

## A case study on the treatment of wastewater sludge from an electronic plant using cement

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**ABSTRACT** Stabilization/Solidification (S/S) is a proven technology for the treatment of hazardous wastes. The process of manufacture and cleaning of electronic components can produce large quantities of waste, including hazardous waste, in the form of effluents, air emissions and solid waste. Direct disposal of these may cause environmental pollution, especially to surface and groundwater. Selection of stabilization/solidification as a remediation technology is also supported by recent developments in the environmental regulations. This paper focused on the laboratory studies of S/S disposal of wastewater sludge from an electronic plant, which generates about 150 tonnes of wastewater sludge per year. Three types of cement with or without activated carbon (AC) were used in this research, which include, Ordinary Portland Cement (OPC), Ground Granulate Blast furnace Slag (GGBS) and Mascrete Cement (MC). The American Nuclear Society (ANS) method indicated only Fe, Al, Cu but these were below the Standard B, EQA, 1974 while other metals were not detected. A comparison between Toxicity Characteristics Leaching Procedure (TCLP) and Japanese Leaching Test (JLT-13) methods indicated that JLT-13 gave lower leaching. The percentage of cement and activated carbon influenced TCLP and JLT-13 results.

**ABSTRAK** Penstabilan/Pemejalan (S/S) merupakan salah satu teknologi yang telah terbukti dapat memberi rawatan kepada sisa berbahaya. Proses-proses membuat dan membersihkan daripada komponen elektronik dapat menghasilkan sisa buangan dalam jumlah yang besar termasuk sisa berbahaya dalam bentuk kumbahan, pancaran udara dan sisa pepejal. Apabila sisa-sisa buangan ini dibuang secara langsung tanpa rawatan terlebih dahulu dapat mencemarkan alam sekitar terutama air di permukaan dan air bawah tanah. Kajian ini lebih tertumpu pada kajian makmal dimana sisa enapcemar sebuah kilang elektronik yang menghasilkan 150 tan sisa enapcemar setiap tahun telah digunakan sebagai sampel. Tiga jenis simen (OPC, GGBS dan MC) ditambah dengan atau tanpa karbon aktif (AC) telah digunakan dalam kajian ini. Kaedah ANS mendapati bahawa hanya Fe, Al, Cu dikenal pasti dan kepekataannya dibawah piawai B, EQA 1974 dan kepekatan logam-logam berat lain tidak dapat dikenal pasti. Perbandingan antara kaedah TCLP dan JLT-13 ialah didapati bahawa kaedah JLT-13 dapat mengurangi kadar resapan berbanding TCLP. Peratus simen dan karbon aktif dapat mempengaruhi bacaan TCLP dan JLT-13.

(Solidification/stabilization, activated carbon, OPC, GGBS, MC, ANS, TCLP, JLT-13)

### INTRODUCTION

There is little doubt that there is growing concern about the menaced by materials classified as hazardous finding their way into the environment, particularly in response to the occurrence of several disasters, for example, the outbreak of Minamata and Itai-itai diseases in Japan, to the Chernobyl and Bopal incidents in USSR and India, respectively. The handling and disposal of toxic and hazardous substances and wastes have since attracted the attention of all nations and have become a global issue.

Like many other industries, 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 categories as toxic and hazardous. The

government in showing its sensitivity to the potential gravity of environmental deterioration, has taken positive action and promulgated several legislations to combat the growing menace of hazardous and toxic wastes [2]

According to DOE, there were some 125,000 tonnes of hazardous and toxic waste accumulated from 1987 to 1993, amounting to an average of 15,625 tonnes per year. This low quantity was due to lack of legislation and inaccurate quantification. In 1994 (Table 1), however, when the management came into perspective, the waste generated increased to 417,000 tonnes. The quantity increased steadily to 487,000 tonnes and peaked at 631,521 tonnes in 1996 when the country's economy was booming. The sudden fall in the nation's economy after 1997 is depicted by the decrease in the generation of hazardous wastes corresponding to the slowdown in several industrial activities [2].

Of the total waste in 1998, the metal finishing industry has been identified to generate the most (34%). Mineral sludges are mainly from metal industries, while paint, dye and ink sludges are derived from textile and printing industries. Heavy metal sludges are mostly the product of wastewater treatment from electroplating and electronics industries [2].

Commonly encountered waste disposal scenarios include, where appropriate, incineration, physical, chemical or biological treatment, consignment to landfill and marine disposal. When wastes are consigned to landfill, problems arise often as a result of long-term release of toxic constituents into the surrounding environment due to fluid percolation through the deposit [4]. The US generates about 260 million tonnes hazardous waste a year, while China generates 30 million tonnes and Malaysia 390,000 tonnes a year. The three major issues in hazardous waste management are lack of waste

minimization and cleaner technologies, transboundary movements of hazardous waste and management of wastes from non-industrial sources [2].

One group of technologies which aims to minimize both the release and mobility rates of such environmental pollutants is known as solidification/stabilization or S/S [3]. Solidification is a technology for treating hazardous, radioactive, and mixed waste, debris, and contaminated environmental media. The objective is to reduce the hazard (solubility, leaching, toxicity) of specific contaminant so that the resulting waste forms can be disposed of in approved/licensed facilities [4]. In general, the stabilization chemistry and technologies that are applied to hazardous and low-level radioactive waste also applicable to mixed wastes. However, innovative technologies are required for unique processing requirements/limitations and for some specific waste streams. Treatment technologies related to chemical stabilization and fixation include vitrification (high-level mixed wastes), sintering, hydrothermal processing and hot isostatic pressing. These processes have the same objective as stabilization/fixation but are carried out at higher temperatures and require rigorous off-gas controls. Most stabilized waste forms are processed at ambient temperatures and have ventilation controls appropriate for the radioactive and chemical contaminants present in the waste. In solidification the waste is incorporated into a monolithic solid with a reduced surface area over which leaching can occur. Solidification process do not necessarily imply that any form of chemical reaction has occurred. The term stabilization on the other hand describes disposal technologies which chemically alter hazardous wastes to produce less toxic or mobile forms [6]. The most important factor determining weather a particular solidification/stabilization (S/S) process and its process parameters are effective in treating a

Table 1. Scheduled waste generated in 1994-1998.

Year	Waste generated (tonnes)
1994	417,000
1995	487,000
1996	631,521
1997	279,511
1998	398,518

Source: Annual Reports (1995-1999), Department of Environment

particular kind of waste, is the reduction in the short-and long-term leachability of the waste [5]. The leaching mechanisms involved in solidified waste are very complex. The rate of leaching from a waste can be controlled by diffusion and convection in the waste matrix and surface phenomena at the interface, such as diffusion and leachant renewal in the aqueous solution. In this paper, the S/S of wastewater sludge from an electronic plant using cement was investigated. The efficiency of solidification was tested using TCLP, ANS and JLT-13.

## MATERIAL AND METHODS

### Collection of samples

The wastewater sludge was obtained from Matsushita Company, in Shah Alam, Selangor.

### Sample preparation

Wastewater sludge (solid) was homogenized with cement by using a blender for 3 minutes. Water was added slowly into the wastewater sludge to promote hydration. The mixture was then mixed at high speed for 3-4 minutes upon attainment of the pre-determined water: cement ratio [7]. The resulting waste-loaded grout paste was transferred to specified moulds. The mixture was hand-compacted to yield a good compaction. The moulds were covered with Lucite sheets and left undisturbed for 24 h 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. In the first trial, 50% cement loading (three types cement) and 50% of wastewater sludge were used. In the second set of trials, AC (10% of the waste loading) was added to the cement, which was reduced in weight correspondingly, whereas the wastewater sludge remained as before at 50%, respectively. The solidified matrices from either trial were used for TCLP, ANS 16.1 (modified) and JLT-13 leach tests.

### American nuclear Society ANSI/ANS (Leach Test)

During the test, the solidified specimens were suspended in the leachant by using nylon fishing line. The ratio of the leachant volume and the external geometric surface area of the solid specimens was maintained at about  $10 \pm 0.2$  during the leaching interval. Ultra pure water of resistivity = 18 Mohm-cm (processed by

ELGASTAT@UHQPS) was used as the leachant in this test.

The leaching of samples was monitored over a period of 28 days (sampling at the 1<sup>st</sup>, 3<sup>rd</sup>, 7<sup>th</sup>, 14<sup>th</sup> and 28<sup>th</sup> 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. The leachate was collected into plastic bottles, acidified with nitric acid and stored in refrigerator until metal analysis was carried out. Inductively Coupled-Plasma-Atomic Emission Spectroscopy (ICP-AES) model 2000 BAIRD was used to analyze the metal concentration in the leachate.

### Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP protocol was performed using the solidified samples which were manually crushed to a particle size smaller than 9.5 mm. Prior to the performance of the 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  $3.00 \pm 0.05$ . 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 temperature of  $25 \pm 2^\circ\text{C}$  in an incubation shaker. At the end of the 18 hours contact time, the leachants were then filtered through a 0.8  $\mu\text{m}$  pore size borosilicate glass fibre filter, to separate the solid and liquid phase. Measurement of pH of the filtrate was taken by using Hanna instrument membrane pH meter, equipped with a standard glass electrode. The filtrate was collected in 100 ml polyethylene bottles, acidified with 1 ml of nitric acid and stored in refrigerator at 4°C until metal analysis was carried out by using ICP-AES.

### Japanese Leaching Test (JLT-13)

For this test, the solidified waste matrixes were crushed to particle size between 0.5-5 mm after 28 days of curing. Extraction buffer of hydrochloric acid and sodium hydroxide at pH  $6.00 \pm 0.05$  was used at a ratio of 10: 1 (buffer: solid). The buffer was added to the crushed waste matrixes in a HDPE container and mechanically shaken for 6 hours continuously at 200 rpm.

After 6 hours, the leachate was filtered using 0.45µm cellulose membrane filter. pH and heavy metals in the JLT leachate were determined as before.

**RESULTS AND DISCUSSION**

The untreated electronic industry wastewater sludge contained 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 (Table 2).

**ANS 16.1(modified)**

*Leaching rate*

The leaching rate, *l*, was calculated using equation:

$$l = \frac{a_n}{A_0} \times \frac{V}{S}$$

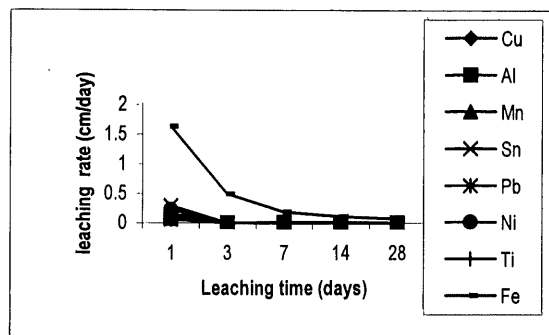
where *a<sub>n</sub>* is the amount of constituent of interest (metal) leached during interval *n* (mg), *A<sub>0</sub>* is the

amount of constituent of interest initially present in the specimen (mg), *V/S* is the specimen volume/surface area ratio (cm). The leaching rate of the heavy metals of concern from (OPC, MC and GGBS) cement treated samples demonstrated a descending trend as the leaching time progressed (Figures 1, 2 and 3). The leaching rate for Fe was highest at 1.627 cm/day whereas the leaching rate for other metals were low at 0.07 cm/day.

Fe showed the highest initial leaching rate (and a subsequent steep decrease in the rate), followed by Sn, Ni, Mn, Ti, Al and Pb. The leaching rate of Fe with 50% OPC loading decreased 96% from 1.627 cm/day in the first interval to 0.065 cm/day in the final interval (Figure 1), whereas the leaching rate of Fe by using 50% MC loading decreased 96.5% from 1.499 cm/day in the first interval to 0.052 cm/day in the final interval (Figure 2) while the leaching rate of Al by using 50% MC loading decreased 98% from 0.380 cm/day in the first interval to 0.006 cm/day in the final interval (Figure 2).

**Table 2.** Heavy metal content in the wastewater sludge before solidification.

Element	Concentration (mg/l)	TCLP limit (mg/l)	EQA 1974 limit (mg/l)
Cu	30.2	-	1.0
Al	785	-	-
Mn	74.0	-	1.0
Sn	239	-	-
Pb	10.4	0.75	0.5
Ni	14.9	11	1.0
Zn	18.1	4.3	1.0
Ti	0.832	-	-
Fe	834	-	5.0



**Figure 1.** Leach rate of heavy metals, in OPC samples, at OPC/wastewater sludge ratio of 50: 50.

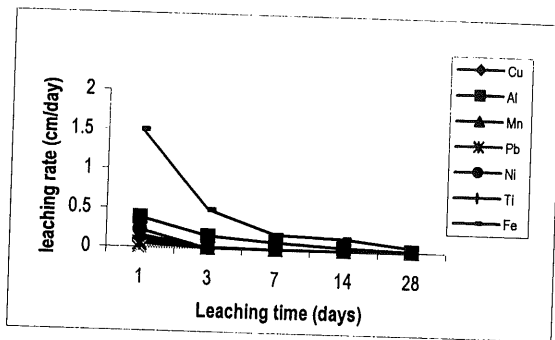


Figure 2. Leach rate of heavy metals, in MC samples, at MC/wastewater sludge ratio of 50: 50.

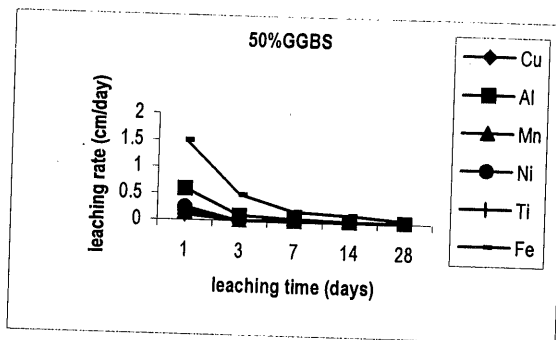


Figure 3. Leach rate of heavy metals, in GGBS samples, at GGBS/wastewater sludge ratio of 50: 50.

When solidified with GGBS, Fe still exhibited the highest initial leaching rate, followed by Al, Ni, Cu, Mn and Ti. The leaching rate of Fe by using 50% GGBS loading decreased 96.5% from 1.499 cm/day in the first interval to 0.052 cm/day in the final interval leaching of. Al also decreased 97.8% from 0.587 cm/day in the first interval to 0.013 cm/day in the final interval (Figure 3).

When 5% activated carbon was added to OPC, MC or GGBS, Fe still showed the highest initial leaching rate, followed by Al and Cu (Figure 4-6). The leaching rate of Fe in 45% OPC+AC loading, decreased 96.5% from 1.96 cm/day in the first interval to 0.069 cm/day in the final interval. The

leaching rate of Cu, in 45% OPC+AC loading, increased 62.3% from 0.04 cm/day in the first interval to 0.106 cm/day in the third interval but Cu loading decreased 80% from 0.01 cm/day until 0.002 cm/day after the seventh interval onwards.

The leaching rate of Fe in 45% MC+AC (Figure 5) loading also, decreased 96.3% from 1.87 cm/day in the first interval to 0.07 cm/day in the final interval, while Fe when solidified with 45% GGBS+AC loading, decreased 96.8% from 1.88 cm/day in the first interval to 0.06 cm/day in the last interval (Figure 6).

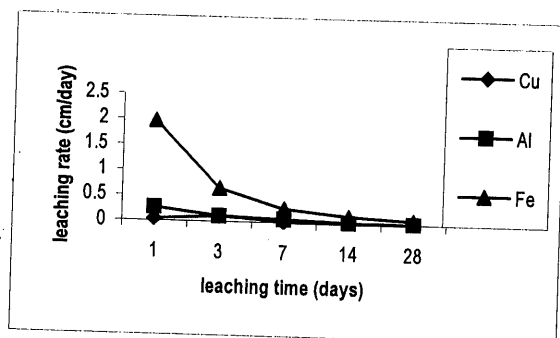


Figure 4. Leach rate of heavy metals, in OPC samples with AC additive at AC/cement/wastewater sludge ratio of 5: 45: 50.

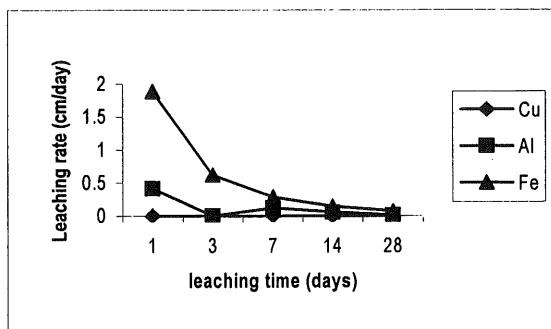


Figure 5. Leach rate of heavy metals, in MC samples with AC additive at AC/cement/wastewater sludge ratio of 5: 45: 50

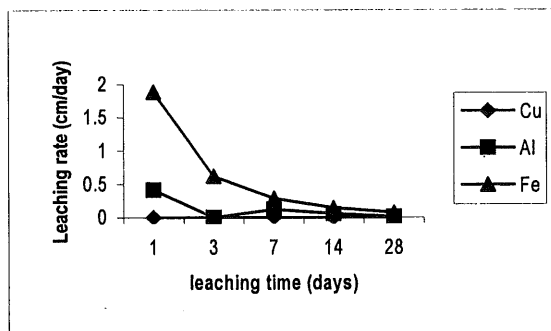


Figure 6. Leach rate of heavy metals, in GGBS samples with AC additive at AC/cement/wastewater sludge ratio of 5: 45: 50.

**Toxicity Characteristic Leaching Procedure (TCLP)**

Wastewater sludge solidified with 45% OPC+5%AC stopped only Pb leaching whereas all other heavy metals leached beyond TCLP standard (Table 3). Mn was the highest metal leaching followed by Al, Fe, Zn, Cu, Ni, Sn and Ti. Fe was above the EQA standard B limit while Zn and Ni were below TCLP standard.

When 45% MC+5% AC was used, it was found that Fe was below EQA standard B limit while Zn was above EQA standard B limit but it was

still below TCLP standard. Mn was higher than EQA standard B limit. With 45% GGBS+5% AC it was found that Fe was below EQA standard B limit and Ni was above standard B but for TCLP standard Ni and Zn were below the limit.

**Japanese Leaching Test (JLT-13)**

In the JLT-13 leach method wastewater sludge solidified with 45% OPC+5% AC immobilized all heavy metals (Mn, Sn, Pb, Ni, Zn and Ti) except Fe, Al and Cu. Similar trend was observed with all other two types of cement (Table 4).

Table 3. TCLP results by using different types of cement.

Element	45% OPC+ 5% AC	45% MC+ 5% AC	45% GGBS+ 5% AC	TCLP Standard	EQA standard B
Cu	3.35	2.44	4.20	-	1.0
Al	5.97	0.971	6.87	-	-
Mn	19.9	24.2	10.4	-	1.0
Sn	0.307	nd	2.32	-	-
Pb	nd	nd	0.11	0.75	0.5
Ni	2.28	3.64	1.9	11	1.0
Zn	2.50	1.81	2.3	4.3	1.0
Ti	0.132	0.116	0.142	-	-
Fe	5.92	4.51	4.87	-	5.0

Nd: not detected  
Unit: mg/l

Table 4. JLT-13 results for different cement types.

Element	45% OPC+ 5% AC	45% MC+ 5% AC	45% GGBS+ 5% AC	JLT-13 standard
Cu	0.773	0.676	1.52	-
Al	3.39	4.49	4.52	-
Mn	nd	nd	nd	-
Sn	nd	nd	nd	-
Pb	nd	nd	nd	0.3
Ni	nd	nd	nd	-
Zn	nd	nd	nd	0.3
Ti	nd	nd	nd	-
Fe	5.87	5.86	5.86	-

Nd: not detected

Unit: mg/l

Based on TCLP and JLT-13 results, it was found that JLT-13 gave 66.6% lower leaching rates.

### CONCLUSION

The results obtained in this study support solidification/ stabilization as an option for electronic industry hazardous waste treatment. Based on TCLP results, wastewater sludge solidified with 45% OPC+5% AC stopped only Pb leaching whereas all other heavy metals leached beyond TCLP standard. Using 45% MC+5% AC and 45% GGBS+5% AC it was found that Fe was below EQA standard B while JLT-13 results, while 45% OPC+5% AC, immobilized all heavy metals (Mn, Sn, Pb, Ni, Zn and Ti) except Fe, Al and Cu. Similar trend was observed with the other the two types of cement. Based on ANS results it was found that GGBS performed better than MC or OPC. For TCLP and JLT-13 all the three cement types gave similar results. Based on TCLP and JLT-13 results it was found that JLT-13 gave 66.6% lower leaching rate.

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