

## CHAPTER 4 SOLIDIFICATION / STABILIZATION (S/S) STUDIES

In this study, an experimental program was carried out to investigate the treatability potential of the brake lining dusts. 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 (Weitzman, 1990). Ordinary Portland Cement (with and without activated carbon) and two types of polymeric resins were utilized in this study.

The objectives of this experiment is:

- (1) to solidify the brake lining waste using cement (with and without activated carbon) or polymeric resins (orthophtalic and vinyl ester),
- (2) the determine the leachability characteristics of the treated/solidified brake lining dust by using 2 leaching procedures: (i). TCLP and (ii). ANS 16.1 (modified), and
- (3) to investigate the hardening time and compressive strength of the monolithic waste form.

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

Table 4.1 Standards guidance for solidified waste form

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

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

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

<sup>b</sup> 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 for full size waste forms to 300 years should produce less than a 10% loss of total carbon in the sample.

## 4.1 MATERIALS & METHODS

### 4.1.1 Collection of Samples

The brake lining dust was obtained from Don Brake (M) Sdn. Bhd. It was collected from the bag house in the manufacturing plant (Refer to plate 3.2). The brake lining dust is greyish in colour as shown in plate 4.1. The dust was handled carefully throughout the experiment. Besides the asbestos and some other fiber materials contents which may cause health hazard if inhaled, the brake lining dust also contains toxic heavy metals that may contaminate groundwater if mishandled.

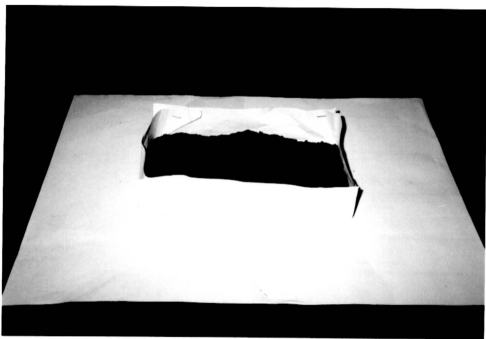


Plate 4.1 Brake lining dust

Laser Defraction Particle Size Analyzer (Coulter, USA) was used to analyze the particle size distribution of the dust prior to the experiment.

#### 4.1.2 Materials

For cement-based S/S, Ordinary Portland Cement (OPC) was used. The typical chemical composition of the OPC is given in the Table 4.2

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

Chemical Compounds	Weight %
SiO <sub>2</sub>	17 - 24
Al <sub>2</sub> O <sub>3</sub>	3 - 8
Fe <sub>2</sub> O <sub>3</sub>	1 - 6
CaO	61 - 67
MgO	0.1 - 4

Source: Glasser, 1997

On the other hand, two types of polymeric resins were used for the polymeric encapsulation. The resins are (i) Ortho Polymal 820, and (ii) Hetron 922 Vinyl Ester. The Polymal 820 resin is produced by Takeda Chemical Industries, whereas Hetron is manufactured by Ashland Chemical Co., Columbus, Ohio. The resins are prepromoted to facilitate room temperature curing. Methyl ethyl ketone (MEK) peroxide was used as the solidification initiator for the resins. Table 4.3 presents data on the physical properties of the two resins.

Table 4.3 Physical data for the two resins used in this project

Resin's Properties	Polymal 820 <sup>a</sup>	Hetron 922 <sup>b</sup>
Resin Type	Orthophthalic	Vinyl Ester
Viscosity, cps	370 - 470	450
Tensile Strength, psi	11,000	12,500
Gel Time, minutes	10 - 30	12 - 20
Specific Gravity, kg/m <sup>3</sup>	1.05 <sup>c</sup>	1.10 <sup>c</sup>
Peak Exotherm, °C	120	187.6

Sources: a: Takeda Chemical Industries

b: Ashland Chemical Co., Columbus

c: These values were determined in this study



### 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), glasswares, and plastic bottles (100ml), ELGASTAT® UHQPS to process ultra pure water. All the apparatus were cleaned thoroughly prior to use. The glasswares 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 for Cement-Based S/S

#### *Trial Mix*

Cement was mixed with brake lining dusts at various ratios. Ultra pure water was added to promote the hydration of cement-sludge paste. Suitable water/cement ratio was determined to allow good workability of the cement paste. The resulting mixture was then transferred to steel-moulds and cured for 24-hours to ascertain their solidibility within the period. The cement:dust ratio and the corresponding water/cement ratio used are summarized in Table 4.4.

Table 4.4 Test run conditions for cement-based solidification

Binding Agent		Brake Lining Dust	Water/Cement	Number of Samples		
Type	Amount (wt %)	Amount (wt %)	Ratio	TCLP	ANS 16.1 (modified)	Comp. Strength
Cement	60	40	0.89	2	1	4
	50	50	1.2	2	1	4
	40	60	1.63	2	1	4
	30	70	2.5	2	1	4
AC:Cement	4:56	40	1.06	2	1	4
	5:45	50	1.57	2	1	4
	6:34	60	2.23	2	1	4
	7:23	70	3.6	2	1	4

AC: Activated Carbon

**Mixing, Casting and Curing**

Specimens were prepared by first homogenizing the lining dust with cement using blender for 1 minute. Water was added slowly into the dry mix to promote hydration. The mixture was mixed at high speed for 3-4 minutes upon attainment of the predetermined water/cement ratio. These procedures are 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 mixture was hand-compacted to yield good compaction before placing the next layer.

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, to prevent excessive water loss by evaporation. At the end of this period, the specimens were

demoulded and further cured for 27 days under the dry condition, to simulate the curing condition as normally encountered in landfill situation.

In the initial trial, four different cement loadings (30, 40, 50 and 60 wt %) were mixed with brake lining dust. In the second trial, 4g, 5g, 6g and 7g of activated carbon was added to the cement which was reduced accordingly. This is because activated carbon have 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 the sorbent in the waste mixture (Conner, 1990).

#### **4.1.5 Preparation of Sample Specimens for Polymeric Encapsulation**

##### **Trial Mix**

Initial curing experiments were carried out with and without brake lining dusts to determine the suitable initiator ratios for curing each resin-waste mixture. Initiator proportions had to be increased to ensure resin hardening within a reasonable time (24-hours). After this preliminary study, initiator ratio was fixed for the remaining tests. The number of samples prepared for evaluation and various waste loading are reported in Table 4.5.

##### **Mixing, Casting and Curing**

The preparation of test specimens was done by mixing a predetermined amount of polymerization initiator at room temperature into a batch of resin. The lining dusts were then added to the initiated resin and intimately mixed for 2-3 minutes in order to obtain

Table 4.5 Test run conditions for polymeric encapsulation

Binding Agent		MEK Peroxide	Lining Dust	Number of Samples		
Type	Amount (%)	Amount (%)	Amount (%)	TCLP	ANS 16.1 (modified)	Comp. Strength
Polymal	60	3	40	1	1	4
	60	5	40	1	1	4
	50	3	50	1	1	4
	50	5	50	1	1	4
	45	5	55	1	1	4
Hetron	60	3	40	1	1	4
	60	5	40	1	1	4
	50	3	50	1	1	4
	50	5	50	1	1	4
	45	5	55	1	1	4

rapid dispersion and even distribution of the dusts throughout the mixture. Upon the completion of mixing, the resulting mixture was transferred to specified moulds (scoop was used when necessary). The mixture was hand-compacted before placing the next layer in order to obtain good compaction.

Three different loadings were prepared (60, 50 and 45 wt %) because below a resin loading of 40%, the added dust occasionally agglomerated and complete wetting of dust particle was difficult. Thus 45% resin loading was prepared and it was estimated that 50% loading would most likely be the feasible upper limit. To investigate the variation in hardening time, 3% and 5% MEK peroxide were added to the 50% and 60% resin loading, whereas only 5% MEK peroxide was used in 45% resin loading.

## 4.2 LEACHING TESTS

### 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 crushed to a particle size smaller than 9.5 mm. 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 and sodium hydroxide adjusted to a pH of  $4.93 \pm 0.05$ .

The leaching procedure involves 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  $25 \pm 2^{\circ}\text{C}$  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  $0.8\mu\text{m}$  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, acidified with 1ml of nitric acid and stored in refrigerator at  $4^{\circ}\text{C}$  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 dust. 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 a modification of that proposed by the American Nuclear Society for solidified low-level radioactive wastes in standard ANSI/ANS 16.1, which is conducted for a total of 90-days.

The modified ANS 16.1 static leaching procedure involves the following steps: the solidified specimens prepared were cylindrical with thickness-to-diameter ratio of 0.3, as shown in the Plate 4.2.

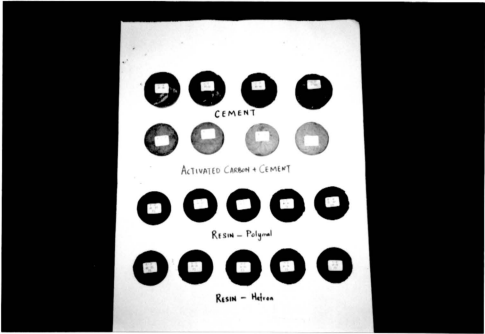


Plate 4.2 Solidified specimens used for ANS 16.1 (modified) leaching test.



Plate 4.3 Suspended sample specimen in beaker.

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 as shown in Plate 4.3.

The ratio of the leachant volume and the external geometric surface area of the solid specimens is maintained at about  $10 \pm 0.2$  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, unreleased report).

The leaching of samples were monitored over a period of 28 days (sampling at the 1st., 3rd., 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 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 a function of the leaching time:

$$l = \frac{a_n}{A_o} \times \frac{V}{S \cdot t_n} \quad (1)$$

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),

$$CFL = \frac{\sum a_n}{A_o} \times \frac{V}{S} \quad (2)$$

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

$$D = \pi \left( \frac{(a_n / A_o)}{(\Delta t)_n} \right)^2 \left( \frac{V}{S} \right)^2 T \quad (3)$$

where

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

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

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

$$L_i = \frac{1}{n} \sum \left[ \log \left( \frac{\beta}{D_i} \right) \right]_n \quad (4)$$

where  $\beta$  is a defined constant ( $1.0 \text{ cm}^2/\text{s}$ ),  $n$  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. It was recorded by visual observation and hand-pressing the specimens at predetermined duration: every six hours for cement treated samples and the first six hours for the resin treated samples, as the resin treated samples solidified immediately after mixing.

### 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 50mm cube specimens) C109/C 109M-95 testing protocols. Plate 4.4 shows the cement-based and the polymeric resin solidified specimens used for determining the strength of the solids formed. This study determines the suitability of solids for landfill stacking on top of another. The stronger the solid formed, the more suitable for secure landfill disposal.

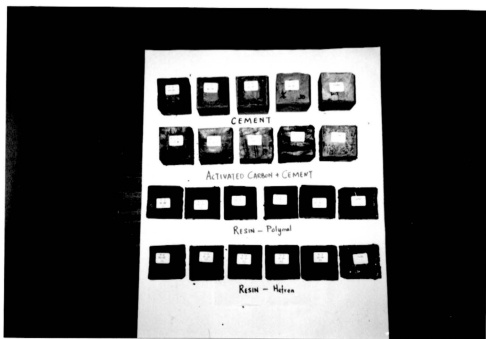


Plate 4.4 Solidified specimens for compressive strength test

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

$$f_m = \frac{P}{A} \tag{5}$$

where

- $f_m$  = compressive strength in psi or [MPa],
- $P$  = total maximum load in lbf or [N] and
- $A$  = area of loaded surface in in<sup>2</sup> or [mm<sup>2</sup>].

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), as shown in Plate 4.5.



Plate 4.5 Hydraulic compressive strength apparatus (model ELE)

## 4.4 RESULTS AND DISCUSSION

Table 4.6 reports the grain size distribution of the brake lining dust based on the results obtained from Laser Defraction Particle Size Analyzer.

Table 4.6 Grain size distribution of the brake lining dust

%<	10	25	50	75	90
Size ( $\mu\text{m}$ )	24.88	72.62	182.1	327	567.3

The estimated average size of the brake lining dust is  $298.2\ \mu\text{m}$  with standard deviation of  $39.3\ \mu\text{m}$  and mode of  $245.2\ \mu\text{m}$ .

### 4.4.1 TCLP Results

The summary of TCLP leachate analysis data is presented in the Table 4.6, 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 4.7, the TCLP extract of the untreated dust contains the highest concentration of Zn, followed by Ba, Pb, Fe, Cu and Cr. Among these metals, the concentration of Zn, Pb and Cr exceeded the regulatory limit stipulated in Malaysia Environmental Quality (Sewage and Industrial Effluents), 1979, *Standard B*; but within the permitted level for TCLP test, except for Zn and Cu, which have no permitted level stipulated in the TCLP test.

Table 4.7 Summary of TCLP leaching data with initial extraction fluid pH and final pH of the extract<sup>a</sup>

Regulatory Limit for TCLP Test <sup>b</sup>	Initial pH	Final pH	Concentration of metals in Leachate, mg/L					
			Ba	Cr	Zn	Pb	Cu	Fe
			100	5	-	5	-	-
Malaysia EQA <sup>c</sup>	5.5 - 9.0		-	0.05	1	0.5	1	5
Untreated Dust	4.92	12.48	3.8352	0.1835	5.9334	2.6777	0.2035	2.5422
Cement	4.91	11.53	0.4258	0.0553	0.0880	0.6505	0.0241	0.7883
Cement:Dust								
60:40	4.92	12.36	1.9617	0.0437	2.0067	0.8156	0.0374	0.6063
50:50	4.93	11.87	1.8183	0.0403	1.7990	0.7313	0.0364	0.4924
40:60	4.93	11.65	1.6058	0.0379	1.5599	0.6710	0.0356	0.4385
30:70	4.92	11.07	1.3715	0.0336	1.6691	0.7211	0.0319	0.4853
AC:Cement:Dust								
4:56:40	4.93	12.01	1.0420	0.0364	1.4466	0.5936	0.0297	0.4040
5:45:50	4.91	11.13	0.9542	0.0312	1.2318	0.4951	0.0259	0.3216
6:34:60	4.94	11.53	0.8691	0.0296	1.1529	0.4544	0.0242	0.2776
7:23:70	4.93	10.94	0.7985	0.0258	1.2650	0.5251	0.0219	0.2402
Polymal:Dust								
60:40 (3%)	4.91	5.11	0.3513	0.0078	0.4788	0.1497	0.0107	0.1063
60:40 (5%)	4.90	5.08	0.3302	0.0072	0.4290	0.1580	0.0116	0.1080
50:50 (3%)	4.90	5.10	0.4487	0.0100	0.5560	0.2217	0.0150	0.1505
50:50 (5%)	4.92	5.11	0.4280	0.0107	0.5856	0.2046	0.0160	0.1375
45:55 (5%)	4.91	5.16	0.5128	0.0150	0.7233	0.2541	0.0186	0.1741
Hetron:Dust								
60:40 (3%)	4.91	5.15	0.4890	0.0114	0.6177	0.1778	0.0123	0.1243
60:40 (5%)	4.93	5.11	0.4932	0.0119	0.5785	0.1588	0.0129	0.1086
50:50 (3%)	4.93	5.14	0.5507	0.0152	0.7079	0.2011	0.0171	0.1581
50:50 (5%)	4.92	5.18	0.5304	0.0154	0.6455	0.2107	0.0162	0.1520
45:55 (5%)	4.90	5.19	0.5941	0.0194	0.8325	0.2726	0.0211	0.2077

a Duplicate analysis for portland cement and portland cement with activated carbon samples, single analysis for the polymeric resin encapsulated samples.

b United States EPA regulatory limits for TCLP Test.

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

AC: Activated Carbon

Substantial amount of heavy metals are found present in the cement, as shown in Table 4.7. These metals originate mostly in natural raw materials used in the binder manufacture of cement (Conner, 1990). 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, analysed by X-ray fluorescence, is given in Table 4.8.

Table 4.8 Heavy metals composition in OPC.

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

Source: Conner (1990)

NA - not available

The high pH value of the untreated dust and the cement, 12.48 and 11.53 respectively, shows that they are basic in nature. The leachate of the cement based specimens shows very high pH value, ranging from 10.94 to 12.36, and exceeds the limit stipulated in Malaysia EQA. However, the pH value decreases gradually as the cement loading decreases in both cement:dust and AC:cement:dust specimens. In contrast, the TCLP extract of polymeric resins shows a relatively consistent pH value, regardless of the amount of resin used and it is within the EQA regulatory limit.

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 cement-based and polymeric resins TCLP extract, are displayed in Figure 4.1.

It is interesting to note that, the percentage of leachable fraction decreased as the waste loading increased in both cement and cement with activated carbon treated samples. This could be explained by the amphoteric nature of the metals, which have higher solubility at both low and high pH conditions (Zamorani, 1994; Bishop, 1995). This will be further discussed in detail in the next section (4.4.2).

As expected, replacing cement with polymeric resin as binder further reduced the leachability of metals. As indicated in Figure 4.1(c), Polymal reduced the percentage of leachable fraction of all metals of concern to less than 15%, where the reduction was 8.61 - 13.37% for Ba, 3.95 - 8.16% for Cr, 7.23 - 12.19% for Zn, 5.59 - 9.49% for Pb, 5.27 - 9.14% for Cu, and 4.18 - 6.85% for Fe.

Figure 4.1(d) shows that the percentage of leachable fraction in the extract of Hetron treated samples were relatively higher than those from Polymal treated samples. The percentage of leachable fraction was 12.75 - 17.49% for Ba, 6.22 - 10.55% for Cr, 9.41 - 14.03% for Zn, 5.93 - 10.18% for Pb, 6.02 - 10.35% for Cu, 4.27 - 8.17% for Fe. It was also observed that at the same loading, the amount of initiator MEK added to both Polymal and Hetron did not significantly affect the percentage of leachable fraction of the solidified specimens.



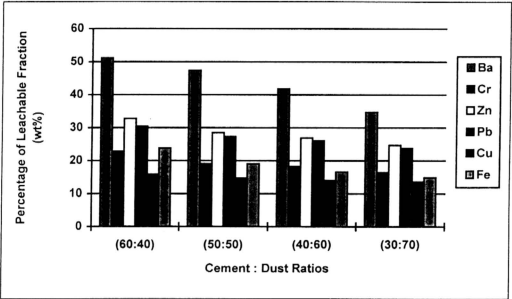


Figure 4.1(a) The percentage of leachable fraction of the heavy metals of concern in the leachate from cement treated samples

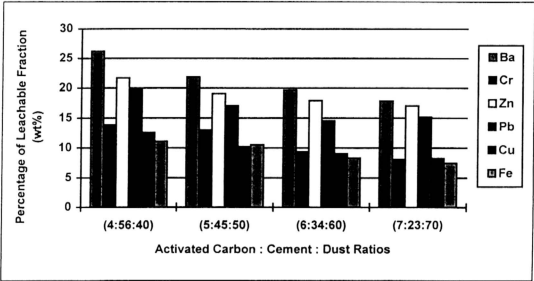


Figure 4.1(b) The percentage of leachable fraction of the heavy metals of concern in the leachate from cement with activated carbon treated samples

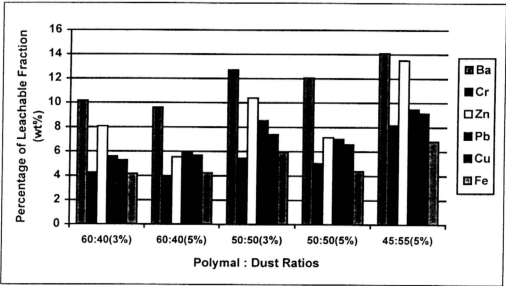


Figure 4.1(c) The percentage of leachable fraction for the heavy metals of concern in the leachate from Polymal treated samples. The initiator percentage is given in the bracket.

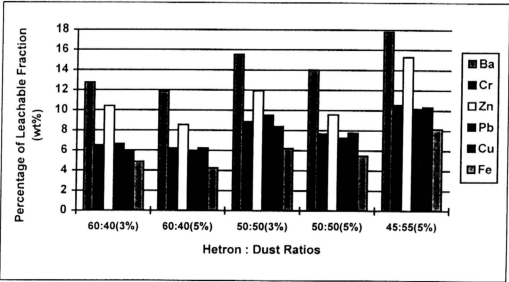


Figure 4.1(d) The percentage of leachable fraction for the heavy metals of concern in the leachate from Hetron treated samples. The initiator percentage is given in the bracket.

Generally, the concentration of the heavy metals in the extract of both Polymal and Hetron were found to increase as the resin loading decreased. This could be due to insufficient resin to bind the dust effectively and hence resulting in higher concentration of heavy metals leached from the “unsolidified” brake lining dust. Retention efficiency improved as more resin was used.

#### **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 metals leaching. The final pH of the TCLP extract for untreated dust, cement, and the cement-based treated samples were basic, ranging from pH 10.94 - 12.36, 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 Cr, Pb, Zn, Cu and Fe that exhibit amphoteric behavior have higher solubility at both low and high pH. Solubility curves for various metal hydroxides at various pH range are shown in Figure 4.2 (Conner,1990).

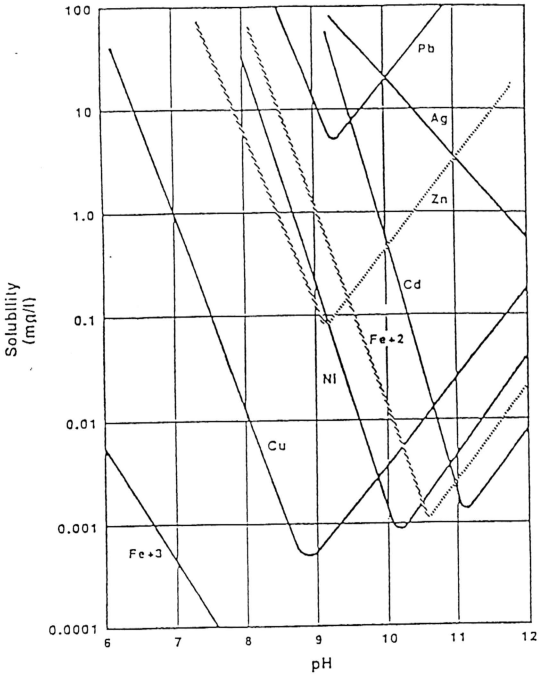
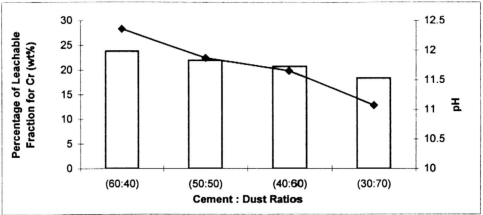


Figure 4.2 Solubilities of metal hydroxides as a function of pH  
(Conner, 1992)

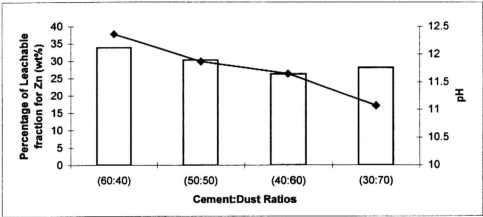
The relationship between the final pH of extract and the percentage of leachable fraction for Cr, Zn, Pb, Cu and Fe in both cement and cement with activated carbon treated waste are illustrated in Figure 4.3 and Figure 4.4 respectively. In Figure 4.3(a), the amphoteric nature of Cr solubility is evident in the plot as the percentage of leachable fraction of Cr decreased as the final pH of the leachate decreased from 12.46 to 11.07. This relationship was consistent for the leaching of Cu as well and shown in Figure 4.3(d). Figure 4.3(b), (c) and (e) showed that the percentage of leachable fraction for Zn, Pb and Fe slightly increased at 70% waste loading, which deviated from the above pattern and this may be caused by insufficient cement to bind the high waste loading effectively.

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 10.94 - 12.01. The slightly lower pH was probably due to the lesser amount of cement which was replaced by activated carbon.

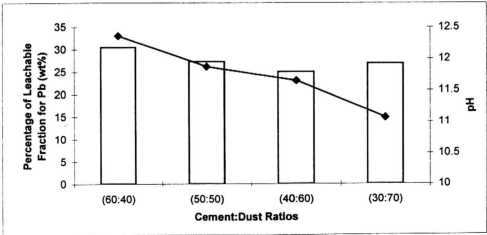
Figure 4.4 shown that the percentage of leachable fraction of the heavy metals that exhibit amphoteric behaviour, followed a similar pattern as the cement treated samples, but less pronounced, as the final pH in the extract decreased. For Zn, Pb and Fe, the respective Figure 4.4(b), (c) and (e) indicated that the leachable fraction of these metals followed similar trend, except at 70% waste loading, the respective metals leached increased, which deviated from the above pattern. This may be caused by insufficient cement to bind the high waste loading effectively.





(a)

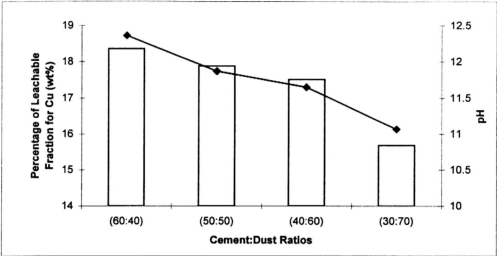


(b)

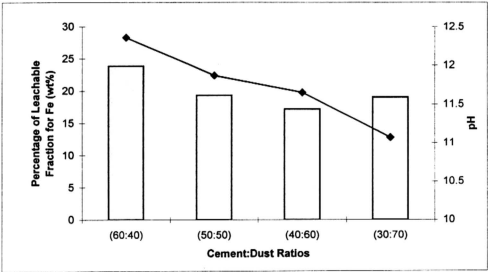


(c)



Figure 4.3 The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of cement treated samples (  heavy metal leached,  pH).

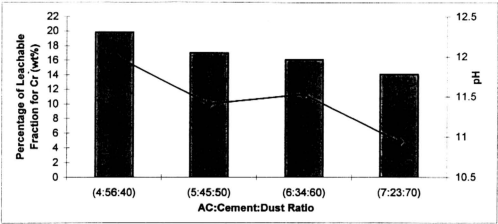


(d)

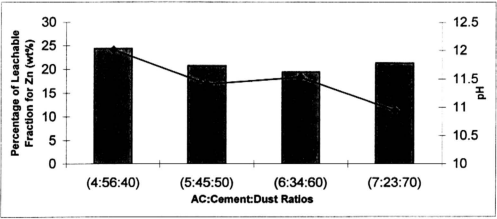


(e)

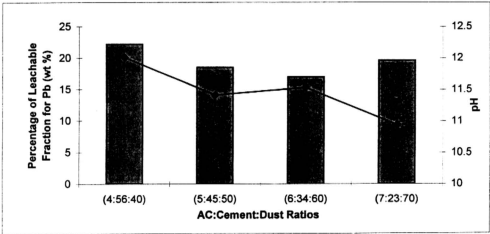
Figure 4.3 (Continued) The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of cement treated samples (  heavy metal leached,  pH).



(a)



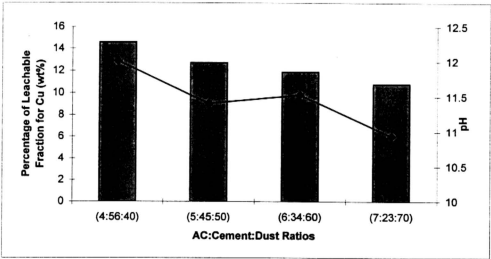
(b)



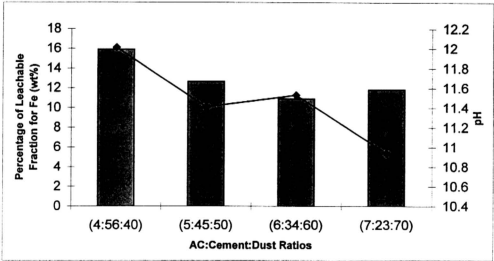
(c)

Figure 4.4 The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of cement with activated carbon treated samples (  heavy metal leached, ◆ pH).





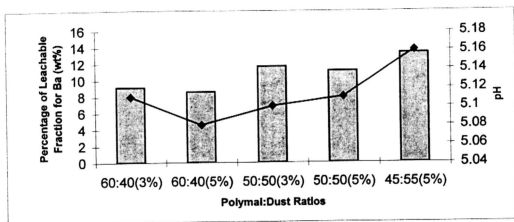
(d)



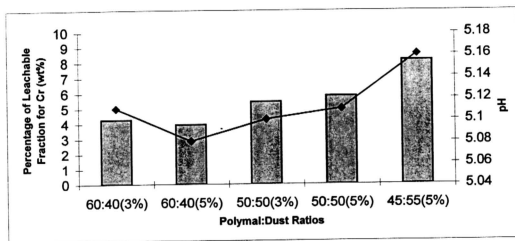
(e)

Figure 4.4 (Continued) The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of cement with activated carbon treated samples (■ heavy metal leached, —◆— pH).

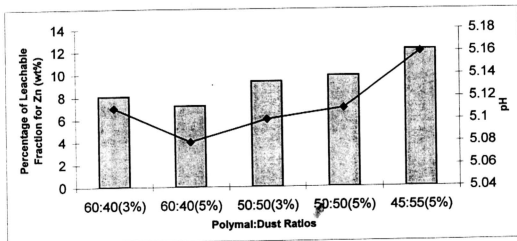
On the other hand, the final pH of the extract in both polymeric resins vary dramatically with the final pH of the extract of cement-based treated samples, but little with its initial pH. The final pH of the extract ranged between 5.08 - 5.16 and 5.15 - 5.19 for Polymal and Hetron treated samples respectively, throughout the various loading and this is within the Malaysia EQA regulatory limits. As shown in the respective Figure 4.5 and Figure 4.6, the percentage of the leachable fraction for the heavy metals of concern in the extract of Polymal and Hetron treated samples, showed little or no apparent pH dependence.





(a)

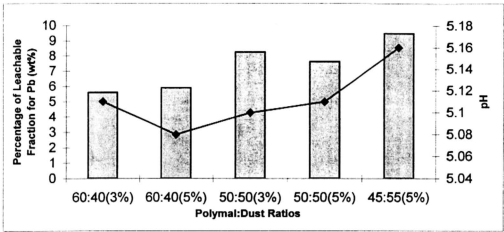


(b)

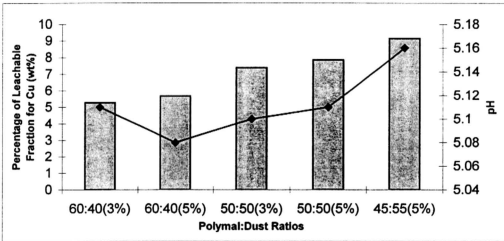


(c)

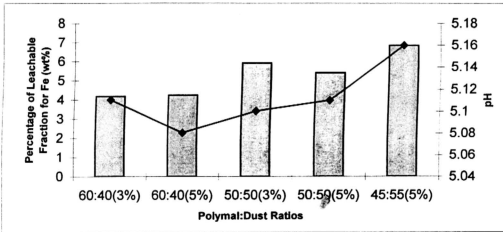
Figure 4.5 The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of Polymal treated samples (  heavy metal leached,  pH).





(d)



(e)



(f)

Figure 4.5 (Continued) The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of Polymal treated samples (  heavy metal leached,  pH).

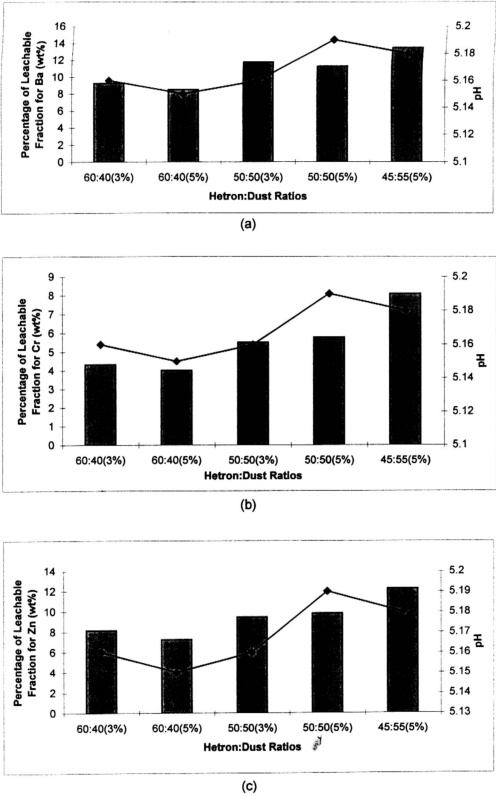
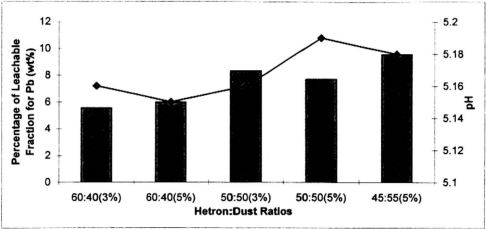
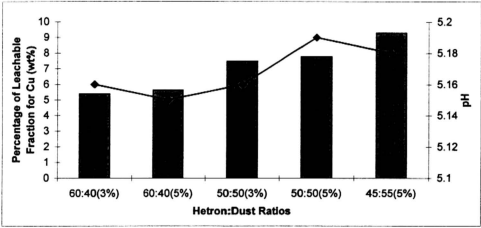


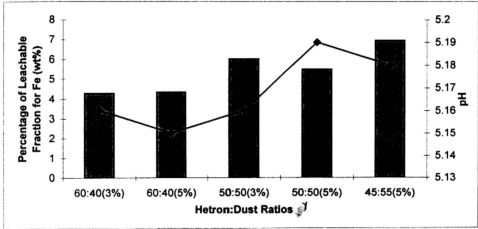
Figure 4.6 The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of Hetron treated samples ( ■ heavy metal leached, ◆ pH).





(d)



(e)



(f)

Figure 4.6 (Continued) The percentage of leachable fraction and the pH changes for the heavy metals of concern in the TCLP extract of Hetron treated samples (  heavy metal leached,  pH).

4.4.3 ANS 16.1 (MODIFIED)

Leaching Rate

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

Example:

Heavy metal analyzed: Zn in specimen at cement:dust ratio of 60:40

Initial amount in specimen, *A*<sub>o</sub> = 0.9493 mg/L

Blank (leachant) = 0 mg/L

Volume of leachant, *V*<sub>L</sub> = 650ml

Volume of the solidified specimen, *V* =  $\pi r^2 h$  = 29.855cm<sup>3</sup>

Surface area of the circular solidified specimen,

$$S = 2\pi r^2 + 2\pi rh = 63.5889\text{cm}^2$$

$$V/S = 0.4695\text{cm}$$

Table 4.9 Sample calculation of leaching rate for Zn, *l* (cm/day), in cement treated sample with cement:dust ratio of 60:40.

Leaching Interval (n) a	Duration (Δt) (days) b	As Analyzed (mg/L) c	Blank (cement) (mg/L) d	Corrected (mg/L) e = c - d	a <sub>n</sub> (mg/L) f=0.65*e	a <sub>n</sub> / A <sub>o</sub> g=f/A <sub>o</sub>	<i>l</i> (cm/day) h=(g*0.4695)/ Δt
1	1	0.0662	0.0058	0.0604	0.0393	0.0414	0.0194
2	2	0.0595	0.0026	0.0569	0.0370	0.0390	0.0092
3	4	0.0714	0.0028	0.0686	0.0446	0.0470	0.0055
4	7	0.0848	0.0031	0.0817	0.0531	0.0559	0.0037
5	14	0.0911	0.0033	0.0878	0.0571	0.0601	0.0020

As shown in Figure 4.7, the leaching rate of all the heavy metals of concern from cement treated samples demonstrated a descending trend as the leaching time progressed.

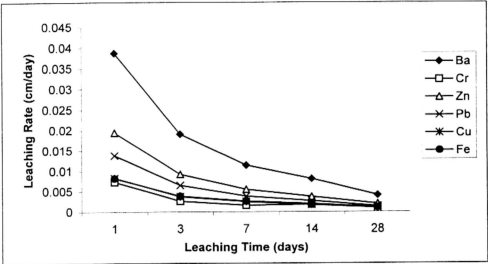
Ba showed the highest leaching rate and gave the most pronounced decrease of the leaching rate among the heavy metals of concern. The leaching rate of Ba in 60% cement loading (Figure 4.7 (a)) decreased from 0.038cm/day in the first interval, to 0.020cm/day in the second interval, and further decreased to 0.013cm/day, 0.010cm/day and 0.005cm/day in the third, fourth and final intervals. Similar trend was observed in the 50% and 40% cement loading, but at a lower leaching rate, decreased from 0.032cm/day - 0.005cm/day to 0.029cm/day - 0.004cm/day within the 28 days of leaching. respectively. The decrease in Ba leaching rate was due to the decreasing amount of cement loading.

The leaching rate of other heavy metals increased as the dust loading increased. The leaching rate of Zn increased from 0.020cm/day - 0.004cm/day in 40% dust loading, to 0.024cm/day - 0.004cm/day and 0.025cm/day - 0.005cm/day in 50% and 60% dust loading, respectively. In 70% dust loading, the leaching rate of Zn even exceeded the leaching rate of Ba in the first two intervals.

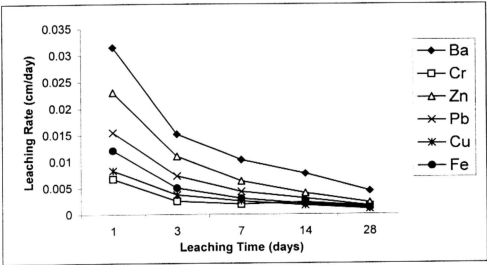
While the leaching rate of Pb was relatively close to the leaching rate of Zn, the leaching rate of Cr, Cu and Fe were also very close to each other, particularly after the third interval until the end of the fifth interval.

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 (De Groot and Sloot, 1992).



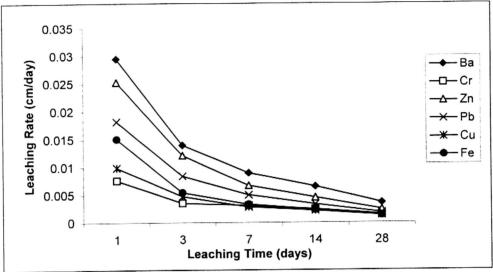


(a)

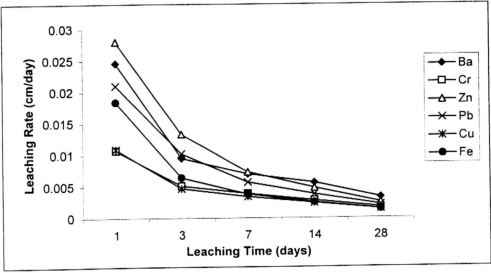


(b)

Figure 4.7 Leaching rate of the heavy metals of concern in cement treated samples at cement:dust ratios of (a) 60:40 and (b) 50:50.



(c)



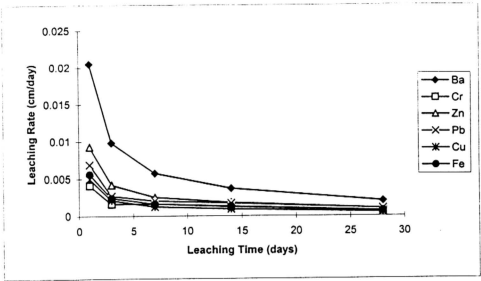
(d)

Figure 4.7 (Continued) Leaching rate of the heavy metals of concern in cement treated samples at cement:dust ratios of (c) 40:60 and (d) 30:70.

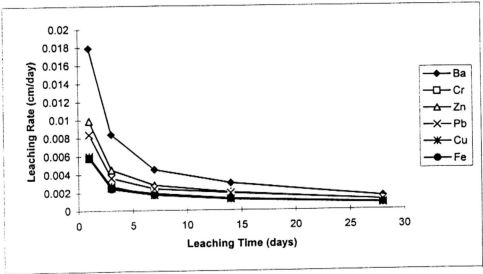
As can be seen in Figure 4.8, the trace metals in cement with activated carbon treated samples demonstrated similar leaching trend as the cement treated samples, where Ba showed the highest leaching rate, followed by Zn and Pb, whereas the leaching rate of Cr, Cu and Fe were approximately the same, except in 70% waste loading, concentration of Fe exceeded the concentration of the other two metals (Cr and Cu).

It was observed that the leaching rate of the heavy metals in cement with activated carbon treated samples were generally lower than the cement treated samples. The leaching rate of Ba in 56% cement loading decreased from 0.020cm/day in the first interval to 0.002cm/day in the final interval. It further decreased to 0.018cm/day - 0.002cm/day and 0.015 - 0.002cm/day at the end of 28th day, as the cement loading decreased to 45% and 34% respectively. The Ba content in cement has reduced as the cement loading decreased, thus the leaching of Ba also decreased.

On the other hand, the leaching rate of other heavy metals were distinctly different compared to the leaching rate of Ba, but increased as the dust loading increased. In 40% dust loading, the leaching rate of Zn decreased from 0.0095cm/day to 0.003cm/day at the end of the final interval, it gradually increased to 0.010cm/day - 0.002cm/day and 0.014cm/day - 0.0030cm/day in 50% and 60% dust loading respectively. Zn leaching rate had exceeded Ba leaching rate in the 70% dust loading (Figure 4.8 (d)).

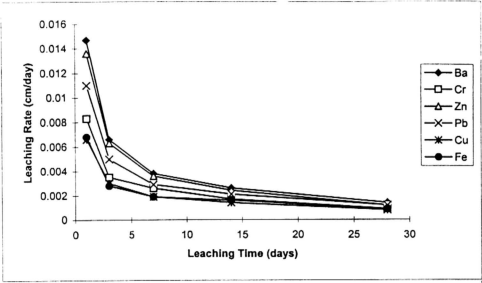


(a)

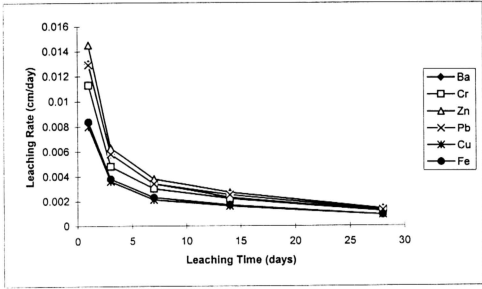


(b)

Figure 4.8 Leaching time of the heavy metals of concern in cement with activated carbon treated samples at the activated carbon:cement:dust ratios of (a) 4:56:40 and (b) 5:45:50.



(c)



(d)

Figure 4.8 (Continued) Leaching time of the heavy metals of concern in cement with activated carbon treated samples at the activated carbon:cement:dust ratios of (c) 6:34:60 and (d) 7:23:70.

As for polymeric resin treated samples, only the leaching of Zn, Ba and Pb can be detected, whereas Cr, Cu and Fe were below detection limit for all the ratios investigated, within the 28 days leaching period. Figure 4.9 and Figure 4.10 showed the leaching rate of the three heavy metals detected in leachate was in descending leaching rates as the leaching time progressed for both Polymal and Hetron solidified specimens respectively.

As shown in Figure 4.9 and Figure 4.10, the heavy metals leached from the resin solidified specimens at a lower rate as compared to the cement treated and cement with activated carbon treated samples. This shows that the Polymal dan Hetron resins were able to retain the heavy metals more effectively in the solidified specimens.

Zn contributed the highest leaching rate among the metals leached out from the Polymal solidified specimens. The leaching rate of Zn declined gradually as the leaching time progressed; except in 60% resin loading with 3% and 5% MEK initiator. On the other hand, the leaching rate of Ba was relatively constant (average of 0.001cm/day) throughout the leaching period (Figure 4.9), while the leaching of Pb only occurred after second interval and decreased slowly in the subsequent intervals.

It was observed that the heavy metals leaching rate increased as the lining dust loading increased. As an example, the leaching rate of Zn in 60% Polymal with 3% and 5% MEK initiator, decreased in the range of 0.0022cm/day - 0.0007cm/day, the leaching rate increased to 0.0030cm/day - 0.0010cm/day and 0.0045cm/day - 0.0014cm/day in 50% and 45% Polymal loading respectively (Figure 4.9).

rate increased to 0.0030cm/day - 0.0010cm/day and 0.0045cm/day - 0.0014cm/day in 50% and 45% Polymal loading respectively (Figure 4.9).

Similar leaching trend was observed in Hetron solidified samples (Figure 4.10), except that higher leaching rate was observed in all the Hetron solidified specimens at various ratios. Obviously, Polymal has demonstrated better retention capability than Hetron.

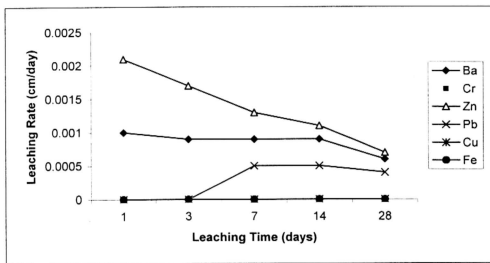
In addition, it is noteworthy that the amount of MEK initiator added did not seem to affect the leachability of the trace metals in both of the Polymal and Hetron solidified samples, as there is no apparent relationship between the amount of MEK initiator and the leaching rate.

Cumulative Fraction Leached (CFL)

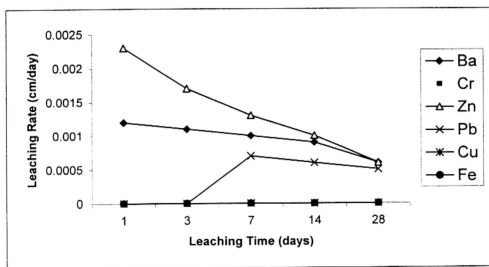
CFL was calculated according to equation (2) in section 4.2.2. and shown in Table 4.10.

Table 4.10 Sample calculation of CFL for Zn in cement treated sample with cement:dust ratio of 60:40

Leaching Interval (n) a	$a_n/a_0$ b	$\Sigma(a_n/a_0)$ c	V/S (cm) d	CFL (cm) $e = c * d$
1	0.0414	0.0414	0.4695	0.0194
2	0.0390	0.0804	0.4695	0.0378
3	0.0470	0.1274	0.4695	0.0598
4	0.0559	0.1833	0.4695	0.0861
5	0.0601	0.2434	0.4695	0.1143



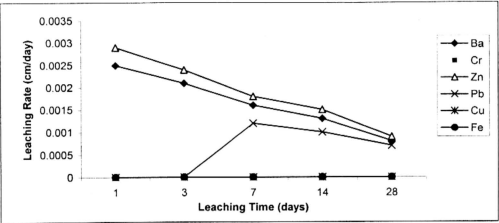
(a)



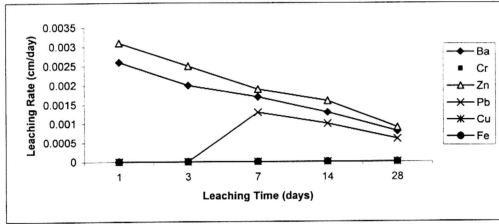
(b)

Figure 4.9 Leaching time of the heavy metals of concern in the Polymal treated samples at Polymal:Dust ratios of 60:40 with (a) 3% and (b) 5% of MEK initiator.

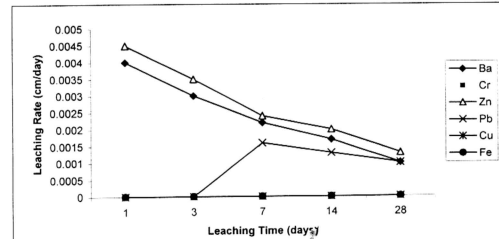




(c)

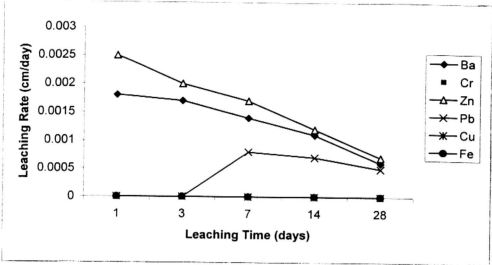


(d)

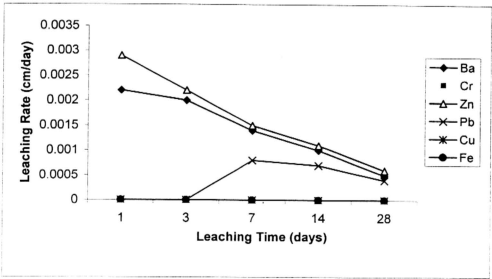


(e)

Figure 4.9 (Continued) Leaching time of the heavy metals of concern in the Polymal treated samples at Polymal:Dust ratios of 50:50 with (c) 3% and (d) 5% of MEK initiator and (e) 45:55 with 5% MEK initiator.



(a)



(b)

Figure 4.10 Leaching time of the heavy metals of concern in the Hetron treated samples at Hetron:Dust ratios of 60:40 with (a) 3% and (b) 5% of MEK initiator.

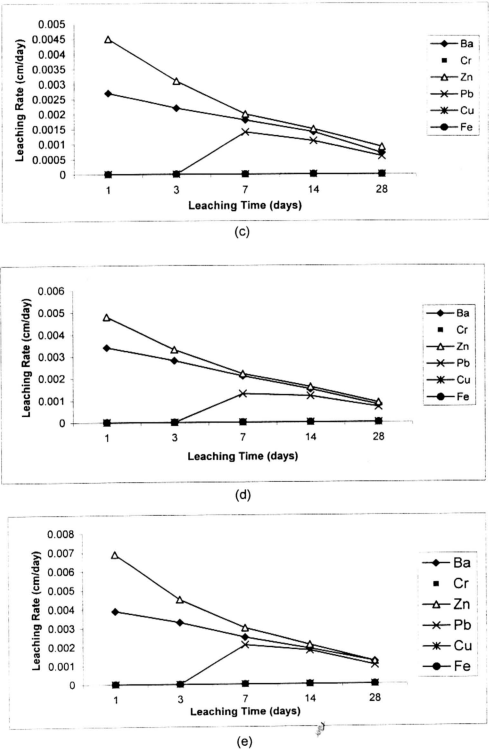


Figure 4.10 (Continued) Leaching time of the heavy metals of concern in the Hetron treated samples at Hetron:Dust ratios of 50:50 with (c) 3% and (d) 5% of MEK initiator and (e) 45:55 with 5% MEK initiator.

Figure 4.11 and Figure 4.12 showed the cumulative fraction leached for the heavy metals of concern for cement treated and cement 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 4.11, Ba contributed the highest CFL among the metals of concern and far above the CFL values of other heavy metals. CFL for Ba was 0.24cm, 0.218cm, 0.191cm and 0.157cm in 60%, 50%, 40% and 30% cement loading respectively. The leaching of Ba from cement treated samples declined as the cement loading decreased, probably this is the reason for the decline of CFL of Ba.

On the other hand, CFL of other heavy metals increased as the lining dust loading increased. This is clearly evident from the increase of CFL of Zn at the end of the leaching interval, where it increased from 0.114cm in 40% dust loading, to 0.129cm and 0.142cm in 50% and 60% lining dust loading respectively. It was slightly below CFL of Ba in 70% lining dust loading, which is 0.152cm.

The CFL values of Pb are below the CFL of Zn considerably, particularly at 40% and 50% lining dust loading. CFL of Pb increased gradually, from 0.08cm in 40% lining dust loading, to 0.091cm, 0.105cm and 0.12cm at 50%, 60% and 70% lining dust loading

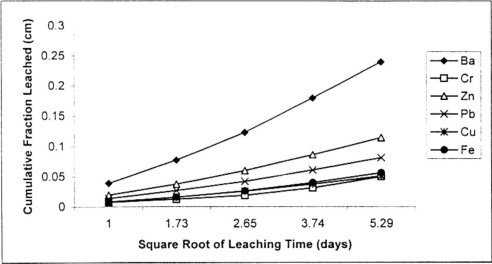
respectively. The CFL of Cr, Cu and Fe were quite close to each other, especially at 40% and 50% lining dust loading, whereas the CFL for Fe was slightly higher at 60% and 70% lining dust loading.

Similar patterns were observed in cement with activated carbon treated samples, where the CFL of all the heavy metals at each AC:Cement:Dust ratio was linearly related with square root of leaching time (Figure 4.12).

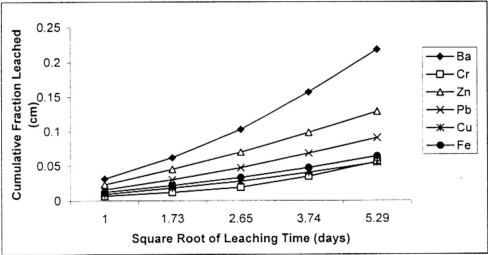
It was observed that the CFL of Ba reduced by approximately 50% after addition of activated carbon. In Figure 4.12 (a), the CFL of Ba declined to 0.117cm as compared to 0.240cm in 60% cement without activated carbon (Figure 4.11 (a)). Similarly, the CFL of Ba was 0.095cm, 0.080cm and 0.072cm (as shown in Figure 4.12 (b), (c) and (d) respectively) as compared to the respective cement treated samples.

CFL of Zn was 0.054cm, 0.06cm, 0.0745cm and 0.081cm in 56%, 45%, 34% and 23% cement loading respectively, which has decreased by 53% - 58% as compared to purely cement treated samples. CFL of other heavy metals declined as well, but less pronounced as Ba and Zn. For Pb, CFL has decreased by 38% - 43%, whereas the decreased of Cr, Cu and Fe was 18% - 38%, 33% - 45% and 35% - 42% respectively.

For the resin treated samples, the plots reported in Figure 4.13 and Figure 4.14 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.

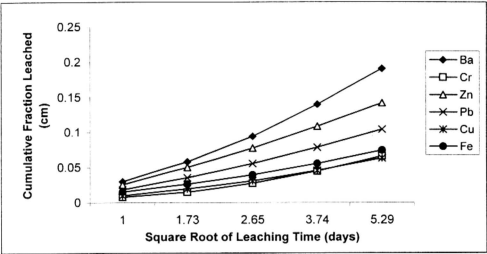


(a)

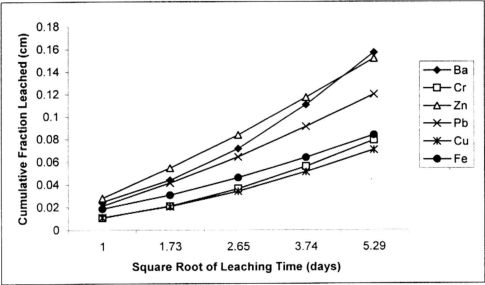


(b)

Figure 4.11 Cumulative Fraction Leached for the heavy metals of concern in cement treated samples at the cement:dust ratios of (a) 60:40 and (b) 50:50.

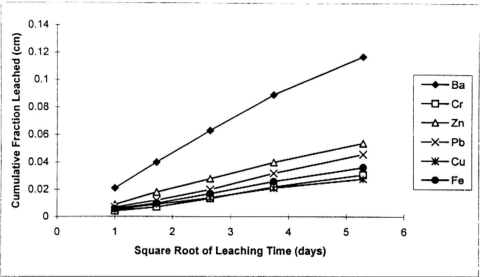


(c)

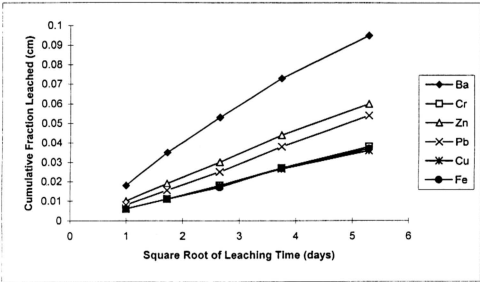


(d)

Figure 4.11 (Continued) Cumulative Fraction Leached for the heavy metals of concern in cement treated samples at the cement:dust ratio of (c) 40:60 and (d) 30:70.



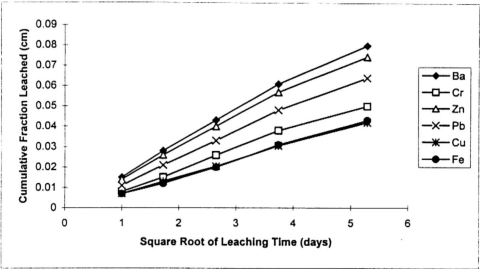
(a)



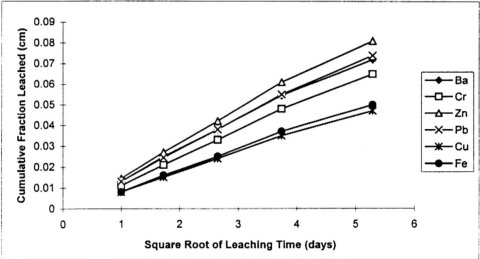
(b)

Figure 4.12 Cumulative Fraction Leached for the heavy metals of concern in cement with activated carbon treated samples at the activated carbon:cement:dust ratios of (a) 4:56:40 and (b) 5:45:50.





(c)



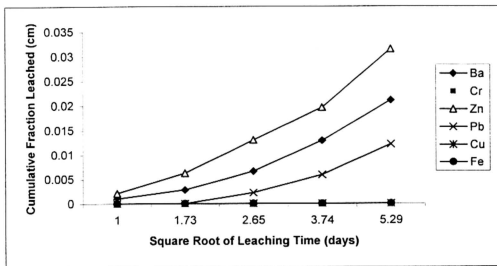
(d)

Figure 4.12 (Continued) Cumulative Fraction Leached for the heavy metals of concern in cement with activated carbon treated samples at the activated carbon:cement:dust ratios of (c) 6:34:60 and (d) 7:23:70.

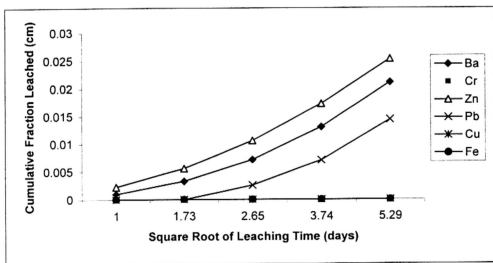
The leaching trend for detected heavy metals (Zn, Ba and Pb) were consistent for all the resin:dust ratios, where Zn contributed the highest CFL, followed by Ba and Pb, but in descending trend as the dust loading increased. As compared to cement and cement with activated carbon, it was observed that the CFL for the heavy metals decreased further after solidified using polymeric resins, but increased as the lining dust loading increased.

In Figure 4.13, the CFL for Zn increased from 0.032cm in 60% Polymal loading to 0.052cm in 45% Polymal loading, which represent approximately 1.7% - 3.7% leaching as compared to the untreated lining dust. For Ba and Pb, the CFL has reduced to approximately 1.7 % - 3.1% (0.021cm - 0.045cm) and 1.3% - 2.8% (0.012cm - 0.029cm) respectively, as compared to untreated dust.

On the other hand, the heavy metals detected in Hetron treated samples showed slightly higher CFL in all ratios, as compared to Polymal treated samples. The CFL of Zn in 60% Hetron loading was 0.031cm, and gradually increased as the Hetron loading decreased, which showed a CFL of 0.060cm in 45% Hetron loading. The CFL for Ba and Pb ranged from 0.028cm - 0.052cm and 0.016cm - 0.036cm respectively, when Hetron loading decreased from 60% to 45% (Figure 4.14).



(a)



(b)

Figure 4.13 Cumulative Fraction Leached for the heavy metals of concern in Polymal treated samples at the Polymal:Dust ratios of 60:40 with (a) 3% and (b) 4% MEK initiator.

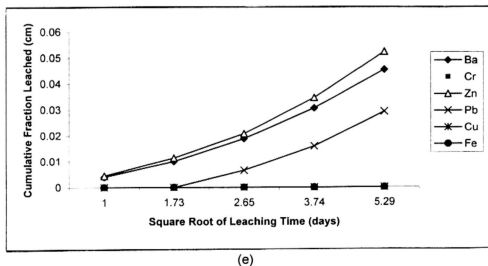
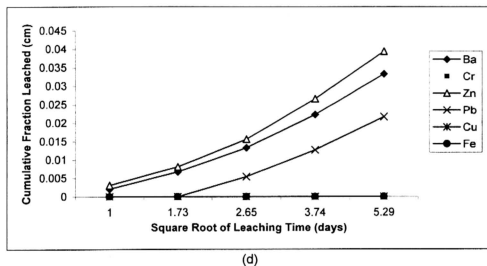
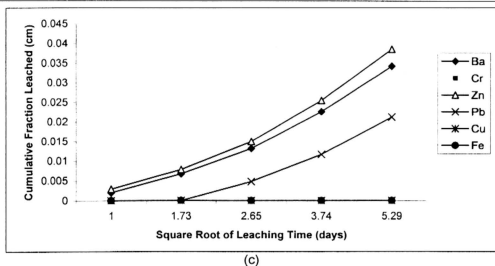
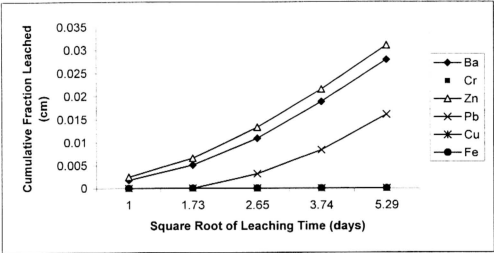
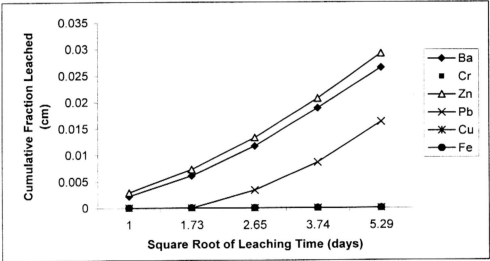


Figure 4.13 (Continued) Cumulative Fraction Leached for the heavy metals of concern in Polymal treated samples at the Polymal:Dust ratios of 50:50 with (c) 3% and (d) 5% MEK initiator and (e) 45:55 with 5% MEK initiator.

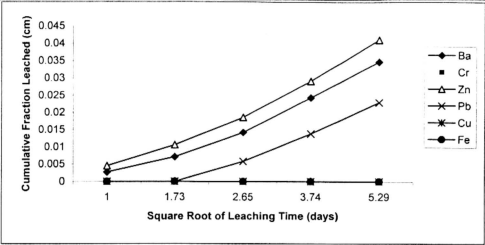


(a)

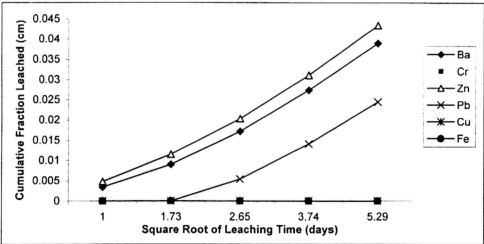


(b)

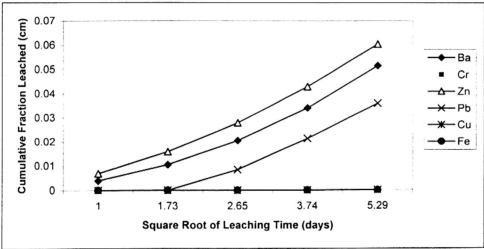
Figure 4.14 Cumulative Fraction Leached for the heavy metals of concern in Hetron treated samples at the Hetron:Dust ratios of 60:40 with (a) 3% and (b) 5% MEK initiator.



(c)



(d)



(e)

Figure 4.14 (Continued) Cumulative Fraction Leached for the heavy metals of concern in Hetron treated samples at the Hetron:Dust ratios of 50:50 with (c) 3% and (d) 5% MEK initiator and (e) 45:55 with 5% MEK initiator.

**Leachability Index ( $L_i$ )**

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 4.11.

Table 4.11 Sample calculation of diffusivity coefficient and Leachability Index ( $L_i$ ) for Zn in cement treated sample with Cement:Dust ratio of 60:40 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 <sup>2</sup> /s) g = $\pi.f^2.d^2.c$	$L_i$ h = log(1/g)
1	86400	21600	0.4695	0.0414	4.791667e-7	3.434e-9	8.46
2	172800	161225	0.4695	0.0390	2.256944e-7	5.687e-9	8.25
3	345600	413967	0.4695	0.0470	1.359954e-7	5.302e-9	8.28
4	604800	881258	0.4695	0.0559	9.242725e-7	5.213e-9	8.28
5	1209600	1762516	0.4695	0.0601	4.968585e-8	2.952e-9	8.53

The  $L_i$  for Zn will be obtained by averaging the  $L$  value of each interval.

$$L_i = [8.46 + 8.25 + 8.28 + 8.28 + 8.53]/5$$
$$= 8.36$$

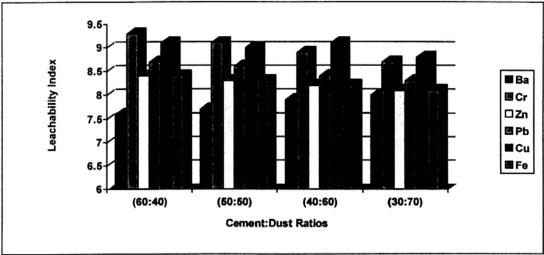
The ANS 16.1 (modified) leachability indices of the six heavy metals for cement-based solidification and polymeric encapsulation, at various ratios, are shown in Figure 4.15 and Figure 4.16 respectively. The leachability indices obtained in this study exceeded the guidance value of leachability index of 6 (Morgan and Bostick, 1992), which clearly indicate that the toxic heavy metals are well retained in the solidified specimens. The mean value of  $L_i$  with its associated standard deviation are presented in the appendix 2.

It was observed that the cement with activated carbon (Figure 4.15 (b)) is relatively superior in retaining the heavy metals than cement alone (Figure 4.15 (a)), where the  $L_i$  of heavy metals in cement and cement with activated carbon ranged from 7.6 to 9.1 and 8.3 to 9.4 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 4.11 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)).

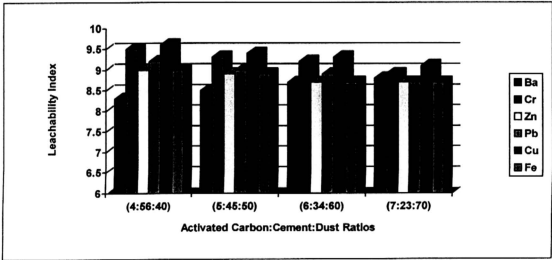
As shown in Figure 4.16 (a), Polymal treated samples exhibited slightly better performance than Hetron treated samples (Figure 4.16 (b)) particularly in resin:dust ratio of 60:40. The  $L_i$  of heavy metals in Polymal and Hetron treated samples were in the range of 9 - 10 and 9 - 9.8 respectively. It was also observed that the two resins exhibited higher  $L_i$  than cement and cement with activated carbon treated samples generally, which indicates better retention capability of the heavy metals. However, retention capability declined as the waste loading increased.

In addition, it is noteworthy that the amount of MEK initiator added did not have any significant effect on the leachability of the heavy metals investigated.



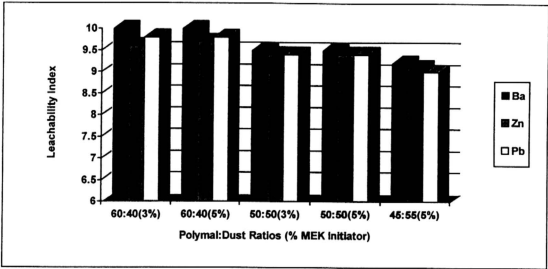


(a)

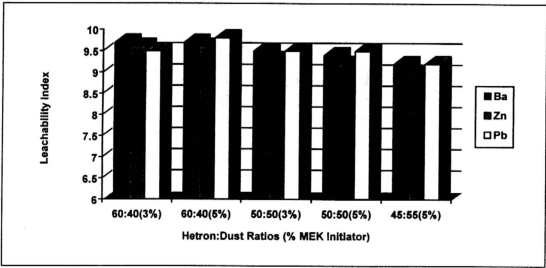


(b)

Figure 4.15 Leachability Index for the (a) cement and (b) cement with activated carbon treated samples.



(a)



(b)

Figure 4.16 Leachability Index for (a) Polymal and (b) Hetron treated samples.

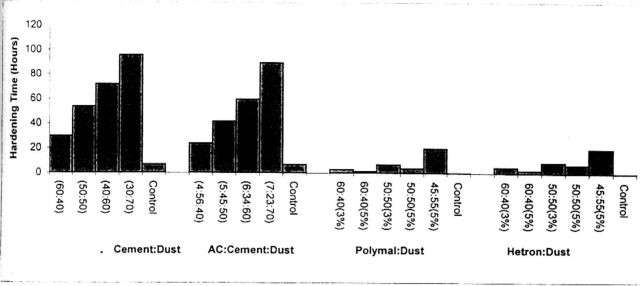


Figure 4.17 Hardening time of cement, cement with activated carbon, Polymal and Hetron at different ratios.

Compressive Strength

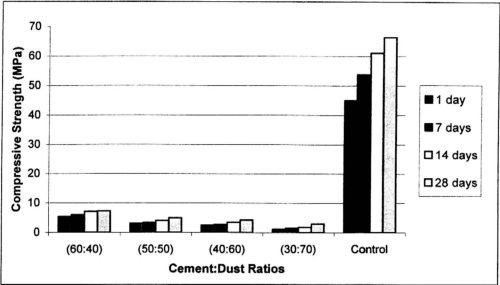
Figure 4.18 (a), (b), (c) and (d) illustrate the compressive strength development of various binder/dust ratio at the 1st, 7th, 14th and 28th days curing. Generally, polymeric resin solidification presents greater compressive strength ( 53 - 68 MPa) than the cement-based solidification ( 1 - 12 MPa) and the compressive strength of solidified forms varied with the loading of the brake lining dust.

As shown in the Figure 4.18(a), the compressive strength of solidified specimens increased as the cement loading increased and also as the days progressed. The readings ranged between 0.44 - 1.64 MPa for 30% cement loading, 1.64 - 3.64 MPa for 40% cement loading, 3.08 - 5.63 MPa for 50% cement loading and 5.71 - 9.29 MPa for 60% cement loading, after 1, 7, 14 and 28 days respectively.

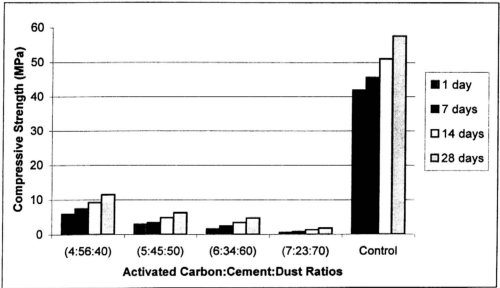
However, the compressive strength reading for all cement:dust ratios were far below that of the control (cubes of cement-water mixture without addition of dust), which was 44.77, 52.19, 60.91 and 67.77 MPa after 1, 7, 14 and 28 days respectively. This may be due to the presence of phenol and formaldehyde in the brake lining dust that retarded the cement hydration.

In the cement with activated carbon treated samples, slightly higher compressive strength of the solidified specimens were observed in addition to the compressive strength increased with the cement content and also as the day progressed (Figure 4.18(b)). The compressive strength readings after 1, 7, 14 and 28 days curing, ranged from 0.52 - 1.84 MPa, 1.6 - 4.74 MPa, 2.92 - 6.28 MPa and 5.94 - 11.49 MPa in 30%, 40%, 50% and 60% cement with activated carbon, respectively.

However, the compressive strength of the solidified specimens were still far below the control (without brake lining dust) which ranged from 41.93 - 57.62 MPa as the days progressed to 28 days. It has been reported that pre-adsorption of inhibiting contaminants (like phenol, formaldehyde) by activated carbon that has an extended polynuclear, microcrystalline structure results in higher compressive strength development (Pollard, *et al.*, 1990).



(a)



(b)

Figure 4.18 Compressive strength of solidified waste after 1, 7, 14 and 28 days of solidification for (a) cement and (b) cement with activated carbon treated samples.

As for the resins (Figure 4.18 (c) and (d)), the compressive strength readings were relatively constant as the days progressed over 28 days. Generally, higher compressive strength were observed for Hetron treated samples and the control, except in 60% resin loading, where Polymal treated samples showed higher compressive strength of 60 - 67MPa.

It was interesting to note that the controls of both types of resins (cubes of resins without addition of dust) showed relatively lower compressive strength as compared to the 60% resin loadings. This was probably because the presence of lining dust acted as filler and enhanced the compressive strength of the solidified forms. However, the compressive strength tends to decrease as the resin loading is reduced. The higher percentage of initiator added to the resin did not seem to cause any significant effect on the compressive strength of the solidified specimens.

The compressive strength can be improved by increasing the cement content, but this decreases the waste loading, increases the volume of the final waste form and hence increases 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).

4.5 COST EVALUATION

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

The annual costs for cement-based S/S and polymeric resin encapsulation are presented in Table 4.12. The computed values are based on the generation rate of 300 metric tones of brake lining dust per annum at the binder:dust ratio of 50:50.

Table 4.12 (a) Annual cost for cementitious S/S

	Unit Cost (RM)	Cement Cost (RM)	Cement + AC Cost (RM)
Material cost - cement	0.2/kg	60,000	54,000
AC	6/kg		180,000
Transportation	67/ metric ton	40,200	40,200
Disposal	495/ metric ton	297,000	297,000
Total		397,200	571,200

Table 4.12 (b) Annual cost for polymeric resin encapsulation

	Unit Cost (RM)	Polymal Cost (RM)	Hetron Cost (RM)
Material cost - Polymal	18.5/kg	5,550,000	-
Hetron	16/kg	-	4,800,000
MEK	15/kg	225,000	225,000
Transportation	67/ metric ton	40,200	40,200
Disposal	495/metric ton	297,000	297,000
Total		6,112,200	5,362,200

As illustrated in Table 4.12, the annual cost of cementitious based S/S is less than the polymeric resins and obviously cement is the cheapest binding agent. However the associated costs are far above the present disposal cost (which is about RM283,000).

On the other hand, the leaching of heavy metals have been demonstrated reduced significantly with the presence of binding agent, particularly the Polymal and Hetron resins.