Journal of Metals, Materials and Minerals, Vol.19 No.2 pp.85-89, 2009

Effect of Black Rice Husk Ash Substituted OPC on Strength and Leaching of Solidified Plating Sludge

Rungroj PIYAPHANUWAT[1] and Suwimol ASAVAPISIT[1, 2*]

[1] Department of Environmental Technology, School of Energy Environmental and Materials, King Mongkut's University of Technology Thonburi, 126 Pracha U-thit Road, Bangmod, Thung-kru, Bangkok 10140, Thailand
[2]National Center of Excellence for Environmental and Hazardous Waste Management, Department of Environmental Engineering, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

Abstract

Strength and leachability of the solidified plating sludge using OPC and BHA as solidification binders were investigated. BHA was used to replace OPC at 0, 20 and 30 wt.%, and was used to solidify 30 and 50 wt.% of the plating sludge. Results showed that no strength was observed during the first 7 days of curing when OPC was used to solidify the plating sludge. But when 20 and 30 wt.% of BHA were used to substitute OPC, the solidified wastes containing 50 wt.% of the plating sludge gave strength of 4.5 kg/cm^2 at the age of 3 and 4.1 kg/cm^2 at the age of 7 days, respectively. Leachability of Zn and Cr from the solidified wastes containing all level of the plating sludge did not exceed the criteria for waste acceptable at landfills, which is regulated at 100 and 25 mg/m^2 by NEN 7375;2004. The dominant leaching mechanism for all samples was surface wash-off.

Key words: Black rice husk ash, Strength, Leachability

Introduction

Electroplating is a processing which uses metallic coating on an object. The wastewater derived from the electroplating activities contains dissolved heavy metals, suspended solid, grease and oil. Heavy metals present in the plating wastewater are normally removed by adjusting pH of wastewater to between 7.5 and 8.5 with hydrating lime. Several metal hydroxides which have minimum solubility within this pH range are removed as sludge. Due to the amphoteric characteristic of several metal hydroxides, the heavy metal-containing sludge is therefore not allowed to be disposed of in the landfill without any further treatment. The most economic treatment method for heavy metal-containing sludge is to turn the semi-solid sludge into monolith by adding solidification binders. Ordinary Portland cement (OPC) type I can be used as solidification binder alone, or can be used in combination with pozzolanic materials such as pulverized fuel ash (PFA), blast furnace slag (BFS) and rice husk ash (RHA).

Several metal oxides and hydroxides are known to cause negative effects on cement-based solidified waste products. Olmo, *et al*. (2001), Hamilton, *et al*. (1999) and Qian, *et al*. (2003). These effects include the increase of initial and final setting times, a reduction of strength development and an increase a leachability of heavy metals. This has sometimes effected that the quality of the solidified wastes does not meet the minimum requirement for disposal in the landfill. Previous works found that partial replacement of OPC by condensed silica fume (CSF), pulverized fuel ash (PFA) and synthetic rice husk ash (RHA) in a pozzolan-based solidification of heavy metal-containing sludge could increase the rate of strength development of the solidified wastes, especially during the first two weeks of curing.[4, 2, 3]

Black rice husk ash (BHA) is an industrial waste generated from biomass power plant. It is derived by burning rice husk in a fluidized bed incinerator. The ash obtained from this combustion process has a high unburned carbon content. This

E-mail : Num_r.piyaphanuwat@hotmail.co.uk, Suwimol.asa@kmutt.ac.th

has caused that the use of BHA in construction material applications does not receive much interest although the silica content of BHA is about 90%. Several researches reported that BHA was added in concrete to increase durability property, used to improve dispersive soil, and blended with lime to solidified heavy metal before dispose in landfill a result, BHA was used to improve properties of polymer.[5, 12] In this work, BHA was used to replace OPC at the levels of 0, 20 and 30% by weight. The pozzolan-based binders (OPC and BHA) were used to solidify the plating sludge. Strength development and leachability of heavy metals from the solidified wastes were evaluated.

Materials and Experimental Procedures

OPC type 1 was supplied by the Siam Cement Public Company Limited (elephant brand). The chemical compositions of OPC were measured by X-ray fluorescence and are shown in Table 1. BHA was brought from a biomass power plant in Ampour Wat Sing, Chai Nat province. BHA was ground for 4 hours to particle size of less than 45 µm by Loss Angeles abrasion machine. The silica (SiO_2) content of BHA is 93.18 % by weight 28-day strength activity index is 92.63 % following ASTM C 311-07. The plating sludge (Ps) was brought from the wastewater treatment plant of an electroplating industry located in Bangkok, Thailand. The sludge was oven dried and ground to a particle size less than 50 mm. One gram of dry sludge was digested with 5 ml of concentrated nitric acid, 1 ml of hydrogenperoxide and 1 ml of hydrogenfluoride using microwave digestion, and the concentration of heavy metals present in the sludge was analysed by atomic absorption spectroscopy (AAS). Iron, chromium and zinc were present in the plating sludge at concentrations of 0.52, 0.28, and 26.3 wt%.

Table 1. Chemical composition of OPC

Chemical composition	% wt.
SiO_2	24.2
Al_2O_3	4.35
Fe_2O_3	3.01
CaO	65.2
MgO	0.62
Na_2O	0.08
K_2O	0.062

Sample Preparation

BHA was used to replace OPC at levels of 0, 20 and 30 wt.% and dry-mixed to obtain a homogeneous solidification binder. The plating sludge was added to the solidification binder at 30 and 50 wt.%. The water to solid (w/s) ratio of all mixes was determined by flow table test following ASTM 305-94. Mix proportions and water requirement for each mix are shown in Table 2. After mixing, the slurry was transferred into plastic cylinder mould. After demoulding the sample specimens were sealed with cling film to avoid carbonation and curing under ambient condition.

Table 2. Water to solid ratio of all mixes

Sample	w/s
100 wt.% OPC (OPC)	0.31
OPC+30wt.% Ps (O3Ps)	0.25
OPC+50wt.% Ps (O5Ps)	0.23
OPC+20wt.% wt.BHA (O2B)	0.35
OPC+20wt.% BHA+30wt.% Ps (O2B3Ps)	0.30
OPC+20wt.% BHA+50wt.% Ps (O2B5Ps)	0.27
OPC+30wt.% BHA (O3B)	0.37
OPC+30wt.% BHA+30wt.% Ps (O3B3Ps)	0.33
OPC+30wt.% BHA+50wt.% Ps (O3B3Ps)	0.31

Unconfined Compressive Strength

The sample specimens were used for compression test following ASTM D1633-96. The size of the cylindrical samples was modified to 37 mm in diameter and 74 mm in height. Compressive strength of the solidified wastes was determined after curing for 1, 3,7,14, 28, 56 and 91 days. A set of five samples was used for this test and the arithmetic average with 95% of confidence interval was made from five samples.

Tank Leaching Test

Metal leaching from the solidified wastes was assessed using Tank test following Environment Agency NEN 7375-2004.[1] The cylindrical specimens cured for 28 days were immersed in deionised water. The ratio between the volume of deionised water (V_L) and the volume of the sample (V_S) is equal to 4.0. The leachant was renewed at 8 different times over a total period of 64 days. After each contacting time the leachates were filtered through a 0.45 µm. filter paper (Whatman no. 42). Part of the leachate was used for pH and conductivity measurement and the remainder used for the analysis of heavy metal concentration by AAS.

Results and Discussion

Strength of Cement Blended with BHA Paste

The strength development of cement paste and cement containing different amounts of BHA is shown in Figure 1. Results showed that the early age (during the first 7 days of curing) of strength development in cement blended with BHA was lower compared with the controlled cement paste, but thereafter, the strength was developed to higher values. The high strength development was observed from cement containing 20 wt.% BHA during the 14 to 91 days of curing. This is caused by the calcium hydroxide that was produced during OPC hydration and which increased to the level that is enough to dissolve silica from BHA. As a result, the secondary calcium silicate hydrate generated from reaction between calcium hydroxide and soluble silica from BHA is the cause of additional strength gain in cement blended with BHA.(4, 2, 3)

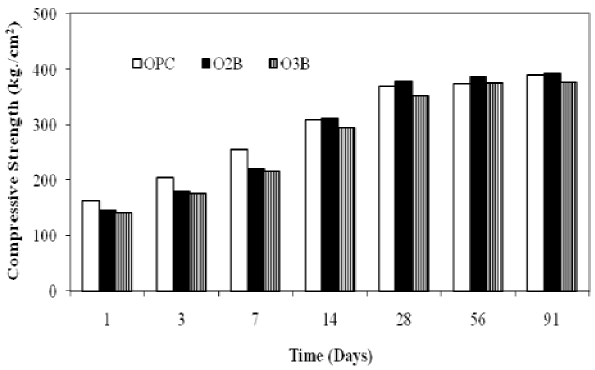

Figure 1. Strength development of OPC containing 0, 20 and 30 %wt. of BHA.

Strength of the Solidified Plating Sludge

The strength development of all cement-based solidified wastes containing 30 and 50 wt.% plating sludge did not develop during the first 7 days. Thereafter, however the strength was developed, as shown in Figure 2(a-b). The negative effect was caused by adding of plating sludge that contained several heavy metals on the strength development of cement-based solidified waste. The high alkalinity of cement causes the heavy metal to become soluble, the heavy metals interfere with the hydration, which leads to develope a low strength. Several researches have reported that $Zn(OH)_2$ causes the hydration retardation among the metal hydroxides, a high strength development was found after 7 days for cement.(11, 8, 7. 9)

Experimental results showed that the strength development of cement blended 20 and 30%wt. BHA solidified wastes was higher than using only OPC as solidification binder. A similar result was found in Li, *et al*. (2001) and Asavapisit, *et al*. (2001) research works. Both research reported that pozzolanic materials substituted OPC and reduced the alkalinity of the solidified wastes system. It is possible that the alkalinity of the OPC containing 20 and 30 wt.% BHA solidified plating sludge at the levels of 30 and 50 wt.% was reduced to a level suitable for immobilization of several metal hydroxides and lead to reduce the soluble metal ions which become soluble at high alkalinity in systems.(4) From the study, the cement blended with 30 wt.% BHA could solidify the 50 wt.% plating sludge and gave the unconfined compressive strength at 28 days, which is more than the minimum requirement for disposal in a secure landfill (3.5 kg/cm^2).

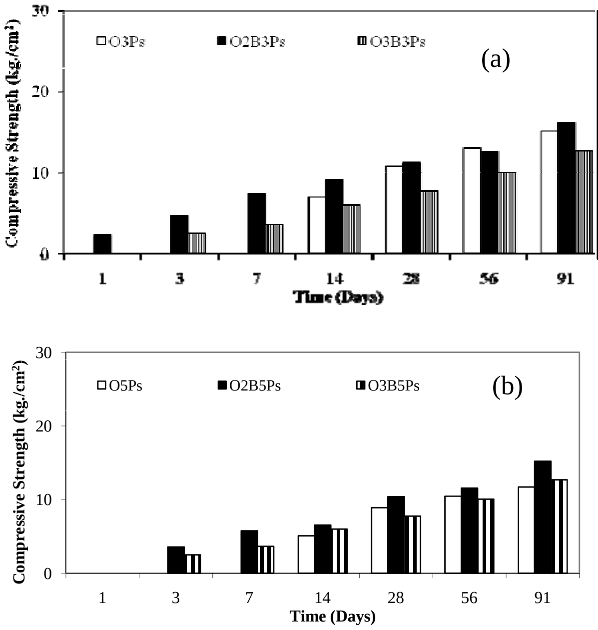

Figure 2. Strengths development of the solidified wastes containing OPC, BHA and plating sludge at (a) 30 wt.% and (b) 50 wt % plating sludge.

Tank Test Result

Table 3 shows pH of the leachates, total concentration of heavy metals in the leachates and mechanisms of metal leaching from cement and cement blended BHA solidified plating sludge. Leachate pHs of cement blended BHA was lower than that of pure cement paste. This is because the reduced proportion of OPC in the mix and the consumption of $Ca(OH)_2$ which is a hydration product by BHA during pozzolanic reaction can lead to low alkalinity of the system.(10) In addition, pH of the leachates contacting with cement and cement blended BHA solidified plating sludge decreased while increasing the amount of the plating sludge in the mix.

replace OPC at 20 wt.%. However, Zn and Cr were leached from all samples at concentrations lower than 100 and 25 mg/m^2, which are the criteria for waste acceptable to dispose of at landfills.

Leaching mechanism of Fe, Cr and Zn from all cement-based solidified samples was surface wash - off. This was done according to NEN 7375;2004 by determining the gradient of a log – log plot of cumulative leaching vs. time.(1) Gradients below 0.35 indicate either surface wash–off or depletion. Gradients between 0.36 and 0.65 indicate diffusion controlled release, whereas as gradient greater than 0.65 indicate dissolution. According to these criteria, the slopes for different leaching intervals which were determined from

Table 3. pH, total concentration and mechanism of solidified waste.

Samples	Interval								Total concentration (mg/ m^2)			Mechanism
	1	2	3	4	5	6	7	8	Fe*	Zn**	Cr***	
OPC	12.20	12.34	11.68	12.01	11.77	11.61	11.23	11.03	-	-	-	-
O3Ps	12.08	12.15	11.36	11.73	11.57	11.38	11.08	10.55	5.644	7.866	4.671	Surface wash -off
O5Ps	12.09	12.17	11.30	11.48	11.37	11.20	11.00	10.52	7.163	12.44	6.347	Surface wash -off
O2B	12.12	12.21	11.37	11.81	11.47	11.39	11.19	10.68	-	-	-	-
O2B3Ps	12.02	12.08	11.26	11.48	11.40	11.26	11.01	10.52	1.186	5.117	2.391	Surface wash -off
O2B5Ps	11.99	12.00	11.22	11.38	11.28	11.11	10.93	10.47	1.813	8.423	4.080	Surface wash -off
O3B	12.08	12.19	11.32	11.78	11.43	11.36	11.08	10.63	-	-	-	-
O3B3Ps	12.00	12.07	11.26	11.44	11.31	11.20	10.92	10.41	1.448	5.835	2.299	Surface wash -off
O3B5Ps	11.91	11.98	11.19	11.32	11.22	11.08	10.87	10.32	2.304	9.438	4.138	Surface wash -off

* Fe is not heavy metal
** Zn limitation is 100 mg/m^2
*** Cr limitation is 25 mg/m^2

Fe, Cr and Zn were the three heavy metals selected for studying metal leaching from the cement-based solidified wastes because these three metals were present in the plating sludge at concentrationa much higher than other heavy metals. Results showed that in the presence of 50 wt.% of the plating sludge, respectively, leaching of Fe, Zn and Cr from the control sample was 7.16, 12.44 and 6.35 mg/m^2, and decreased to 1.81, 8.42 and 4.08 mg/m^2 when BHA was used to

linear regression (r_c) through the data point indicate that the dominant leaching mechanism for Fe, Cr and Zn was surface wash-off (< 0.35).

Conclusions

Using BHA as a partial substitute for OPC as solidification binder can produce solidified wastes with ultimate strength higher than the control. It is possible that adding BHA reduces the alkalinity of cement to a level suitable for the immobilization of plating sludge, especially when OPC was blended with 20 wt.% BHA. Result showed that when OPC was replaced by 20 wt.% BHA, the solidified waste could contain up to 50 wt.% and gave enough strength for disposal in the landfill within 3 days.

The leaching mechanism of all cement and blended cement solidified plating sludges was surface wash-off. Leachability of Fe, Cr and Zn from all samples was lower than the maximum level of metal leaching. The plating sludge could be loaded at 50 wt.% to the cement blended with 30 wt.% BHA and resulted in the minimum acceptable 28-day strength for landfilling.

Acknowledgements

This research work was funded by The Royal Golden Jubilee Ph.D program of the Thailand Research Fund. The Department of Civil Engineering, Faculty of Engineering, KMUTT, deserves appreciation for providing access to its laboratories and for its assistance with the experiment.

Reference

1. Agency, U.S.E.P. 2005. *Determination of leaching of inorganic components with the diffusion test 'The Tank Test*'. Netherlands Normalisation Institute Standard.

2. Asavapisit, S., Naksrichum, S. and Harnwajanawong, N. 2005. Strength, leachability and microstructure characteristics of cement-based solidified plating sludge. *Cem. Concr. Res.* **35(6)** : 1042-1049.

3. Asavapisit, S. and Ruengrit, N. 2005. The role of RHA-blended cement in stabilizing metal- containing wastes. *Cem. Concr. Compos.* **27(7-8)** : 782-787.

4. Asavapisit, S., Nanthamontry,W. and Polprasert, C. 2001. Influence of condensed silica fume on the properties of cement-based solidified wastes. *Cem. Concr. Res.* **31** : 1147-1152.

5. Chatveera, B. and Lertwattanaruk, P. 2009. Evaluation of surface resistance of cement mortars containing black rice husk ash. *J. Environ. Manage.* **90** : 1435-1441.

6. Hamilton, I.W. and Sammes, N.M. 1999. Encapsulation of steel foundry bag house dusts in cement mortar. *Cem. Concr. Res*. **29(1)** : 55-61.

7. Hanna, R.A., Barrie, P. J., Cheeseman, C. R., Hills, C.D., Buchler, P.M. and Perry, R. 1995. Solid state 29Si and 27Al NMR and FTIR study of cement pastes containing industrial wastes and organics. *Cem. Concr. Res.* **25(7)** : 1435-1444.

8. Hills, C.D., Koe, L., Sollars, C.J. and Perry, R. 1992. Early heat of hydration during the solidification of a metal plating sludge. *Cem. Concr. Res.* **22** : 822-832.

9. Hills, C.D., Sollar,C.J. and Perry, R. 1993. Ordinary portland cement based solidification: the role of OPC reviewed. *Cem. Concr. Res.* **23** : 196-212.

10. Li, X.D., Poon, C. S., Sun, H., Lo, I. M. C. and Kirk, D. W. 2001. Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials. *J. Hazard. Mater.* **82** : 215-230.

11. Olmo, F., Chacon, I.,E. and Irabien, A. 2001. Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of portland cement. *Cem. Concr. Res.* **31(8)** : 1213-1219.

12. Piyaphanuwat, R., Asavapisit, S. and Buddhawong, S. 2005. Effects of elevated temperature curing on strength and leachability of the solidified wastes using lime and BHA as solidification binde. *Suranaree J. Sci. Technol.* **12(2)** : 91 – 97.

13. Qian, G., Sun, D.D. and Tay, J.H. 2003. Characterization of mercury- and zinc-doped alkali- activated slag matrix: Part II. Zinc. *Cem. Concr. Res.* **33(8)** : 1257-1262.