Thammasat Int. J. Sc. Tech., Vol. 10, No. 4, October-December 2005

Immobilization of the Plating Sludge by Activation of Pulverized Fuel Ash with Sodium Silicate Solution

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Abstract

This research work investigated the solidification of plating sludge using hydrated lime and pulverized fuel ash (PFA) as solidification binder at different proportions. The proportions between lime-PFA at ratio of 25:75, 30:70 and 35:65 were studied. The sodium silicate (Na_2SiO_3) solution was used as chemical activator for cementitious material at 0, 4, 6 and 8 vol./wt.% and the plating sludge was added to the solidification binder at 0, 10, 20, 30, and 50 wt.%. Compressive strength and leachability of heavy metals from the solidified wastes were determined. Experimental results showed that the 28-day strength of the solidified wastes decreased from 186 to 44, 20 and 6.5 kg/cm^2 when the plating sludge was added at 10, 30 and 50 wt.%, respectively and a significant increase in strength was observed at the age of 56 and 91 days except for those containing 50 wt.% plating sludge. However, the plating sludge was added to lime-PFA cements with 6 vol./wt.% Na_2SiO_3 solution up to 50 wt.% and gave strength of the solidified wastes greater than 3.5 kg/cm^2 which, meets the standard criteria for landfilling. The Toxicity Characteristic Leaching Procedure (TCLP) results showed that the concentration of Cu in leachates extracted from the solidified wastes containing 20 and 30 wt.% plating sludge was higher than the regulatory limit of 2 mg/L which was defined by the Ministry of Industry and the USEPA.

Keywords: immobilization, pulverized fuel ash, sodium silicate, plating sludge, strength, leaching

1. Introduction

Heavy metal-containing sludge is generated from various manufacturing industries including metal plating, photography, battery, paints and pesticide. It is estimated that 1.7 million tons of the metal sludge is generated every year [1]. A great amount of heavy metals present in the sludge such as chromium, copper, lead and zinc are persistent in the aquatic system. These heavy metals are highly toxic to flora and fauna. Their disposal by means of incineration is a costly process [2]. Such wastes demand some treatments such as stabilization and solidification (S/S) to minimize their environmental impacts before being placed in the landfill [3].

S/S processes aim to immobilize the toxic constituents of hazardous wastes to prevent them leaching from the waste once disposed. Cement-based or pozzolan-based processes are most suitable for inorganic wastes containing heavy metals. PFA is one of several pozzolanic materials commonly used in the pozzolan-based process. PFA is generated from the coal combustion process in thermal power plants [4]. Most pozzolans do not undergo self-cementing reactions, but in the presence of lime and water can produce cementitious materials and act in a similar manner to hydraulic cement. [5] The slow pozzolanic reaction has made the pozzolan-based solidification processes unattractive for some applications, although these types of treatment often have reduced costs.

Some recent research has shown that the slow pozzolanic reaction could be accelerated using either chemical or thermal activation [6-9]. Several alkali activators have been used for activating PFA including Portland cement, lime, sodium hydroxide (NaOH), sodium carbonate

(Na_2CO_3), sodium sulfate (Na_2SO_4) and sodium silicate (Na_2SiO_3) solution [10-11]. In this work, lime and PFA were used as low-cost solidification binders to solidify the zinc-cyanide electroplating sludge. Na_2SiO_3 was used to activate the pozzolanic reaction between lime and PFA. Strength and metal leaching from the solidified wastes were determined to assess the performance of the solidified products prior to landfilling.

2. Experimental procedure

2.1 Materials

PFA was brought from the Electricity Generating Authority of Thailand (EGAT) in Lumpang Province. It was screened through sieve No. 325 to remove PFA with particle size greater than 45 μm. The data on chemical composition of PFA was obtained by EGAT and is shown in Table 1.

Reagent grade Na_2SiO_3 solution was used throughout this work as chemical activator. The alkali modulus between sodium oxide (Na_2O) and silicon dioxide (SiO_2) was adjusted to 1:1 with NaOH. The final concentration of SiO_2 in sodium silicate solution was 21.28 wt.%.

Electroplating sludge was brought from a wastewater treatment plant of the zinc-cyanide process located in Bangkok, Thailand. The plating sludge was oven dried and ground to a particle size less than 0.5 mm. The ground sludge was digested using microwave digestion (Milestone, method no. 328). The concentration of heavy metals was analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) as shown in Table 2.

2.2 Sample preparation

Lime-PFA cement samples were prepared using lime and PFA at the ratio of 25:75, 30:70 and 35:65. Sodium silicate solution was added to the optimum proportion between lime and PFA at 0, 4, 6 and 8 vol./wt.% of cementitious binder. A water-to-solid ratio for each mixture was obtained by conducting normal consistency following ASTM 187-86 [12] and is shown in Table 3. The initial pHs of Na_2SiO_3 solutions increased from 12.46 to 12.51 when the amount of Na_2SiO_3 solution increases from 4 to 8 vol./wt.%.

The slurry was mixed following ASTM 305-94 standard test [13] to achieve a uniform distribution, and later transferred to the cylindrical plastic mold. The optimum concentration for Na_2SiO_3 was selected by determining the strength development of lime-PFA cement pastes during the first 28 days of curing under room temperature (30-32 °C). The plating sludge was then loaded to the optimum mix design at 0, 10, 20, 30 and 50 wt.%. Water requirement for each mix is shown in Table 3.

2.3 Unconfined compressive strength test

Cylindrical samples with 50 mm in diameter and 100 mm in height were tested for strength and were measured following ASTM D 1633-96 test method [14]. The strength development of lime-PFA pastes and alkali-activated PFA pastes was determined after curing for 1, 3, 7, 14, 21 and 28 days, whereas those of the solidified wastes were tested at the age of 1, 3, 7, 14, 21, 28, 56 and 91 days. A set of three samples was used for the test to ensure the reproducibility of the results.

2.4 Leaching test

Metal leaching from the solidified wastes was assessed using TCLP, as defined by the U.S. EPA SW-846. Samples used for leaching testing were cured for 28 days and ground to a particle size less than 9.5 mm. The samples were extracted with 0.1 N acetic acid solution (initial pH of 2.88) and rotated in an end-over-end manner at 30 rpm for 18 hours. The leachates was filtered through a 0.45 μm. membrane filter to remove suspended solids. pH of the leachates was measured and the concentration of heavy metals present in the leachates were determined by ICP-AES. Leachates were analyzed in triplicate and the mean values were reported.

3. Results and discussion

3.1 Strength development of Lime-PFA cement

Fig. 1 shows strength development of lime-PFA cements containing lime and PFA at the ration of 25:75, 30:70 and 35:65. Experimental results showed that cement pastes made from lime and PFA at the ration of 25:75 gave the highest strength at all curing duration observed. This is because the PFA used in this work has CaO content around 16 wt.% which does not undergo self-cementing reactions like OPC.

Addition of hydrated lime to PFA increases the pH of the system. This results in the dissociation of SiO_2 from the surface of PFA particles and SiO_4^{4-} was obtained. The SiO_4^{4-} was then reacted with Ca^{2+} dissociated from lime and as a result, CSH gels were formed, which are responsible for strength development of lime-PFA cement [15].

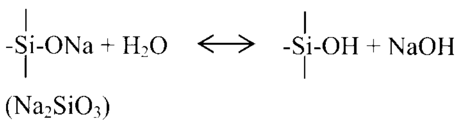
In addition, the rate of strength development was observed to decrease at increasing amount of lime. This is because the amount of PFA reduced when lime was added at an increasing amount, and as a result, less CSH gels were produced. From this experimental result, lime-PFA cement at the ration of 25:75 was selected for further study.

3.2 Strength development of Lime-PFA cements in the presence of Na_2SiO_3

Compressive strength of lime-PFA cements in the presence of Na_2SiO_3 solution, as a function of curing time, is shown in Fig. 2. A significant higher rate of strength development of lime-PFA cements with Na_2SiO_3 solution was observed compared to those without. Strength of lime-PFA cements with 4, 6 and 8 vol./wt.% of Na_2SiO_3 solution increased by 329, 1012 and 1259 %, respectively at the age of 1 day. It is observed that the strength increased at a decreasing rate when the curing duration was increased.

When Na_2SiO_3 solution was added to the mixture of lime-PFA cements, it hydrolyzes and forms NaOH. This increases the pH value of the system and resulted in the breakdown of the covalent bonds of Ca-O, Si-O and Al-O from the glassy surface of PFA particles as shown in the following reactions:

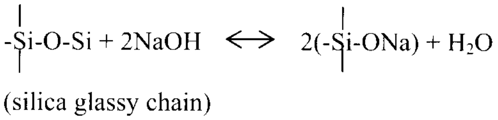
i) Na_2SiO_3 hydrolyzes with H_2O and forms NaOH.



$$-\mathrm{Si}-ONa + H_2O \longleftrightarrow -\mathrm{Si}-OH + NaOH$$

(Na_2SiO_3)

ii) NaOH disintegrates Si-O.



$$-\mathrm{Si}-O-\mathrm{Si} + 2NaOH \longleftrightarrow 2(-\mathrm{Si}-ONa) + H_2O$$

(silica glassy chain)

Na ion in $-\mathrm{Si}-ONa$ is replaced by Ca ion dissociated from Ca-O, and CSH gels are formed [16-17].

Lime-PFA cements activated with 8 vol./wt.% Na_2SiO_3 solution gave higher strength than those activated with 6 vol./wt % Na_2SiO_3 solution, but was not statistically significant. In the following experiment, lime-PFA cement with 6 vol./wt.% Na_2SiO_3 solution was selected for further study on waste loading.

3.3 Strength development of the solidified wastes

Strength development of lime-PFA cements activated with 6 vol./wt.% Na_2SiO_3 solution, and in the presence of the plating sludge at different concentrations, is shown in Fig.3. Addition of the plating sludge to lime-PFA cement resulted in significant strength reduction at all curing durations. When the plating sludge was added at 10 wt.%, the strength of the solidified wastes decreased from 47.7 to 2.8 kg/cm^2 at the age of 1 day. This is generally known to be caused by the retardation effects from several metals present in the plating sludge, especially zinc hydroxide [18-21].

The strength of the solidified waste decreased with increasing concentration of the plating sludge. It was found that the 28-day strength of the solidified wastes decreased from 186 to 44, 27, 20 and 6.5 kg/cm^2 when the plating sludge was added at 10, 20, 30 and 50 wt.%, respectively. Strength reduction of the solidified wastes could also be resulted from the dilution effect with a less reactive binder when the plating sludge was added at an increasing amount. In addition, lime-PFA cement with 6 vol./wt.% Na_2SiO_3 solution can contain up to 50 wt.% plating sludge and has strength around 6.5 kg/cm^2 which meets the regulation for landfilling of the Ministry of Industry (3.5 kg/cm^2).

3.4 Metals leaching from the solidified wastes

Table 4 shows pH of leachates and concentration of heavy metals in TCLP leachates. Experimental results showed that pH values of the extraction fluid increased from 2.8 to 11.3, 11.9, 11.7, 10.8 and 9.0 after contact with samples containing 0, 10, 20, 30 and 50 wt.% plating sludge, respectively. Leachate pHs were observed to decrease with increasing concentration of the plating sludge. This is from the dilution effect on lime-PFA cements when the concentration of the plating sludge increased.

TCLP results showed that concentrations of Pb and Cd in TCLP leachates were below analytical detection limits, whereas Cr and Zn were found at concentrations lower than the U.S. EPA regulatory limit of 5 mg/L. In addition, Cu was found at concentration greater than 2 mg/L, regulated by the Ministry of Industry, when the plating sludge was added at 20 and 30 wt.%, except for the sample containing 50 wt.% plating sludge. It is possible that the TCLP leachate after contacting with a sample containing 50 wt.% plating sludge had a pH value of 9, which is the pH value for minimum solubility of Cu. As a result, solubilization of Cu from the solidified wastes was low [3].

4. Conclusions

The following conclusions can be drawn:

1. The highest compressive strength observed during 28 days of curing was obtained from lime-PFA cement at the ration of 25:75.
2. A significant high rate of strength development was found from lime-PFA cements with Na_2SiO_3 solution during the first 14 days of curing.
3. The plating sludge can be loaded as high as 50 wt.% to the lime-PFA cements with 6 wt.% Na_2SiO_3 solution and has compressive strength that meets the minimum requirement for placing in the landfill.
4. Leachability of heavy metals, for example Pb, Cr, Cd, and Zn, did not exceed the regulatory limits of the U.S.EPA and the Ministry of Industry, except for Cu.
5. Effect of curing duration on leachability of heavy metals from the solidified wastes and durability to corrosion by various acid solutions is under investigation.

5. Acknowledgements

The authors would like to give special thanks to the National Science and Technology Development Agency for provision of financial support to this work. The Electricity Generating Authority of Thailand (EGAT) deserved appreciation for provision of PFA. The authors would also wish to acknowledge the Department of Civil Engineering and Department of Civil Technology Education, Faculty of Engineering KMUTT, for providing access to their laboratories.

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Table 1. Chemical composition of PFA (wt. %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	Na_2O	Loss on Ignition
38.20	21.91	14.57	16.07	2.60	2.91	1.89	1.07	0.10

Table 2. Concentration of heavy metals in the plating sludge (mg/kg dry sludge)

Lead	Chromium	Cadmium	Zinc	Iron	Copper
2752	39819	145	191658	78235	2194

Table 3. Water solid ratio for each mixture (wt.% of cementitious binder)

Composition of	Water/Solid	Water/Solid in the presence of Na_2SiO_3 solution
Lime : PFA		
25 : 75	33.0	35.0
30 : 70	35.0	-
35 : 65	37.0	-
Cementitious binder : Sludge		
90 : 10	38.0	39.8
80 : 20	39.0	40.6
70 : 30	40.0	41.4
50 : 50	42.0	43.0

Table 4. pH and metal concentrations in TCLP leachates.

Sample	Solidified waste (Binder : Sludge)	Concentration (mg/L)						pH
		Pb	Cr	Cd	Cu	Fe	Zn	
		5*	5*	1*	2**	-	5**	
Lime-PFA + 6 vol./wt.% Na_2SiO_3	100 : 0	BD	BD	BD	BD	0.04	BD	11.34
	90 : 10	BD	BD	BD	0.83	0.02	1.47	11.90
	80 : 20	BD	0.02	BD	2.32	0.27	1.35	11.68
	70 : 30	BD	0.13	BD	2.61	0.25	2.25	10.75
	50 : 50	BD	0.18	BD	0.84	0.45	4.05	9.02

*: US.EPA Regulatory limits
**: Ministry of Industry, Thailand Regulatory limits
BD = Below analytical detection limit.

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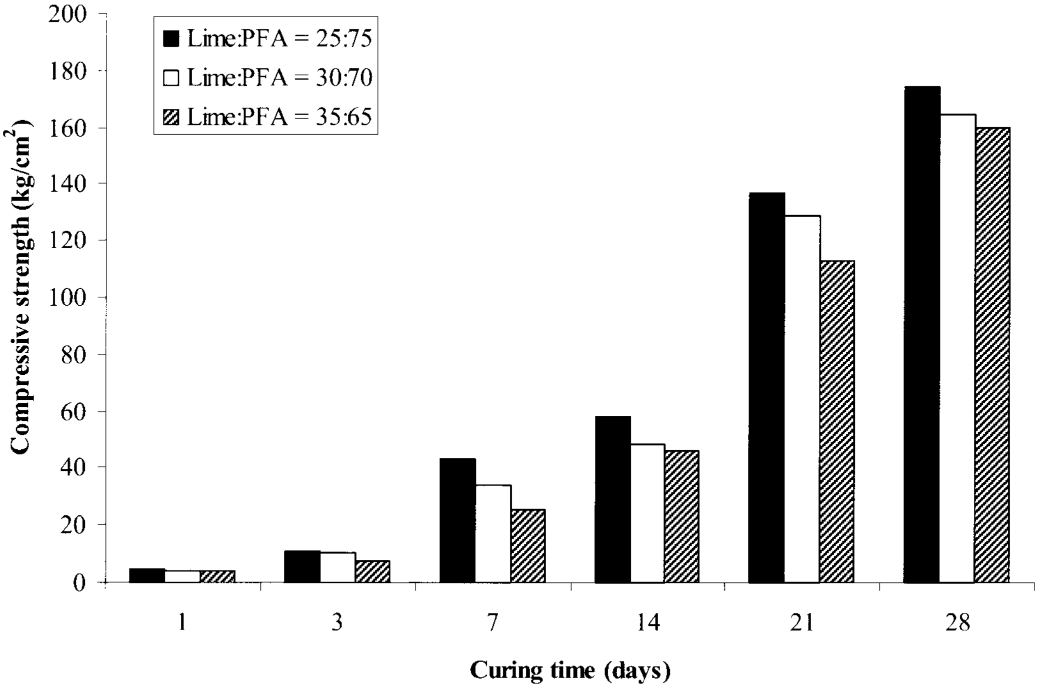

Figure 1 Strength development of lime-PFA cements

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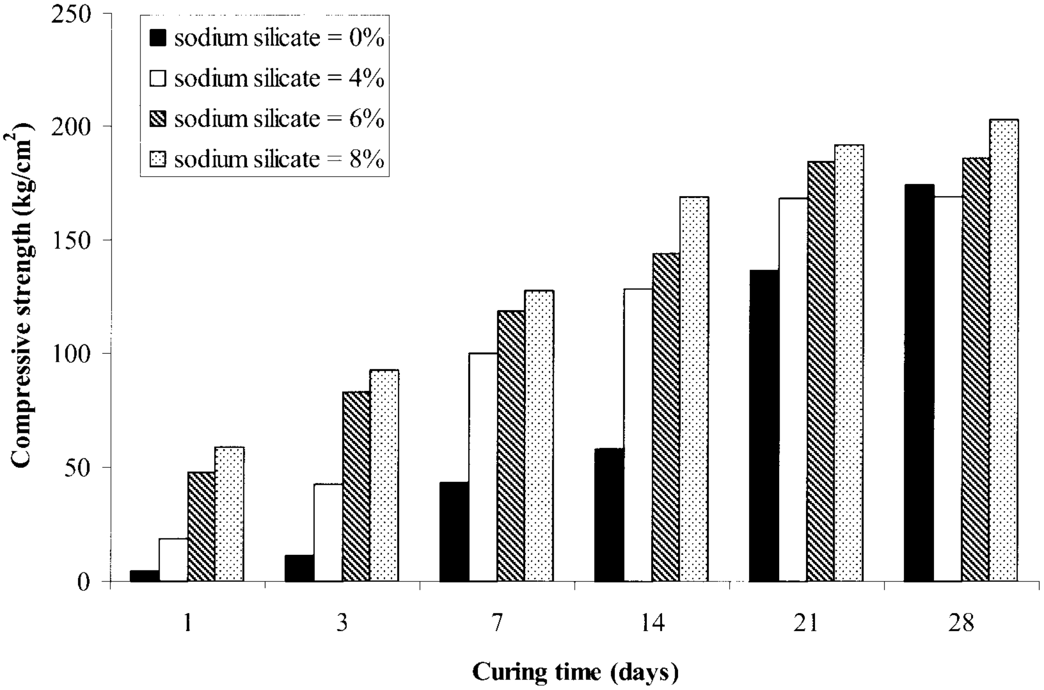

Figure 2 Strength development of lime-PFA cements in the presence of Na_2SiO_3

Immobilization of the Plating Sludge by Activation of Pulverized Fuel Ash with Sodium Silicate Solution

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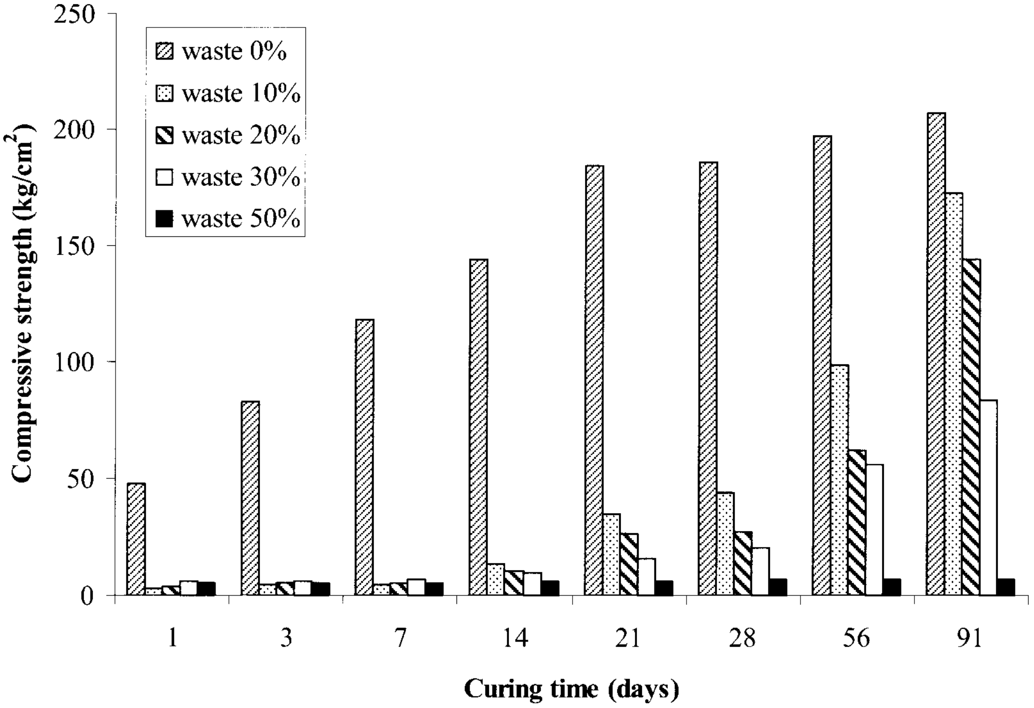

Figure 3 Strength development of lime-PFA cements with Na_2SiO_3 solution 6 vol./wt.% and in the presence of the plating sludge.