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Immobilization of metal-containing waste in alkali-activated lime–RHA cementitious matrices

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Abstract

This research investigated the immobilization potential of alkali-activated lime–rice husk ash (RHA) for synthetic $Cr(OH)_3$, $Fe(OH)_3$, $Zn(OH)_2$ and zinc cyanide plating sludge. The binder consists of hydrated lime and RHA at a weight ratio of 45:55. Waterglass (Na_2SiO_3) with $SiO_2/Na_2O \approx 3$ and anhydrous sodium carbonate (Na_2CO_3) were used as alkali activator between 0 and 8 wt.% of the binder. Results showed that $Zn(OH)_2$ addition causes a considerable strength development in control and sodium silicate-activated samples but only after 14 days. Similar observations were found for the sample loaded with 10 wt.% plating sludge but this only occurred after 28 days. A possible explanation for these phenomena is that the initial formation of calcium zincate, which has a set retarding effect, inhibits early strength development. At later ages, calcium zincate dissolves and Zn is taken up in the formation of C–S–Z–H solid solutions leading to strength development. These phenomena were not observed from the sodium carbonate-activated lime–RHA matrices. In these, it is believed that zinc/calcium carbonates readily form inhibiting calcium zincate and C–S–Z–H formation. Despite this, carbonate-containing mixes with up to 30 wt.% plating sludge gave a 14-day strength and Cr concentration in TCLP leachate that meet the regulatory limit for landfilling.

Keywords: Rice husk ash; Hydrated lime; Plating sludge; Alkali activators; Strength; Leaching

1. Introduction

Rice husk, an agricultural residue, is generated in Thailand in large quantities each year. The husk is partly used as bulking agents for composting of animal manure or as biomass fuel to replace fossil fuel in generating heat for drying rice or electricity [1,2]. The remaining husk is burned at the rice fields, causing environmental problems. If rice husk is burned under controlled conditions, the resultant ash (RHA) can be used as a supplementary cementing material due to its high reactive silicon dioxide content. Several studies have been conducted on the use of rice husk ash as a mineral additive to improve the performance of concrete [3–8]. Its application in hazardous waste treatment is relatively new and is under investigation.

Previous study found that the interfering effects caused by both synthesized metal hydroxides ($Zn(OH)_2$, $Cr(OH)_3$ and $Fe(OH)_3$) and plating sludges, derived from electroplating processes and containing these heavy metal hydroxides, on cement hydration was reduced when OPC was substituted by 10 wt.% reactive RHA during the solidification process [9]. This paper investigates the use of RHA, in this case, activated with hydrated lime rather than OPC, as a matrix for the immobilization of metals in zinc cyanide plating sludge. The plating sludge was generated from the wastewater treatment plant of a zinc-cyanide plating industry. Cyanide in the plating wastewater was first removed by chemical oxidation with ozone. Sodium hydroxide was then added to adjust pH of the remaining wastewater to around 7.5 to transform the soluble metals into metal hydroxides. These metal hydroxides were separated from wastewater by filtration through sand drying beds. The sludge was then oven dried in the laboratory and is subsequently referred to as the plating sludge (PS). The cementitious properties, as well as the immobilization performance of the binder

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Table 1
Setting time characteristics of the metal sludge–cement matrices

Identity	Setting time (min)	
	Initial	Final
Lime + RHA	415	615
Lime + RHA + 8% Na_2SiO_3	122	200
Lime + RHA + 8% Na_2CO_3	122	205
Lime + RHA + 10% $Cr(OH)_3$	466	595
Lime + RHA + 10% $Fe(OH)_3$	480	615
Lime + RHA + 10% $Zn(OH)_2$	2637	4050
Lime + RHA + 8% Na_2SiO_3 + 10% $Cr(OH)_3$	138	250
Lime + RHA + 8% Na_2SiO_3 + 10% $Fe(OH)_3$	175	255
Lime + RHA + 8% Na_2SiO_3 + 10% $Zn(OH)_2$	3480	4851
Lime + RHA + 8% Na_2CO_3 + 10% $Cr(OH)_3$	135	215
Lime + RHA + 8% Na_2CO_3 + 10% $Fe(OH)_3$	167	235
Lime + RHA + 8% Na_2CO_3 + 10% $Zn(OH)_2$	355	510
Lime + RHA + 10% PS	908	2340
Lime + RHA + 20% PS	681	4020
Lime + RHA + 30% PS	403	5928
Lime + RHA + 8% Na_2SiO_3 + 10% PS	1294	2157
Lime + RHA + 8% Na_2SiO_3 + 20% PS	525	2934
Lime + RHA + 8% Na_2SiO_3 + 30% PS	146	5495
Lime + RHA + 8% Na_2CO_3 + 10% PS	627	1101
Lime + RHA + 8% Na_2CO_3 + 20% PS	338	1328
Lime + RHA + 8% Na_2CO_3 + 30% PS	133	1451

are compared with and without activation by sodium silicate or sodium carbonate solutions using real and model waste systems.

2. Experimental

2.1. Materials

The rice husk was obtained from the rice milling plant in Phranakorn-Sri-Ayuthaya province, located in the central region of Thailand. The dried rice husk was burned to remove fixed carbon and volatile organic carbon before firing at 650 °C for 1 h in a muffle furnace [9]. The rice husk ash (RHA) was removed from the furnace and rapidly cooled to ambient temperature (between 30–32 °C) by spreading on a tray. The RHA was then ground using a Los Angeles abrasion machine until the maximum amount retained, when wet-sieved on a No. 325 (45 μm) sieve, was less than 34%. The synthetic RHA has 90.2% SiO_2 and gave a 28-day strength activity index with Portland cement of 97.7%.

Two analytical grade chemicals were used as activators: waterglass (sodium silicate solution with $SiO_2/Na_2O \approx 3$, pH sol. $5\% \leq 11.50$; supplied by Panreac Quimica SA) and anhydrous sodium carbonate (Na_2CO_3); supplied by Ajax Finechem.

Plating sludges were obtained from the wastewater treatment plant of a zinc-cyanide plating plant located in Bangkok, Thailand. Analysis[1] showed that the main metal constituents were chromium (17.6 g/kg of dried sludge), iron (60.8 g/kg) and zinc (341 g/kg). In efforts to simulate sludge performance, model sludges were prepared by precipitating metal hydroxides from 1 N solutions of chromium, iron and zinc nitrate (prepared from metal nitrates (Ajax Finechem) dissolved in deionised water). Precipitation was maximized by adjusting the pH with sodium hydroxide solution (Ajax Finechem AnalaR; 1 M) to pH 7.5 for $Cr(OH)_3$ and $Fe(OH)_3$, and 9.5 for $Zn(OH)_2$ (pH of minimum solubility). The precipitated metal hydroxide sludges were oven dried at 105 °C and ground to a particle size of less than 500 μm using a mortar and pestle.

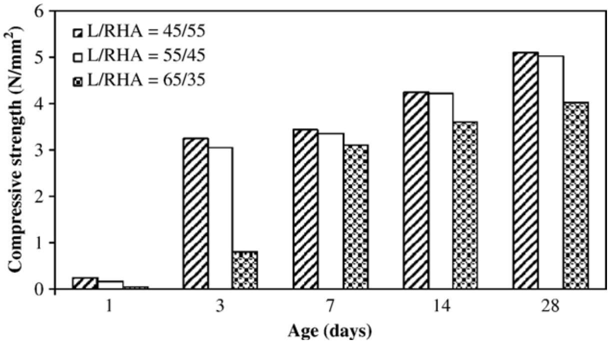

Fig. 1. Strength development of lime-RHA cement at different proportions of lime and RHA.

2.2. Sample preparation

Cement samples were prepared using hydrated lime and RHA in the weight ratio of 45:55, 55:45 and 65:35. Waterglass solution and Na_2CO_3 were dissolved in the mix water and then were slowly added to the lime–RHA mixes such that waterglass and Na_2CO_3 concentrations were 0, 4, 6 and 8% of the binder (hydrated lime and RHA), and water to solid ratio in all cases

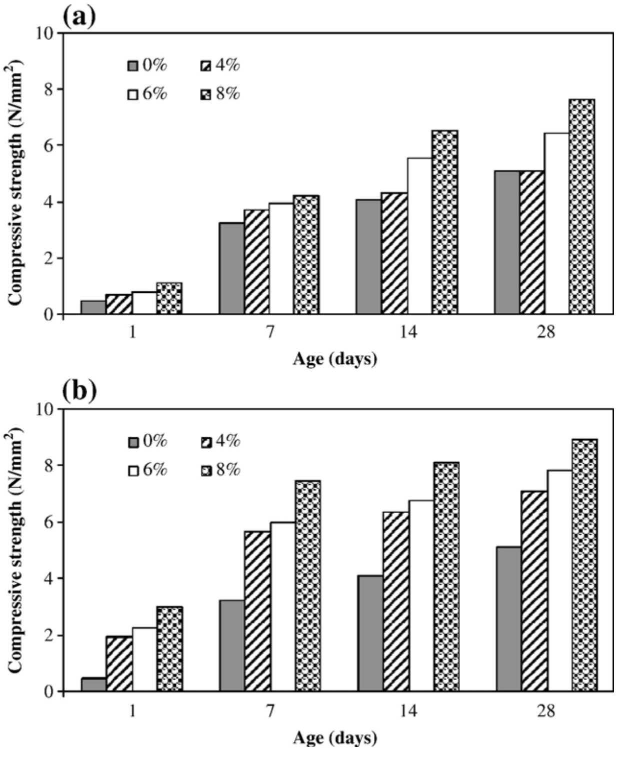

Fig. 2. Strength development of lime-RHA cement at the ratio of 45:55 and in the presence of (a) waterglass and (b) Na_2CO_3.

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[1] Portions of sludges were dried at 105 °C, ground to pass a 500 mm sieve and digested using concentrated nitric acid. Metal concentrations were analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES).

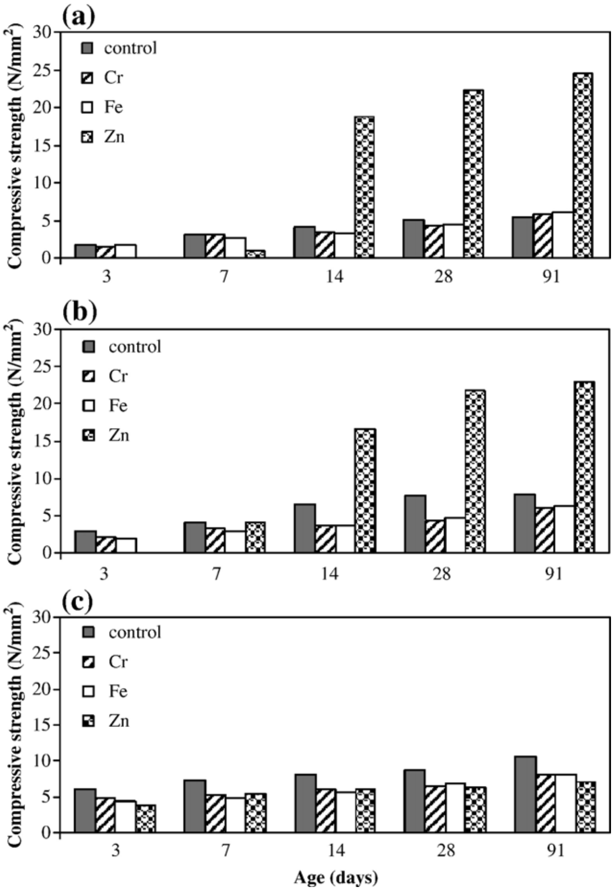

Fig. 3. Strength development of lime-RHA cement in the presence of metal hydroxides; (a) control; (b) waterglass and (c) Na_2CO_3.

was 0.955. The slurries were mixed following the standard test method ASTM C 305-94 to achieve a uniform consistency before being transferred to plastic moulds. The samples were then allowed to set and harden in the sealed plastic moulds to avoid carbonation prior to testing. On demoulding, samples were wrapped with shrink film to prevent the loss of moisture and cured in this condition at room temperature (28–32 °C).

2.3. Setting time

The standard test method, ASTM C 191-92, was modified to determine the setting time of the cement–metal waste mixes, as follows. Samples were prepared at a w/s ratio of 0.45. The mixture was then transferred into the apparatus and the excess paste was removed. The penetration of the needle into the samples was determined every 15 min. The final setting time was obtained when the needle did not sink visibly into the mix. Setting time data are reported in Table 1.

2.4. Compressive strength

The unconfined compressive strength of cylindrical samples (50 mm in diameter and 100 mm in height) of the solidified wastes was determined following ASTM D 1633-96. The compressive strengths of the sludge-free cement samples were determined after curing for 1, 7, 14 and 28 days whereas those of samples containing metal hydroxide sludge were determined at the age of 3, 7, 14, 28 and 91 days. A set of five samples was used for compression testing at each curing duration and the arithmetic average was taken. These data are summarized in Figs. 1–4.

2.5. Leaching characteristics

The optimum solidification binder involving lime, RHA and chemical activators was determined based on strength development data obtained during 28 days of curing (see Figs. 1 and 2). Hydrated lime and RHA in the weight ratio 45:55, with 8% waterglass or 8% Na_2CO_3 and a 10–30 wt.% loading of plating sludge was selected for subsequent leaching studies.

Metal leaching from the solidified wastes aged 91 days was assessed using the toxicity characteristic leaching procedure (TCLP), as defined by the US EPA. Samples were crushed to pass a 9.5 mm sieve and extracted with acetic acid solution (pH 2.88) in a quantity equal to 20 times the surface area of the sample. The extractions took place in vessels, which were rotated end over end at 30 rpm for 18 h. Leachates were then filtered using a 0.45 μm membrane filter to remove suspended solids and were divided into two portions; for pH and for ICP-AES analysis. Metal concentrations were measured in triplicate

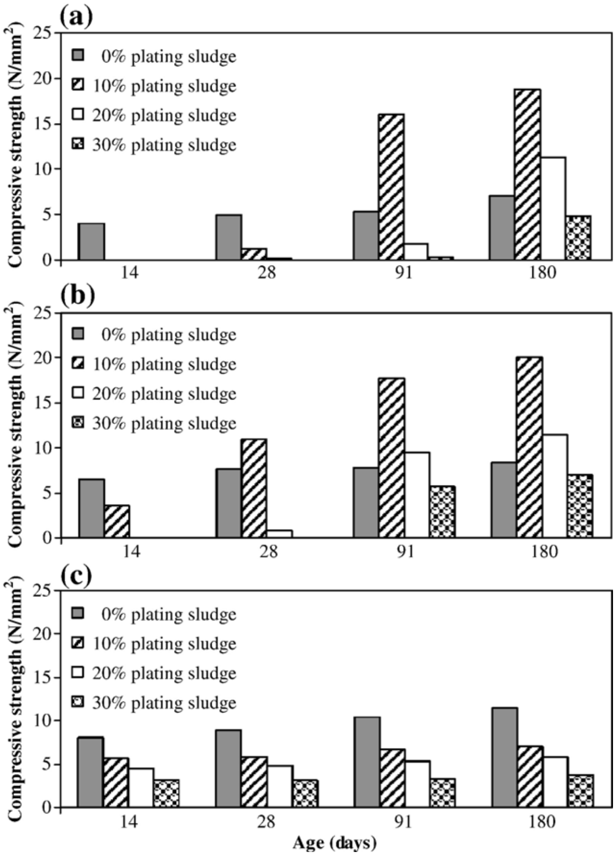

Fig. 4. Strength development of lime-RHA cement in the presence of plating sludge; (a) control; (b) waterglass and (c) Na_2CO_3.

Table 2
pH and metal concentration (mg/L) in TCLP leachates from samples aged 91 days

Identity	Concentration (mg/L)			
	pH	Zn	Fe	Cr
Regulatory limit		*	*	5
Lime+RHA+10% PS	11.80	0.09	1.06	0.28
Lime+RHA+20% PS	11.83	2.34	0.34	0.24
Lime+RHA+30% PS	11.69	2.26	0.42	0.25
Lime+RHA+8%Na_2SiO_3+10% PS	8.12	0.13	0.77	0.25
Lime+RHA+8%Na_2SiO_3+20% PS	11.71	12.29	0.27	0.27
Lime+RHA+8%Na_2SiO_3+30% PS	10.86	21.15	0.32	0.29
Lime+RHA+8%Na_2CO_3+10% PS	8.58	0.09	0.77	0.27
Lime+RHA+8%Na_2CO_3+20% PS	8.22	0.84	0.26	0.26
Lime+RHA+8%Na_2CO_3+30% PS	7.44	10.35	0.33	0.30

Remark: *not regulated.

and data, reported in Table 2, are arithmetic averages of metal concentrations.

3. Results and discussion

Table 1 and Figs. 1–4 indicate the setting and strength development properties respectively within the system studied. The strength data for binder only (Fig. 1) show an increase in the strength of paste derived from all lime/RHA compositions although the maximum rate of strength development is observed for the 45/55 (lime/RHA) weight ratio. The superior performance of this composition over the higher lime content samples, especially up to 3 days, indicates the beneficial contribution of RHA as a reactive component of the system [the 28-day strength activity index is 97.7%].

The influence of activators on the 45/55 (lime/RHA) blend is highlighted in Fig. 2. In this case, hydrating water contains sodium silicate or sodium carbonate at weight ratios relative to the binder, of 0–8%. Strength development is enhanced by both activators, generally increasing with increasing levels of addition, but more so by the sodium carbonate with higher rates of strength development and higher 28 day strengths. The enhancement with sodium silicate can be attributed to the increased availability of soluble silicate ions to calcium ions from the hydrating lime, to form C–S–H gel. This supplements the pozzolanic reaction between lime and RHA. However, the role of carbonate is less clear. Precipitation of calcium carbonate may act as nucleation sites for C–S–H formation, with the calcium carbonate having a micro-aggregate role or precipitated calcium carbonate may deposit in pores, thus enhancing compressive strength.

The addition of synthetic wastes (metal hydroxides at 10% by weight of the binder) has variable influence on strength development (Fig. 3). The chromium and iron hydroxides tend to reduce strength marginally in all systems (with and without activators) but the behaviour of Zn-containing matrices is distinctly different as reported by previous research [9–12]. With no activator, the Zn-containing sample has no strength at 1 day because it has not yet set (see setting time data, Table 1) and has only achieved initial set by 2 days. This confirms the previously reported retardation effect observed for Zn [9] and it is not until 3 days that strength gain becomes significant. In fact, relatively high rates of strength development and high final strengths are observed (Fig. 3). A possible explanation for this effect is the intercalation of Zn into C–S–H to provide gel compositions of the form $Ca_4[(Si_{6-\triangle}v_{\triangle-n}Zn_nO_{18-2\triangle})H_{2(p-n)}Ca_{2-p}]_q(OH)_{8(1-q)}.mH_2O$, (C–S–Z–H) as reported by Tomasseo and Kersten [13]. The various terms in the compositional representation have structural significance and the reader is referred to the original paper for detailed compositional information. The same authors report that calcium zincate ($CaZn_2(OH)_6.2H_2O$), disappeared in their analysis after about 14 days and this offers a possible explanation for the delayed setting observed in the present study although no systematic mineralogical analysis was carried out in the present work to confirm this. The same trends are observed in the set of data corresponding to metal hydroxide-loaded samples activated by sodium silicate and we assume that the same explanation as was offered for the non-chemically activated pastes, is applicable.

By contrast, the data corresponding to sodium carbonate activation show no strength gain at 14 days. The only difference between these and previously discussed systems is that there is now the potential for carbonates of Ca and Zn to form following the progressive incongruent dissolution of C–S–H and C–S–Z–H phases [14]. Leach test data (Table 2) show that whilst leached concentrations of Fe and Cr remain low, the Zn concentrations are considerably higher from all of the $Zn(OH)_2$-containing matrices. There does not appear to be any correlation between the observed strength behaviour nor the observed setting times with leached Zn concentrations although there is no expectation that there should be, particularly as the sequence of precipitation and redissolution of Zn-bearing phases appears to be rather complex [14] and the TCLP conditions are not representative of the aqueous environment within a cement system.

The final set of strength data (Fig. 4) indicate the strength development in samples loaded with actual plating sludge. It is important to emphasise that $Zn(OH)_2$ is the principal component of the sludge and appears to dominate the strength characteristics of the pastes according to the model waste systems discussed above. However, the degree of loading has a significant effect on strength and on setting time. Firstly, the sodium silicate, at 10% loading and sodium carbonate-activated samples (at 10, 20 and 30% loading) develop strength at 14 days, which is not apparent in the water-activated control. The 10% loading in the sodium silicate-activated system is capable of significant strength development from 14 days whilst the higher loadings are unable to gain sufficient strength to test until 28 days. It is difficult, based on the available data, to be precise on explanations for the strength characteristics observed but we suggest, based on the arguments presented in [13] and [14], that the strength maximum observed at 10% PS loading in control and waterglass activated systems arises due to competing effects. At low loadings, the C–S–H gel binder is tolerant of Zn (perhaps as it is incorporated into the gel (C–S–Z–H) [14]) but at higher levels, other, less stable Zn-bearing phases e.g. calcium zincate, may also contribute to a developing microstructure. However, these would have a disruptive influence on the matrix microstructure as they dissolve leading to the lower observed strengths. Finally, the sodium carbonate-activated pastes, whilst not developing as high strengths as some of the other systems tested, achieve measurable strengths at 14 days and this remains approximately for the duration of the testing period for all levels of sludge addition.

Given the dominant concentrations of Zn in the plating sludges, it is interesting to note that the highest Zn concentration leached from any of the specimens tested corresponds to a sodium silicate-activated matrix containing a sludge loading of 30%. The leached concentration corresponds to only 2.5% of the available Zn suggesting that either much of the Zn is trapped in soluble form within a disconnected pore network or that it is associated with hydration products. The corresponding figure for the 20% sludge loading is 1.4% but at 10%, this is 0.02%. It is proposed that the higher levels of addition have introduced sufficient Zn to saturate the available C–S–Z–H. The lower leached concentration in the corresponding sodium carbonate-activated paste may be attributed to Zn incorporation in $(Zn,Ca)CO_3$-related phases [14].

4. Conclusions

This study has focused primarily on a search for a technical solution to the disposal of sludges from the zinc-cyanide plating process. The objectives were to develop a matrix from readily available resources within which wastes could be stabilized and which would meet the necessary strength requirements for disposal in landfill. The main conclusions of the study are:

- RHA represents a suitable silica source for acceptable strength development when activated by slaked lime.
- Rate of strength development can be enhanced by up to 45% using waterglass (sodium silicate) and by up to 65% with sodium carbonate solutions, at 28 days.
- Synthetic waste preparations showed that despite long setting times, Zn additions initiated considerable strength development after 14 days in control and sodium silicate-activated systems. These characteristics were absent in the sodium carbonate-activated samples.
- The behaviour of the Zn-loaded samples is attributed to the formation of C–S–Z–H solid solutions of the form $Ca_4[(Si_{6-\triangle}v_{\triangle-n}Zn_nO_{18-2\triangle})H_{2(p-n)}Ca_{2-p}]_q(OH)_{8(1-q)}.mH_2O$ [13] which are subject to dissolution in the presence of carbonate; lower strengths were observed in the sodium carbonate-activated systems.
- The trials with plating sludge suggest that paste performance is dominated by the presence of Zn.
- The hydrated lime and RHA at the weight ratio of 45:55 and activated with 8% sodium carbonate is capable of containing up to 30 wt.% plating sludge and gave the quality of the solidified wastes that meets the minimum requirement for landfilling (the standard criteria for strength of the solidified waste that can go for landfilling is 0.34 N/mm^2).

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