

The role of RHA-blended cement in stabilizing metal-containing wastes

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Received 14 June 2004; accepted 2 March 2005

Abstract

Time to final setting, strength development and leachability of heavy metals from the solidified wastes using reactive rice husk ash (rRHA)-blended cement as solidification binder were investigated. The rRHA was prepared by firing at 650 °C for 1 h. Synthetic metal hydroxides and plating sludge were solidified using cement blended with 0, 10, 20 and 30 wt.% rRHA. Experimental results showed that synthetic $\text{Zn}(\text{OH})_2$ and the plating sludge caused rapid setting for cement paste but prolong the final setting for rRHA-blended cements. The rate of strength development was also decreased during the first 14 days of curing. However, these interfering effects were reduced when cement was blended with 10 wt.% rRHA. In addition, the plating sludge could be loaded at 30 wt.% to the cement blended with 10 wt.% rRHA and gave both the 28-day strength and metal concentration in TCLP leachates that meet the regulatory limits for landfilling.

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Keywords: Rice husk ash; Plating sludge; Setting; Strength; Leaching

1. Introduction

Rice husk is an external covering of rice, which is generated during dehusking of paddy rice. The rice husk accounts for 20 wt.% of the paddy produced. The husk is bulky in characteristic and therefore causes problems during its handling and disposal. In developing countries, rice husk is normally used as bulking agents for composting of animal manure or as biomass fuel to replace fossil fuel in generating heat for drying rice or generating electricity [1,2]. The high silicon content of rice husk also makes it more favorable to be used as part substitute for ordinary Portland cement (OPC) in low cost concrete for rural housing [3,4].

The rice husk ash rich in silica content was obtained by burning rice husk to remove the volatile organic carbon such as cellulose and lignin. Studies by James and Rao [5] have shown that a complete destruction of the organic matter from rice husk was achieved at a minimum temperature of around 400 °C. The silica present in the ash can be amorphous or crystalline and its reactivity depends primarily on burning conditions. The amorphous silica in the ash begins to transform to crystalline, which does not exhibit pozzolanicity when the rice husk was burnt at temperature above 750 °C [6–8].

Several research works have been conducted on the use of rice husk ash as mineral additive to improve the performance of concrete [9–13]. However, its application in hazardous waste treatment is relatively new and is under investigation. In this work, the optimum condition for preparing the reactive rice husk ash (rRHA) was studied by burning the rice husk at different temperatures ranging from 400 °C to 800 °C for 1 h. The

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rRHA was then partly used to replace OPC for solidifying the synthetic metal hydroxides and the zinc-cyanide plating sludge. The final setting time, strength development and leachability of the solidified wastes were examined.

2. Experimental

2.1. Materials

Commercial Portland cement Type 1 was supplied by The Siam Cement Public Company Limited (elephant brand) and its chemical composition is shown in Table 1.

The rice husk used throughout this work was brought from the rice milling plant in Ayuthaya province which is located in the central region of Thailand. The dried rice husk was fired at temperatures of 400, 500, 550, 600, 650, 700 and 800 °C for 1 h in the muffle furnace. The rice husk ash (RHA) was removed from the furnace and rapidly cooled down to ambient temperature between 30 °C and 32 °C by spreading on a tray. The RHA was then ground to particle size less than 45 µm using Los Angeles abrasion machine. X-ray fluorescence (XRF) was used to determine the percentages of SiO₂ present in the RHA. The 28-day strength activity index with Portland cement was tested. The properties of RHA firing at various temperatures are shown in Table 2. The optimum temperature of 650 °C was employed to prepare the rRHA which was used throughout the experiment. This temperature was selected from the strength activity index results and the SiO₂ content as shown in Table 2.

Three synthetic metal hydroxides, Cr(OH)₃, Fe(OH)₃ and Zn(OH)₂, were used in this work because they were present in the zinc-cyanide plating sludge at high concentrations. Cr(OH)₃, Fe(OH)₃ and Zn(OH)₂ were obtained by adjusting the pHs of 1 N metal nitrate solutions with sodium hydroxide solution to 7.5, 7.5

and 9.5, respectively. These three metal hydroxide sludges were oven dried at 105 °C and ground to a particle size of less than 500 µm using mortar and pestle.

The plating sludge was brought from 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 500 µm. The ground sludge was digested using concentrated nitric acid and the concentration of heavy metals was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES). Cr, Fe and Zn were present in the plating sludge at the concentration of 17.6, 60.8 and 341 g/kg dry sludge, respectively.

2.2. Sample preparation

The rRHA was used to substitute for OPC at 0, 10, 20 and 30 wt.% and were used as solidification binders to solidify the synthetic metal hydroxides and the zinc-cyanide plating sludge. The synthetic metal hydroxides were added to the solidification binders at 0 and 10 wt.% whereas zinc-cyanide plating sludge was added at 0, 10, 20 and 30 wt.%, respectively. The optimum water to solid (W/S) ratio for each mix was obtained by conducting flow tests following ASTM C 230-90. The mix designs for metal hydroxides and the plating sludge are shown in Table 3. The slurry was mixed following the standard test method ASTM C 305-94 to achieve a uniform distribution of the solidification binders and wastes before being transferred to the plastic mould. The cement solidified metal wastes were allowed to solidify in the sealed plastic moulds to avoid carbonation prior to testing.

Table 1
Oxide content of OPC (elephant brand)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	LOI
21.16	6.04	3.15	63.96	0.87	0.05	0.54	2.88	1.39

Table 2
Characteristics of RHA firing at various temperatures

Temperature (°C)	SiO ₂ (%)	LOI (%)	Strength activity index (28 days)
400	85.2	10.3	75.0
500	87.8	7.7	92.0
550	88.3	7.1	94.2
600	89.5	6.5	94.1
650	90.2	4.9	97.7
700	90.5	4.0	93.4
800	94.6	1.3	79.2

Table 3
Mix designs of the solidified wastes

Identity	W/S ratio	Identity	W/S ratio
OPC + 0R	0.45	OPC + 0R	0.45
OPC + 10R	0.5	OPC + 10R	0.5
OPC + 20R	0.5	OPC + 20R	0.5
OPC + 30R	0.6	OPC + 30R	0.6
OPC + 0R + 10%Cr	0.45	OPC + 0R + 10%PS	0.5
OPC + 10R + 10%Cr	0.45	OPC + 10R + 10%PS	0.5
OPC + 20R + 10%Cr	0.55	OPC + 20R + 10%PS	0.6
OPC + 30R + 10%Cr	0.65	OPC + 30R + 10%PS	0.6
OPC + 0R + 10%Fe	0.45	OPC + 0R + 20%PS	0.5
OPC + 10R + 10%Fe	0.45	OPC + 10R + 20%PS	0.6
OPC + 20R + 10%Fe	0.55	OPC + 20R + 20%PS	0.6
OPC + 30R + 10%Fe	0.65	OPC + 30R + 20%PS	0.7
OPC + 0R + 10%Zn	0.45	OPC + 0R + 30%PS	0.6
OPC + 10R + 10%Zn	0.45	OPC + 10R + 30%PS	0.6
OPC + 20R + 10%Zn	0.55	OPC + 20R + 30%PS	0.7
OPC + 30R + 10%Zn	0.65	OPC + 30R + 30%PS	0.7

Remarks: R = rice husk ash; Cr = chromium hydroxide; Fe = ferric hydroxide; Zn = zinc hydroxide; PS = plating sludge.

2.3. Time of setting

A standard test method for time of setting of cement mixes were determined by means of Vicat Needle (ASTM C 191-92). The cement/rRHA/metal waste mixes were prepared as those given in Table 3. A method of test for normal consistency of hydraulic cement (ASTM C 187) was used for determining the mix water. The slurry was then transferred into the ring and the excess mix was removed. The penetration of the needle into the samples was observed for every 15 min. The values of the final setting time were averaged from at least four observations.

2.4. Compressive strength

The unconfined compressive strength of the solidified wastes was done following ASTM D 1633-96. The size of the cylindrical sample was modified to 50 mm in diameter and 100 mm in height. The compressive strength of the solidified samples was determined after curing for 1, 3, 7, 14, 28, 56 and 91 days except for those containing the plating sludge which were determined at the age of 14, 28, 56, 91 and 180 days. A set of five samples was used for compression test at each curing duration and the arithmetic average was taken from five replicates.

2.5. Leaching test

Metal leaching from the solidified waste samples was assessed using toxicity characteristic leaching procedure (TCLP) as defined by the US EPA on the samples cured for 28 days. The leachates were filtered through a 0.45 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 ICP-AES. Each leachate was analyzed in triplicate and the mean values were reported to ensure the reproducibility of the data.

3. Results and discussion

3.1. Time of setting

The final setting time of cement/metal hydroxide mixes and cement/plating sludge mixes is shown in Table 4. The mixes containing 10 wt.% Cr(OH)₃ or Fe(OH)₃ have similar final setting time with respect to the control.

An accelerated setting was observed when Zn(OH)₂ was added to cement. Time to final setting decreased from 207 min for cement paste to 99 min for cement with 10 wt.% Zn(OH)₂. This phenomena was the same as that found by other researchers that the cement paste showed unusual rapid setting but was not hard [14,15]. Asavapisit et al. [16] have reported that SO₄²⁻ concentration was reduced and rapidly disappeared from solution during cement hydration in the presence of Zn(OH)₂. This indicates that the rapid setting of cement could possibly be due to insufficient SO₄²⁻ to prevent the tricalcium aluminate hydration.

The opposite effect occurred when rRHA was substituted for OPC. The time to final setting increased from 99 to 354, 801 and 993 min when Zn(OH)₂ was added to cement blended with 0, 10, 20 and 30 wt.% rRHA, respectively. Zn(OH)₂ was reported to accelerate the hydration of calcium aluminate but retard the hydration of silicate [15]. It is possible that when the amounts of

Table 4
The final setting time for cement/metal waste mixes

Identity	W/S ratio	Final setting (min)	Identity	W/S ratio	Final setting (min)
OPC + 0R	0.26	207	OPC + 0R	0.26	207
OPC + 10R	0.34	209	OPC + 10R	0.34	209
OPC + 20R	0.43	249	OPC + 20R	0.43	249
OPC + 30R	0.52	248	OPC + 30R	0.52	248
OPC + 0R + 10%Cr	0.25	210	OPC + 0R + 10%PS	0.28	38
OPC + 10R + 10%Cr	0.32	189	OPC + 10R + 10%PS	0.37	180
OPC + 20R + 10%Cr	0.41	183	OPC + 20R + 10%PS	0.45	1055
OPC + 30R + 10%Cr	0.51	198	OPC + 30R + 10%PS	0.53	1034
OPC + 0R + 10%Fe	0.23	316	OPC + 0R + 20%PS	0.30	29
OPC + 10R + 10%Fe	0.31	298	OPC + 10R + 20%PS	0.37	621
OPC + 20R + 10%Fe	0.40	250	OPC + 20R + 20%PS	0.46	1120
OPC + 30R + 10%Fe	0.49	300	OPC + 30R + 20%PS	0.54	1560
OPC + 0R + 10%Zn	0.30	99	OPC + 0R + 30%PS	0.30	95
OPC + 10R + 10%Zn	0.38	354	OPC + 10R + 30%PS	0.37	804
OPC + 20R + 10%Zn	0.45	801	OPC + 20R + 30%PS	0.46	1302
OPC + 30R + 10%Zn	0.51	993	OPC + 30R + 30%PS	0.56	1790

rRHA in the cement mixes increased, the negative effects on silicate hydration also increased and this leads to longer final setting time.

The zinc-cyanide plating sludge affected the final setting time of cement and rRHA-blended cements in a similar manner to the synthetic Zn(OH)_2 but the effect on hydration reactions was more severe. This can be associated with the high concentration of Zn(OH)_2 present in the plating sludge (341 g/kg dry sludge). In addition, the presence of other metal hydroxides in the plating sludge may enhance the retardation effect of zinc hydroxide [17].

3.2. Compressive strength

Results of strength development of cement paste containing rRHA as cement replacement material can be seen in Fig. 1. The influence of rRHA resulted in strength reduction of blended cements at all levels of replacement during the first 14 days of curing. This was caused by the slow pozzolanic reaction of rRHA compared to the hydration reactions of the OPC. However, it was found that the blended cements with 10 and 20 wt.% replacement had higher rate of strength development than the control at 28 and 91 days, respectively.

A reduction in strength of blended cements was observed when 10 wt.% of Cr(OH)_3 , Fe(OH)_3 and Zn(OH)_2 were added (Fig. 2(a)–(c)). The strength was not developed for the samples containing Fe(OH)_3 and Zn(OH)_2 during 1 and 3 days, respectively. The high alkalinity of cement systems causes the amphoteric metal hydroxides to become soluble. These soluble heavy metals interfere with the cement hydration and lead to lower strength development. Although Zn(OH)_2 causes the most severe hydration retardation among the metal hydroxides studied during the early age (7 days), a considerable high rate of strength development was observed after 7 and 14 days for cement and cement blended with 10% rRHA.

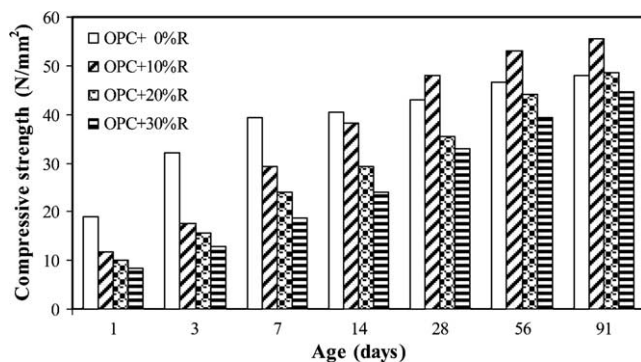


Fig. 1. Strength development of cement paste containing various amounts of rRHA.

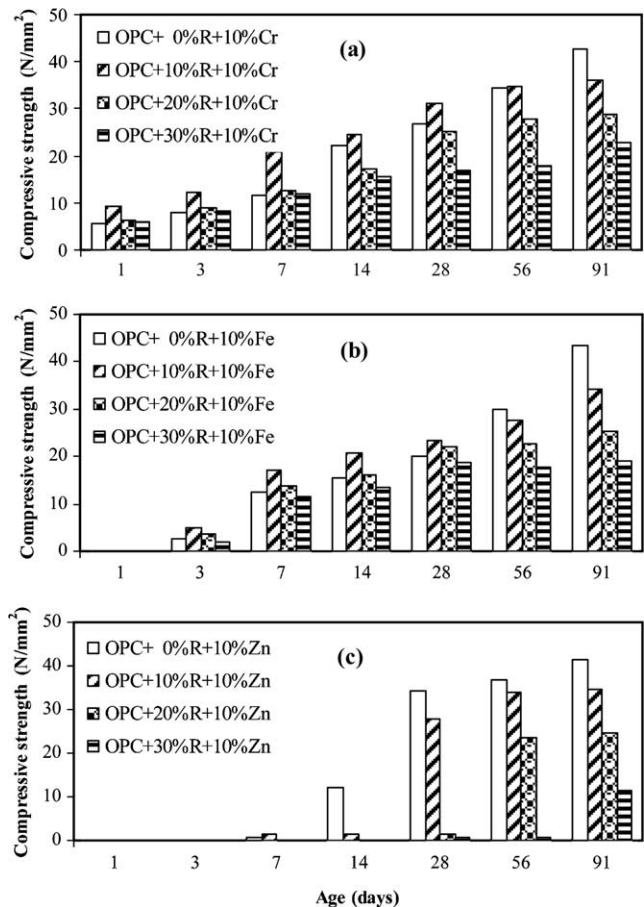


Fig. 2. Strength development of cement-based solidified metal hydroxides: (a) Cr(OH)_3 ; (b) Fe(OH)_3 and (c) Zn(OH)_2 .

An interesting observation was found for samples containing Cr(OH)_3 and Fe(OH)_3 . A higher rate of strength development during the first 28 days of curing was observed from cements blended with 10 wt.% rRHA compared to those without. It is possible that the chemical composition especially alkalinity of cements blended with rRHA is suitable for stabilization of the amphoteric Cr(OH)_3 and Fe(OH)_3 . As a result, less Cr(OH)_3 and Fe(OH)_3 are soluble and therefore the interfering effect on cement hydration is reduced. Similar effect has been reported [18] for the severe hydration retardation caused by Pb(OH)_2 on OPC being reduced due to the pozzolanic effect of condensed silica fume.

Similar observations were obtained from samples containing the plating sludge but the strength development during the first 7 days of curing was very low (Fig. 3(a)–(c)). A significant strength reduction is believed to be caused by the synergistic effect between Zn(OH)_2 and other metal hydroxides present in the plating sludge. Experimental results showed that the plating sludge could be loaded at 30 wt.% to the cement blended with 10 wt.% rRHA and gave the 28-day strength greater than 0.34 N/mm^2 [19,20] which is the minimum requirement for landfilling.

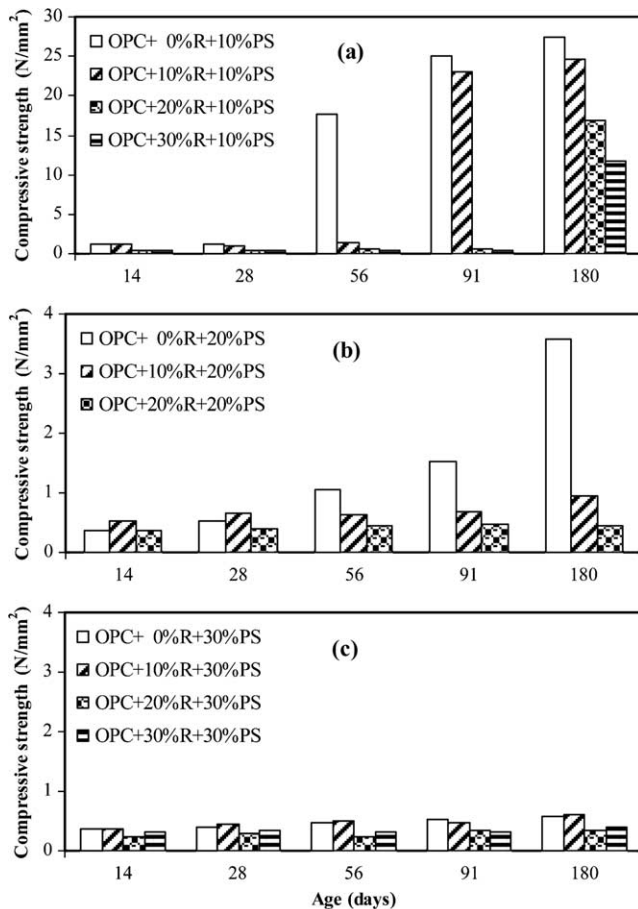


Fig. 3. Strength development of cement-based solidified plating sludge: (a) 10%PS; (b) 20%PS and (c) 30%PS.

3.3. Metal leachability

The pH values for TCLP leachates obtained from the solidified metal hydroxides were in the range of 11.6–12.5 as shown in Table 5. Leachate pHs were found to decrease with the addition of rRHA in the cement mixes. This is because $\text{Ca}(\text{OH})_2$ which is one of the hydration products produced from OPC hydration was consumed during the pozzolanic reaction of rRHA. As a result, the acid neutralization capacity of the cement blended with rRHA has reduced. However, the release of synthetic metal hydroxides from the solidified samples was very low due to the high resultant leachate pHs under TCLP leaching condition.

Higher leachate pHs extracted from the solidified plating sludges was observed in comparison with the solidified metal hydroxides (Table 6). This is believed to be caused by the interfering effects of heavy metals present in the plating sludge on the hydration reactions of OPC and as a result most of the cement clinkers were left unreacted. CaO was therefore dissociated from the unreacted cement clinkers when they were in contact with TCLP leachate and increased the pH values of

Table 5

Leachate pHs and concentration of metals in TCLP leachates of the solidified metal hydroxides

Identity	pH	Concentration (mg/L)		
		Cr	Fe	Zn
OPC + 0R + 10%Cr	12.5	0.3	n.d.	n.d.
OPC + 10R + 10%Cr	12.1	0.3	n.d.	n.d.
OPC + 20R + 10%Cr	11.8	0.4	n.d.	n.d.
OPC + 30R + 10%Cr	11.8	0.4	n.d.	n.d.
OPC + 0R + 10%Fe	12.4	n.d.	0.1	n.d.
OPC + 10R + 10%Fe	12.1	n.d.	0.1	n.d.
OPC + 20R + 10%Fe	11.8	n.d.	0.1	n.d.
OPC + 30R + 10%Fe	11.6	n.d.	0.1	n.d.
OPC + 0R + 10%Zn	12.4	n.d.	n.d.	1.5
OPC + 10R + 10%Zn	12.2	n.d.	n.d.	1.5
OPC + 20R + 10%Zn	11.6	n.d.	n.d.	1.5
OPC + 30R + 10%Zn	11.7	n.d.	n.d.	1.8

n.d. = not detected.

Table 6

Leachate pHs and concentration of metals in TCLP leachates of the solidified plating sludges

Identity	pH	Concentration (mg/L)		
		Cr	Fe	Zn
OPC + 0R + 10%PS	12.3	0.3	0.2	2.9
OPC + 10R + 10%PS	12.1	0.4	0.5	3.1
OPC + 20R + 10%PS	12.3	0.4	0.2	2.6
OPC + 30R + 10%PS	12.7	0.5	0.3	2.5
OPC + 0R + 20%PS	12.5	0.5	1.3	3.6
OPC + 10R + 20%PS	12.4	0.5	2.0	3.2
OPC + 20R + 20%PS	12.5	0.5	2.2	3.2
OPC + 30R + 20%PS	12.4	0.5	2.6	2.5
OPC + 0R + 30%PS	12.4	0.5	3.7	3.7
OPC + 10R + 30%PS	12.3	0.5	4.5	3.9
OPC + 20R + 30%PS	12.3	0.5	4.1	2.8
OPC + 30R + 30%PS	12.1	0.5	4.4	2.2

n.d. = not detected.

the leachates to between 12.1 and 12.7. It was observed that leachability of heavy metals increased with increasing the amount of waste loading. The concentration of heavy metals especially chromium in leachates does not exceed the TCLP limits (5 mg/L). This is because the solubility of most amphoteric metal hydroxides was controlled by the high leachate pH.

4. Conclusion

1. The presence of $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ have no apparent effect on final setting time. However, the presence of $\text{Zn}(\text{OH})_2$ caused rapid setting when added to cement whereas delayed setting was observed when $\text{Zn}(\text{OH})_2$ was added to cement blended with rRHA.
2. $\text{Zn}(\text{OH})_2$ causes severe hydration retardation on both cement and cement blended with rRHA. Although no

strength was developed for all samples containing $\text{Zn}(\text{OH})_2$ during the first three days of curing but a considerable high rate of strength was developed after that.

3. The interfering effect caused by both the synthetic metal hydroxides and the plating sludge on cement hydration was reduced when cement was blended with 10 wt.% rRHA. It is possible that the alkalinity of the blended-cement system was suitable for stabilization of heavy metals.
4. The acid neutralization capacity of cement-based solidified wastes was reduced when rRHA was used to substitute for OPC. However, concentration of heavy metals in the TCLP leachates was very low due to the high resultant leachate pHs.
5. The plating sludge could be loaded at 30 wt.% to the cement blended with 10 wt.% rRHA and resulted in either the minimum acceptable 28-day strength or the maximum level of metal leaching that meets the minimum requirement for landfilling.

Acknowledgements

This research work was funded by the Thailand Research Fund. The authors would like to thank Miss Orraporn Chanpenkun for her help with some experiments. The Department of Civil Engineering and Department of Civil Technology Education, Faculty of Engineering, KMUTT deserve appreciation for providing access to their laboratories and for their assistance with the experiment.

References

- [1] Kapur T, Kandpal TC, Garg HP. Electricity generation from rice husk in Indian rice mills: Potential and financing viability. *Biomass Bioenergy* 1996;10:393–403.
- [2] Soponronnarit S, Yapha M, Prachayawarakorn S. Cross-flow fluidized bed paddy dryer: prototype and commercialization. *Drying Technol J* 1995;13:2207–16.
- [3] Ajiwe VIE, Okeke CA, Akigwe FC. A preliminary study of manufacture of cement from rice husk ash. *Bioresource Technol* 2000;73:37–9.
- [4] Cisse IK, Laquerbe M. Mechanical characterisation of filler sandcretes with rice husk ash additions: Study applied to Senegal. *Cement Concrete Res* 2000;30:13–8.
- [5] James J, Rao S. Silica from rice husk through thermal decomposition. *Thermochim Acta* 1986;97:329–36.
- [6] Hanafi S, Abo-El-Enein SA. Surface properties of silicas produced by thermal treatment of rice-husk ash. *Thermochim Acta* 1980;37:137–43.
- [7] Yu Q, Sawayama K, Sugita H, Shoya M, Isojima Y. The reaction between rice husk ash and $\text{Ca}(\text{OH})_2$ solution and the nature of its product. *Cement Concrete Res* 1999;29:37–43.
- [8] Ibrahim DM. Crystallite growth of rice husk ash silica. *Thermochim Acta* 1981;45:79–85.
- [9] Ismail MS, Waliuddin AM. Effect of rice husk ash on high strength concrete. *Constr Build Mater* 1996;10:521–6.
- [10] Zhang MH, Lastra R, Malhotra VM. Rice-husk ash paste and concrete: some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste. *Cement Concrete Res* 1996;26:963–77.
- [11] Jaubertie R, Rendell F, Tamba S, Cisse I. Origin of the pozzolanic effect of rice husks. *Constr Build Mater* 2000;14:419–23.
- [12] Coutinho JS. The combined benefits of CPF and RHA in improving the durability of concrete structures. *Cement Concrete Composites* 2003;25:51–9.
- [13] Isaia GC, Gastaldini ALG, Moraes R. Physical and pozzolanic action of mineral additions on the mechanical strength of high-performance concrete. *Cement Concrete Composites* 2003;25:69–76.
- [14] Stephan D, Mallmann R, Knöfel D, Härdtl R. High intakes of Cr, Ni, and Zn in clinker Part II. Influence on the hydration properties. *Cement Concrete Res* 1999;29:1959–67.
- [15] Diet JN, Moszkowicz P, Sorrentino D. Behaviour of ordinary Portland cement during the stabilization/solidification of synthetic heavy metal sludge: macroscopic and microscopic aspects. *Waste Manage* 1998;18:17–24.
- [16] Asavapisit S, Fowler G, Cheeseman CR. Solution chemistry during cement hydration in the presence of metal hydroxide wastes. *Cement Concrete Res* 1997;27:1249–60.
- [17] Olmo IF, Chacon E, Irabien A. Influence of lead, iron(III) and chromium(III) oxides on the setting time and strength development of Portland cement. *Cement Concrete Res* 2001;31:1213–9.
- [18] Asavapisit S, Nanthamontry W, Polprasert C. Influence of condensed silica fume on the properties of cement-based solidified wastes. *Cement Concrete Res* 2001;31:1147–52.
- [19] Stabilization/Solidification of CERCLA and RCRA Wastes-Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities: EPA 625/6-89-022; U.S. Environmental Protection Agency, May 1989.
- [20] Guide Specification for Military Construction-Stabilization/Solidification of Contaminated Materials: CEGS-02445; U.S. Army Corps of Engineers. December 1995.