

EFFECT OF VARIOUS POZZOLANS ON PROPERTIES OF THE SOLIDIFIED WASTES

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Abstract

The effects of pozzolanic materials on the properties of cement-based solidified plating sludge were studied. Black rice husk ash (BHA), pulverized fuel ash (PFA) and synthetic rice husk ash (sRHA) were used at 20 wt% to replace ordinary Portland cement (OPC). Electroplating sludge was added to the solidification binders at 30 and 50 wt%. Compressive strength, setting time, and static leaching test were determined. Results showed that the plating sludge could be loaded to the solidification binders containing PFA, and gave a 1-day strength that meets the minimum requirement for landfilling (3.5 kg/cm²), but no strength was developed during the first 7 days for the control. Rapid initial and final setting times were observed from OPC/BHA/PS and OPC/PFA/PS mixes except for OPC/sRHA/PS mixes. Results on leaching test found that cumulative concentration of interested heavy metals (Zn, Cr, and Fe) especially chromium does not exceed the regulatory limit of 5 mg/L.

Keywords: Pozzolans, plating sludge, strength, setting, leaching

Introduction

Stabilization/Solidification (S/S) processes are common treatment technology for heavy metal-containing waste. The hazardous components in the waste are converted to less hazardous or non hazardous waste forms which are environmentally acceptable for disposal in the landfill. Ordinary Portland cement (OPC) is normally used as solidification binder or can be used in combination with pozzolanic materials as OPC replacement material. The advantage of this technology is to minimize the release of hazardous components into the environment

after being disposed of in a landfill.

Several researchers reported that heavy metals present in the waste affect the quality of the solidified products. These heavy metals interfere with the hydration reactions of cementitious binders. As a result, the solidified waste products exhibit one or a combination of the following effects, for example, an impede setting time, an increase release of heavy metals, a reduction of strength and a decrease durability to the aggressive environment (Diet *et al.*, 1998; Stephan *et al.*, 1999; Olmo *et al.*,

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2001; Fitch and Cheeseman, 2003; Qiao *et al.*, 2007). Previous works found that the use of pozzolanic materials to substitute OPC can improve the performance of cement-based solidified wastes (Park, 2000; Asavapisit *et al.*, 2001, 2005; Asavapisit and Ruengrit, 2005). Therefore, an understanding of the effects of pozzolanic materials on the properties of the solidified waste products is necessary to improve the long-term performance after disposal in the landfill.

In this research work, Black rice husk ash (BHA), Pulverized fuel ash (PFA) and synthesis rice husk ash (sRHA) were used to replace OPC at the level of 20 wt%. The plating sludge was added to the solidification binders at 30 and 50 wt%. Initial and final setting times, strength development and leaching of heavy metals from cement-based solidified plating sludge were investigated.

Materials and Method

Materials

OPC Type 1 which was used throughout this experiment was supplied by the Siam Cement Public Company. Three types of pozzolanic materials, black rice husk ash (BHA), pulverized fuel ash (PFA) and synthetic

rice husk ash (sRHA), were used in this work. PFA was gained from the Electricity Generating Authority of Thailand (EGAT) in Lampang province. BHA was brought from the biomass power plant in Chai-Nat province. sRHA was obtained by burning the rice husk at 500°C in a muffle furnace to remove the volatile organic carbon for 1 h, followed by firing it at 650°C for 1 h. The ash was removed from the furnace and rapidly cools down to ambient temperature. PFA, BHA and sRHA were then ground to a particle size of less than 45 mm using Los Angeles Abrasion machine. Approximate amount of 7 Kgs of PFA, BHA and sRHA were ground using 10 steel balls, 3 of which having diameter of 2.5 inches and another 7 balls having diameter of 1 inch. The total weight of these 10 balls is 10 Kgs. The oxide content of PFA, BHA and sRHA was examined by the X-ray fluorescence (XRF) and is shown in Table 1.

Electroplating sludge was obtained from the wastewater treatment plant which was derived from electroplating process. The sludge was air dried and followed by oven dried for 24 h to remove excess water, and then ground to a particle size of less than 0.5 mm. The sludge was digested using microwave digestion, and the concentration of heavy metals was analyzed using Atomic Absorption Spectroscopy

Table 1. Chemical compositions of sRHA, BHA, and PFA

Oxides (%)	sRHA	BHA	PFA
Na ₂ O	0.13	0.07	1.35
MgO	0.43	0.23	1.87
Al ₂ O ₃	0.05	0.31	15.80
SiO ₂	92.44	93.18	25.60
P ₂ O ₅	0.87	0.47	0.16
SO ₃	0.23	0.05	3.10
K ₂ O	2.95	1.86	2.25
CaO	0.43	0.40	14.90
MnO ₂	0.17	0.11	0.08
Fe ₂ O ₃	0.12	0.26	13.90
LOI	1.70	2.90	ND
%Carbon content	0.06	1.37	ND

ND = not detected

(AAS). Zn, Fe, and Cr were presented in the sludge at 263, 52, and 28 g/kg dry sludge, respectively

Sample Preparation

BHA, PFA and sRHA were used to replace OPC at the level of 20 wt%, and the plating sludge was added to the samples at the level 0, 30, and 50 wt%. Flow table tests (ASTM D 5873 - 05) were used to determine the w/s (water to solid) ratio of all samples. The slurry was mixed following the standard test methods ASTM C 305 - 06 to achieve a uniform distribution of the plating sludge before being transferred into the cylindrical plastic mould. The samples were allowed to set and harden in a carbon dioxide-free atmosphere to avoid carbonation.

Setting Time

Initial and final setting times of the solidified wastes were determined using Vicat needle (ASTM C191 - 08). The mixture of cement-plating sludge was transferred into the apparatus and the excess mixture was removed. The needle was released and allowed to free-fall on the sample every 15 min except for the sample containing PFA. The penetration of the needle into the sample was recorded. The final setting time was obtained when the needle

did not sink visibly into the paste.

Unconfined Compressive Strength

The unconfined compressive strength of cement-based solidification/stabilization products was done following ASTM D1633 – 00 (2007). Samples were prepared with the same mix proportions to those used for setting time determination (Table 2). Cylindrical plastic mould with diameter of 50 mm and 100 mm was used to prepare sample specimens for compression test. The sample specimens were wrapped with cling-film to prevent the loss of water and cured under ambient condition. The compressive strength of specimens was tested at the age of 1, 3, 7, 14, 28, 56, and 91 days. The load was given to the smooth surface of the specimen at a constant rate of 1mm/min. A set of four samples was used for compression test. The average value was made from four samples.

Leaching Test

Metal leaching from the solidified wastes was assessed using a static leaching test on monolithic samples hydrated for 28 days. The synthetic acid rain was used as leachant and was prepared from sulfuric and nitric acid solutions at the ratio of 80:20 by volume and dilute with deionized water to a pH of 3. The monolith was

Table 2. Initial and final setting times of various mixes

Identity	W/S ratio	Initial setting time (min)	Final setting time (min)
OPC	0.31	172	191
OPC+30%PS	0.28	53	74
OPC+50%PS	0.26	361	512
OPC+20%BHA	0.35	162	182
OPC+20%BHA+30%PS	0.33	56	102
OPC+20%BHA+50%PS	0.30	426	676
OPC+20%PFA	0.28	174	190
OPC+20%PFA+30%PS	0.26	12	25
OPC+20%PFA+50%PS	0.24	150	189
OPC+20%sRHA	0.44	175	200
OPC+20%sRHA+30%PS	0.43	1,370	1,667
OPC+20%sRHA+50%PS	0.36	1,154	1,453

wrapped with a plastic net and suspended in the leachant. The ration of leachant volume to surface area was 20:1.

Samples were contacted with the leachant for a period of 1, 3, 5, 7, 14, 28, and 56 days. The leaching test was performed in duplicate to confirm the data. Leachates were then filtered through a 0.45 μm filter paper to remove suspended solids. The filtrates were measured for pH and heavy metals concentration by AAS.

Results and Discussion

Setting Time

Table 2 shows the initial and final setting times of cement-based solidified plating sludge containing BHA, PFA and sRHA as cement replacement material at 20 wt%. The initial and final setting times of OPC were 172 and 191 min, respectively. The acceleration of initial and final setting time was observed when the plating sludge was added to OPC at 30 wt%. The initial and final setting times of OPC were reduced from 172 and 191 min to 53 and 74 min with 30 wt% addition of the plating sludge. $\text{Zn}(\text{OH})_2$ was reported to accelerate the hydration of calcium aluminate but retard the hydration of silicate. The initial formation of calcium zincate precipitates was not only covers cement grains but also inhibit gypsum dissolution. As a result, the occurrence of flash setting was observed (Asavapisit *et al.*, 1997).

However, when the plating sludge was loaded to OPC at 50 wt%, the initial and final setting times of OPC were increased from 172 and 191 min to 361 and 512 min. The formation of calcium zincate precipitates increase with increasing the amount of the plating sludge. It is possible that the hydrated calcium aluminate phase, like the calcium silicate cements phases, are also rapidly coated with calcium zincate precipitates. In addition, the presence of other metal hydroxides in the plating sludge may enhance the retardation effect of $\text{Zn}(\text{OH})_2$ (Diet *et al.*, 1998).

Rapid setting time was also found for both initial and final setting times when the plating sludge was added at 30 wt% to cement

blended with BHA and PFA. The opposite result was found for all cement-based solidified waste samples containing sRHA as cement replacement material. This may be cause by the reactivity of silica (SiO_2) present in the sRHA, with soluble species of heavy metals. As a result, the delay formation of hydration products was observed and this leads to longer setting time.

Unconfined Compressive Strength

Strength development of cement-based solidified wastes containing various amounts of the plating sludge is shown in Figures 1(a)-(c). Results showed that compressive strength of cement paste increased from 162 kg/cm^2 to 254, 368 and 419 kg/cm^2 at the age of 1, 7, 28, and 91 days, respectively (Figure 1(a)). The hardened cement incorporating PFA gave significantly higher strength than the control (cement paste) at all curing duration observed. Similar results were found for samples containing BHA. It could be possible that these ashes were ground to a very high fineness and that the percentages of the ashes retained on the sieve no. 325 were 24, 27, and 29 for PFA, BHA and sRHA, respectively.

A higher rate of strength development was obtained from sample containing PFA compared to those containing BHA and sRHA. The amount of mix water for each sample has a significant effect on strength. Experimental results show that samples containing sRHA required more water during sample preparation than those containing BHA and PFA (Table 2). sRHA and BHA requires more water than PFA because sRHA and BHA particles are not spherical in shape like PFA. This results in larger interparticular voids which are occupied by water. In addition, sRHA needs more water than BHA because BHA was obtained by burning rice husk in fluidized bed gasifier and the volatile carbon is not completely removed. The presence of carbon in BHA has made BHA a hydrophobic material (does not prefer water). This is why BHA requires less water for the mix than sRHA.

When the plating sludge was added to

OPC at 30 and 50 wt%, no strength was gained during the first 7 days of curing (Figure 1(b)-(c)). The solidified wastes containing 30 and 50 wt% of the plating sludge gave strength of 7 and 5 kg/cm² at the age of 14 days and increased to 17 and 12 kg/cm² at the age of 91 days, respectively. It was observed that the presence of the plating sludge resulted in a significant

reduction of strength compared to the control (cement paste). This was caused by both the negative effects from heavy metal-containing waste and a decreased proportion of OPC with the increased addition of the plating sludge. As a result, the products from hydration reactions of the binders especially C-S-H gels were reduced.

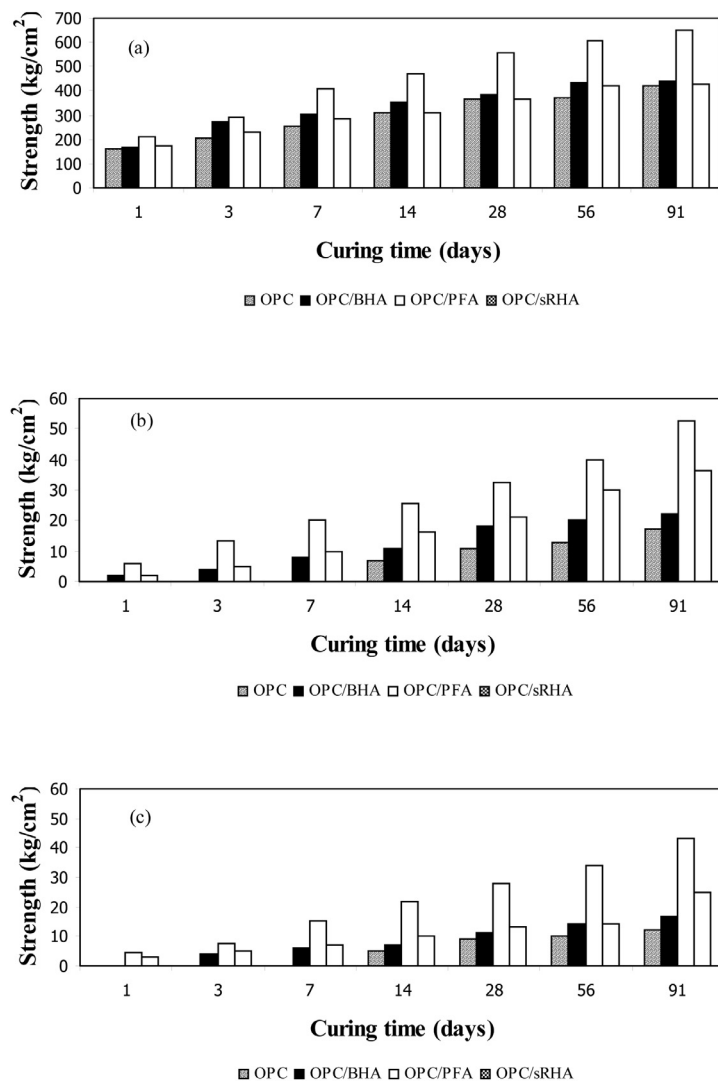


Figure 1. Strength development of the solidified wastes containing various amount of the plating sludge; a) 0 wt%, b) 30 wt% and c) 50 wt%

It was found that when PFA was used to replace OPC at the level of 20 wt%, the solidified wastes containing all level of the plating sludge had enough strength for disposal in the landfill at the age of 1 day. (The regulatory limit for compressive strength of the solidified waste was defined by the Ministry of Industry to be more than 3.5 kg/cm²). Similar observations were found for samples containing BHA and sRHA. The solidified wastes incorporating BHA and sRHA could contain up to 50 wt% of the plating sludge and can be disposed of at the age of 3 days.

Static Leaching Test

The leachability of waste constituents from cement-based solidified waste products after disposal in the landfill is the most important factor determining the effectiveness of the treatment process. Leaching of contaminants may occur when cement-based solidification 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.

Leachability of heavy metals from cement-based solidified waste samples was investigated using static leaching test. Synthetic acid rain with an initial pH value of 3.0 was

used as leachant. Results showed that pH of the leachates after contacting with cement-based solidified wastes containing 50 wt% of the plating sludge increased from an initial pH of 3.0 to between 11 and 12 (Figure 2) at the end of the leach test. A rapid increase of pH values could be caused either by the release of calcium hydroxide and decalcification of calcium oxide from the cement matrix or dissolution of calcium oxide from unhydrated cement clinkers. Leachability of Zn, Cr and Fe from cement-based solidified samples is shown in Figures 3 ((a) – (c)). Concentration of Zn, Cr and Fe in the leachates increased with exposure time especially during the first 7 days of contacting with the leachant and decreased with increasing leaching time thereafter. This is because when the solidified wastes exposed to acid leachant the chemical equilibrium of the pore water is disturbed and this initiates dissolution of insoluble species at the surfaces of solid phases. The rate of solubilization is controlled by both the solubility of each species and the concentration of soluble species in the solution near the surface (van der Sloot, 2002).

It is observed that concentration of Zn and Cr in the leachates after contacting with samples containing sRHA was lower than those containing PFA and BHA. It could be possible that the highly reactive surface of sRHA could adsorb the soluble species of heavy metals better than PFA and BHA. However, the

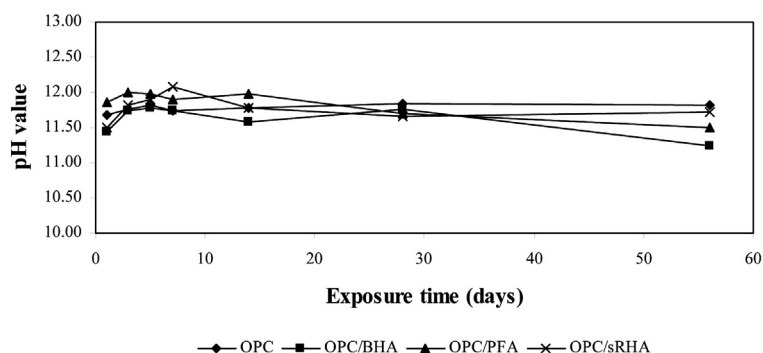


Figure 2. pH values of the leachate after contacting with the solidified wastes containing 50 wt% of the plating sludge versus exposure time

cumulative concentration of Zn, Cr and Fe after 56 days of leaching was lower than 2.6, 2.7, and 0.6 mg/L, respectively. It is believed that the release of excess alkalinity from the solidified wastes increased the leachate pH to the optimum range for metal immobilization and this was indirectly responsible for the reduced leachability of heavy metals.

Conclusions

Strength development, setting time and leachability of heavy metals were used to study the effect of pozzolanic materials on the properties of cement-based solidified plating sludge. Results from this experimental work are summarized as follows:

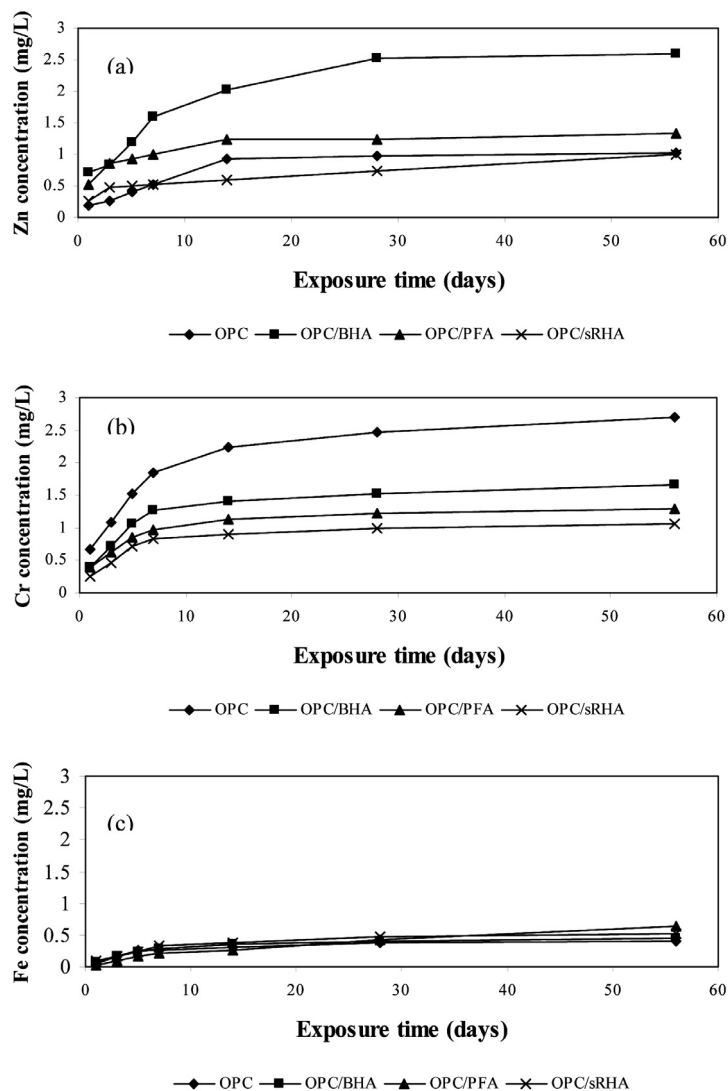


Figure 3. Cumulative concentration of heavy metals in the leachate after contacting with the solidified wastes containing 50 wt% of the plating sludge; a) Zn, b) Cr and c) Fe

1. The solidified wastes containing PFA as cement replacement material gave higher rate of strength development compared to those containing BHA and sRHA.

2. Addition of the plating sludge to OPC/sRHA mix increased the initial and final setting times of the solidified wastes whereas for those of OPC and OPC/PFA mixes, rapid initial and final setting times were observed.

3. Lower leachability of Zn and Cr was observed from samples with BHA, PFA and sRHA as replacement for OPC but was not significant. The cumulative concentration of Zn and Cr throughout the experiment was lower than 2.6 and 2.7 mg/L.

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