-AES was used to analyze the metal concentration in the leachate.

The results of this leaching test were recorded in terms of leaching rate (*l*), cumulative fraction leached (*CFL*) relative to the total mass of the waste sample, and subsequently used to derive the effective diffusion coefficient (*D*) and Leachability Index (L_i) (ANS, 1986; De Angelis, *et al.*, 1992; Kim, *et al.*, 1992)

1. Leaching rate, *l* (cm/day), as function of the leaching time:

$$l = \frac{a_n}{A_o} X \frac{V}{S.t_n}$$

where

a_n = amount of the constituent of interest leached during interval n (mg/L)

A_o = amount of the constituent of interest initially present in the specimen (mg/L)

V/S = ratio of specimen volume to surface area (cm)

t_n = the leaching time since the beginning of the first leaching interval (s)

2. Cumulative Fraction Leached, CFL (cm)

$$CFL = \frac{\sum a_n}{A_o} X \frac{V}{S}$$

3. Effective diffusivity, D (cm^2/sec), a measure of the diffusivity of the heavy metals of concern in the monolithic specimen of solidified/stabilized waste for each leaching interval

$$D = \pi\left(\frac{a_n / A_o}{(\Delta t)_n}\right)\left(\frac{V}{S}\right)^2 T$$

where

$\Delta t_n = t_n - t_{n-1}$, duration of the n leaching interval (sec)

$T = \left[\frac{1}{2}\left(t_n^{1/2} + t_{n-1}^{1/2}\right)\right]^2$, leaching time representing the cumulative time in the middle of the interval n (sec)

4. Leachability Index, L_i , (dimensionless), which gives an indicator of the effectiveness of the S/S technique for control of leaching

$$L_i = \frac{1}{n}\sum\left[\log\left(\frac{\beta}{D_i}\right)\right]_n$$

where β is a defined constant (1.0 cm^2/s), n is the number of leach periods for which analytical results were obtained and D_i is the effective diffusivity of constituent i. Leachability Index is defined as a material parameter that characterizes the resistance of the solidified waste to leaching of constituents. Larger value of the L_i imply the smaller values for contaminant diffusing (i.e. a lower value for contaminant release rate) (Morgan and Bostick, 1992).

4.3 PHYSICAL TEST

4.3.1 Hardening Time

The hardening time is the time taken for the specimens to harden at room temperature. It was recorded by visual observation and hand-pressing the specimens at predetermined duration : every six hours.

4.3.2 Compressive Strength Test

This test is aimed at determining the mechanical strength development characteristics of the solidified matrix formed. Specimens for compressive strength test were prepared according to the American Standard Testing Material (ASTM) Test Method for Compressive Strength of Hydraulic Cement Mortars (using 2-in or 50 mm cube specimens) C109/C 109M-95 testing protocols. This study determined the solubility of solids for landfill stacking on top of another. The stronger the solid formed, the more suitable for secure landfill disposal.

Total maximum loads were recorded at the point of fracture and the compressive strength is determined as follows :

$$f_m = \frac{P}{A}$$

where

f_m = compressive strength in psi or [MPa]

P = total maximum load in lbf or [N]

A = area of loaded surface in in^2 or [mm^2]

Compressive strength measurements were performed on the cube specimens in duplicate at the 1st., 7th., 14th. and 28th. days curing (98% RH, 30 ± 3°C) using a calibrated, hand operated hydraulic compression apparatus (model ELE).

4.4 RESULTS AND DISCUSSION

4.4.1 TCLP Results

The summary of TCLP leachate analysis data is presented in the Table 4.5, which includes the regulatory limit for TCLP test (US EPA method 1311, 1992) and Malaysia Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Standard B.

As shown in Table 4.5, the TCLP extract of the untreated waste contains Ti only. Ti is not listed in Malaysia Environmental Quality (Sewage and Industrial Effluents), 1979, Standard B; but the concentration is quite high. Substantial amount of heavy metals are found present in the OPC and white cement. These metals originate mostly in natural raw materials used in the binder manufacture of cement. Thus the binder composition must be taken into consideration in the leachability of the treated waste. The composition of the heavy metals of concern, in OPC and white cement, analysed by X-ray fluorescence, is given in Table 4.4 (Sora, *et al.*, 2002).

Table 4.4
Heavy metal composition in OPC and white cement

	Composition (ug/kg)					
Trace metals	Ba	Cr	Zn	Pb	Cu	Fe
	276±10	53±5	80±1	37±1	43±10	NA

Source : Sora, *et al.* (2002) NA – not available

Table 4.5
Summary of TCLP leaching data with initial extraction fluid pH and final pH of the extract[a]

	Initial pH	Final pH	Concentration of metals in leachate, mg/L					
			Ti	Ba	Zn	Pb	Cu	Fe
Regulatory Limit for TCLP Test[b]			-	100	-	5	1	5
Malaysia EQA[c]	5.5 – 9.0		-	-	1	0.5	1	5
Untreated Waste	4.90	12.22	1.5298	-	-	-	-	-
OPC	4.91	11.53	-	0.4173	0.0758	0.6449	0.0202	0.7765
White cement	4.90	12.04	-	0.4155	0.0750	0.6670	0.0211	0.6832
OPC:waste								
50:50	4.93	12.33	0.7812	0.2214	0.0315	0.2600	0.0080	0.2376
40:60	4.92	11.71	0.8139	0.1987	0.0258	0.2462	0.0075	0.2042
30:70	4.90	11.45	0.8628	0.1696	0.0255	0.2011	0.0063	0.1669
20:80	4.92	11.12	0.9148	0.1323	0.0236	0.1898	0.0050	0.1312
10:90	4.93	10.96	0.9592	0.1080	0.0213	0.1507	0.0038	0.0932
White cement:waste								
50:50	4.91	12.40	0.7921	0.2298	0.0305	0.2610	0.0077	0.2145
40:60	4.93	11.81	0.8093	0.2015	0.0278	0.2363	0.0073	0.1845
30:70	4.93	11.54	0.8659	0.1789	0.0262	0.2010	0.0065	0.1483
20:80	4.92	11.20	0.9194	0.1425	0.0249	0.1805	0.0052	0.1079
10:90	4.92	11.07	0.9500	0.1188	0.0201	0.1515	0.0038	0.0800
AC:OPC:waste								
3:47:50	4.93	12.03	0.3809	0.1065	0.0170	0.1258	0.0038	0.1312
4:36:60	4.93	11.37	0.4085	0.0934	0.0157	0.1116	0.0034	0.1118
5:25:70	4.94	11.15	0.4345	0.0836	0.0135	0.1025	0.0030	0.0909
6:14:80	4.93	10.73	0.4635	0.0719	0.0112	0.0909	0.0025	0.0769
7:3:90	4.92	10.50	0.4865	0.0593	0.0099	0.0793	0.0020	0.0637
AC:white cement:waste								
3:47:50	4.94	12.10	0.3855	0.1151	0.0154	0.1247	0.0037	0.1161
4:36:60	4.94	11.47	0.4238	0.1018	0.0137	0.1101	0.0032	0.0991
5:25:70	4.94	11.25	0.4329	0.0844	0.0134	0.1034	0.0028	0.0772
6:14:80	4.93	10.88	0.4574	0.0785	0.0121	0.0894	0.0026	0.0670
7:3:90	4.93	10.72	0.4819	0.0677	0.0110	0.0767	0.0022	0.0574

a Duplicate analysis for OPC and white cement and OPC and white cement with activated carbon samples.

b United States EPA regulatory limits for TCLP test.

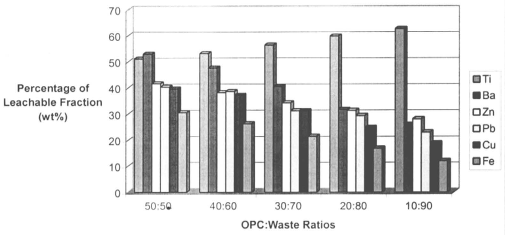
c Regolatory limit stipulated in Malaysia Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Standard B.

AC : Activated Carbon

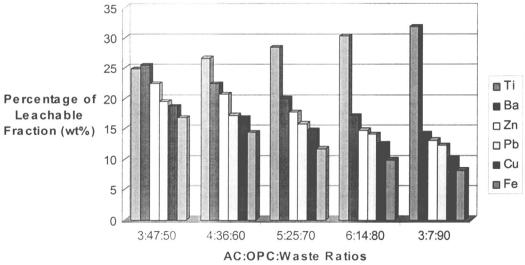
The high pH value of the untreated waste, OPC and white cement, 12.52,11.53 and 12.10 respectively, shows that they are basic in nature. The leachate of the specimens shows very high pH value, ranging from 10.20 to 12.33, and exceeds the limit stipulated in Malaysia EQA. However, the pH value decreases gradually as the cement loading decreases in both cement:waste and AC:cement:waste specimens.

The percentage of leachable fraction, *f*, of each metal of concern (in terms of percentage of the untreated quantity) at various waste loadings, for both OPC-based and white cement based extract, are displayed in Figure 4.1. The extraction for the waste does not contain Ba, Pb, Cu, Zn and Fe so the leachable fraction for these heavy metals calculated relative to the amount in OPC and white cement.

As can be seen in the Figure 4.1(a) and (c), cement was able to immobilize the Ti of concern to a certain extent, depending on the cement loading. Among the heavy metal tested, Ti and Ba contributed the highest percentage of leachable fraction. Ti showed a descending trend as the waste loading decreased, ranging from 62.7% in 90% waste loading to 51.1% in 10% waste loading in OPC treated sample and for white cement treated sample it was 62.1% in 90% waste loading to 51.8% in 10% waste loading.. Comparatively the percentage of leachable fraction of Ba decreased as the cement loading decreased and it was 53% in 50% OPC loading to 25.9% in 10% OPC loading. While for the white cement treated samples, the percentage of leachable fraction was 55.3% 50% cement loading to 28.4% in 10% cement loading. The high solubility of barium hydroxide in the cement itself could contribute to the high concentration of Ba in the extract.

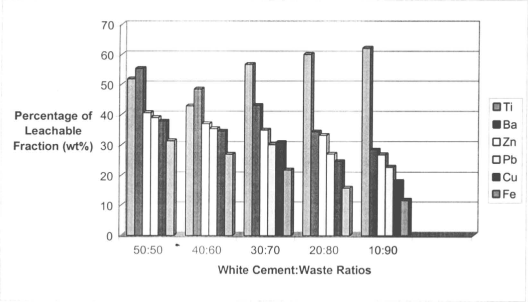


(a)

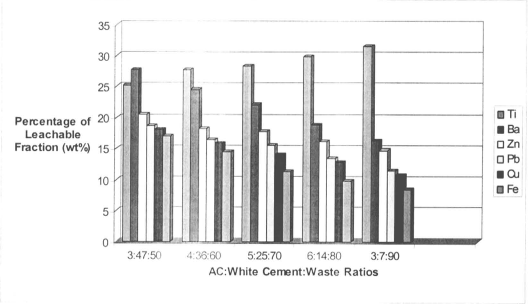


(b)

Figure 4.1 The percentage of leachable fraction of the heavy metals of concern in the leachate from (a) OPC and (b) OPC with activated carbon treated samples



(c)



(d)

Figure 4.1 (Continued) The percentage of leachable fraction of the heavy metals of concern in the leachate from (a) white cement and (b) white cement with activated carbon treated samples

Zn contributed the next highest leachable fraction after Ba with 41.6% to 28.1% and 40.7% to 26.8% in 50% and 10% OPC and white cement loading respectively. The percentage of leachable fraction of Pb in the OPC treated extract was reduced to 40.3% - 23.0%; similarly 39.6% - 18.9% for Cu and 30.6% - 12.0% for Fe. The same trend observed for white cement treated extract with leachable fraction of 40.7% - 26.8% for Zn, 39.1% - 22.7% for Pb, 37.9% - 18.0% for Cu and 31.4% - 11.7% for Fe.

Generally, the addition of activated carbon with cement reduced the leaching of all the metals concern considerably as compared with merely cement binding. As shown in Figure 4.1 (b), the percentage of leachable fraction for Ti has reduced from 62.7% in waste without activated carbon to 31.8% for 50% OPC loading. The percentage of leachable fraction for Ba was reduced by 25.5% to 14.2% as the percentage of activated carbon was increase by 3% to 7%. Similarly, the percentage of leachable fraction for other metals decreased as well, with addition of activated carbon at various waste loading. The leachable fraction decreased by 22.4% - 13.1% for Zn, 19.5% - 12.3% for Pb, 18.7% - 10.2% for Cu and 16.9% - 8.2% for Fe. The same trend was observed for white cement with activated carbon treated samples (Figure 4.1 (d)). The leachable fraction for Ti was reduced to 31.5% - 25.2% and for Ba it was 27.7% - 16.3% . Similar trend was observed for Zn, Pb, Cu and Fe where the percentage of leachable fraction decreased as the percentage of activated carbon increased.

4.4.2 Effects of final pH of TCLP Extract on Metals Leaching

Measurement of pH in the extract can help to elucidate the pH dependence of metal leaching. The final pH of the TCLP extract for untreated waste, OPC, white cement and the cement-based treated samples were basic, ranging from pH 10.2 – 12.33, indicating an appreciable acid neutralization (buffering capacity in the samples that offset initial TCLP extraction fluids.

It is widely accepted that cement waste forms rely heavily on pH control for metal contaminant, whereby metal hydroxides normally have minimum solubility in the pH range of 7.5 – 11. However, some metals such as Ti, Cr, Pb, Zn, Cu and Fe that exhibit amphoteric behaviour have higher solubility at both and low and high pH.

The other heavy metals such Zn, Pb, Cu and Fe was only leached out from the cement and not the waste. The amphoteric nature of Ti solubility is evident in the plot as the percentage of leachable fraction for Ti decreased as the final pH of the leachate decreased from 12.03 – 10.66 for OPC treated sample and 12.15 – 10.70 for white cement treated samples. The final pH of the extract of cement with activated carbon treated samples were relatively lower than those from cement treated samples, ranging from pH 10.10 – 11.62. The slightly lower pH was probably due to the lesser amount of cement which was replaced by activated carbon.

ANS 16.1 (MODIFIED)

Leaching Rate

The leaching rate *l* (cm/day) is calculated according to equation (1)

Example:

Heavy metal analysed : Ti in specimen at OPC:waste ratio of 50:50

Initial amount in specimen, A_o = 1.3462 mg/L

Blank (leachant) = 0 mg/L

Volume of Leachant, V_l = 700ml

Volume of the solidified specimen, $V = \pi r^2 h = 35.473 cm^3$

Surface area of the circular solidified specimen,

$$S = 2\pi r^2 + 2\pi rh = 70.296 cm^2$$

V/S = 0.5046cm

Table 4.6
Sample calculation of leaching rate for Ti, *l* (cm/day), in cement treated sample with OPC:waste ratio of 50:50

Leaching Interval (n) a	Duration (Δt) (days) b	As analysed (mg/L) c	a_n (mg/L) d=0.70*c	a_n / A_o e=d/A_o	*l* (cm/day) f=(e*0.5046)/ Δt
1	1	0.1137	0.0796	0.0591	0.0298
2	2	0.1533	0.1073	0.0797	0.0201
3	4	0.1010	0.1185	0.0880	0.0111
4	7	0.2027	0.1419	0.1054	0.0076
5	14	0.1150	0.1084	0.0805	0.0029

The leaching rate of Ti in 90% waste loading (Figure 4.2 (e)) decreased from 0.0416 cm/day in the first interval, to 0.0333 cm/day in the second interval, and further decreased to 0.0244 cm/day, 0.0159 cm/day and 0.0137 in the third, fourth and final intervals. Similar trend was observed 80%, 70%, 60% and 50% waste loading, but at lower leaching rate, decreased from 0.0397 cm/day – 0.0128 cm/day, 0.0365 cm/day – 0.0083 cm/day, 0.0272 cm/day – 0.0042 cm/day to 0.0298 cm/day – 0.0051 cm/day within the 28 days of leaching respectively. The increase in leaching rate was due to the increasing amount of waste loading.

The leaching rate of Ba in 50% OPC loading (Figure 4.2 (a)) decreased from 0.0356 cm/day in the first interval, to 0.0233 cm/day in the second interval, and further decreased to 0.0159 cm/day, 0.0108 cm/day and 0.0073 cm/day in the third, fourth and final intervals. Similar trend was observed in the 40%, 30%, 20% and 10% OPC loading, but at lower leaching rate, decreased from 0.0306 cm/day – 0.0065 cm/day, 0.0281 cm/day – 0.0053 cm/day, 0.0197 cm/day – 0.0047 cm/day to 0.0144 cm/day – 0.0009 cm/day within the 28 days of leaching respectively. The decrease in Ba leaching rate was due to the decreasing amount of cement loading.

While the leaching rate of Pb was relatively close to the leaching rate of Zn, the leaching rate of Cu and Fe were also very close to each other. Rapid loss of heavy metals was observed on the first interval, and this was probably due to the surface wash off of the solidified specimens (Li, 2001).

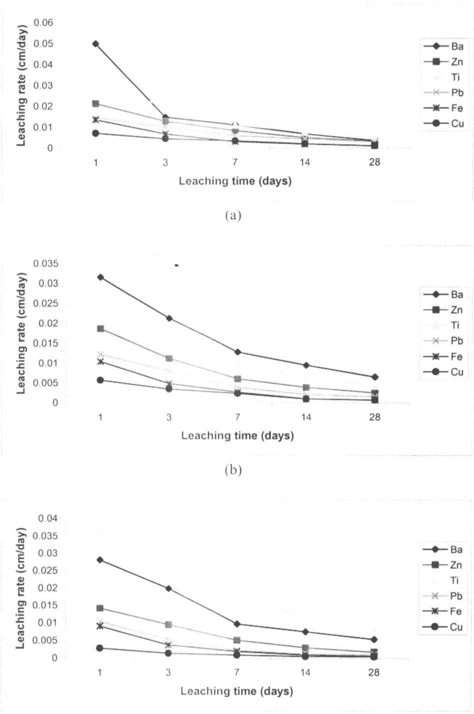
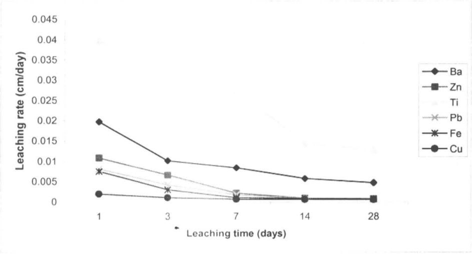
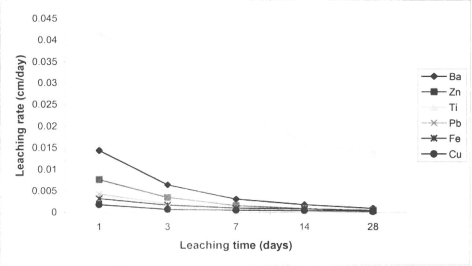


Figure 4.2 Leaching time of the heavy metals of concern in OPC treated samples at OPC:waste ratios of (a) 50:50, (b) 40:60 and (c) 30:70.



(d)



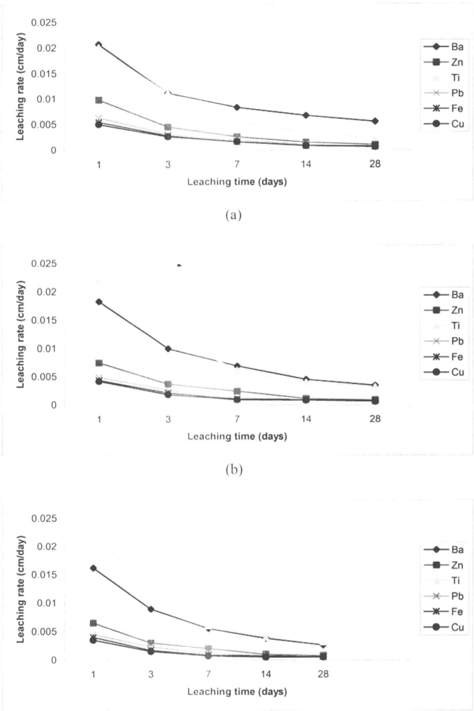
(e)

Figure 4.2 (Continued) Leaching rate of the heavy metals of concern in OPC treated samples at OPC: waste ratios of (d) 20:80 and (e) 10:90

As can be seen in Figure 4.3, the trace metals in cement with activated carbon treated samples demonstrated similar leaching trend as the OPC treated samples, where Ba and Ti showed the highest leaching rate, followed by Zn and Pb, whereas the leaching rate of Cu and Fe were approximately the same.

It was observed that the leaching rate of the heavy metals in OPC with activated carbon treated samples were generally lower than the OPC treated samples. The leaching rate of Ti in 90% waste loading decreased from 0.0271 cm/day in the first interval to 0.0055 cm/day in the final interval. It further decreased to 0.0258 cm/day – 0.0037 cm/day, 0.0219 cm/day – 0.0032 cm/day, 0.0219 cm/day – 0.0032 cm/day and 0.0201 cm/day – 0.0024 cm/day at the end of 28th day, as the waste loading decreased to 80%, 70%, 60% and 50% respectively. The Ti content in sample has reduced as the waste loading decreased, thus the leaching of Ti also decreased.

On the other hand, the leaching of Ba also decreased as the OPC loading decrease. In 47% OPC loading, the leaching rate of Ba decreased from 0.0207 cm/day to 0.0055 cm/day at the end of the final interval. It gradually decreased to 0.0183 cm/day – 0.0032 cm/day and 0.0162 cm/day – 0.0026 cm/day in 36% and 25% OPC loading respectively. Leaching rate of other heavy metals were distinctly different compared to the leaching rate of Ba, but also decreased as the OPC loading decreased.

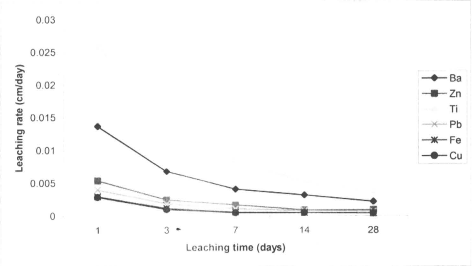


(a)

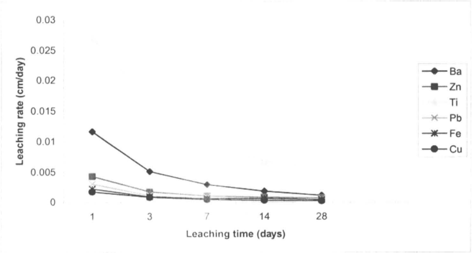
(b)

(c)

Figure 4.3 Leaching time of the heavy metals of concern in OPC with activated carbon treated samples at activated carbon:OPC:waste ratios of (a) 3:47:50, (b) 4:36:60 and (c) 5:25:70.



(d)



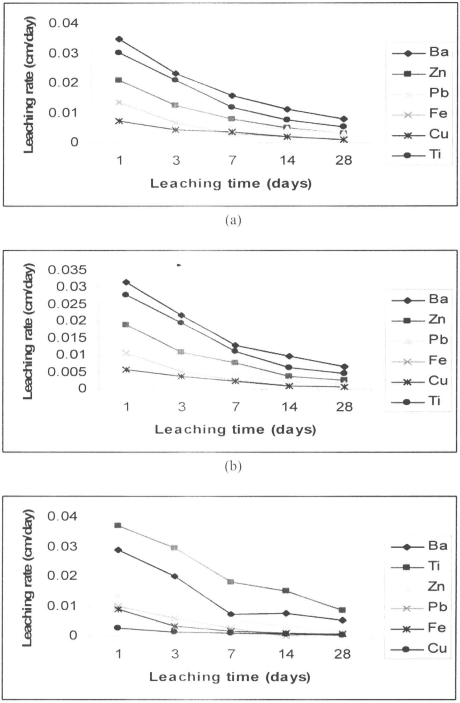
(e)

Figure 4.3 (Continued) Leaching time of the heavy metals of concern in OPC with activated carbon treated samples at activated carbon:OPC:waste ratios of (d) 6:14:80 and (e) 7:3:9.

For white cement treated samples, the leaching trend was similar as the leaching trend for OPC treated samples. Ba and Ti showed the highest leaching rate. The leaching rate of Ti in 90% waste loading (Figure 4.4 (a)) decreased from 0.041 cm/day in the first interval, to 0.0333 cm/day in the second interval and further decreased to 0.0251 cm/day, 0.0177 cm/day and 0.013 cm/day in the third, fourth and final intervals. Similar trend was observed in the 80%. 70%, 60% and 50% waste loading but at a lower leaching rate, decreased from 0.039 cm/.day – 0.0128 cm/day, 0.037 cm/day – 0.009 cm/day, 0.027 cm/day – 0.0045 cm/day and 0.0301 cm/day – 0.0055 cm/day within the 28 days of leaching respectively. The decrease in Ti leaching rate was due to the decreasing amount of waste loading.

The leaching rate of Ba decreased as the white cement loading decreased. The leaching rate of Ba decreased from 0.0365 cm/day – 0.008 cm/day in 50% white cement loading, to 0.0322 cm/day – 0.006 cm/day and 0.0297 cm/day – 0.0049 cm/day in 40% and 30% white cement loading respectively.

While the leaching rate of Zn was relatively close to the leaching rate of Pb. The leaching rate of Cu and Fe were also very close to each other, particularly after the third interval for 30%, 20% and 10% white cement loading.

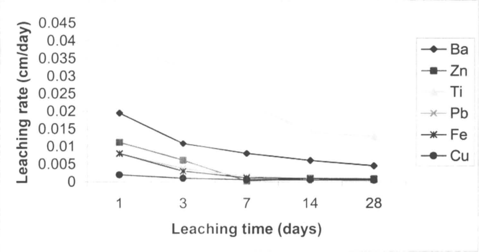


(a)

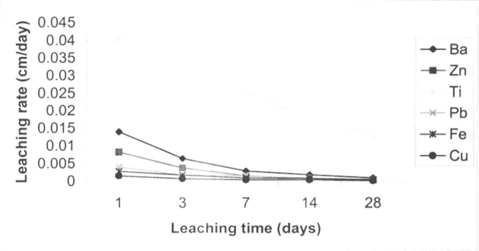
(b)

(c)

Figure 4.4 Leaching time of the heavy metals of concern in white cement treated samples at white cement:waste ratios of (a) 50:50, (b) 40:60 and (c) 30:70.



(d)



(e)

Figure 4.4 (Continued) Leaching rate of the heavy metals of concern in white cement treated samples at white cement: waste ratios of (d) 20:80 and (e) 10:90

As can be seen in Figure 4.5, the leaching trend in white cement with activated carbon treated samples is similar as in OPC with activated carbon treated samples where Ba and Ti showed the highest leaching rate followed by Zn and Pb, whereas the leaching rate of Cu and Fe were approximately the same.

It was observed that the leaching rate of all the heavy metals in white cement with activated carbon treated samples were generally lower than the white cement treated samples. The leaching rate of Ti decreased from 0.03 cm/day – 0.003 cm/day, 0.0271 cm/day – 0.0088 cm/day and 0.0261 cm/day – 0.0069 cm/day in 90%, 80% and 70% waste loading respectively. The Ti content in waste has reduced as the waste loading decreased, thus the leaching of Ti also decreased.

On the other hand, the leaching of Ba also decreased as the white cement loading decrease. In 47% white cement loading, the leaching rate of Ba decreased from 0.0208 cm/day to 0.0063 cm/day at the end of the final interval. It gradually decreased to 0.0178 cm/day – 0.0034 cm/day and 0.0166 cm/day – 0.0028 cm/day in 36% and 25% white cement loading respectively. Leaching rate of other heavy metals were lower than Ba and it decreases as the white cement loading decreases. Similar leaching rate was observed for Zn and Pb and for Cu and Fe.

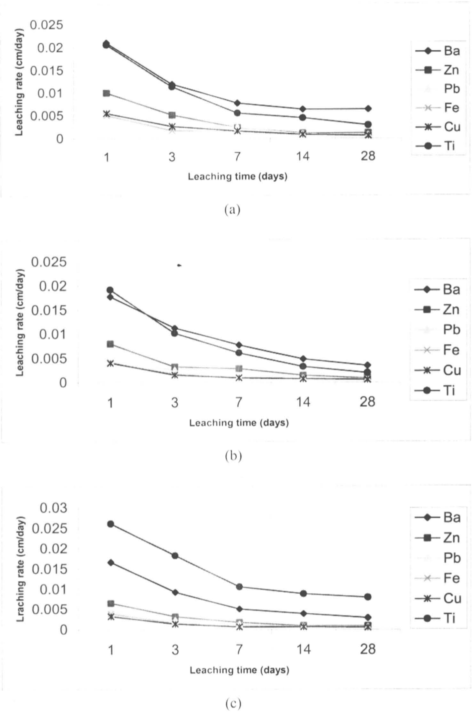
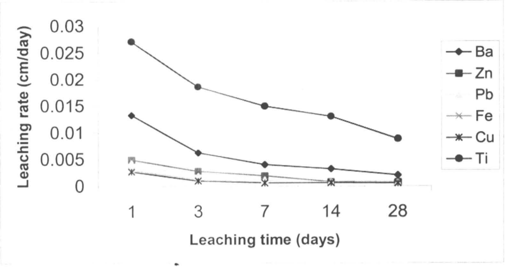
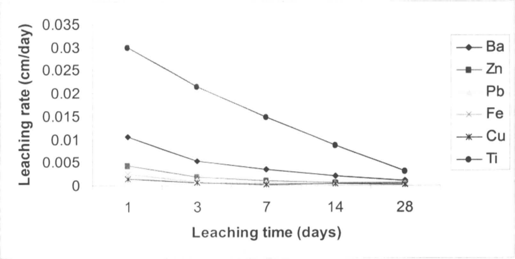


Figure 4.5 Leaching time of the heavy metals of concern in white cement with activated carbon treated samples at activated carbon:white cement:waste ratios of (a) 3:47:50, (b) 4:36:60 and (c) 5:25:70.



(d)



(e)

Figure 4.5 (Continued) Leaching time of the heavy metals of concern in white cement with activated carbon treated samples at activated carbon:white cement:waste ratios of (d) 6:14:80 and (e) 7:3:9.

Cumulative Fraction Leached (CFL)

CFL was calculated according to equation (2) in section 4.2.2 and shown in Table 4.7.

Table 4.7

Sample calculation of CFL for Ti in OPC treated sample with OPC:waste ratio of 50:50

Leaching interval (n)	a_n	Σa_{no}	$\Sigma a_n / A_o$	V/S (cm)	CFL (cm)
a		b	c	d	E=c*d
1	0.0796	0.0796	0.0523	0.5046	0.0264
2	0.1073	0.1869	0.0894	0.5046	0.0451
3	0.1185	0.3054	0.1419	0.5046	0.0716
4	0.1419	0.4473	0.1786	0.5046	0.0901
5	0.1084	0.5557	0.2162	0.5046	0.1091

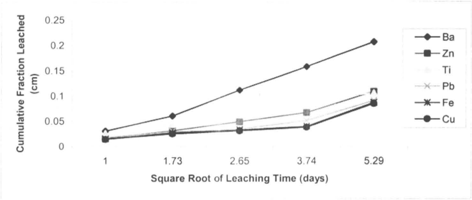
Figure 4.6 and Figure 4.7 showed the cumulative fraction leached for the heavy metals of concern for OPC and OPC with activated carbon treated samples versus the square root of leaching time respectively. As demonstrated in these figures, the linearity relationship between cumulative fraction leached and square root of leaching time indicated that diffusional process is the main transport phenomenon for the leaching of the trace metals (Bishop, *et al.*, 1992; Morgan and Bostick, 1992; De Groot and Van Der Sloot, 1992).

As shown in Figure 4.6, Ba and Ti contributed the highest CFL among the metals of concern and far above the CFL values of other heavy metals. CFL for Ti was 0.1488cm, 0.141cm, 0.129cm, 0.1185cm and 0.106cm in 90%, 80%, 70%, 60% and 50% waste loading respectively. The leaching of Ti from OPC treated samples increase as the waste loading increases, probably this is the reason for the increase of CFL of Ti.

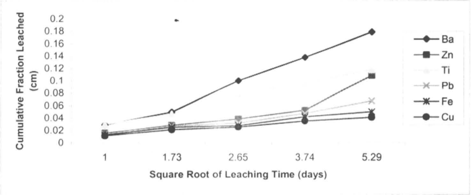
As for Ba, CFL decreased as the OPC loading decreased from 0.207cm, 0.179cm and 0.142cm in 50%, 40% and 30% OPC loading respectively. The leaching of Ba from OPC treated samples declined as the OPC loading decreased, probably this is the reason for the decline of CFL of Ba.

On the other hand, CFL of other heavy metals decreased as the OPC loading decreased. It is clearly seen from the CFL of Zn at the end of the leaching interval, where it decreased from 0.1088cm in 50% OPC loading, to 0.0723cm and 0.0596cm in 40% and 30% OPC loading respectively. The CFL values of Pb are below the CFL of Zn decreasing from 0.1088cm in 50% OPC loading to 0.0311cm in 10% OPC loading.

Similar patterns were observed in OPC with activated carbon treated samples, where the CFL of all the heavy metals at each AC:OPC:waste ratio was linearly related with square root leaching time (Figure 4.7). It was observed that the CFL of Ti reduced approximately 22% after addition of activated carbon. In Figure 4.7 (e), the CFL of Ti declined to 0.1009cm as compared to 0.1488cm in 90% waste without activated carbon (Figure 4.6 (a)). The CFL of Ti was decreasing from 0.0985cm, 0.0918cm, 0.0852cm to 0.0832cm as in 80%, 70%, 60% and 50% waste loading.



(a)



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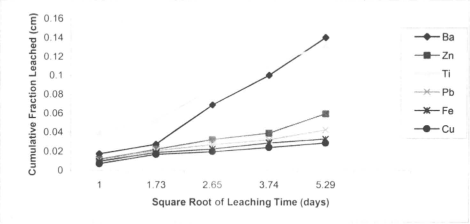
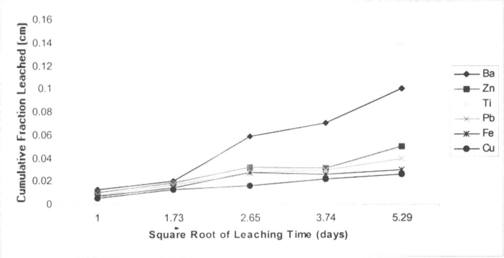
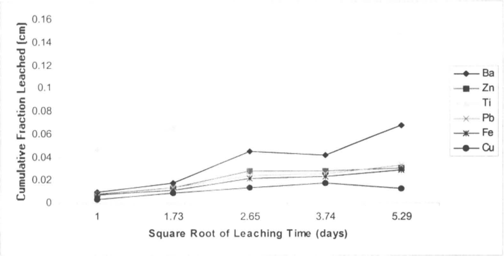


(c)

Figure 4.6 Cumulative Fraction Leached for the heavy metals of concern in OPC treated samples at the OPC:waste ratios of (a) 50:50, (b) 40:60 and (c) 30:70

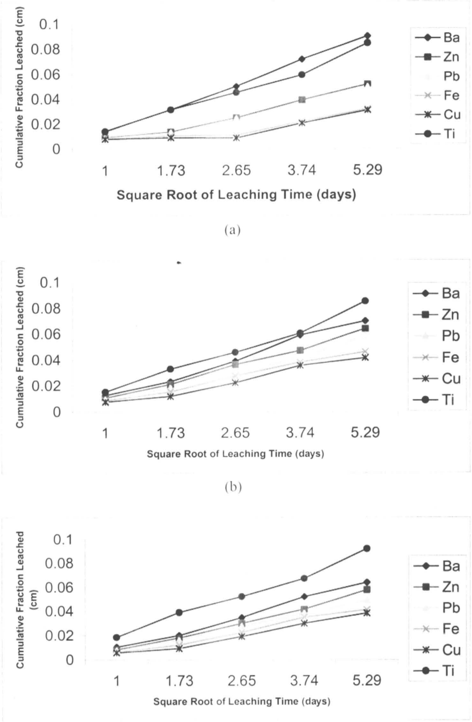


(d)



(e)

Figure 4.6 (Continued) Cumulative Fraction Leached for the heavy metals of concern in OPC treated samples at the OPC:waste ratios of (d) 20:80 and (e) 10:90

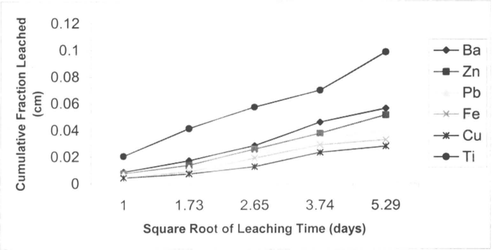


(a)

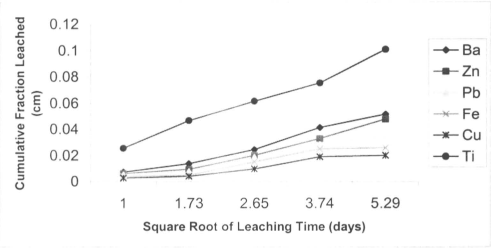
(b)

(c)

Figure 4.7 Cumulative Fraction Leached for the heavy metals of concern in OPC with activated carbon treated samples at the AC:OPC:waste ratios of (a) 3:47:50, (b) 4:36:60 and (c) 5:25:70



(d)



(e)

Figure 4.7 (Continued) Cumulative Fraction Leached for the heavy metals of concern in OPC with activated carbon treated samples at the AC:OPC:waste ratios of (d) 6:14:80 and (e) 7:3:90

CFL of Ba was 0.09cm, 0.07cm, 0.0639cm, 0.0562cm and 0.0515cm in 47%, 36%, 25%, 14% and 3% OPC loading respectively, which has decreased by 56% - 60% as compared to purely OPC treated samples. CFL of Zn decreased from 0.0516cm to 0.0477cm. CFL of other heavy metals declined as well, but less pronounced as Ba and Zn. For Pb, CFL has decreased by 35% - 45%, whereas the decreased of Cu and Fe was 18% - 40% and 25% - 55% respectively.

For the white cement treated samples, the plots reported in Figure 4.8 and Figure 4.9 also demonstrated that the heavy metals leached according to a diffusional-controlled phenomenon, since the CFL is linearly related to the square root of leaching time. As shown in Figure 4.8, Ti and Ba contributed the highest CFL among the metals of concern and far above the CFL values of other heavy metals. CFL for Ti was 0.1009cm, 0.0985cm, 0.0918cm, 0.0852cm and 0.0845cm in 90%, 80%, 70%, 60% and 50% waste loading respectively. While the CFL for Ba was decreased from 0.2042cm in 50% white cement loading to 0.0659cm in 10% white cement loading.

On the other hand, CFL of other heavy metals also decreased as the white cement loading decreased. CFL of Zn decrease from 0.1065cm in 50% white cement loading to 0.0296cm in 10% white cement loading. The CFL value for Pb is slightly lower than Zn. The CFL of Cu and Fe were quite close to each other

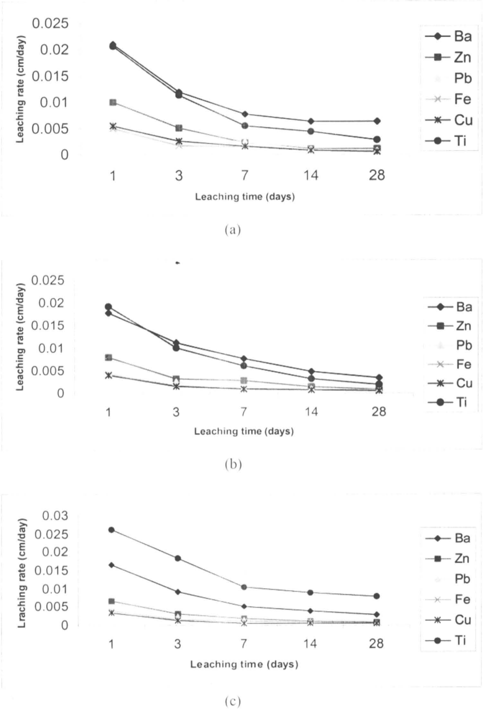
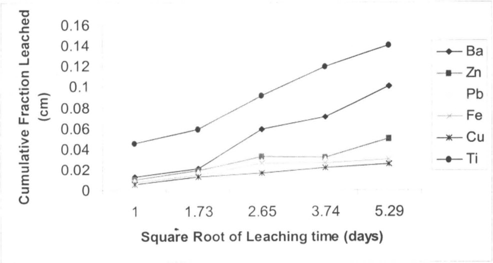
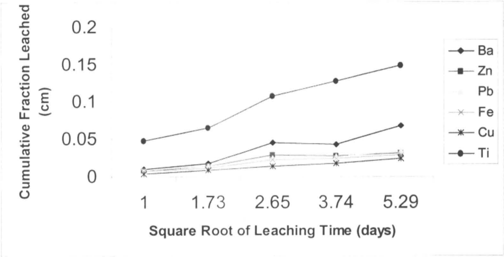


Figure 4.8 Cumulative Fraction Leached for the heavy metals of concern in white cement treated samples at the white cement:waste ratios of (a) 50:50, (b) 40:60 and (c) 30:70

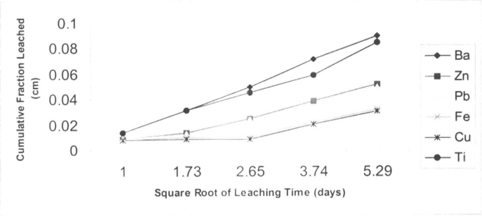


(d)

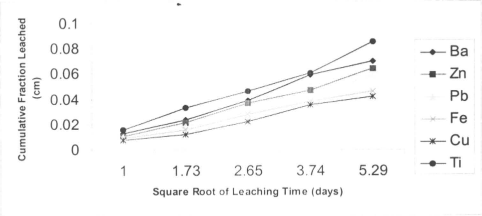


(e)

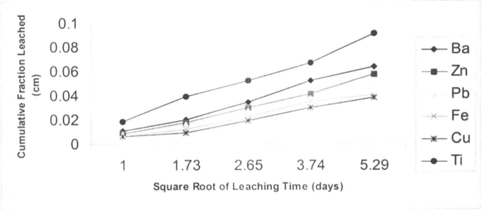
Figure 4.8 (Continued) Cumulative Fraction Leached for the heavy metals of concern in white cement treated samples at the white cement:waste ratios of (d) 20:80 and (e) 10:90



(a)

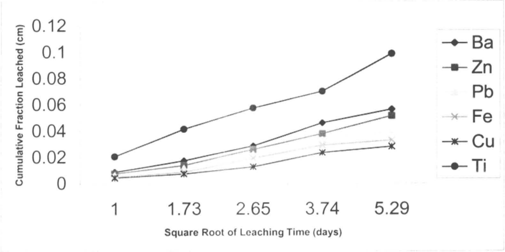


(b)

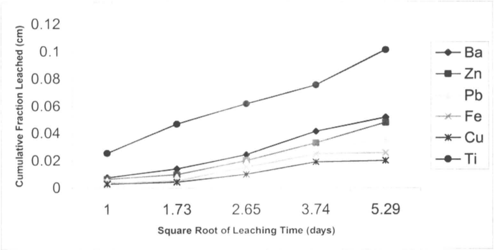


(c)

Figure 4.9 Cumulative Fraction Leached for the heavy metals of concern in white cement with activated carbon treated samples at the AC:white cement:waste ratios of 3:47:50, (b) 4:36:60 and (c) 5:25:70



(d)



(e)

Figure 4.9 (Continued) Cumulative Fraction Leached for the heavy metals of concern in white cement with activated carbon treated samples at the AC:white cement:waste ratios of (d) 6:14:80 and (e) 7:3:90

Similar patterns were observed in white cement with activated carbon treated samples, where the CFL of Ti and Ba was the highest. The CFL of Ti reduced by approximately 22% after addition of activated carbon. In Figure 4.9 (e), the CFL of Ti decline to 0.1015cm as compared to 0.1220cm in 90% waste without activated carbon (Figure 4.8 (e)). Similarly the CFL of Ti was 0.1383cm, 0.113cm, 0.1167cm and 0.0987cm in 80%, 70%, 60% and 50% waste loading respectively.

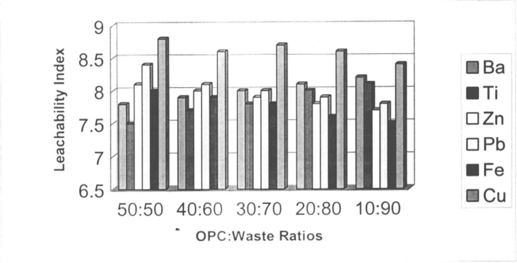
CFL of Ba was 0.0888cm, 0.0685cm, 0.0630cm, 0.0542cm and 0.0501cm in 50%, 40%, 30%, 20% and 10% white cement loading. The CFL of Ba was reduced by approximately 55% after addition of activated carbon. On the other hand, the CFL of Zn, Pb, Cu and Fe were also reduced as the cement loading decreased.

Leachability Index

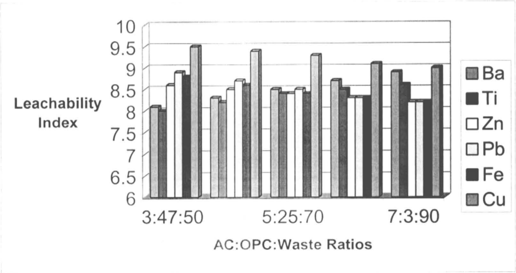
The effective diffusivity (D) and Leachability Index (L_i) were calculated according to equations (3) and (4), and a sample calculation is shown in Table 4.8.

Table 4.8
Sample calculation of diffusivity coefficient and Leachability Index (L_i) for Ti in OPC treated sample with OPC:waste ratio of 50:50 at each interval.

Leaching interval (n) a	Leaching duration $T=(\Delta t)_n$(s) b	T (s) c	V/S (cm) d	a_n / A_o e	$[a_n / A_o]$ $[1/\Delta t_n]$ (cm) f=e/b	D (cm^2/s) g= $\pi.f^2.d^2.c$	L_i h= log(1/g)
1	86400	21600	0.5046	0.1011	1.1701e-6	2.3656e-8	7.43
2	172800	161225	0.5046	0.0587	3.3970e-7	1.4882e-8	7.53
3	345600	413967	0.5046	0.0876	2.5347e-7	2.1275e-8	7.57
4	604800	881258	0.5046	0.0930	1.5377e-7	1.6668e-8	7.50
5	1209600	1762516	0.5046	0.0960	7.9365e-8	8.8805e-9	7.47

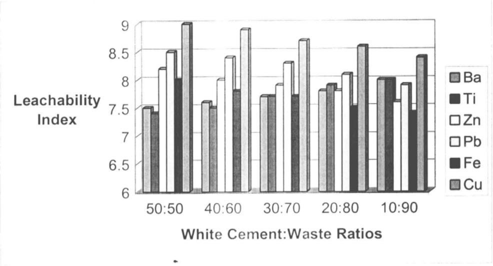


(a)

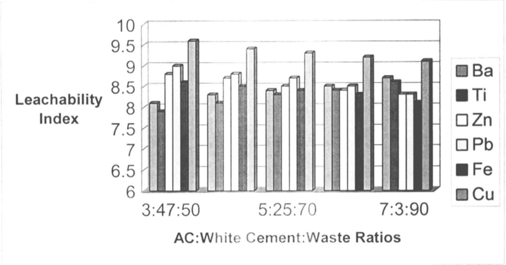


(b)

Figure 4.10 Leachability Index for the (a) OPC and (b) OPC with activated carbon treated samples.



(a)



(b)

Figure 4.11 Leachability Index for the (a) white cement and (b) white cement with activated carbon treated samples

The L_i for Ti will be obtained y averaging the L value of each interval.

$L_i = [7.43+7.53+7.57+7.5+7.47] / 5$

$= 7.50$

The ANS 16.1 (modified) leachability indices of the six heavy metals for the two type of cement-based solidification, at various ratios, are shown in Figure 4.10 and Figure 4.11 respectively. The leachability indices obtained in this study exceeded the guidance value of leachability index of 6 (Morgan and Bostick, 1992), which clearly indicate that the toxic heavy metal are well retained in the solidified specimens.

It was observed that the OPC and white cement with activated carbon is relatively superior in retaining the heavy metals than cement alone, where the L_i of heavy metals in cement and cement with activated carbon ranged from 7.4 to 9.0 and 8.0 – 9.5 respectively. Despite small differences in L_i values of the heavy metals, there is a correlation that when the waste loading was increased, the L_i values decreased, except for Ba. This result was consistent with the CFL of Ba as shown in Figure 4.10 where Ba demonstrated the highest CFL and hence tend to have smaller value of L_i (i.e. smaller value of L_i imply larger amount of contaminant diffusing from the solidified waste forms (Morgan and Bostick, 1992)).

4.2.3 PHYSICAL CHARACTERISTIC

Hardening time

The hardening time of the mixture was recorded and illustrated in Figure 4.12. Generally, the untreated waste took longer time to harden, 25-40 hours, whereas hardening time is significantly reduced to 15-30 hours for cement-based binder solidification. The controls (without the waste) of cement and cement with activated carbon hardened within a day.

Compressive strength

Figure 4.13 (a), (b), (c) and (d) illustrate the compressive strength development of various binder/waste ratio at the 1st, 3rd, 7th, 14th and 28th days curing. Generally the solidification presents great compressive strength and the compressive strength of solidified forms varied with the loading of the waste and the curing time.

As shown in the Figure 4.13(a) and (b), the compressive strength of solidified specimens increased as the cement loading decreased and also as the days progressed. The readings ranged between 68 – 73 MPa for 50% cement loading, 69 – 75 MPa for 40% cement loading, 71 – 76 MPa for 30% and 20% cement loading and 73 – 78MPa for 10% cement loading, after 1, 7, 14 and 28 days respectively.

While in Figure 4.13(b), the readings ranged between 67 – 71 MPa for 50% cement loading, 70 – 74 MPa for 40% cement loading, 71 – 77 MPa for 30%, 71 – 80 MPa for 20% cement loading and 73 – 79 MPa for 10% cement loading, after 1, 7, 14 and 28 days respectively.

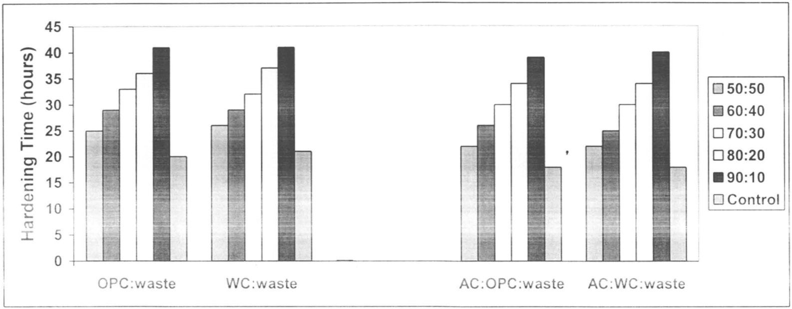
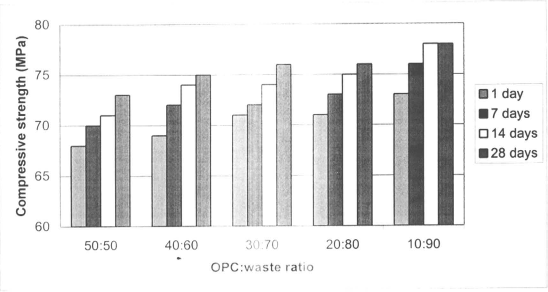


Figure 4.12 Hardening time of cement and cement with activated carbon samples at different ratios.

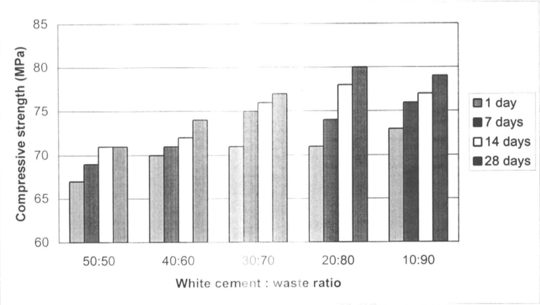
In the OPC and white cement with activated carbon treated samples, slightly higher compressive strength of the solidified specimens were observed. In Figure 4.13(c) the compressive strength readings after 1, 7, 14 and 28 days curing, ranged from 70 – 75MPa, 71 – 78 MPa,73 – 78 MPa, 75 – 80 MPa and 76 – 82 MPa in 50%, 40%, 30%, 20% and 10% cement with activated carbon, respectively.

The compressive strength for the white cement and activated treated samples are almost the same as OPC. Based on Figure 4.13(d), the compressive strength readings after 1, 7, 14 and 28 days curing, ranged from 70 – 76MPa, 70 – 77 MPa,72 – 78 MPa, 74 – 81 MPa and 75 – 81 MPa in 50%, 40%, 30%, 20% and 10% cement with activated carbon respectively.

The compressive strength can be improved by decreasing the cement content, which can increase the waste loading, decreased the volume of the final waste form and hence decreased the treatment and disposal cost. It must be remembered that the intent is to stabilize a waste for disposal, not create a strong cement structure contaminated with hazardous materials. In this regard, the strategy is to utilize the minimal amount of binder/additives to meet the performance criteria (EPA/ORIA,1996).

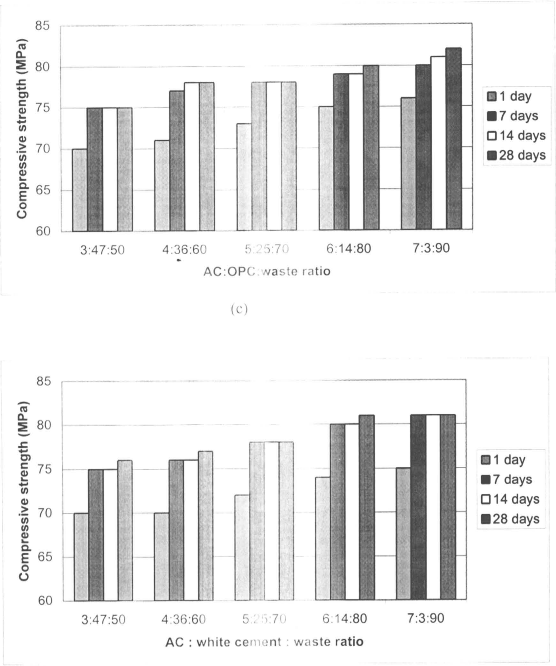


(a)



(b)

Figure 4.13 Compressive strength of solidified waste after 1,7, 14 and 28 days of solidification for (a) OPC and (b) white cement treated samples.



(c)

(d)

Figure 4.13 (Continued) Compressive strength of solidified waste after 1,7, 14 and 28 days of solidification for (a) OPC and (b) white cement with activated carbon treated samples.

4.5 COST EVALUATION

The material cost and disposal cost for cement-based S/S were computed. It should be highlighted that the operating cost, such as energy usage, water, labour, maintenance have not been taken into consideration. Note that the values presented below are illustration purpose only.

The annual cost for cement-based S/S is presented in Table 4.9 and Table 4.10. The computed values are based on the generation rate of 45 metric tonnes of waste per annum at the binder : waste ratio of 50:50.

Table 4.9
Annual cost for cementitious S/S

	Unit Cost (RM)	OPC Cost (RM)	White cement Cost (RM)
Material cost - OPC	1 / kg	45,000	
- WC	1.5 / kg		67,500
Transportation	70 / metric ton	3150	3150
Disposal to landfill	550 / metric ton	24,750	24,750
Total		72,900	95,400

Table 4.10
Annual cost for cementitious S/S with activated carbon

	Unit Cost (RM)	OPC Cost (RM)	White cement Cost (RM)
Material cost - OPC	1 / kg	45,000	
- WC	1.5 / kg		67,500
- AC	6.5/kg	8775	8775
Transportation	70 / metric ton	3150	3150
Disposal to landfill	550 / metric ton	24,750	24,750
Total		81,675	104,175

As illustrated in Table 4.9 and Table 4.10, the annual cost of cementitious based S/S with or without activated carbon is more expensive than the present disposal cost which is about RM60,000.