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Solidification of electroplating sludge using alkali-activated pulverized fuel ash as cementitious binder

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Abstract

This work investigated the potential for utilization of alkali-activated PFA as solidification binder to treat electroplating sludge. The sludge was solidified using 30 wt.% of lime and 70 wt.% of PFA. Two alkali activators, Na_2SiO_3 and Na_2CO_3, were added at 0, 4, 6, and 8 wt.%. Results showed that early strength development of lime-PFA cements with Na_2SiO_3 and Na_2CO_3 was considerably higher than those without. Addition of electroplating sludge resulted in reduced strength. The strength reduction was greater when 4% Na_2SiO_3 activator was used than when 8% Na_2CO_3 activator was used. A higher pH of Na_2SiO_3 solution (pH = 13.5) compared to that of Na_2CO_3 solution (pH = 11.9) resulted in resolubilization of metal hydroxides from the electroplating sludge, which competed with calcium ion for soluble silicate. In addition, Pb, Cd, and Cu were not found in the toxicity characteristic leaching procedure (TCLP) leachates. Cr, Zn, and Fe were detected and in some cases Cr exceeded U.S. EPA allowable limits.

Keywords: Electroplating sludge; Pulverized fuel ash; Alkali activation; Strength; Leaching

1. Introduction

Stabilization/solidification processes are waste treatments designed to improve the handling and physical characteristics of liquids or semisolids and decrease the degree of hazard of the disposed wastes. These processes are based on hydraulic reactions of hydraulic cements or pozzolanic reactions between Portland cement or lime and pozzolanic materials such as pulverized-fuel ash, cement kiln dust, and rice husk ash [1,2]. The development of hydration products provides an interlocking framework to physically encapsulate waste particles and is also responsible for the strength development of the monolithic solid. The leaching characteristics of the treated waste are expected to reduce because of the reduced surface area exposed to the environment and the isolation of the waste from the environment due to the formation of the low permeability cement matrix.

Pozzolanic materials are high in SiO_2 and often also in Al_2O_3, and low in CaO. 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 [3]. The slow pozzolanic reactions have 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 reactions could be accelerated using either chemical or thermal activation [4–7].

Several research works on cements have been based on the activation of granulated blast-furnace slags by alkalis [8–13]. The hydration products and pore structure characteristics of these alkali-activated slag cement concrete and mortar varied with the nature and dosage of activators. Na_2SiO_3 was found to be the most effective activator among NaOH, Na_2CO_3, Na_3PO_4, and Na_2SiO_3 for certain types of granulated blast furnace slag [9,12]. Only a small amount of work has been done on the alkali activation of PFA [14,15].

PFA is discharged every year in large quantities from power plants. There is an increasing interest to find new uses for this type of ash, other than construction applications. In this work, alkali-activated PFA was used as low-cost cementitious binder to solidify the electroplating sludge. Compressive strength and leachability of heavy metals from the solidified electroplating sludge were deter-

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mined to assess the potential for utilization of alkali-activated PFA as a solidification binder.

2. Experimental procedure

2.1. Materials

PFA used in this investigation was a pozzolanic waste generated during the combustion of coal at the Electricity Generating Authority of Thailand (EGAT) in Lumpang Province. PFA was then ground to a particle size of less than 45 μm using Los Angeles Abrasion Machine. Chemical composition of PFA was determined by X-ray fluorescence and is shown in Table 1. The main composition of SiO_2, Al_2O_3, and Fe_2O_3 contents of PFA was 73.34%, which was classified as pozzolans class F following ASTM C 618-97.

Sodium silicate ($Na_2SiO_3 \cdot 5H_2O$) and anhydrous sodium carbonate (Na_2CO_3) were used as chemical activators for lime-PFA cement during solidification of electroplating sludge.

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 of less than 0.5 mm. The ground sludge was digested using concentrated nitric acid and the concentration of heavy metals was analysed using atomic absorption spectroscopy (AAS) as shown in Table 2.

2.2. Sample preparation

Lime-PFA cement samples were prepared using 30 wt.% of lime and 70 wt.% of PFA. Two alkali activators, Na_2SiO_3 and Na_2CO_3, were added to activate reactions between lime and PFA at 0, 4, 6, and 8 wt.% of lime/PFA mixtures. A water-to-solid ratio of 0.5 was used for all mixes. Na_2SiO_3 and Na_2CO_3 were first dissolved in mix water and then added to the lime-PFA mixtures. The initial pHs of Na_2SiO_3 and Na_2CO_3 solutions were in the range of 13.5–13.6 and 11.8–11.9, respectively. The slurry was then mixed following the ASTM C 305-94 standard test method to achieve a uniform distribution, and later transferred to the cylindrical plastic mould.

The optimum concentration for each activator was selected by determining the strength development of lime-PFA cement pastes during the first 14 days. Electroplating sludge was then loaded to the optimum mix design at 0, 10, 20, 30, and 50 mass%. Strength development as a function of curing time and metal leaching from the solidified wastes were tested to evaluate the performance of the solidified waste forms.

Table 1
Chemical composition of pulverized fuel ash (wt.%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	Na_2O	LOI
39.7	21.69	11.95	12.76	3.65	2.82	2.09	1.39	0.17

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

Lead	Chromium	Cadmium	Zinc	Iron	Copper
124.3	43,058	6.7	155,254	7644	19.1

2.3. Unconfined compressive strength test

Compressive strength of the solidified wastes was measured following ASTM D 1633-96 test method, using 50 mm in diameter and 100 mm in height molded cylinders as test specimens. The strength development of the alkali-activated PFA pastes was determined after curing for 1, 3, 7, and 14 days, whereas those of the solidified wastes were tested at the age of 14, 28, 56, and 91 days. A set of five samples was used for the compression test and the arithmetic average was made from five observations.

2.4. Leaching test

Metal leaching from the solidified wastes was assessed using toxicity characteristic leaching procedure (TCLP), as defined by the U.S. EPA, on the samples cured for 28 days. The leachates were filtered through a 0.4-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 AAS. Each leachate was analysed in triplicate and the mean values were reported to ensure the reproducibility of the data.

3. Results and discussion

3.1. Strength development of lime-PFA cements in the presence of Na_2SiO_3 and Na_2CO_3

Compressive strength of lime-PFA cements in the presence of Na_2SiO_3 and Na_2CO_3 as a function of curing time is shown in Fig. 1a and b. Results show that the rate of strength development of lime-PFA cements in the presence of Na_2SiO_3 and Na_2CO_3 was considerably higher compared to those without. Several researchers [14–16] reported that the high pH of Na_2SiO_3 and Na_2CO_3 solutions resulted in the breakdown of the covalent bonds of Ca–O, Si–O, and Al–O from the glassy surface of PFA. This causes the dissolution of calcium, silicon, and aluminium ions, and as a result, calcium silicate hydrate (CSH) gels are formed, which is responsible for the early strength development of lime-PFA cements.

The maximum rate of strength development of lime-PFA cements was achieved at 4% dosage of Na_2SiO_3 and 8% dosage of Na_2CO_3. Strength of lime-PFA cements with 4 wt.% of Na_2SiO_3 increased by 66.7%, 87.5%, 200%, and

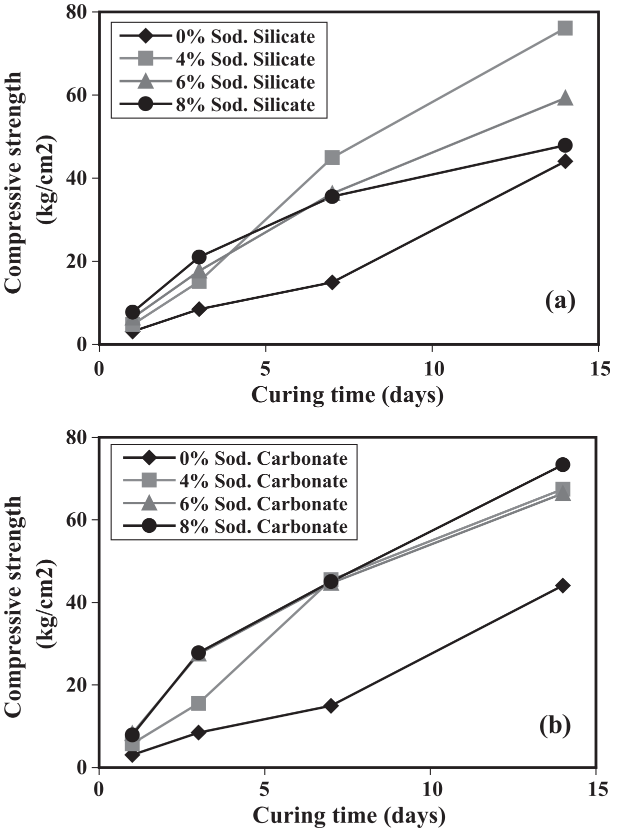

Fig. 1. Strength development of lime-PFA cements in the presence of chemical activators: (a) Na_2SiO_3 and (b) Na_2CO_3.

72.7%, whereas those with 8 wt.% addition of Na_2CO_3 gave an increase of strength by 167%, 250%, 200%, and 66% after curing for 1, 3, 7, and 14 days, respectively. The calcium ion is likely to dissociate into the solution more than silicon and aluminium ions because the Ca—O bond is much weaker than Si—O and Al—O bonds. In the presence of Na_2SiO_3, the calcium ion in the solution reacts rapidly with the silicon ion, hydrolyzed from Na_2SiO_3, and formed CSH gels. The precipitation of these CSH gels on the surface of PFA is retarded and controlled by the diffusion of ions through the precipitated products [16].

When Na_2CO_3 is added, the concentration of soluble silicate in the solution is much lower at the beginning than when soluble Na_2SiO_3 is added. The soluble silicate ions, which dissociate from PFA, are slowly accumulated in the solution until the conditions for precipitation of the hydration products are reached. The hydration products are formed far away from PFA particle [17]. As a result, the dissolution of ions from the surface of PFA and the precipitation of the hydration products continue at a higher rate, and therefore the rate of the strength development was higher.

3.2. Compressive strength of the solidified wastes

Fig. 2a and b show the strength development of alkali-activated (4% Na_2SiO_3 or 8% Na_2CO_3) PFA cements containing electroplating sludge in different concentrations. It is observed that the rate of strength development of the solidified electroplating sludge decreased with increasing concentration of the sludge. This reduction in strength was reported to be caused by the resolubilization of metal hydroxides from electroplating sludge in the highly alkaline environment of lime-PFA cements [18]. These soluble metals were then reacted with soluble silicates and carbonates. It could be possible that these metal silicates and carbonates were deposited on the surface of PFA and were responsible for hydration retardation between lime and PFA [19]. In addition, strength reduction of the solidified wastes could be resulted from the dilution effect with a less reactive binder when the plating sludge was added at an increasing amount.

The addition of electroplating sludge at increasing concentration to the lime-PFA cements with 4 wt.% of Na_2SiO_3 resulted in a greater reduction in strength of the solidified wastes as compared to those with 8 wt.% of Na_2CO_3. It can be hypothesized that the higher pH of Na_2SiO_3 solution (pH = 13.5) compared to that of Na_2CO_3 solution (pH = 11.9) results in extensive resolubilization of several metal hydroxides from the electroplating sludge due to the amphoteric characteristic of most metal hydroxides. As a

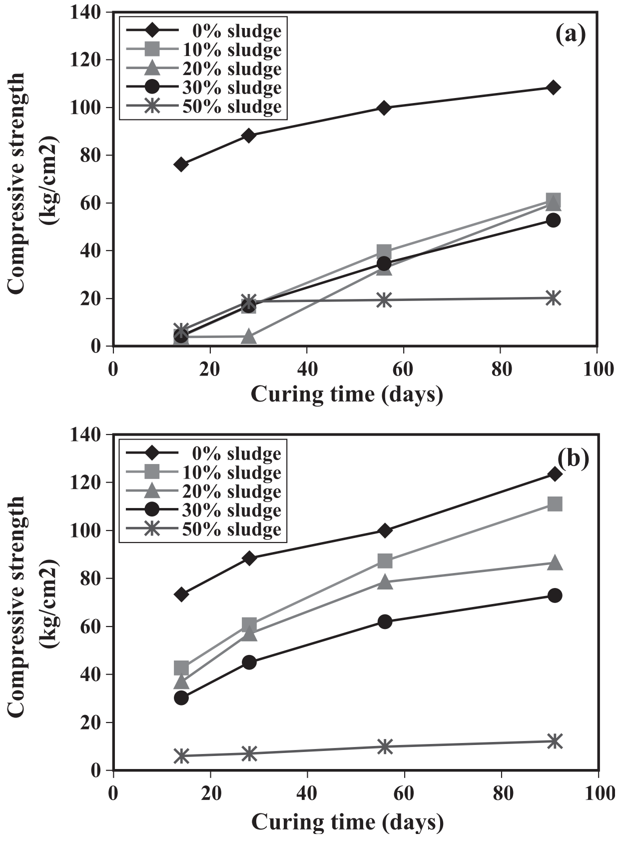

Fig. 2. Strength development of alkali-activated PFA cements containing electroplating sludge at different concentration: (a) 4% Na_2SiO_3 and (b) 8% Na_2CO_3.

Table 3
Final pHs and metal concentrations in the TCLP leachates from the solidified electroplating wastes

Sample	Electroplating sludge (wt.%)	Concentration (mg/l)						Final pH
		Pb	Cr	Cd	Zn	Fe	Cu	
Lime/PFA + 4 wt.% Na$_2$SiO$_3$	10	bd	3.1	bd	102	4.5	bd	11.9
	20	bd	8.6	bd	197	5.7	bd	11.8
	30	bd	18.0	bd	205	6.1	bd	11.7
	50	bd	7.9	bd	174	5.3	bd	9.7
Lime/PFA + 8 wt.% Na$_2$CO$_3$	10	bd	2.7	bd	77	3.8	bd	9.8
	20	bd	4.4	bd	118	3.9	bd	9.6
	30	bd	6.0	bd	124	4.2	bd	9.1
	50	bd	9.7	bd	185	4.3	bd	8.4

bd = Below analytical detection limit.

result, soluble metal hydroxides are present in the solution at high concentration and compete with calcium ion for soluble silicate.

3.3. Metals leaching from the solidified wastes

The final values of pH and metal concentrations in the TCLP leachates from the solidified electroplating wastes are shown in Table 3. It was found that leachate pHs from the solidified electroplating wastes with 4 and 8 wt.% of Na$_2$SiO$_3$ and Na$_2$CO$_3$ decreased from 11.9 to 9.7 and from 9.8 to 8.4, respectively, when the concentration of electroplating sludge increased from 10 to 50 wt.%. This is because the lime-PFA cement content decreased when the concentration of electroplating sludge increased, and consequently, the ability of the solidified waste matrices to neutralize acid was reduced.

Pb, Cd, and Cu concentrations were below analytical detection limit of AAS. Cr, Zn, and Fe levels were detected. Results showed that the concentration of Cr in the leachates exceeded the U.S. EPA regulation for TCLP (5 mg/l) when the electroplating sludge was loaded by more than 10 and 20 wt.%, respectively. Metal concentrations in the leachates tended to increase as the initial metal concentration was growing in the solidified wastes, but there is no linear relationship between the amount of metal leached and the initial concentration. In addition, metal leaching from the solidified wastes with 8 wt.% Na$_2$CO$_3$ was found in a lower concentration than from those with 4 wt.% Na$_2$SiO$_3$. This is likely because leachate pHs from the solidified wastes with 8 wt.% Na$_2$CO$_3$ ranged between 8.4 and 9.8, being adequate to stabilize most metal hydroxides whose solubilities are strongly pH dependent.

4. Conclusions

1. The early strength development of lime-PFA cements in the presence of Na$_2$SiO$_3$ and Na$_2$CO$_3$ was considerably higher than the strength development of those without these compounds. The maximum strength development was achieved at 4 and 8 wt.% dosage of Na$_2$SiO$_3$ and Na$_2$CO$_3$, respectively.
2. The addition of electroplating sludge in an increasing concentration to the lime-PFA cements with 4 wt.% of Na$_2$SiO$_3$ resulted in a greater reduction in strength of the solidified wastes than for those with 8 wt.% of Na$_2$CO$_3$.
3. Pb, Cd, and Cu leachate concentrations were below the analytical detection limit of AAS. Higher concentrations were measured for Cr, Zn, and Fe. The quantity of Cr, Zn, and Fe leached tended to increase as the initial concentration of these metals and leachate pHs were growing. For higher loading percentages, the Cr leached was above U.S. EPA limits.

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References

[1] C.C. Wiles, A review of solidification/stabilization technology, J. Hazard. Mater. (14) (1987) 5–21.
[2] M.J. Cullinane Jr., L.W. Jones, Solidification and stabilization of hazardous wastes, Hazard. Mater. Cosntr. 2 (1) (1989) 9–17.
[3] H.F.W. Taylor, Cement Chemistry, Academic Press, Great Britain, 1990, pp. 290–298.
[4] C. Shi, X. Wu, M. Tang, Hydration of alkali-slag cements at 150 °C, Cem. Concr. Res. 21 (1991) 91–100.
[5] C. Shi, R.L. Day, Chemical activation of blended cements made with lime and natural pozzolans, Cem. Concr. Res. 23 (1993) 1389–1396.
[6] C. Shi, R.L. Day, Acceleration of strength gain of lime-pozzolan cements by thermal activation, Cem. Concr. Res. 23 (1993) 824–832.
[7] D.M. Roy, Alkali-activated cements: opportunities and challenges, Cem. Concr. Res. 29 (1999) 249–254.
[8] F. Collins, J.G. Sanjayan, Early age strength and workability of slag pastes activated by NaOH and Na$_2$CO$_3$, Cem. Concr. Res. 28 (1998) 655–664.
[9] C. Shi, Strength, pore-structure and permeability of alkali-activated slag mortars, Cem. Concr. Res. 26 (1996) 1789–1799.
[10] F. Collins, J.G. Sanjayan, Workability and mechanical properties of alkali activated slag concrete, Cem. Concr. Res. 29 (1999) 455–458.
[11] F. Collins, J.G. Sanjayan, Effects of ultra-fine materials on workability and strength of concrete containing alkali-activated slag as the binder, Cem. Concr. Res. 29 (1999) 459–462.
[12] T. Bakharev, J.G. Sanjayan, Y.B. Cheng, Alkali activation of Australian slag cements, Cem. Concr. Res. 29 (1999) 113–120.
[13] S. Song, H.M. Jennings, Pore solution chemistry of alkali-activated ground granulated blast-furnace slag, Cem. Concr. Res. 29 (1999) 159–170.
[14] Y. Fan, S. Yin, Z. Wen, J. Zhong, Activation of fly ash and its effects on cement properties, Cem. Concr. Res. 29 (1999) 467–472.
[15] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes: a cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.

[16] C. Shi, R.L. Day, A calorimetric study of early hydration of alkali-slag cements, Cem. Concr. Res. 25 (1995) 1333–1346.
[17] C. Shi, R.L. Day, Pozzolanic reaction in the presence of chemical activators: Part II. Reaction products and mechanism, Cem. Concr. Res. 30 (2000) 607–613.
[18] S. Asavapisit, G. Fowler, C.R. Cheeseman, Solution chemistry during cement hydration in the presence of metal hydroxide wastes, Cem. Concr. Res. 27 (1997) 1249–1260.
[19] J.R. Conner, Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold, New York, 1990, pp. 82–91.