Malaysian Journal of Science **24** : 39 - 47 (2005)

Electronics Wastewater Sludge Treatment using S/S with Ordinary Portland Cement

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Received 25 April 2005, accepted in revised form 29 June 2005

ABSTRACT Ordinary Portland Cement (OPC) with or without Activated Carbon (AC) in varying concentrations was used to solidify/stabilize (S/S) wastewater sludge from an electronics plant. In this research the solidification/stabilization method was used to immobilize heavy metal content. To analyze leachability and leach treatment, TCLP and ANS methods were used. Untreated wastewater sludge contains high concentrations of Fe, Al, Sn, Mn, Cu and Ni. Solidification with OPC reduced the leachable fraction of these heavy metals in the solidified matrix of the wastewater sludge. Based on the Toxicity Characteristics Leachability Procedure (TCLP) and the American Nuclear Society (ANS) 16.1 (modified) leach protocol, the initial pH of the extract was 5.9, however, the pH of the final extract ranged between 6.07 and 6.26. The Leachability Indices (L_i) obtained ranged between 4 and 9.1 for cement without AC and 7 to 9.2 with AC, compared to standard guidance value of $L_i \geq 6$. The resulting solid matrices exhibited a compressive strength ranging from 1 to 7.1 MPa, while the standard requirement is 414 kpa (60 psi). Results show that the solidification and stabilization method can immobilize and reduce heavy metal leaching.

ABSTRAK *Ordinary Portland Cement* (OPC) dengan ataupun tanpa karbon teraktif (AC) dalam kepekatan yang berbeza-beza telah digunakan untuk pemejalan/penstabilan (S/S) enapcemar daripada sebuah kilang elektronik. Dalam kajian ini pemejalan/penstabilan telah digunakan untuk menghalang pergerakan kandungan logam berat. TCLP dan ANS telah digunakan untuk menganalisis kadar lesapan sisa enapcemar sebelum dan selepas rawatan,. Sisa enapcemar tanpa rawatan mengandungi kepekatan Fe, Al, Sn, Mn, Cu dan Ni yang tinggi. Pemejalan dengan menggunakan OPC dapat mengurangkan kandungan lesapan (*leachable fraction*) logam berat dalam matriks pejal sisa enapcemar. Berdasarkan hasil TCLP dan ANS, sebelum rawatan sisa enapcemar ini didapati mempunyai nilai pH 5.9. Bagaimanapun, selepas rawatan pH berada dalam julat 6.07 hingga 6.26. Indeks lesapan (*leachability index*) adalah di antara 4 - 9.1 bagi rawatan simen sahaja dan 7 - 9.2 bagi rawatan simen dan campuran karbon teraktif dengan piawai ≥ 6. Matriks pejal yang terhasil mempunyai kekuatan tekanan (*compressive strength*) dari 1 hingga 7.1 MPa di mana standard pempiawainya adalah 414 KPa (60 psi). Keputusan menunjukkan bahawa kaedah pemejalan/penstabilan (S/S) boleh menghalang dan mengurangkan kadar lesapan logam berat.

(Solidification/stabilization, activated carbon, OPC, ANS, TCLP)

INTRODUCTION

Malaysia has been facing numerous assaults on its environment, particularly in recent years due to an accelerated pace of industrialization in the country. The implementation of various development plans, notably the Industrial Master Plan (IMP), which is primarily aimed at maximizing the growth potential of the manufacturing sector, has substantially increased the number of polluting sources. Of particular public concern is the significant proportion of these industries which are associated with the generation of wastes categorized as Scheduled Wastes. One of the consequences of this development is the increasing quantity and diversity of chemicals being used and the types of toxic and hazardous wastes generated by the industries and other non-industrial sources [1]. The government in showing its sensitivity to the potential gravity of environmental deterioration has taken positive actions and promulgated several legislations to combat the growing menace of hazardous and toxic wastes [2].

The immobilization of organic materials in cement-based solidification is limited, since it depends on the waste characteristics and heavy metal content [3]. Various additives are used to reduce the organic contaminants' interference with cement hydration and to enhance stabilization [4]. For mixed wastes, the solidification/stabilization (S/S) could also incorporate activated carbon (AC) or exchanged clay [5]. The efficiency of S/S treatment could be evaluated by total waste analysis for organics or leachibility studies using various methods, permeability tests, unconfined compressive strength, treated waste and/or leachate toxicity endpoints and durability testing [6].

Data obtained from ANS 16.1 (modified) method was recorded in terms of Leaching Rate (*l*) and Cumulative Fraction Leached (CFL) relative to the total mass in the waste sample. Subsequently, from these calculations, the Effective Diffusivity (*D*) and Leachability Index (*Li*) were also obtained [7, 8].

The objective of this paper is to study the solidification/stabilization of the wastewater sludge as an ultimate treatment and disposal option, for an electronics plant waste. The efficiency of solidification was tested using TCLP, ANS and the solidified matrix was also tested for compressive strength.

MATERIALS AND METHODS

Sample preparation

Wastewater sludge was obtained from Matsushita (M) Sdn. Bhd in Shah Alam. The sludge was homogenized for three minutes with cement using a blender. Water was added slowly into the wastewater sludge to promote hydration. The mixture was then mixed at high speed for three to four minutes upon attainment of the pre-determined water: cement ratio. The resulting waste-loaded grout paste was transferred to moulds of specific dimensions. The moulds were covered with Lucite sheets and left undisturbed for 24 hrs at room temperature (27-34°C) and relative humidity 92%. The specimens were removed from the moulds and further cured for 27 days under dry condition to simulate the curing condition as normally practiced before landfilling. Ordinary Portland Cement (OPC) with or without Activated Carbon (AC) was used in this research. The combination of OPC, AC and waste are given in Table 1.

Table 1. Combination of OPC, AC and waste

Ordinary Portland Cement (% weight)	Activated Carbon (% weight)	Waste (% weight)
10	-	90
20	-	80
30	-	70
40	-	60
50	-	50
1	9	90
12	8	80
23	7	70
34	6	60
45	5	50

Leach tests

Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP protocol (U.S. EPA method 1311, 1992) was performed using the solidified samples that were crushed to particle size smaller than 9.5 mm and transferred to flasks. A buffer of acetic acid and sodium hydroxide adjusted to pH 3.00 ± 0.05 was used as the appropriate extraction fluid. A liquid-to-solid ratio of 20:1 was used. The flasks were then covered with parafilm, capped with aluminium foil, and then mechanically shaken for 18 hrs continuously at 300 rpm at a temperature of 25 ± 2°C.

After 18 hours contact time, leachates were filtered through a 0.8-μm pore size borosilicate glass fiber filter to separate the solid and liquid phases. The filtrate, i.e., the TCLP extract, was tested for pH using a Hanna Instrument Membrane pH meter. Heavy metals in the TCLP extract were analyzed using Inductively Couple Plasma-Emission Spectroscopy (ICP-AES, Baird Model 2000). The results of this extraction test are expressed in terms of the percentage of leachable fraction f, for each element, which is defined as the amount of a particular heavy metal extracted relative to the amount originally present in untreated dust [7].

American Nuclear Society [ANSI/ANS 16.1 (modified)]

Solidified specimens of thickness-to-diameter ratio 0.3 were suspended into the leachant (ultrapure water of resistivity = 18 Mohm-cm, processed by ELGASTAT^R UHQPS) using a nylon fishing line. The leachant was contained in plastic beakers made of nonreactive polypropylene. Neither the beaker nor the fishing line contributed to the concentration of heavy metals in the leachate [2]. The ratio of the leachant volume (cm^3) to the external geometry surface area (cm^2) of the solid specimen was maintained at about 10 ± 0.2 (cm) throughout the static leaching procedure [7]. The leaching was carried out over a 28 day period as follows (i.e., not over the 90-day period as is normally done for low-level radioactive wastes): the specimen was transfered into fresh leachant after one, two, four, seven and 14 days: next, the leachate samples from the first, third, seventh, 14th, and 28th days were analyzed for pH and heavy metals, as was the case for the TCLP leachate samples.

Compressive strength test

The physical strength of the solidified matrix is important because it determines the suitability of the solids for secure landfill stacking. Cubic specimens (50 mm cube specimens) prepared according to the ASTM Test Method for Compressive Strength of Hydraulic Cement Motars (C109/C 109M-95) testing protocols, were used for the compressive strength test. Total Maximum loads were recorded at the point of fracture and the compressive strength was determined using the formula:

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

where f_m is compressive strength (psi or MPa), P is total maximum load (lbf or N) and A is the area of loaded surface (in^2 or mm^2). Compressive strength was determined on duplicate specimens after 7, 14 and 28 days of curing (98% RH, 30 ± 3°C) using a calibrated hand operated hydraulic compression apparatus (model ELE).

RESULTS AND DISCUSSION

TCLP results

As shown in Figure 1, TCLP of the untreated electronics industry wastewater sludge contain Fe which was at 834 mg/l followed by Al, Sn, Mn, Cu, Zn, Ni, Pb and Ti at concentrations of 785 mg/l, 239 mg/l, 74 mg/l 30.2 mg/l 18.1 mg/l 14.9 mg/l, 10.4 mg/l and 0.832 mg/l, respectively. Pb, Ni and Zn were above the TCLP and EQA (1974) standard limit while Cu, Mn and Fe were only above the EQA (1974) standard limit for industrial effluent.

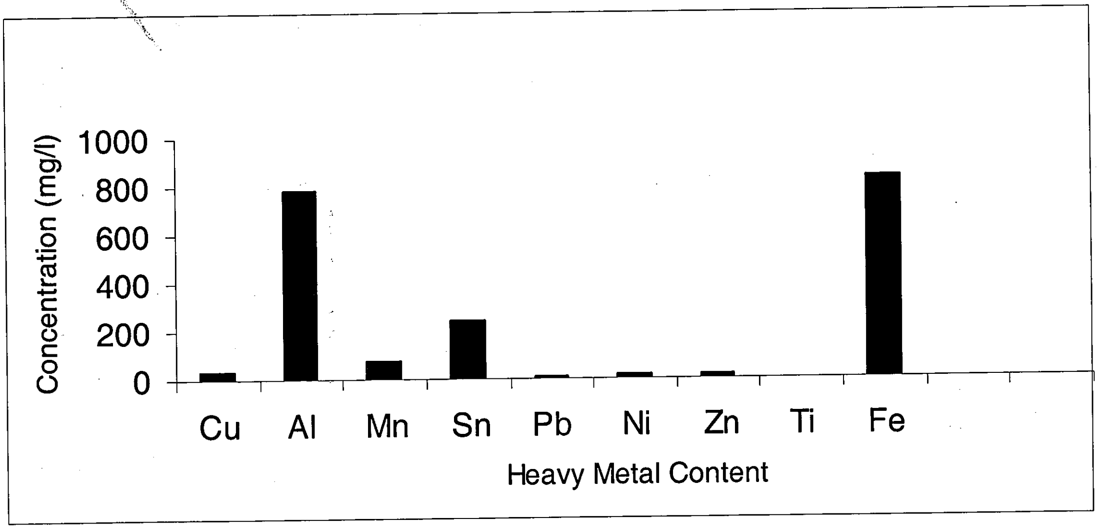
Cu concentration in OPC-treated TCLP leachate ranged between 0.79 and 0.87 mg/l, whereas it was between 0.35 and 0.84 mg/l in OPC with AC-treated TCLP leachate. Wastewater sludge solidified with OPC with or without AC stopped only Pb leaching. Al was the highest metal leaching followed by Ni, Fe, Zn, Sn, Ti and Cu (Table 2).

Table 2. Summary of TCLP leach data for OPC solidified matrix, including initial and final pH of the extract

	Initial pH (fixed)	Final pH	Concentration of metals in leachate, mg/l								
			Cu	Al	Mn	Sn	Pb	Ni	Zn	Ti	Fe
Regulatory limit for TCLP Test [a]			---	---	---		0.75	11	4.3	---	---
Malaysia EQA [b]	5.5-9.0		1.0	---	1.0	---	0.5	1.0	1.0	---	5.0
Untreated WW Sludge	5.91	11.38	30.2	785	74.0	239	10.4	14.9	18.1	0.832	834
OPC : WW Sludge											
10:90	5.92	6.11	0.87	17.5	0.98	2.54	nd	8.59	4.12	0.66	10.9
20:80	5.93	6.07	0.79	17.3	0.95	2.43	nd	7.86	4.31	0.58	9.74
30:70	5.91	6.10	0.83	16.8	0.97	2.39	nd	7.74	3.75	0.59	6.41
40:60	5.90	6.15	0.81	17.1	0.89	1.85	nd	7.23	3.87	0.57	5.87
50:50	5.92	6.14	0.82	16.7	0.88	2.06	0.58	6.81	3.38	0.48	5.88
OPC : AC: WW Sludge											
1:9:90	5.92	6.23	0.76	11.3	0.76	1.47	Nd	7.44	3.47	0.32	5.92
12:8:80	5.90	6.24	0.84	11.4	0.69	1.19	Nd	6.46	3.26	0.34	5.87
23:7:70	5.87	6.22	0.44	5.23	0.70	0.39	Nd	3.26	2.62	0.28	4.59
34:6:60	5.89	6.25	0.42	5.07	0.74	0.02	Nd	3.21	2.59	0.26	4.89
45:5:50	5.89	6.26	0.35	5.97	0.71	0.31	Nd	2.28	2.50	0.132	5.92

[a] Federal Register 63 No. 100, May 26, 1998
[b] Regulatory limit stipulated in Malaysia Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulation, 1979, *Standard B*
nd: not detected

Figure 1. Heavy metal concentration in untreated wastewater sludge



Effect of final pH of TCLP extract on metal leaching

According to Conner [8], the leaching of some metals relies heavily on pH. Some heavy metals, such as Cr, Pb, Zn, Cu and Fe, exhibit amphoteric behavior and have higher solubility at both high and low pH. The pH of the initial extract was in range of 5.9, however, the pH of the final extract ranged between 6.07-6.15 and 6.22-6.26 for OPC with and without AC treated samples, respectively and there is little relationship between pH and heavy metal concentration (Cu, Ni, Zn and Fe) in leachate (Table 2). According to Chan *et al.* [9] they found that there is little or no apparent relationship between pH and the percentage of leachable fraction of heavy metals when they treated Automobile Brake Industry waste using OPC.

ANS 16.1 (modified) leaching rate

According to De Groot and Van der Sloot [10], based on the value of leach rate, *l* (cm/day), for each metal, rapid loss of heavy metals was recorded on the first interval, probably due to surface wash off of the solidified specimens. Only Ni and Fe were detected when the leachate was tested using ANS technique, whereas Cu, Al, Mn, Sn, Ti and Pb were below detection limit for OPC without AC in all the ratios investigated (Figure 2). The leach rate of all heavy metals decreased over the 28-day leaching period for OPC without AC. All the metals leached were below EQA limit, showing that OPC retained the metals quite effectively. Leach rate of Fe was the highest for OPC with or without AC (Figures 2 and 3).

Only Cu, Al and Fe were detected when the leachate was tested using ANS technique (Figure 3). The leach rate of all three heavy metals decreased over the 28-day leaching period for OPC with AC. This result shows that Fe was the highest concentration followed by Al and Cu.

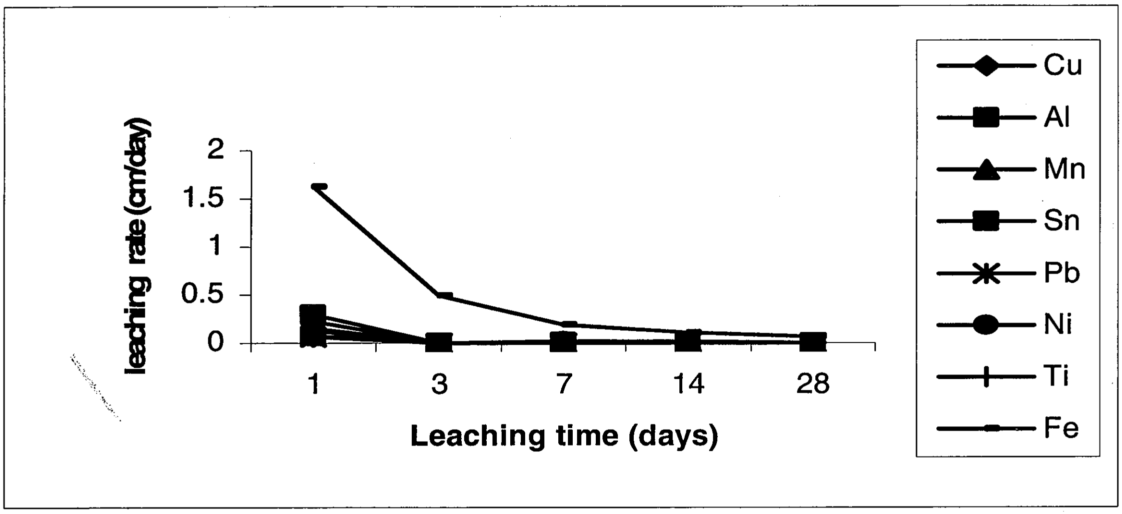


Figure 2. Leach rate of heavy metals in OPC treated samples at cement: waste ratio of 50:50

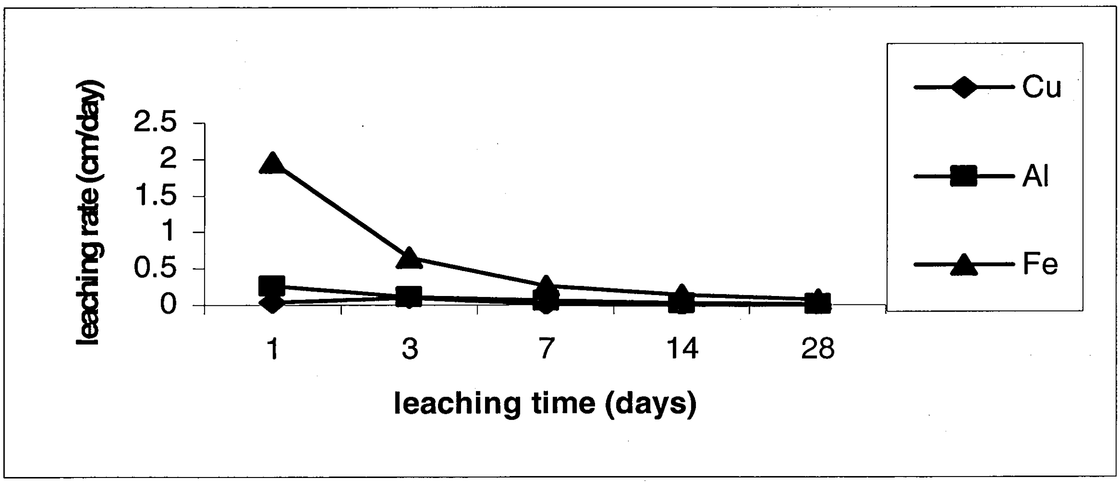


Figure 3. Leach rate of heavy metals in OPC and AC treated samples at cement: waste: AC ratio of 45:50:5

Cumulative fraction leached (CFL)

Cumulative Fraction Leached was calculated using Equation CFL = $\frac{\sum a_n}{A_0} x \frac{V}{S}$ and these are shown in Table 3 and see next page for L_i in Figure 4 (OPC without AC) and Figure 5 (OPC with AC).

Leachability Index (Li)

The effective diffusivity *(D_i)* and Leachability Index *(L_i)* for Fe were calculated according to Equation: $D_i = \pi\left(\frac{(a_n/A_0)}{(\Delta t_n)}\right)^2\left(\frac{V}{S}\right)^T$ and $L_i = \frac{1}{n}\sum\left[\log\left(\frac{\beta}{D_i}\right)\right]^n$ and the results are shown in Figure 4 (OPC without AC) and Figure 5 (OPC with AC). For an example, the sample calculation for D_i and L_i for Fe in cement treated sample is shown in Table 4.

The L_i for Fe was obtained by averaging the L values of each interval, L_i = [4.104 + 6.043 + 7.085 + 7.322 + 8.453]/5 = 6.6014]. The standard guidance value for solidified waste form [11, 12] for Leachability Index is ≥ 6.

Table 3. Sample calculation of CFL for Fe in cement treated sample with cement: sludge ratio of 50:50

Leaching Interval (n) a	a_n/A_o b	$\sum(a_n/A_o)$ c	V/S (cm) d	CFL (cm) e = c* d
1	0.627	0.627	0.4695	0.294
2	0.492	1.119	0.4695	0.525
3	0.185	1.304	0.4695	0.6122
4	0.169	1.473	0.4695	0.692
5	0.065	1.538	0.4695	0.722

Table 4. Sample calculation of diffusivity coefficient (D_i) and Leachibility Index (L_i) for Fe in cement treated sample.

Leaching Interval (n) a	Leaching Duration b	T (s) c	V/S (cm) d	a_n/A_0 e	$[a_n/A_o][1/t]$ (cm) f = e/b	D (cm^2)/s) $g=\pi f^2 d^2 c$	L_i h=log (1/g)
1	8640	21600	0.4695	0.627	7.2569e-5	7.8774e-5	4.104
2	172800	161225	0.4695	0.492	2.8472e-6	9.0510e-7	6.043
3	345600	413967	0.4695	0.185	5.3530e-7	8.2145e-8	7.085
4	604800	881258	0.4695	0.169	2.7943e-7	4.7651e-8	7.322
5	1209600	1762516	0.4695	0.065	5.3737e-8	3.5245e-9	8.453

From these results (Table 4) there is a correlation between leaching intervals and leachability index (Figure 6). The results show that Leaching Index of heavy metal was depended on the leaching interval. If the leaching Interval increased, the leaching index will increase also. The ANS 16.1 (modified) leachibility indices of the eight heavy metals for cement based solidification with and without AC at various ratios, are shown in Figure 4 and Figure 5, respectively.

Compressive strength test

Cement-based solidification exhibited a compressive strength of 1-7.1 MPa (Figures 7 and 8). The strength decreased as the percentage of cement loading was reduced, the compressive strength being 4.8-6.4 MPa for 50% cement which reduced to 2.0-2.9 MPa when 10% cement was used (Figure 7). Addition of AC to cement improved the compressive strength, as seen in Figure 8. In this case, increasing the cement loadings also increased the solid matrix strength. The compressive strength reading after 7, 14 and 28 days of curing ranged from 2.2-5.0, 2.4-5.4, and 2.9-7.1 MPa, respectively, corresponding to 10%, 20%, 30%, 40% and 50% cement with AC. The standard guidance for solidified waste form is given in Table 5.

Table 5. Standard 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 and compressive strength after 90 days
Immersion	See 1983 TP[b]	414 kPa compressive strength after 30 cycles
Thermal cycling	ASTM B 553	

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

[b] The 1983 Branch technical Position (TP) paper calls for a multistep procedure for biodegradation testing: if observed culture growth rated "greater than 1" is observed following a repeated ASTM G 21 test or any growth is observed following a repeated test of ASTM G22 test longer term testing for (at least 6 month) 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.

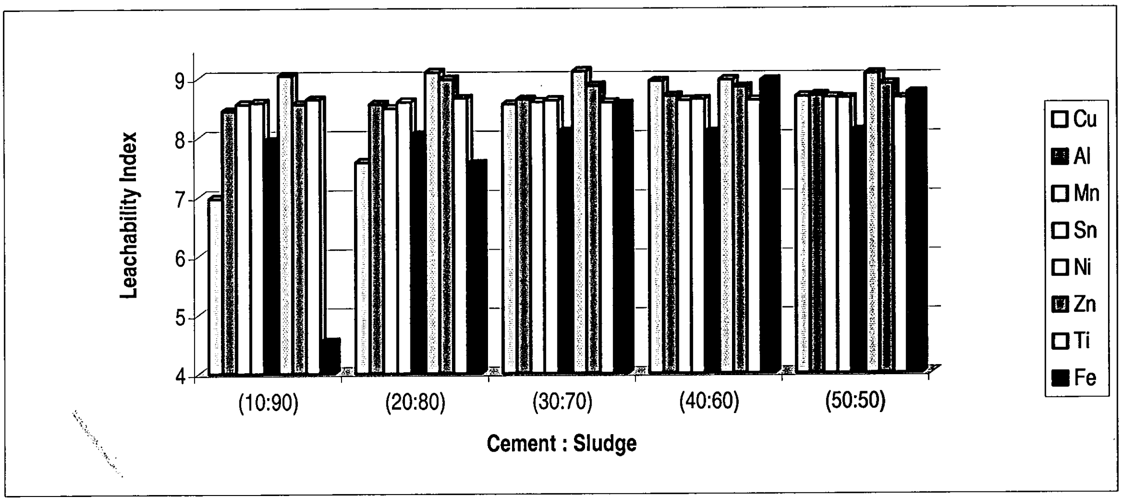


Figure 4. Leachability Index for metals in cement solidified matrix without AC treated sample.

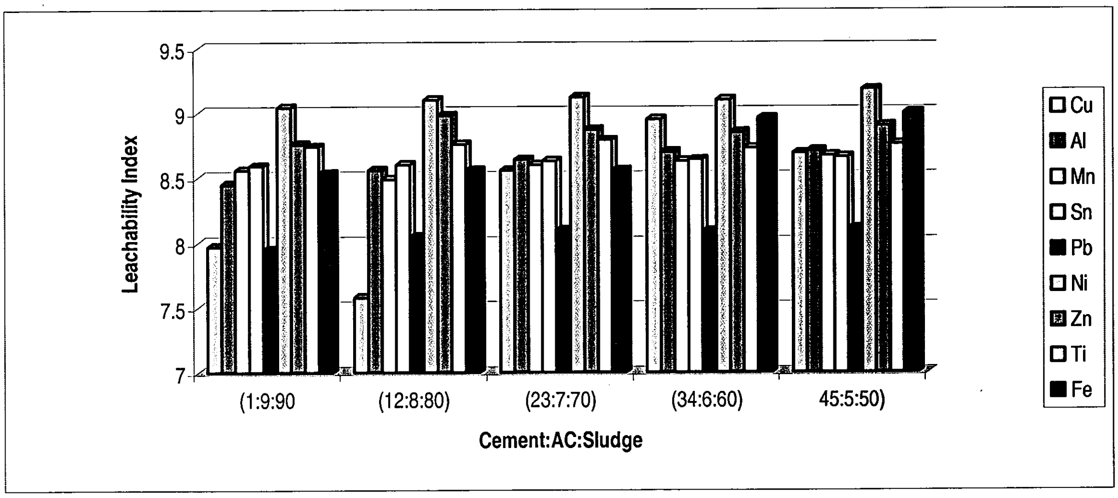


Figure 5. Leachability Index for the OPC with AC solidified matrix samples.

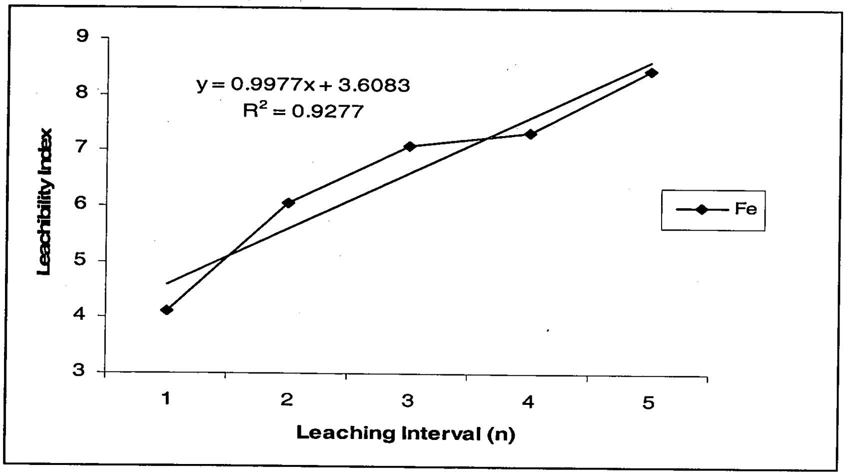


Figure 6. Correlation between leaching interval (n) and Leaching Index (L_i)

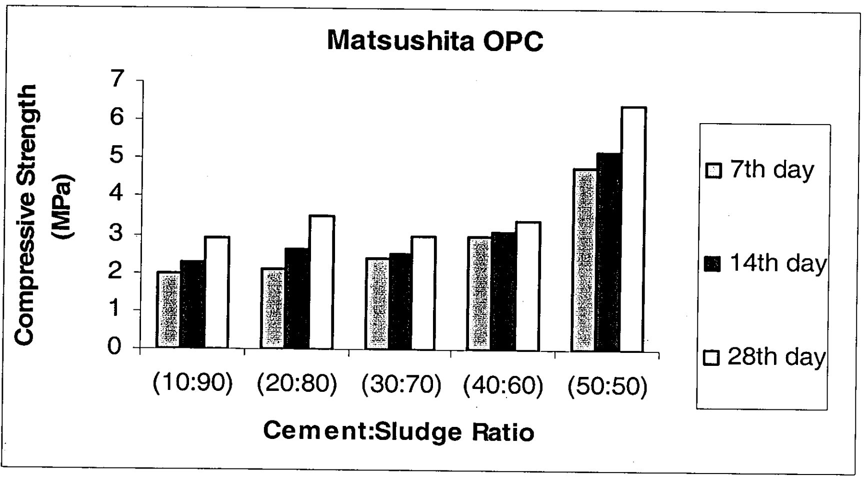


Figure 7. Compressive strength of solidified waste of cement without AC additive samples after 7, 14, and 28 days of solidification

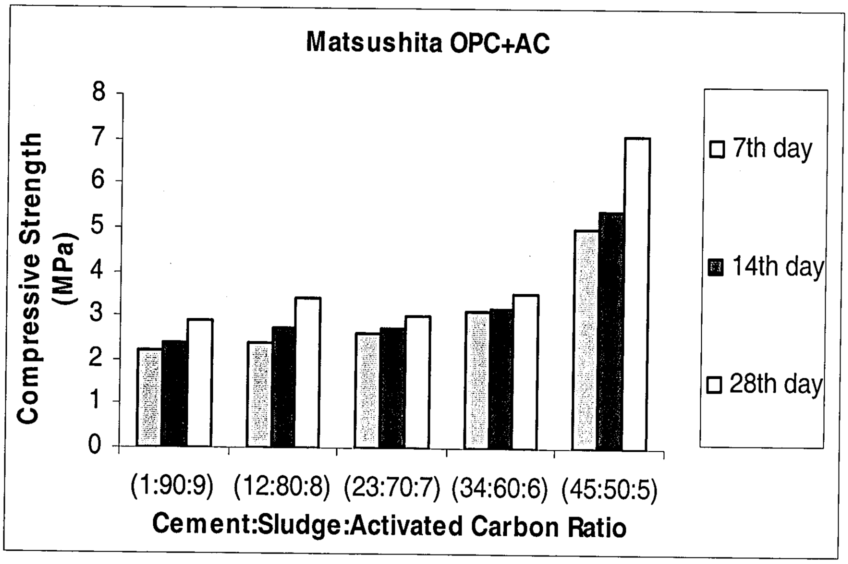


Figure 8. Compressive strength of solidified waste matrix of cement with AC samples after 7, 14, and 28 days of solidification

CONCLUSION

Solidification/stabilization of electronic waste with OPC was able to stabilize Al, Sn, Mn, Cu, Zn, Ni, Pb within the Environmental Quality Act, 1974 standard, but Fe was still higher than EQA 1974 standard. AC addition also immobilized heavy metals and decreased the number of elements leached from eight (Cu, Al, Mn, Sn, Pb, Ni, Ti and Fe) to three elements (Cu, Al and Fe). The compressive strength of the samples depended on the ratio of cement applied. The Leachability indices (L_i) obtained ranged between 4 and 9.1 for cement without AC and 7 and 9.2 with AC (Guidance Limit = 6) indicating that S/S was able to retain heavy metals within the solidified matrix.

Acknowledgements Authors wish to thank Matsushita (M) Sdn. Bhd in Shah Alam for technical support. The research was funded by a PJP Grant from the University of Malaya.

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