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Leaching Behavior of Heavy Metals from the Solidified Plating Sludge under Various Leaching Conditions

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Abstract

This research work investigates leaching behavior of heavy metals from the solidified zinc-cyanide electroplating sludge using TCLP, DLT and leaching under controlled pH. OPC and OPC + 10 wt.% PFA are used as solidification binders. The plating sludge is loaded to the solidification binder at 10 wt.% and a water-to-solid ratio of 0.5 is used throughout this work. TCLP results show that Cr concentrations in the leachates do not exceed the limit specified by the US.EPA. Under DLT leaching conditions, Zn, Fe and Cr are leached from the monolithic samples when in contact with 0.1N acetic acid leachant (pH = 3) at a higher rate than deionized water and the pH 5 synthetic acid rain. When leachate pHs are controlled at 4, the concentration of all three metals in the leachates are the highest. Reduction in concentration of these three metals in the leachates is observed when leachate pHs are increased to the alkali pH values.

Keywords: Leaching, OPC, PFA, TCLP, DLT, Controlled pH

Introduction

Cement-based stabilization/solidification (S/S) processes are potential treatments for a wide variety of wastes, and particularly those containing heavy metals. Current solidification processing normally involves simply mixing waste with ordinary Portland cement (OPC) and/or other pozzolanic materials. The relative simplicity of cement-based solidification processes has made this an attractive pre-landfill waste treatment technology for selected wastes. Immobilization of waste constituents by the cementitious binders occurs due to both chemical and physical effects, with the effectiveness of the containment process normally being assessed by completing relatively short-term leaching tests [1-2].

The leachability of waste constituents from cement-based S/S products after landfilling is the most important factor determining the effectiveness of the treatment process. Leaching is a complex mechanism involving transport of contaminants, normally by diffusion, through the interconnected pores of the solidified waste. The release of contaminants may occur when cement-based S/S products are in contact with landfill leachate. Permeation of landfill leachate through the connected porosity into the solidified waste may cause solubilization of waste components and particularly amphoteric heavy metals, which can have highly pH dependent solubilities [3].

Several factors were reported to have effect on leachability of waste components from cement-based solidified waste products. These factors include the acid neutralization capacity of the cement matrix, pH dependence of waste constituents, the open porosity of the S/S waste, leachant composition, and the surface of the product-to-volume of the leachant ratio [4-10]. Consequently, more reliable leaching test methods have been developed to evaluate the release of inorganic constituents from the cement-based solidified waste forms.

In this research work, leaching behaviors of heavy metals from cement-based solidified plating wastes were assessed using various leaching tests. The Toxicity Characteristic Leaching Procedure (TCLP), the Dynamic Leach Test (DLT) and leaching under controlled pHs were used to determine the concentrations of heavy metals in the leachates and leachate pHs.

Materials And Methods

Materials

OPC Type 1 used throughout this research work was from The Siam Cement Public Company Limited. The pulverized fuel ash (PFA), a pozzolanic waste generated during the combustion of coal, was brought from the Electricity Generating Authority of Thailand (EGAT) in Lumpang Province. PFA was then ground to a particle size of less than 45 μm using a Los Angeles Abrasion Machine. The data of oxide contents of OPC and PFA was obtained by the suppliers and is shown in Table 1.

Electroplating sludge was brought from a wastewater treatment plant of zinc-cyanide process located in Bangkok, Thailand. The Cr (VI) present in the wastewater was reduced to Cr (III) before hydroxide precipitation. The plating sludge was then oven dried and ground to a particle size of less than 0.5 mm. The ground sludge was digested using concentrated nitric acid and the concentration of heavy metals was analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES). Zn, Fe and Cr are the major metals present in the plating sludge at concentration of 256, 21.1 and 11.9 mg/kg dry sludge, respectively.

Sample preparation

PFA was used to substitute for OPC at 0 and 10 wt.% and the plating sludge was added at 0 and 10 wt.%, respectively. A water to solid ratio of 0.5 was used for all mixes. The slurry was mixed following the standard test method ASTM C 305-94 to achieve a uniform distribution of the plating sludge before being transferred to the cylindrical plastic mould (25-mm high and 25-mm diameter). The mixes were allowed to solidify in the sealed plastic moulds to avoid carbonation prior to testing.

Toxicity Characteristic Leaching Procedure (TCLP)

Metals leaching from the solidified plating wastes were assessed using the Toxicity Characteristic Leaching Procedure (TCLP) as defined by the U.S. EPA on the samples cured for 28 days. The sample specimen was crushed to reduce the particle size to less than 9.5 mm. The crushed sample was extracted with an amount of acetic acid solution (pH 2.88) equal to 20 times the weight, of the sample. The extraction vessels were rotated in an end-over-end manner at 30 rpm for 18 hours. The leachates were filtered through a 0.45 μm membrane filter to remove suspended solids, and were then divided into two portions. One was used for pH measurement and the other for the determination of metals present in the leachates by ICP-AES. Each leachate was analysed in triplicate and the average values were reported to ensure the reproducibility of the data.

Dynamic Leach Test (DLT)

A modified American Nuclear Society test 16.1 (ANSI/ANS 16.1) was used to observe metal leaching from the monolithic samples. Deionized water, 0.1N acetic acid solution and synthetic acid rain were used as leachants. The synthetic acid rain was prepared from 0.1N sulfuric and nitric acid at the ration of 80:20 and diluted with deionized water to a pH of 5. Cylindrical samples, cured for 28 days, were suspended in a plastic net in each acid solution, at a leachant volume to surface area ratio of 20:1.

The leachates were removed to determine the pH and metal concentration and the leachant was replaced periodically after intervals of static leaching. Deionized water and synthetic acid rain were renewed at 2.7 hours, 1, 2, 3, 4, 5, 7, 14, 28, and 43 days, whereas acetic acid solution was renewed after having contact with the sample for 1, 3, 7, 14, 21, 28, 35 and 42 days. This produces severe leaching conditions and allows assessment of leaching performance over longer time periods.

Leaching under controlled pH

Three pH values, 4.0, 8.0 and 11.0, were selected to observe leaching behavior of metals from the solidified plating wastes. Leachants were prepared from deionized water and adjusted to the desired pH values with 0.1N nitric acid solution and sodium hydroxide solution. Both crushed and monolithic samples curing for 28 days were extracted under designated pH values. The amount of leachant used was equal to 20 times the weight of the sample for the crushed sample and was equal to 20 times the surface area of the sample for the monolithic sample. During extraction, leachate pHs were controlled to the designated pH values using 0.1N nitric acid solution and sodium hydroxide solution. The sample and the leachant were allowed to contact in a shaker until leachate pH was nearly constant for 24 hours. Leachates were then filtered through a 0.45 μm membrane filter before ICP-AES analysis for metal concentrations.

Results and discussion

Leachability of metals under TCLP

Leachate pHs and metal concentration in TCLP leachates are shown in Table 2. Experimental results showed that the pH of acetic acid leachants after having had contact with the solidified samples changed from an initial pH of 2.8 to approximately 12.8-13.0 by the end of the tests.

It is known that the main hydration products of OPC are calcium silicate hydrate (CSH) gel and calcium hydroxide (CH) which are highly alkaline. CH has relatively high solubility when the pH of the pore water is below 13, whereas the solubility of CSH gel is low below pHs of approximately 11.5 [11]. CH is therefore the first phase to dissolve when acidic leachant ingresses into the pore water of cement-based solidified wastes. This resulted in an increase leachate pH to its steady-state value while having contact during the test sample.

TCLP results showed that Cr concentrations in the leachates did not exceed the limit specified by the US.EPA in all samples. Although Zn and Fe were not specified by the US.EPA, they were present in the leachates at concentrations lower than 1.8 and 0.5 mg/L, respectively. It was observed that leachability of Zn, Fe and Cr from the solidified waste forms was much lower than from the untreated plating sludge. It is believed that the release of excess alkaline from the solidified wastes increased the leachate pHs to the optimum range for immobilization of some amphoteric metals. This was indirectly responsible for the reduced leachability of metals [3].

Leachability of metals under DLT

DLT leachate pHs are shown in Table 3 and the cumulative metal concentrations in DLT leachates as a function of exposure duration are shown in Figures 1-3. It was observed that leachate pHs for all samples leached in deionized water increased from an initial pH of 6.0 to around 10 and 11 during the first 3 days of contact. The low concentration of H^+ ions present in deionized water was rapidly buffered to an alkali leachate pH by the available CH from the solidified wastes. At longer exposure duration, the leachate pHs were increased, but at a slower rate to a slightly alkaline or near neutral pH. Similar observations were found when a pH 5.0 synthetic acid rain was used as leachant.

A change in pH of 0.1N acetic acid leachant after each exposure duration from 2.8 to between 4.2 and 4.9 was observed in all samples (Table 3). The high concentration of H^+ ions present in acetic acid leachant was reduced during penetrating into the pore water due to reaction with CH. However, the alkalinity obtained from dissolution of CH or decalcification of CSH gel was insufficient to neutralize the acid leachant during the designated contact time. As a result, the pH of all leachates which were in contact with the solidified wastes was lower than 5.0.

No differences in leachability of Fe, Cr and Zn from the solidified wastes were observed during leaching in both reduced water and synthetic acid rain. A higher leaching rate of Fe and Cr was found during the first 3 or 4 days and the rate of leaching reduced with increasing leach time (Fig. 1 and 2). This is because leaching of the amphoteric metal hydroxides is highly pH dependent. During the first 3 or 4 days, leachate pHs of the solidified wastes were neutralized and increased from 6.0 to between 10.2 and 11.0 for deionized water and from 5.0 to between 10.5 and 11.0 for synthetic acid rain. At these highly alkali pHs, Fe and Cr hydroxides started to resolubilize. But after these days, leachate pHs of deionized water and synthetic acid rain were increased to the range of 6.3 to 8.1 and 6.6 to 7.6, respectively where Fe and Cr hydroxides are less soluble.

However, the cumulative amounts of Fe and Cr in leachates after leaching for 42 days were lower than 4.0 and 0.5 mg/l, respectively in all samples. In addition, Zn was found in both leachates at concentration lower than the detection limit of ICP-AES. Similar leaching behavior of Cr and Zn were also observed by other researchers [12-14]. They reported that the amphoteric $Zn(OH)_2$ is insoluble in the pH range between 7 and 13 whereas $Cr(OH)_3$ is most insoluble between pH 5 and 13.

Under 0.1N acetic acid, the cumulative concentrations of Fe, Cr and Zn in the leachates were high and gradually increased with contact time (Fig. 3 a-c). Continued ingression of acidic leachant into the pore water of the solidified wastes disturbs the chemical equilibrium of the wastes and the cement matrices. This may initiate dissolution of insoluble species especially metal hydroxides. The soluble metals are diffused through interconnected pores of the cement matrix into the bulk acid solution as a result of concentration gradient. It could be possible that the higher cumulative concentration of Zn in the leachates compared to that of Fe and Cr was due to higher initial concentration of Zn present in the plating sludge.

Leachability of metals under controlled pH

Table 4 shows concentrations of Fe, Cr and Zn in leachates extracted from crushed and monolithic samples under pH 4.0, 8.0 and 11.0. Experimental results showed that concentrations of Fe, Cr and especially Zn were highest when leachate pH was controlled at 4.0. This is because Fe and Cr hydroxides have minimum solubility at pH around 7.5 whereas Zn hydroxide is around 9.5. The difference between minimum solubility pH of Zn hydroxide and the leachate pH is large compared to that of Fe and Cr hydroxides. As a result, Zn was solubilized and released from the solidified wastes at higher rate. Reduction in concentration of these three metals was observed when leachate pH was increased to the alkali pH value. In addition, the concentration of these three metals in the leachates extracted from the crushed samples was higher compared to that extracted from the monolithic samples. This effect is due to the increase in surface area of contact, which can accelerate the release of metals from the solidified wastes.

Conclusions

pH is an important factor influencing leaching of most heavy metals. Under TCLP leach testing, the pH of the leachant is allowed to rise to its steady-state value in contact with the test sample. This simulates disposal scenarios in which the ground water regime is static and a high pH environment will develop around cement-based solidified wastes tested under this condition. As a result, leaching of most amphoteric metal hydroxides was relatively low and had not exceeded the regulatory limit.

In the DLT leaching test, the leachant is renewed periodically to simulate ground water flow. This produces more severe leaching conditions and allows assessment of leaching performance over longer time periods. Zn, Fe and Cr were leached from the monolithic samples when in contact with the pH 3 acetic acid leachant at a higher rate than deionized water and the pH 5 synthetic acid rain. It was noticed that the pH 3 acetic acid leachant produces leaching data under highly aggressive condition and is rarely found under normal landfill scenarios.

The concentrations of all three metals in the controlled pH 4 leachates were the highest. In addition, the concentration of these metals in the leachates extracted from the crushed samples was higher compared to that extracted from the monolithic samples.

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Table 1 Oxide contents of OPC and PFA.

Component	OPC (%)	PFA (%)
SiO_2	21.2	39.44
Al_2O_3	5.22	21.96
Fe_2O_3	3.08	13.55
CaO	64.73	12.94
MgO	1.04	2.60
Na_2O	0.19	1.41
K_2O	-	2.90
P_2O_5	-	0.16
SO_3	2.01	1.51

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Table 2 Leachate pHs and metal concentrations in TCLP leachates.

Sample ID	pH	Metal Concentration (mg/L)		
		Zn	Fe	Cr
Regulatory level	-	*	*	5
Plating sludge (PS)	5.9	1077	2.83	2.92
OPC	13.0	0.33	0.16	0.24
OPC+10%PS	12.9	1.74	0.19	0.51
OPC+10%PFA	12.9	0.16	0.15	0.24
OPC+10%PFA+ 10%PS	12.8	0.87	0.44	0.54

*not specified by the US.EPA

Table 3 DLT leachate pHs.

Sample ID	Exposure Duration (days)										
	0	0.11	1	2	3	4	5	7	14	28	42
Deionized Water											
OPC	6.0	10.7	10.9	11.0	11.0	8.5	8.3	7.8	7.7	7.6	7.0
OPC+10%PS	6.0	10.6	10.7	11.0	11.1	8.3	8.2	7.8	7.6	7.3	6.6
OPC+10%PFA	6.0	10.6	10.8	11.0	11.1	8.4	8.3	7.8	7.7	7.6	7.0
OPC+10%PFA+ 10%PS	6.0	10.2	10.7	10.8	11.0	8.1	8.2	7.8	7.5	7.3	6.6
Synthetic Acid Rain											
OPC	5.0	10.4	10.9	10.9	11.0	10.0	9.8	9.7	8.0	7.7	6.3
OPC+10%PS	5.0	10.5	10.8	10.9	10.9	10.1	7.6	7.6	7.6	7.2	6.6
OPC+10%PFA	5.0	10.5	10.8	11.0	10.9	10.1	9.6	9.6	8.0	8.0	6.6
OPC+10%PFA+ 10%PS	5.0	10.5	10.7	10.8	10.7	10.2	7.6	7.7	7.5	7.0	6.6
0.1N Acetic Acid Solution	**0**	**1**	**3**	**7**	**14**	**21**	**28**	**35**	**42**		
OPC	2.8	4.6	4.6	4.6	4.9	4.4	4.5	4.5	4.3		
OPC+10%PS	2.8	4.3	4.4	4.6	4.8	4.3	4.5	4.4	4.3		
OPC+10%PFA	2.8	4.6	4.5	4.6	4.9	4.2	4.5	4.4	4.3		
OPC+10%PFA+ 10%PS	2.8	4.4	4.5	4.5	4.8	4.2	4.4	4.5	4.3		

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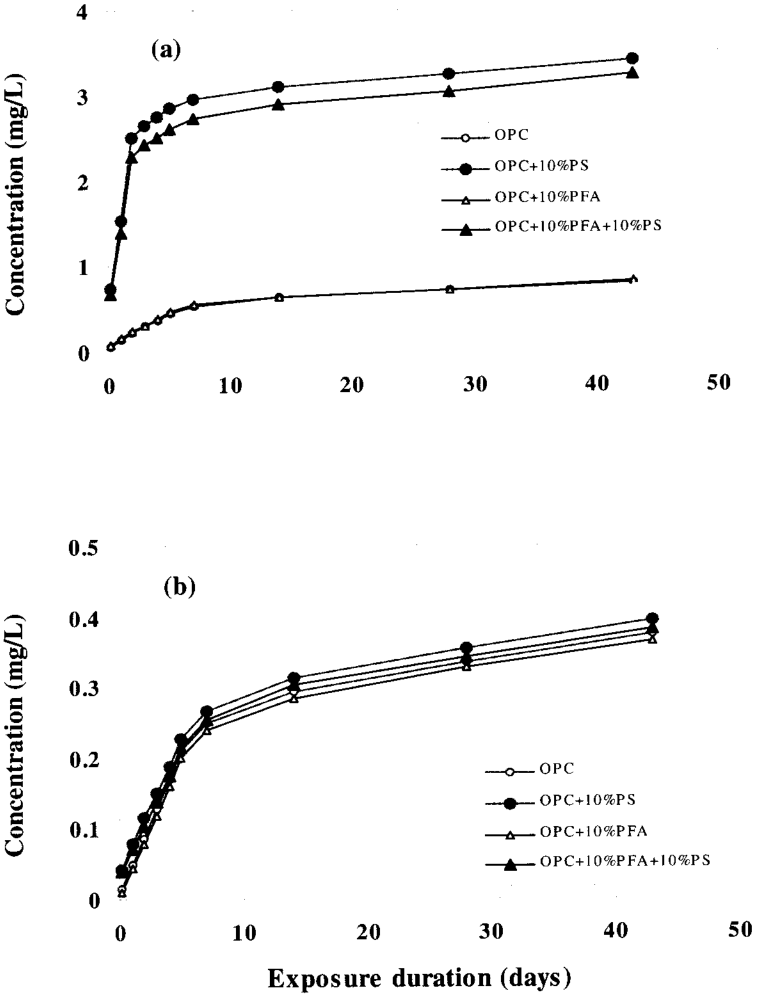

Figure 1 Cumulative metal concentration in deionized water as a function of exposure duration: (a) Fe concentration; and (b) Cr concentration.

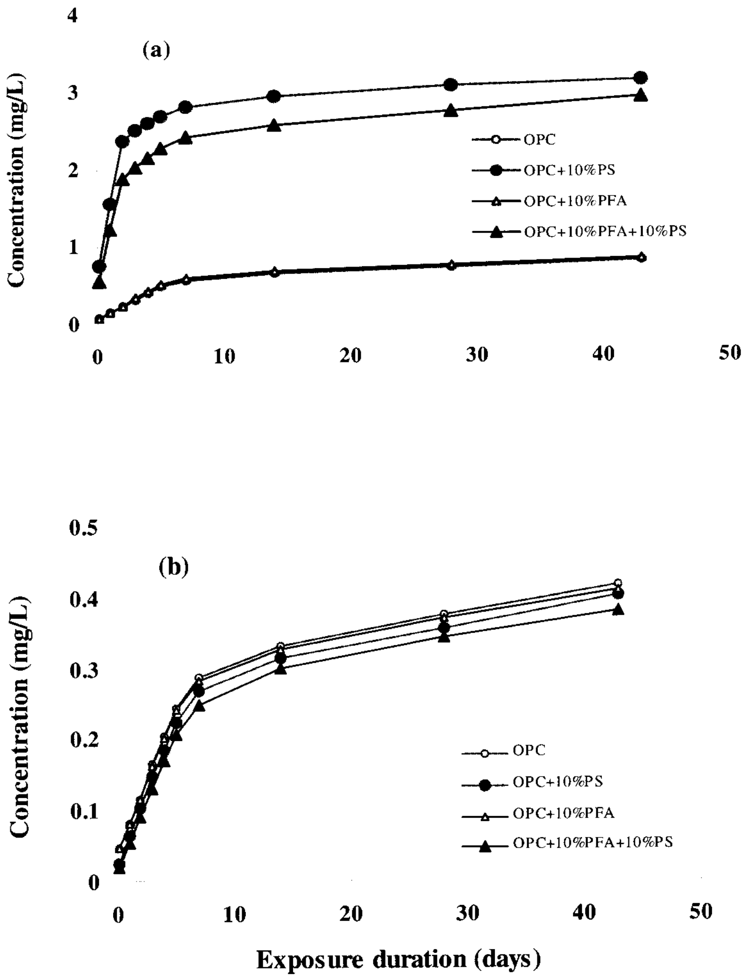

Figure 2 Cumulative metal concentration in synthetic acid rain as a function of exposure duration: (a) Fe concentration; and (b) Cr concentration.

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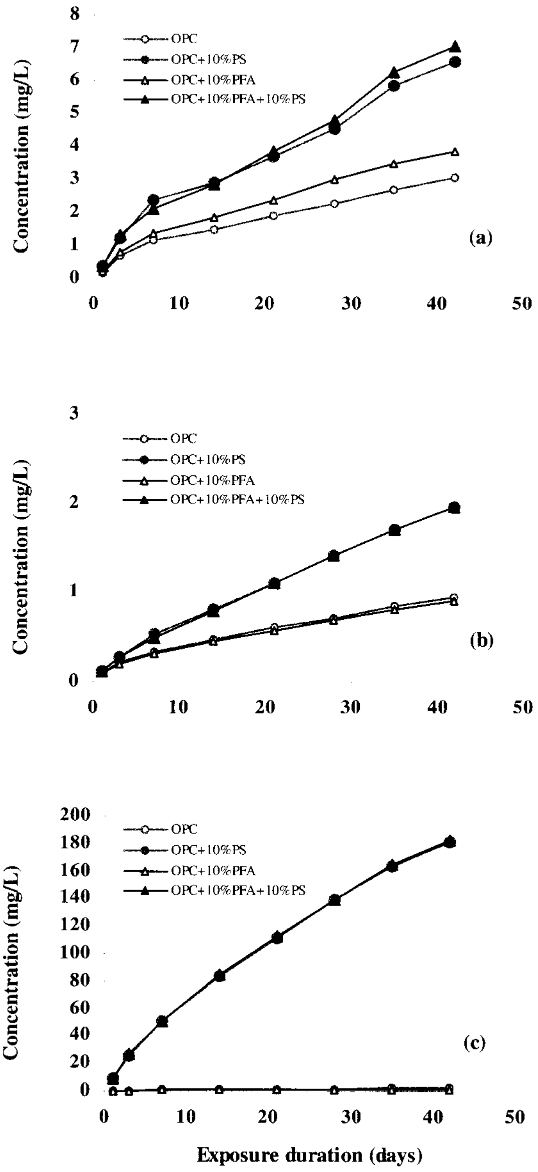

Figure 3 Cumulative metal concentration in 0.1N acetic acid as a function of exposure duration: (a) Fe concentration; (b) Cr concentration; and (c) Zn concentration.

Table 4 Metal concentrations in leachates leaching under controlled pH.

Sample ID	Metal concentration (mg/L)								
	pH 4.0			pH 8.0			pH 11.0		
	Fe	Cr	Zn	Fe	Cr	Zn	Fe	Cr	Zn
Crushed Samples									
OPC	0.23	0.23	0.64	0.14	0.21	ND	0.09	0.12	ND
OPC+10%PS	0.90	0.36	11.13	0.33	0.27	0.37	0.21	0.18	ND
OPC+10%PFA	0.19	0.22	0.56	0.12	0.16	ND	0.09	0.09	ND
OPC+10%PFA+ 10%PS	0.83	0.30	10.33	0.24	0.19	0.26	0.20	0.15	ND
Whole Cylindrical Samples									
OPC	0.14	0.10	0.27	0.11	0.04	ND	0.08	0.03	ND
OPC+10%PS	0.36	0.11	4.45	0.33	0.04	ND	0.10	0.04	ND
OPC+10%PFA	0.17	0.09	0.23	0.11	0.04	ND	0.08	0.03	ND
OPC+10%PFA+ 10%PS	0.34	0.11	4.13	0.30	0.04	ND	0.10	0.03	ND