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Strength, leachability and microstructure characteristics of cement-based solidified plating sludge

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Abstract

The solidification of the stabilized zinc–cyanide plating sludge was carried out using ordinary Portland cement (OPC) and pulverized fuel ash (PFA) as solidification binders. The plating sludge were used at the level of 0%, 10%, 20% and 30% dry weight, and PFA was used to replace OPC at 0%, 10%, 20% and 30% dry weight, respectively. Experimental results showed that a significant reduction in strength was observed when the plating sludge was added to both the OPC and OPC/PFA binders, but the negative effect was minimized when PFA was used as part substitute for OPC. SEM observation reveals that the deposition of the plating sludge on the surface of the clinkers and PFA could be the cause for hydration retardation. In addition, calcium zinc hydroxide hydrate complex and the unreacted di- and tricalcium silicates were the major phases in X-ray diffraction (XRD) patterns of the solidified plating waste hydrated for 28 days, although the retardation effect on hydration reactions but Cr concentration in toxicity characteristic leaching procedure (TCLP) leachates was lower than the U.S. EPA regulatory limit.

Keywords: Strength; TCLP; Plating sludge; SEM; XRD

1. Introduction

Stabilization/solidification processes are waste treatments designed to improve the handling and physical characteristics of liquids or semisolids and decrease the release of hazard to the environment. The processing technique normally involves simply mixing wastes with solidification binders. These processes are based on the hydraulic reactions of the hydraulic cements or pozzolanic reactions between Portland cement or lime and pozzolanic materials. Pulverized fuel ash (PFA) is an example of a pozzolanic material that is frequently used in combination with Portland cement.

The chemical changes that take place as a result of the interaction between waste components and solidification binders play an important role in controlling the quality of cement-based solidified waste products. Several studies have demonstrated that the retardation and, in some cases, inhibition of cement hydration reactions results from the addition of stabilized wastes containing heavy metals [1–3]. The complexity and highly variable of real wastes could

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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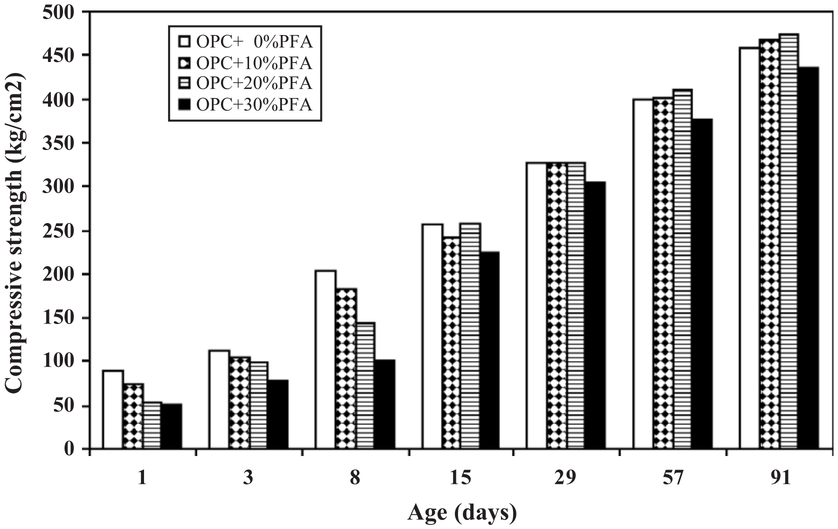

Fig. 1. Strength development of various proportions of OPC/PFA mixes as a function of curing time.

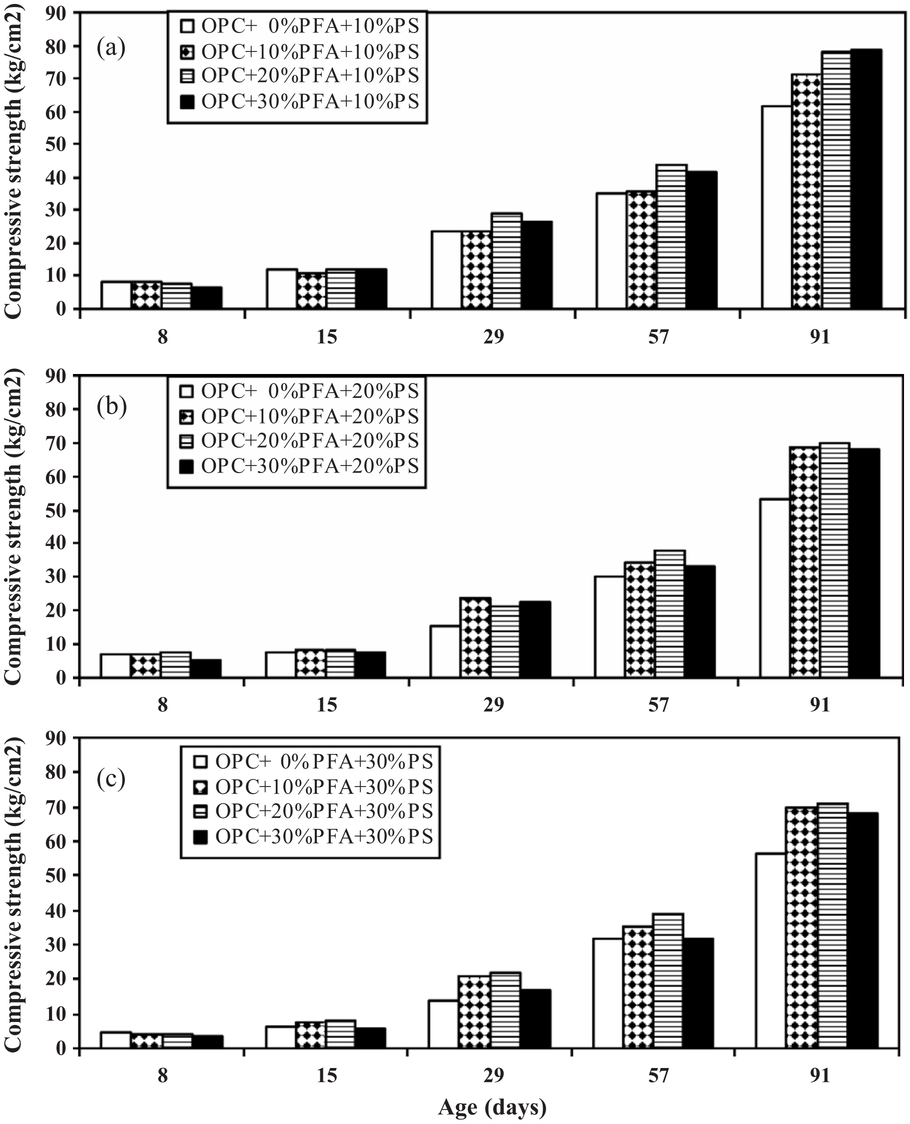

Fig. 2. Strength development of the solidified wastes in the presence of different amounts of the plating sludge: (a) 10 wt.% PS; (b) 20 wt.% PS; and (c) 30 wt.% PS.

induce undesirable effects and produce the solidified wastes with reduced qualities [4].

Several metal oxides and hydroxides (Cr, Cu, Fe, Pb, Zn, Cd and Hg) were reported to promote the growth of large crystals of ettringite [5–7]. This contributes to the expansion of the hardened cement, and, as a result, a decrease in strength was observed. Although strength requirements for solidified wastes are not as important as those for structural concretes, failure to obtain adequate strength is an indicator of a poor microstructure and may be expected to lead to increased leaching [8].

In this work, pulverized fuel ash that is discharged from coal-fired power station was used in combination with ordinary Portland cement (OPC) at different proportions to solidify the stabilized plating sludge from a zinc–cyanide electroplating process. The strength development and leachability of metal contaminants using the toxicity characteristic leaching procedure (TCLP) were studied to evaluate the quality of the solidified waste forms. In addition, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to examine the crystalline phases and the microstructures of the solidified plating wastes.

2. Materials and methods

2.1. Materials

OPC Type 1 used throughout this research work was from The Siam Cement Public Company. 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 oxide contents of OPC and PFA were obtained by the suppliers and are shown in Table 1.

Electroplating sludge was brought from the wastewater treatment plant of a 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 inductively coupled plasma atomic emission spectrometry (ICP-AES). Zn, Fe and Cr were the main metals present in the plating sludge at concentration of 265, 21.1 and 11.9 g/kg dry sludge, respectively.

2.2. Sample preparation

PFA was used to substitute for OPC at 0, 10, 20 and 30 wt.%, and the dried and ground plating sludge was added at 0%, 10%, 20% and 30% dry weight, respectively. The dry solid was mixed with hand prior to the addition of mixing water. 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. The mixes were allowed to solidify in the sealed plastic moulds to avoid carbonation.

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	1078	2.83	2.92
Pulverize fuel ash (PFA)	5.0	2.24	0.29	0.48
OPC+0% PFA+0% PS	13.0	0.33	0.16	0.24
OPC+10% PFA+0% PS	13.0	0.28	0.22	0.29
OPC+20% PFA+0% PS	12.8	0.50	0.07	0.29
OPC+30% PFA+0% PS	12.7	0.54	0.20	0.29
OPC+0% PFA+10% PS	12.9	1.74	0.19	0.51
OPC+10% PFA+10% PS	12.9	0.60	0.16	0.33
OPC+20% PFA+10% PS	12.8	0.55	0.24	0.65
OPC+30% PFA+10% PS	12.8	1.02	0.45	0.68
OPC+0% PFA+20% PS	12.9	2.88	1.17	0.76
OPC+10% PFA+20% PS	12.8	0.69	1.44	0.68
OPC+20% PFA+20% PS	12.8	0.74	1.21	0.63
OPC+30% PFA+20% PS	12.8	1.44	0.92	0.63
OPC+0% PFA+30% PS	12.8	2.70	1.40	0.79
OPC+10% PFA+30% PS	12.8	1.25	1.61	0.56
OPC+20% PFA+30% PS	12.8	1.51	1.24	0.60
OPC+30% PFA+30% PS	12.7	1.17	1.05	0.61

* Not specified by the U.S. EPA.

2.3. Unconfined compressive strength test

The compressive strength of the solidified wastes was done following ASTM D 1633-96 using moulded cylinders as test specimens. The size of the cylindrical sample was modified, 50 mm in diameter and 100 mm in height. The compressive strength of the blended cement pastes was tested after curing for 1, 3, 8, 15, 29, 57 and 91 days. Due to retardation effect, the 1- and 3-day compressive strengths of the samples containing the plating sludge were not measured. A set of five samples was used for compression test, and the arithmetic average with 95% confidence interval was made from five observations.

2.4. Toxicity characteristic leaching procedure (TCLP)

Metal leaching from the solidified plating wastes was 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 h. The leachate was filtered through a 0.45-μm membrane filter to remove suspended solids and was then divided into two portions. One was used for pH measurement and the other for the determination of metals present in the leachate by ICP-AES. Each extraction was done in triplicate, and the average value was reported to ensure the reproducibility of the data.

2.5. X-ray diffraction (XRD)

The crystalline phases present in the solidified waste samples were characterized using Cu-K_α XRD (Philips PW 1710). Samples cured for 28 days were crushed into powder using a mortar and pestle. The powder was sieved through a 150-μm mesh and was scanned from 10° to 70°.

2.6. Scanning electron microscopy (SEM)

A JSM 35 has been used in this work to examine the phase development and microstructure of the solidified plating wastes. Samples for SEM were demoulded from

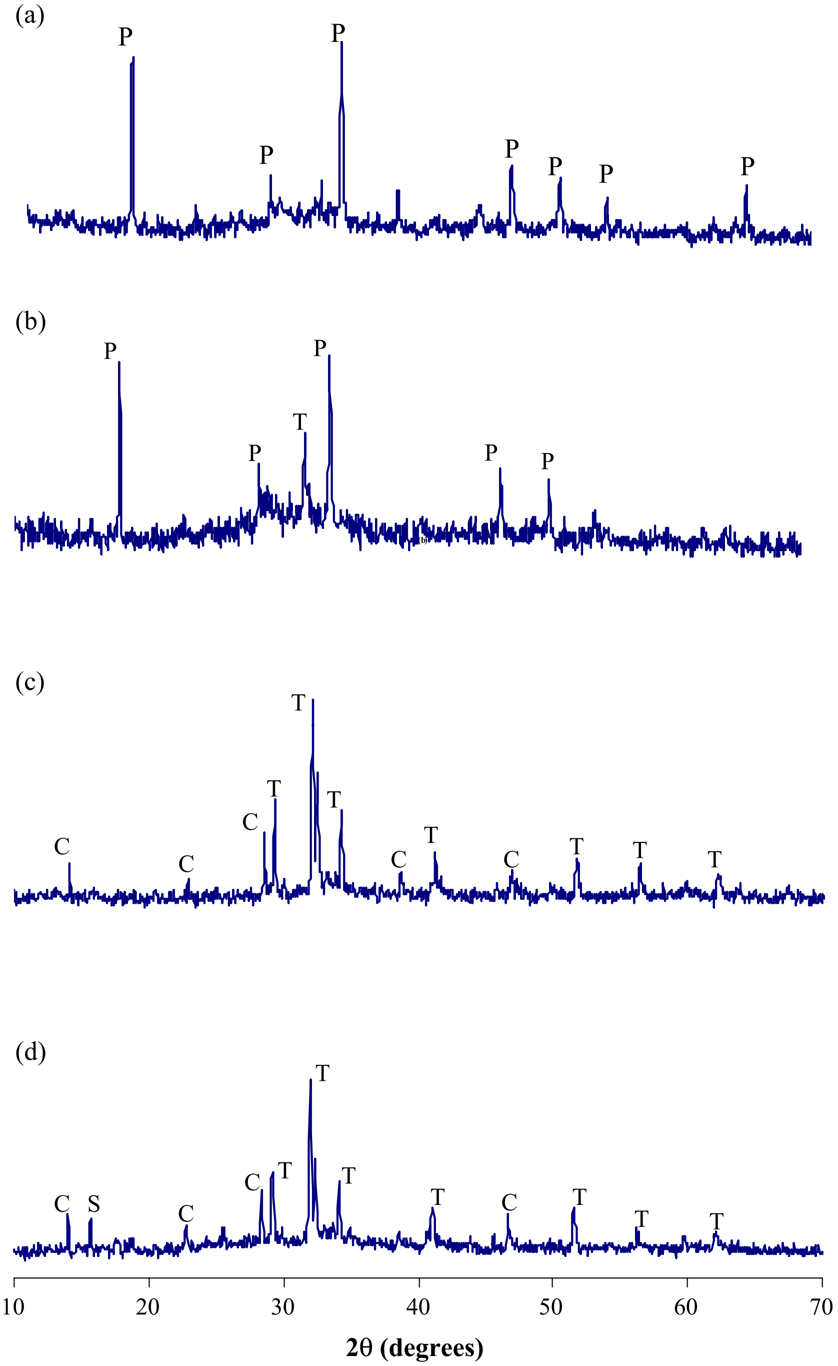

Fig. 3. XRD patterns of cement-based solidified wastes at the age of 28 days: (a) cement paste; (b) OPC/20% PFA paste; (c) OPC/10% PS; and (d) OPC/20% PFA/10% PS. P=portlandite; T=tri- and dicalcium silicate; C=calcium zinc hydroxide hydrate; S=sodium iron oxide hydrate.

cylindrical plastic moulds (25 mm diameter and 25 mm high) after 7 and 28 days of hydration. The sample was crushed, and the central region of the crushed sample with flat surface was selected for analysis. The selected samples were then treated with acetone–alcohol solution to stop the hydration reactions. Carbon was used as a conducting medium to coat the surface of the crushed sample. Carbon-coated samples were kept in a vacuum desiccator for analysis.

3. Results and discussion

3.1. Strength of the blended cement pastes

Fig. 1 shows the strength development of cement paste and cement blended with different amounts of PFA as a function of time. Experimental results showed that the early-age strength development in cement blended with PFA was lower compared with that of the controlled cement paste, followed by a higher strength development at later ages.

The highest strength was observed from cement blended with 20 wt.% PFA during the 29 and 91 days of curing. This is because the calcium hydroxide crystal produced during OPC hydration was consumed during the pozzolanic reaction of PFA, which occurred mostly during these curing durations, and as a result, the secondary calcium silicate hydrate (CSH) gel was formed. It is believed that this secondary CSH gel contributes to the additional strength for the blended cement paste other than the primary CSH gel obtained from the hydration of OPC [9].

3.2. Strength of the solidified plating wastes

The strength development of all solidified wastes incorporating the plating sludge was slowed up to the age of 15 days, but thereafter, the strength was gradually developed to higher values, as shown in Fig. 2a–c. The negative effects caused by the addition of heavy-metal-containing wastes on the strength development of cement-based solidified wastes have been widely reported in the literature [1–3]. Fernández et al. [10] reported that the retardation effect of ZnO was enhanced by the presence of other metal oxides, such as PbO, Cr_2O_3 and Fe_2O_3. It is possible that the presence of several metal hydroxides in the plating sludge, e.g., $Zn(OH)_2$, $Cr(OH)_3$ and $Fe(OH)_3$, at a high concentration could induce severe synergistic negative effects, which retarded the hydration of OPC and the pozzolanic reactions of PFA.

Experimental results showed that the rate of strength development of the solidified wastes using OPC/PFA as solidification binders was higher than using OPC (Fig. 2a–c). Li et al. [11] reported that the replacement of OPC by PFA reduced the alkaline nature of the solidified waste. It could be possible that the alkalinity of the OPC/PFA/PS system reduced to the level that was suitable for immobilization of several metal hydroxides. As a result, the synergistic negative effects caused by the soluble metal ions were reduced [12].

A similar strength development profile of the solidified wastes was observed when the plating sludge was added at an increasing amount (Fig. 2a–c). From the investigation, the plating sludge can be loaded as high as 30 wt.% to the cement blended with 30 wt.% PFA and gave a 29-day compressive strength that meets the minimum requirement for disposal in a secure landfill (3.5 kg/cm^2 or 50 psi).

3.3. TCLP results

Table 2 shows the leachate pHs and metal concentration in TCLP leachates. The pH values of acetic acid leachant after contacting with the plating sludge and PFA increased from an initial pH of 2.8 to 5.9 and 5.0, respectively. The change in pH initiates the resolubilization of metals from the plating sludge and PFA. It was found that Fe and Cr were leached from the plating sludge at much lower concentrations compared with Zn. The release of metal hydroxides from the plating sludge depends on initial concentrations of metal hydroxides present in the plating sludge and the minimum solubility of each metal hydroxide. The pH gradients between leachate (pH 5.9) and the minimum

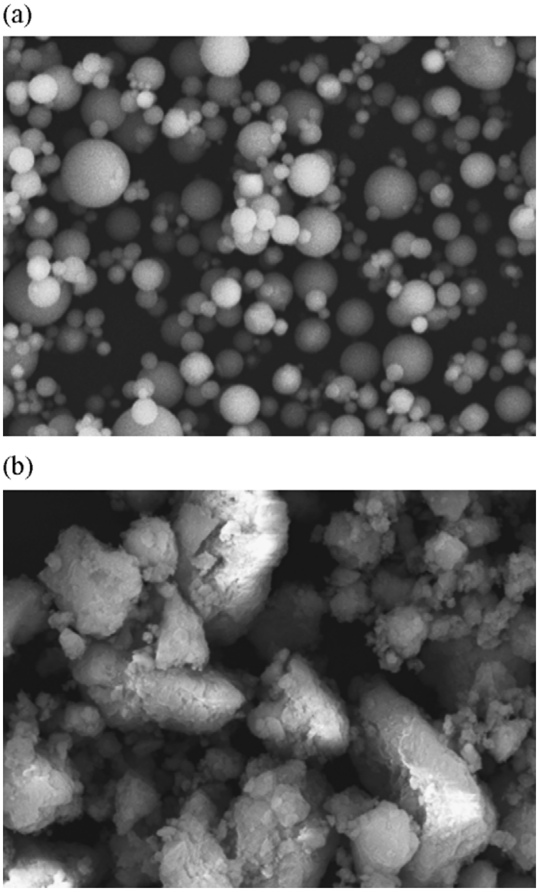

Fig. 4. SEM micrographs of PFA (a) and the plating sludge (b) at a magnification of ×2000.

solubility of Fe and Cr (pH around 7.5 for both metal hydroxides) were smaller than that of Zn (minimum solubility of zinc hydroxide is around 9.5), and therefore, lower leachability of Fe and Cr was observed.

Leachate pHs after contacting with the cement paste increased from an initial pH of 2.8 to 13.0. The dissolution of the available $Ca(OH)_2$ and decalcification of the cement matrix are the main causes of an increase of leachate pH. When OPC was substituted by PFA at increasing amounts, a decrease of leachate pH from 13.0 to 12.7 was noticed. This is because $Ca(OH)_2$, which is highly alkaline, was partly consumed during pozzolanic reactions of PFA, and as a result, the acid neutralization capacity of the OPC/PFA/PS samples decreased [11].

TCLP results showed that the concentration of Cr in the leachate for all solidified waste samples was lower than the limit specified by the U.S. EPA standards. There are no regulatory standards for Zn and Fe because these two metals were not classified as hazardous wastes by the U.S. EPA. In addition, metal concentrations in the TCLP leachates extracted from the cement-based solidified plating wastes were much lower than that extracted from the plating sludge. The TCLP pH found for the stabilized waste is too alkaline for amphoteric metals, such as $Zn(OH)_2$.

3.4. X-ray diffraction

The XRD patterns of cement-based solidified wastes hydrated for 28 days are shown in Fig. 3a–d. Results showed that portlandite [$Ca(OH)_2$] was the major crystalline phases dominated the XRD pattern of cement paste (Fig. 3a). When PFA was blended with OPC at 20 wt.% (Fig. 3b), portlandite and the unreacted di- and tricalcium silicates were detected. There is also a broad and diffuse hump that appears between 28° and 34°. This hump could be either the glass structure of PFA or the formation of poorly crystalline calcium silicate hydrate.

Similar XRD patterns were observed when the plating sludge was added to the OPC and OPC/PFA systems (Fig. 3c–d). Two major crystalline phases detected in these samples were the unreacted di- and tricalcium silicates and calcium zinc hydroxide hydrate. The unreacted di- and tricalcium silicate phases were expected to appear due to the hydration retardation of cementitious materials as a result of plating sludge addition.

Calcium zincate [$CaZn_2(OH)_6?2H_2O$] and some other forms of calcium zinc hydroxy compounds were reported to form during OPC hydration in the presence of zinc [13–15]. The hydrolysis of cement clinker particles results in

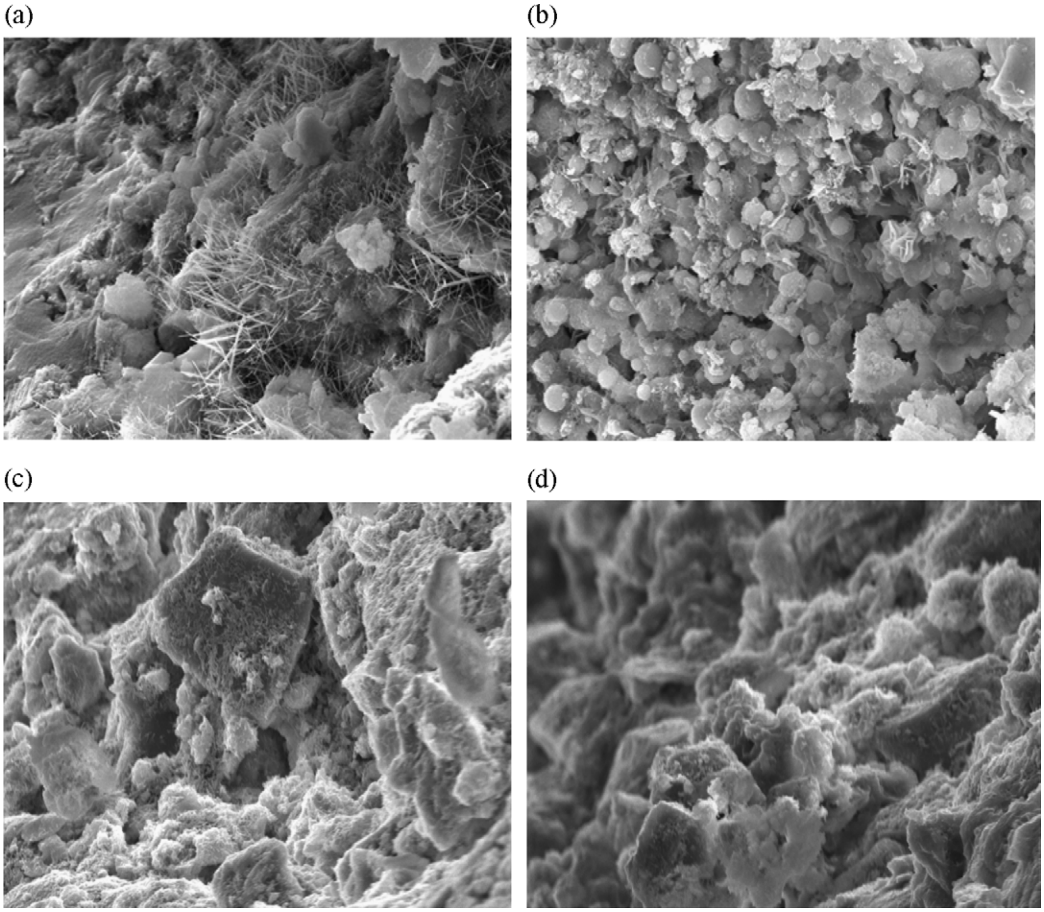

Fig. 5. SEM micrographs of cement-based materials after 7 days of curing at a magnification of ×2000: (a) cement paste; (b) OPC/20% PFA; (c) OPC/10% PS; and (d) OPC/20% PFA/10% PS.

the extensive dissolution of Ca^{2+} and OH^- ions. This initiates the rapid resolubilization of the amorphous zinc hydroxide and transforms to calcium zinc hydroxide hydrate.

3.5. Scanning electron microscopy

SEM micrograph in Fig. 5a reveals that calcium silicate hydrate (CSH) and significant quantities of ettringite (AFt phase) existed in the cement paste hydrated for 7 days. For the OPC/PFA sample, a large amount of the spherical shape PFA (Fig. 4a) and CSH phase are observed, as Fig. 5b shows.

When the plating sludge was added to both the OPC and OPC/PFA systems, there is no evidence of the existence of the hydration products at 7 days. Additionally, the plating sludge was seen everywhere, coating on the surface of both the cement clinkers and PFA, as seen in Fig. 5c–d. Cement hydration is normally a self-inhibiting process and largely controlled by the permeability of the gelatinous coating around the cement clinkers. The deposition of the plating sludge on the surface of the clinkers and PFA results in a dense coating, and this could be the cause for hydration retardation of both cement clinkers and PFA.

At the age of 28 days, a dense microstructure with large crystal of $Ca(OH)_2$ can be seen from both the OPC and OPC/PFA samples (Fig. 6a and b), with some PFA still existing in the OPC/PFA sample (Fig. 6b). Voids and a needle-like calcium silicate hydrates are observed in the OPC/PS and OPC/PFA/PS samples (Fig. 6c and d).

4. Conclusions

This work has shown that the use of PFA as part substitute for OPC as solidification binder can produce the solidified waste with ultimate strength higher than OPC. It could be possible that when the highly alkaline OPC was replaced by PFA, the alkalinity of the OPC/PFA/PS systems was reduced to the level that was suitable for the immobilization of several metal hydroxides. As a result, the synergistic negative effects caused by the resolubilization of the plating sludge on hydration reactions of cementitious binders were reduced.

A decrease in pH of TCLP leachates from 13.0 to 12.7 was observed when PFA was used to replace OPC. Although the acid neutralization capacity of the OPC/PFA/PS samples was lower than that of the OPC/PS samples, Cr

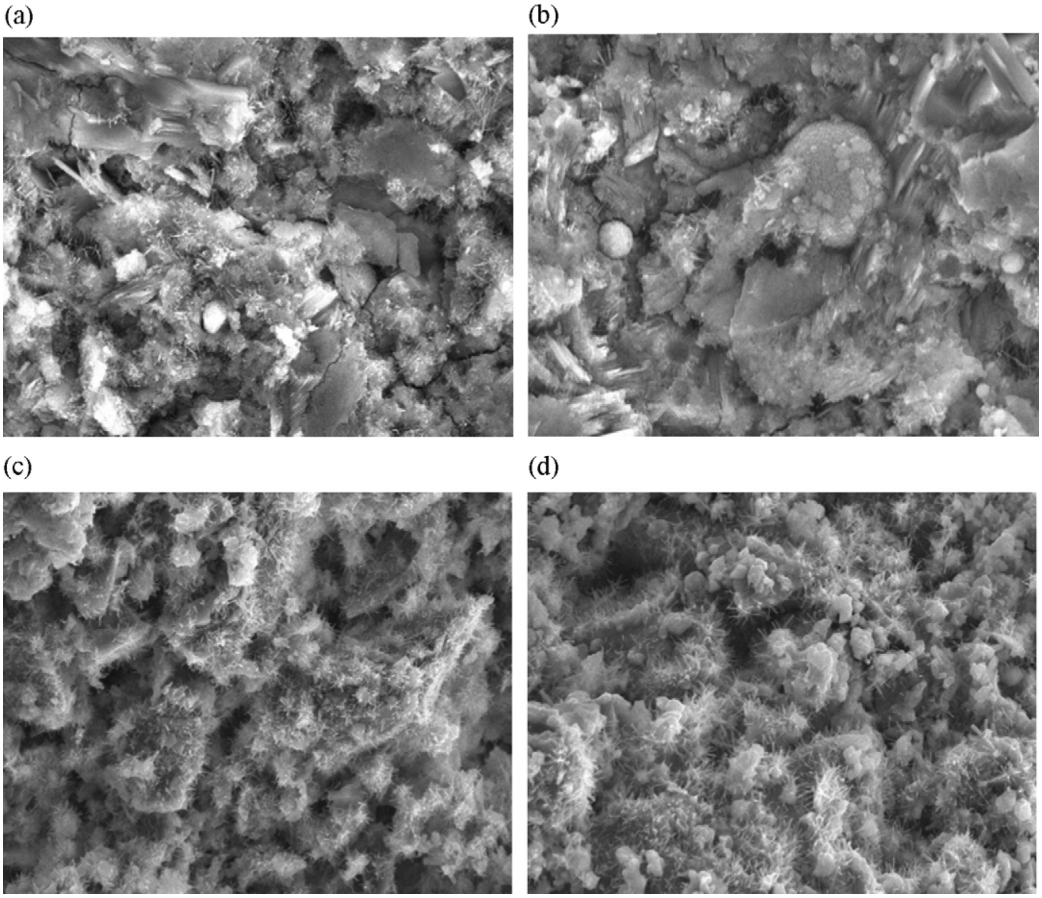

Fig. 6. SEM micrographs of cement-based materials after 28 days of curing at magnification of ×2000: (a) cement paste; (b) OPC/20% PFA; (c) OPC/10% PS; and (d) OPC/20% PFA/10% PS.

concentration in TCLP leachates was not over the limit specified by the U.S. EPA standard. In addition, concentrations of Cr, Zn and Fe in TCLP leachates extracted from the cement-based solidified plating wastes were much lower than that extracted from the plating sludge.

SEM micrographs showed that the dense coating on the surface of cementitious binders was caused by the addition of the plating sludge. This causes hydration retardation of cementitious binders.

Calcium zinc hydroxide hydrate complex, and the unreacted di- and tricalcium silicates were found in the XRD patterns of the 28-day solidified wastes. These crystalline phases are expected to be detected during OPC hydration in the presence of zinc.

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References

[1] R.A. Hanna, P.J. Barrie, C.R. Cheeseman, C.D. Hills, P.M. Buchler, R. Perry, Solid state ^{29}Si and ^{27}Al NMR and FTIR study of cement pastes containing industrial wastes and organics, Cem. Concr. Res. 25 (1995) 1435–1444.

[2] C.D. Hills, L. Koe, C.J. Sollar, R. Perry, Early heat of hydration during the solidification of a metal plating sludge, Cem. Concr. Res. 22 (1992) 822–832.

[3] C.D. Hills, C.J. Sollar, R. Perry, Ordinary portland cement based solidification: the role of OPC reviewed, Cem. Concr. Res. 23 (1993) 196–212.

[4] C.C. Wiles, A review of solidification/stabilization technology, J. Hazard. Mater. 14 (1987) 5–21.

[5] C. Tashiro, J. Oba, K. Akama, The effects of several heavy metal oxides on the formation of ettringite and the microstructure of hardened ettringite, Cem. Concr. Res. 9 (1979) 303–308.

[6] C. Tashiro, H. Takahashi, M. Kanaya, I. Hirakida, R. Yoshida, Hardening property of cement mortar adding heavy metal compound and solubility of heavy metal from hardened mortar, Cem. Concr. Res. 9 (1979) 283–290.

[7] C. Tashiro, J. Oba, The effects of Cr_2O_3, $Cu(OH)_2$, ZnO and PbO on the compressive strength and the hydrates of the hardened C_3A paste, Cem. Concr. Res. 9 (1979) 253–258.

[8] F.P. Glasser, Chemistry of cement—solidified waste forms, in: R.D. Spence (Ed.), Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, USA, 1993.

[9] R.J. Detwiler, J.I. Bhatty, S. Bhattacharja, Supplementary cementing materials for use in blended cements, Research and Development Bulletin RD112T, Portland Cement Association, USA, 1996.

[10] I. Fernández, E. Chacon, A. Irabien, Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement, Cem. Concr. Res. 31 (2001) 1213–1219.

[11] X.D. Li, C.S. Poon, H. Sun, I.M.C. Lo, D.W. Kirk, Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials, J. Hazard. Mater. A 82 (2001) 215–230.

[12] S. Asavapisit, W. Nanthamontry, C. Polprasert, Influence of condensed silica fume on the properties of cement-based solidified wastes, Cem. Concr. Res. 31 (2001) 1147–1152.

[13] I.W. Hamilton, N.M. Sammes, Encapsulation of steel foundry bag house dusts in cement mortar, Cem. Concr. Res. 29 (1999) 55–61.

[14] N.Y.A. Mollah, T.R. Hess, Y.N. Tsai, D.L. Cocke, FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based system—Portland Type V with zinc, Cem. Concr. Res. 23 (1993) 773–784.

[15] S. Asavapisit, G. Fowler, C.R. Cheeseman, Solution chemistry during cement hydration in the presence of metal hydroxide waste, Cem. Concr. Res. 27 (1997) 1249–1260.