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Alkali-Activated Composites of Calcium Carbide and Black Rice Husk Ash for Immobilizing Electroplating Sludge

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This study investigated the use of two waste products, black rice husk ash (BHA) from biomass power plants and calcium carbide residue (CCR) from acetylene gas production as an alkali-activated binder to solidify and stabilize the heavy metal plating sludge (PS) from electroplating plants. Optimum strength of the alkali-activated product was obtained using a weight percentage ratio of CCR to BHA of 60:40. CCR-BHA compacts containing 50 wt % PS developed strength after 3 days, but the addition of 2 wt % Na_2SiO_3 or 4 wt % Na_2CO_3 developed strength in all the samples after 1 day. The CCR-BHA paste containing 50 wt % PS developed a 7-day strength >0.35 MPa in the sample containing 4 wt % Na_2SiO_3 and the same strength was developed after 3 days in the sample containing 4 wt % Na_2CO_3. The Cr concentration of leachate from all the samples was greater than the regulatory limit except for the CCR-BHA paste containing 50 wt % PS and 4 wt % Na_2CO_3. After contacted all samples with synthetic acid rain, less corroded surface was observed from sample containing Na_2SiO_3 and Na_2CO_3. © 2018 American Institute of Chemical Engineers Environ Prog, 00: 000–000, 2018

Keywords: black rice husk ash, calcium carbide residue, electroplating sludge, durability, leachability

HIGHLIGHTS

- This research aims at the management of two kinds of waste, black rice husk ash (BHA), and calcium carbide residue (CCR), as binder to solidify electroplating sludge.
- BHA and CCR were found to successfully contain electroplating sludge.
- Addition of Na_2SiO_3 and Na_2CO_3 was beneficial in that early strength development was observed.
- Addition of both activators reduced both leachability of heavy metals and increased resistant to acid corrosion.

INTRODUCTION

Heavy metal contamination from waste is a global concern for human health and the environment. Stabilization and solidification is the preferred treatment method prior to disposal in the landfill. The release of heavy metals is reduced through the containment within an impermeable matrix. Cement-based solidification technique especially Ordinary Portland cement (OPC) has been demonstrated to be effective and economical for the treatment of heavy metal containing wastes. However, the energy intensive process and a global warming potential material have made the use of OPC for this purpose being disadvantage. Waste residues with composition similar to that of OPC are therefore receiving an increase interest recently as alternative solidification binders [1,2].

The plating sludge (PS) was generated from the wastewater treatment plant of electroplating industry. The wastewater pH was adjusted to around 7.5 to transform the soluble metals into metal hydroxides using calcium hydroxide. These metal hydroxides were separated from wastewater by filtration through the sand drying bed. The sludge contains significant amounts of heavy metals such as iron, chromium and zinc. The heavy metals present in the sludge were normally immobilized by containing within an impermeable solidified cementitious matrix [3–6]. Several researchers [7–11] reported that metal oxides and hydroxides of Cr, Cu, Fe, Pb, Zn, Cd, and Hg promote the growth of large crystal of ettringite. Zinc in different forms such as zinc oxide, and zinc sulfate, zinc nitrated retarded the hydration of cement [12,13]. The $Fe(OH)_3$ and $Cr(OH)_3$ inhibited reaction of cement grain that led to reduction of strength development and increase of setting times [14]. These are the indication of a poor microstructure development and may be expected to lead to an increase leaching [15–18].

Calcium carbide residue (CCR) is a residue from the production of acetylene gas (C_2H_2). It is used in several industries such as fuel for lamp, welding, metal cutting, space heaters, and fruit ripening. Acetylene gas manufacturing generates approximately 1790 metric tons of CCRs per month [19]. Most of the residue was disposed of in landfills where it can cause alkaline contamination of groundwater and soil. Several workers reported a reaction between CCR and pozzolanic materials (containing predominantly silica and alumina) to form C-S-H compounds similar to the products of cement hydration [15,20]. However, the compressive strength of materials produced from CCR and pozzolanic materials was rather low, possibly due to the slow nature of the

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pozzolanic reaction. The slow pozzolanic reaction could be achieved by accelerating the reaction between CCR and pozzolan. This includes particle size reduction of the reactants, the use of elevated curing temperature or addition of alkali activators such as sodium hydroxide, sodium silicate, sodium carbonate and calcium chloride. Calcium chloride is a well-known and inexpensive accelerator used to accelerate the setting and increase the early compressive strength of concrete [21]. Alkali activators have also been used in the reaction between lime and pozzolanic materials to accelerate the pozzolanic reaction and achieve high early compressive strength [22].

The black rice husk ash (BHA) is derived from the use of rice husk as biofuel in the boiler of rice milling plant. The ash is black in color due to incomplete combustion in the boiler but there is silica content >90%. BHA is therefore considering as a valuable source of silica which can be used to react with CCR to produce cementitious materials. The objective of this research work is to use two types of waste residues, BHA and CCR, to treat the zinc-electroplating sludge using stabilization/solidification (S/S) processes. BHA was used in combination with CCR to replace OPC which is a conventional S/S binder. The performance of the solidified wastes was evaluated through the development of strength, setting time, leachability of heavy metals and durability of the solidified waste to corrosion by synthetic acid rain.

EXPERIMENTAL

Materials

The materials in this study were CCR, BHA, and PS. The CCR was from the acetylene gas factory, Samutsakorn province, Thailand and was dried in the sun for 2–3 days to a moisture content of ≈ 2–5%. The BHA was from the fluidized bed incinerator of a small-scale power plant in Chainat province, Thailand. The dried CCR and BHA was ground to a particle size <45 μm using a Los Angeles Abrasion Machine. The chemical composition of these starting materials, determined by Wavelength-Dispersive X-ray Fluorescence Spectrometer (Bruker S4 Explorer), is shown in Table 1.

Table 1. Chemical analysis of PS.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
BHA	93.18	0.31	0.26	0.47	0.23	0.07	1.86
CCR	28.1	3.53	3.83	58.3	3.09	0.159	1.5

The PS was obtained from the wastewater treatment plant of the Electroplating Company, Bangkok, Thailand. The sludge was dried in the sun for 3–4 days to a moisture content of ≈ 2–4%, ground to a particle size of <0.5 μm and digested in a microwave oven with a Milestone 328. The concentration of heavy metals in the digested solution (5 mL concentrated HNO_3, 1 mL H_2O_2 and HF), was determined by ICP (Perkin-Elmer Model no. Optima 3000). Cr, Fe, and Zn were present in the PS at concentration of 28.2, 60.8, and 377 g/kg dried sludge.

Sample Preparation

Mixtures of CCR and BHA were prepared with weight ratios of 70:30, 60:40, 50:50, 40:60, and 30:70. The samples were activated by the slow addition of an aqueous solution of Na_2SiO_3 and Na_2CO_3. The concentrations of Na_2SiO_3 and Na_2CO_3 were 0, 2, and 4% of Na_2O to the CCR and BHA mixes. The optimal proportion of CCR to BHA (CCR:BHA ratio of 60:40) was selected on the basis of 56-day strength development. The mixtures were prepared containing 0, 30 and 50% PS by weight of the optimum binder. The water-to-solid ratio of all the samples was determined using consistency test (ASTM C 187-11) as shown in Table 2.

The slurry was mixed according to ASTM C 305-06, then transferred to a cylindrical plastic mold 35-mm diameter × 70-mm high. The sample was allowed to set and harden for 24 h at room temperature (around 30–35°C) before being demolded, wrapped in shrink film and cured at 32–35°C to avoid carbonation prior to testing.

Compressive Strength

The compressive strengths of the cylindrical samples were determined according to ASTM D 1633-00 after aging for 3, 7, 14, 28, and 56 days. Five replicates of each sample were used for the compaction test and the arithmetic average using a 95% CI was reported.

Table 2. Proportion of water used in CCR-BHA based cement mixtures.

					% Na_2O	
Samples	**CCR (%)**	**BHA (%)**	**Ps (%)**	**W/S**	**as Na_2SiO_3**	**as Na_2CO_3**
C70:30	70	30	-	0.32	-	-
C60:40	60	40	-	0.33	-	-
C50:50	50	50	-	0.34	-	-
C40:60	40	60	-	0.35	-	-
C30:70	30	70	-	0.37	-	-
Control	60	40	-	0.33	-	-
CPs30	42	28	30	0.31	-	-
CPs50	30	20	50	0.29	-	-
CNs2	60	40	-	0.34	2	-
CNs2Ps30	42	28	30	0.32	2	-
CNs2Ps50	30	20	50	0.30	2	-
CNs4	60	40	-	0.35	4	-
CNs4Ps30	42	28	30	0.33	4	-
CNs4Ps50	30	20	50	0.31	4	-
CNc2	60	40	-	0.33	-	2
CNc2Ps30	42	28	30	0.31	-	2
CNc2Ps50	30	20	50	0.29	-	2
CNc4	60	40	-	0.33	-	4
CNc4Ps30	42	28	30	0.31	-	4
CNc4Ps50	30	20	50	0.29	-	4

Setting Time

The setting times of the mixtures were determined using the modified ASTM method C 191-08. The penetration of the needle into the sample was determined every 30 min during the first 2 h, every 15 min from 2–3 h and every 5 min after 3 h. The initial penetration was 25 mm and the final setting time was at 0 mm penetration. A set of three samples was used to determine the setting time and the arithmetic average is reported.

Leaching Test

The leaching of metals from the solidified wastes aged for 28 days was determined by the toxicity characteristic leaching procedure (TCLP) as defined by the US EPA. Samples were crushed to pass a 9.5-mm mesh and extracted with synthetic acid leachant equal to 20 times of the sample weight. The leachant was prepared from concentrate nitric and sulfuric acid at a ratio of 60:40 and diluted with deionized water to a pH of 3. The extractions were carried out in vessels rotated end over end at 30 rpm for 18 h. The leachates were then filtered off using a 0.45 μm membrane filter to remove suspended solids and were divided into two portions for pH and ICP-AES analysis. Metal concentrations were reported as the arithmetic average of triplicate samples.

Durability

The durability of the solidified wastes to acid corrosion was determined on samples cured for 28 days with and without the addition of Na_2SiO_3 and Na_2CO_3 using a modified tank test method (EA NEN 7375:2007). The test solution was synthetic acid rain prepared from 0.01 N of nitric acid and 0.01 N of sulfuric acid at a ratio of 60:40 and the samples were exposed for 0.25, 1, 2, 4, 9, 16, 36, and 64 days. After each exposure time, the sample was dried in an acrylic chamber under N_2 to prevent surface carbonation and the sample durability was determined from the percentage weight loss and difference in surface corrosion. Variation in the chemical compositions of the corrosion layer was determined using X-ray fluorescence.

RESULTS AND DISCUSSION

Optimum Ratio of CCR and BHA

Figure 1 and Table 3 present the strength development and setting times of the CCR-BHA cement samples. CCR reacts with water according to Equation (1), generating C_2H_2 and $Ca(OH)_2$ which increases the pH of the solution to 11.25 [16, 20].

$$CaC_2 + 2H_2O \Rightarrow C_2H_2 + Ca(OH)_2 \tag{1}$$

The monosilicate ions [$SiO(OH)_3^-$] from BHA react with the alkaline $Ca(OH)_2$ forming C-S-H gels; these are similar to the products of OPC hydration and provide strength development of the paste (Figure 1). The maximum rate of strength development occurs in the sample with a CCR:BHA ratio of 60:40, and decreases when the BHA content is lower or higher than 40 wt %. This is because BHA is the silica source for the formation of CSH gels in the presence of lime. If BHA was presence at higher proportion than 40 wt % then lime content was insufficient for hydration reaction with BHA and vice versa, resulting in less CSH gels were produced. The initial and final setting time of the CCR-BHA cement increases with BHA content (Table 3). Based on these results, the mixture containing 60% CCR and 40% BHA was selected for further study.

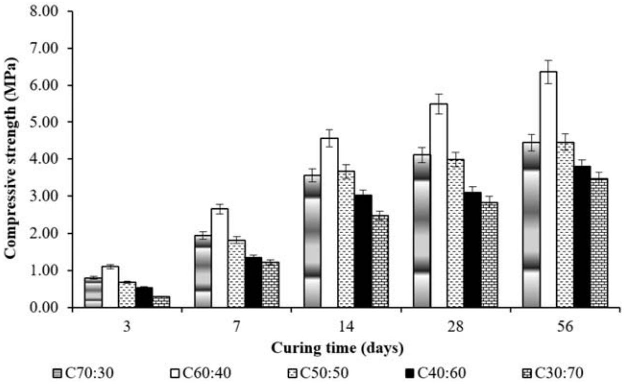

Figure 1. Strength development of CCR-BHA-based cement at different proportions of CCR and BHA.

Table 3. Initial and final setting times of CCR-BHA based cement.

Sample	Initial Setting Time (min)	Final Setting Time (min)
C70:30	120	420
C60:40	127	426
C50:50	135	434
C40:60	219	478
C30:70	222	493

Effect of Alkali Activators on Strength Development of CCR-BHA-Based Cement

The strength development of CCR-BHA based cement with a CCR:BHA weight ratio of 60:40 wt % activated with 0, 2, and 4% of Na_2O from Na_2SiO_3 and Na_2CO_3 (Figures 2 and 3) shows that on day 3 the strength of the mix with 2 and 4% of Na_2O increased from 1.11 MPa in the control sample to 2.54 and 2.13 MPa, respectively. The increase of strength was from the hydrolysis of both Na_2SiO_3 and Na_2CO_3 which generates NaOH and is the cause of increasing the OH^- concentration and pH of the solution [23]. As a result, higher solubility of silica from the surface of BHA particle was obtained leading to an increase formation of C-S-H gel which is responsible for the early strength development. In addition, the readily available SiO_4^- ion from the dissociation of Na_2SiO_3 can immediately react with $Ca(OH)_2$ from CCR to produce C-S-H gel [24–26]. This increase can be explained in terms of the available SiO_4^- ion from Na_2SiO_3, which can immediately react with $Ca(OH)_2$ from CCR to produce C-S-H gel [24–26]. It is observed that at longer curing times (28 days), the strength of the CCR-BHA cement activated with 2 and 4% of Na_2O from Na_2SiO_3 was lower than the control (no activators) as shown in Figure 2. Possible explanation for this phenomenon could arise from the rapid formation of hydration products at the early curing time. This causes the precipitation of these products on the surface of BHA particle and hinders the dissolution of SiO_4^- ion from BHA surface thus slow down the rate of hydration reaction at the later age [24,25].

The CCR-BHA-based cements activated with 2 and 4% of Na_2O as Na_2CO_3 rapidly gained 3-day strengths of 2.1 and 3.45 MPa, respectively (Figure 3), and increase to 5.85 and 6.54 MPa after 28 days, which is approximately 5–20% higher than the control. This resulting from the highly alkali environment induced by Na_2CO_3 which enhances the SiO_4^- ion dissolves from BHA surface, allowing the C-S-H gel to form. Additionally, the Ca^{2+} ion from the CCR can react with CO_3^{2-}

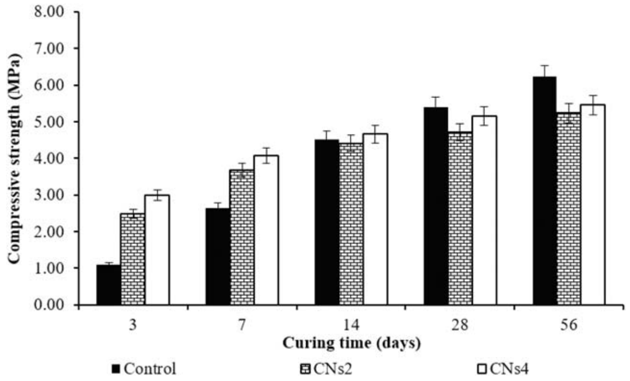

Figure 2. Strength development of CCR-BHA cement at a ratio of 60:40 and in the presence of Na_2SiO_3.

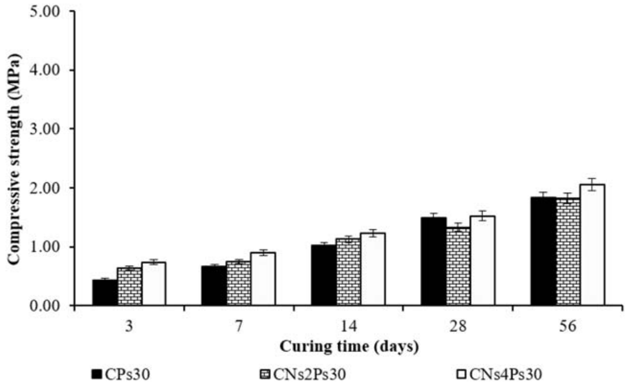

Figure 5. Strength development of CCR-BHA cement with 2% and 4% of Na_2O from Na_2SiO_3 and 30% PS.

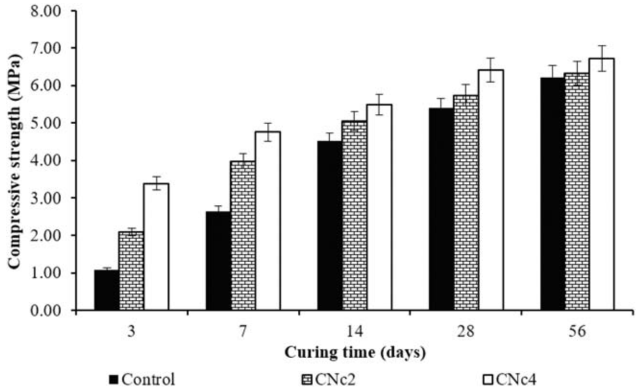

Figure 3. Strength development of CCR-BHA cement at a ratio of 60:40 and in the presence of Na_2CO_3.

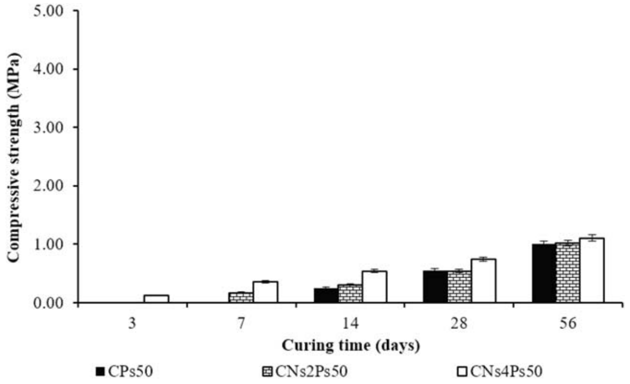

Figure 6. Strength development of CCR-BHA cement with 2% and 4% of Na_2O from Na_2SiO_3 and 50% PS.

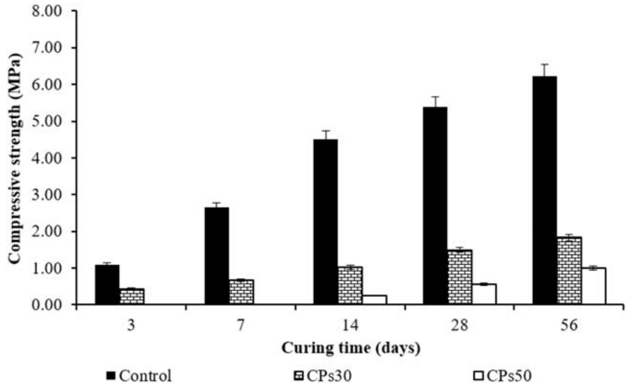

Figure 4. Strength development of CCR-BHA cement in the presence of PS.

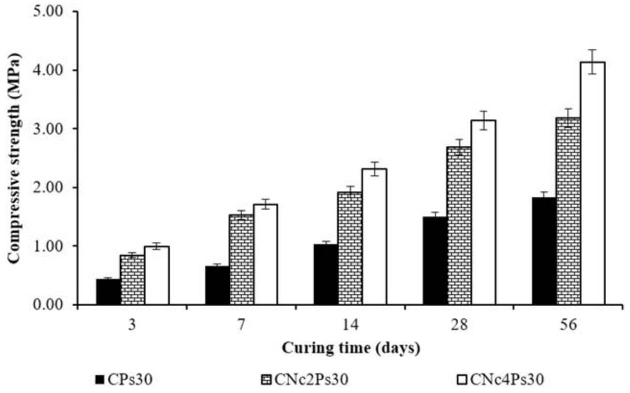

Figure 7. Strength development of CCR-BHA cement with 2% and 4% of Na_2O from Na_2CO_3 and 30% PS.

available from Na_2CO_3 and forms $CaCO_3$ which acts as a micro filler in the cement matrix, providing additional strength [27,28].

Effect of the Alkali Activators on the Strength of the Composites Containing Plating Sludge

The addition of 30 wt % PS to CCR-BHA cement decreased a 3-day strength from 1.11 to 0.45 MPa, and the increase addition to 50 wt % resulted in a product with zero strength (Figure 4). A reduction of strength of the CCR-BHA cement is due to the interference by the heavy metals present in the PS. The high alkalinity of cement composites in the presence of both activators can transform the metal hydroxides present in the PS to various precipitates such as metal silicates or carbonates and deposit on the surface of BHA thus, retards the hydration reaction between BHA and CCR [28]. Similar phenomenon has also been reported in the hydration and geopolymerisation reactions in the presence of the PS [6,29–32]. Previous studies [5,11] have reported that

Zn in particular exerts a high degree of interference in these reactions; the soluble Zn from the PS retards the pozzolanic reactions since it can be incorporated into the C-S-H to provide gels of the form C-S-Z-H [23,33] or linked directly to the ends of the silicate chains via Zn-O-Si bonds [11,32].

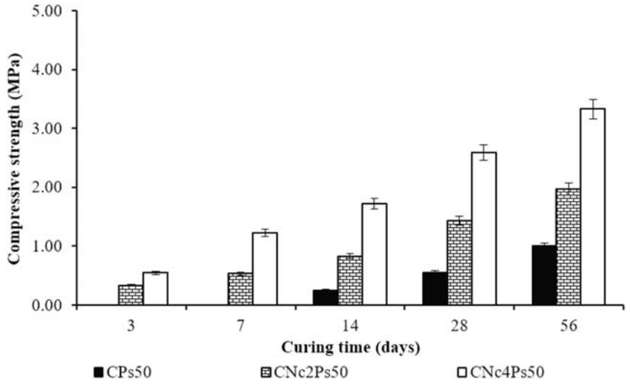

Figure 8. Strength development of CCR-BHA cement with 2% and 4% of Na_2O from Na_2CO_3 and 50% PS.

Table 4. Setting time of CCR-BHA cement solidified PS with Na_2SiO_3 and Na_2CO_3.

Samples	Initial setting time (min)	Final setting time (min)
CPs30	173	502
CNs2Ps30	155	488
CNc2Ps30	150	470
CNs4Ps30	146	467
CNc4Ps30	135	421
CPs50	255	631
CNs2Ps50	213	553
CNc2Ps50	179	511
CNs4Ps50	199	567
CNc4Ps50	169	498

Figures 5–8 show the effect of adding 2 and 4% of Na_2O as Na_2SiO_3 and Na_2CO_3 to composites containing 30 and 50 wt % PS. Strength of the solidified wastes decreases with increased concentration of the PS. Composites containing 50 wt % PS activated with 2% Na_2O from Na_2SiO_3 developed no strength, although composites activated with 2% Na_2O from Na_2CO_3 and those activated with 4 wt % of both activators developed some 3-day strength. The strength developed in all samples activated with Na_2CO_3 was greater than those activated with Na_2SiO_3. Previous workers have reported that heavy metals present in the PS can form metal carbonate such as $ZnCO_3$ and $CaZn(CO_3)_2$ [27,29,33] which can also play an important role as micro fillers in the solidified matrix [23]. Samples containing 50 wt % of PS in composites activated with 4 wt % of Na_2O from Na_2CO_3 or Na_2SiO_3 developed compressive strengths greater than the USEPA standard of 0.35 MPa after 3 and 7 days, respectively.

The final setting time of the compacts containing PS increased with increasing concentration of the PS, from 426 min in the control sample without PS to 502 and 631 min in the samples containing 30 and 50 wt % of PS, respectively (Table 4). The use of 4 wt % Na_2O from Na_2SiO_3 and Na_2CO_3 activators decreased the final setting times of samples containing 50 wt % of PS from 631 to 567 and 498 min, respectively. This retardation of the setting time may be due in particular to the Zn, which occurs in the PS in the highest

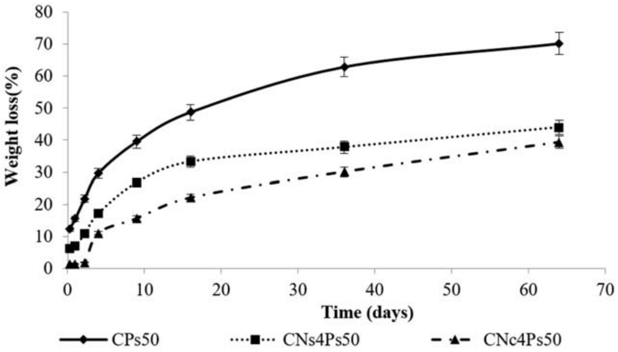

Figure 9. Weight loss of solidified wastes at 28 days.

Table 5. Metal concentrations of leachate from CCR-BHA cement.

	Metal concentrations (mg/L)						
	Fe		Zn		Cr		
Samples	-	% encapsulation	-	% encapsulation	(5 mg/l)	% encapsulation	pH
Control (C60:40)	0.84	-	0	-	0	-	12.87
CNs2	0.78	-	0	-	0	-	12.98
CNs4	0.73	-	0	-	0	-	13.29
C2c4	0.78	-	0	-	0	-	12.99
CNc4	0.93	-	0	-	0	-	13.39
30 wt % Ps	176.6	-	1019.4		77.53		10.62
CPs30	3.82	97.84	6.44	99.37	4.04	94.79	12.65
CNs2Ps30	3.39	98.08	4.87	99.52	3.56	95.41	12.86
CNc2Ps30	2.77	98.43	4.43	99.57	3.06	96.05	12.93
CNs4Ps30	3.55	97.99	4.46	99.56	3.07	96.04	13.10
CNc4Ps30	2.81	98.41	4.06	99.60	2.62	96.62	13.35
50 wt % Ps	298.4		1737.9		128.6		10.89
CPs50	8.42	97.18	9.02	99.48	7.24	94.37	12.08
CNs2Ps50	6.66	97.77	6.62	99.62	6.23	95.15	12.25
CNc2Ps50	6.05	97.97	4.95	99.72	6.20	95.18	12.31
CNs4Ps50	6.76	97.73	6.07	99.65	5.69	95.57	12.12
CNc4Ps50	6.14	97.94	4.54	99.74	3.75	97.08	12.17

CPs50								
Before soaked			After soaked					
Chemical composition		Surface and core	Chemical composition		Surface	Chemical composition		Core
CaO	61.43		CaO	29.02		CaO	29.43	
SiO_2	14.58		SiO_2	31.63		SiO_2	31.13	
Al_2O_3	5.12		Al_2O_3	0.11		Al_2O_3	0.15	
Fe_2O_3	3.31		Fe_2O_3	0.29		Fe_2O_3	0.22	
SO_3	4.35		SO_3	38.76		SO_3	38.89	
MgO	0.51		MgO	0.05		MgO	0.05	
K_2O	0.28		K_2O	0.00		K_2O	0.00	
ZnO	9.51		ZnO	0.00		ZnO	0.00	
Na_2O	0.91	a)	Na_2O	0.14	b)	Na_2O	0.14	c)

Figure 10. Chemical composition and physical appearance of CCR-BHA-based solidified wastes at 28 days: (a) before soaking, (b) surface after soaking, and (c) core after soaking. [Color figure can be viewed at **wileyonlinelibrary.com**]

CNc4Ps50								
Before soaked			After soaked					
Chemical composition		Surface and core	Chemical composition		Surface	Chemical composition		Core
CaO	61.22		CaO	28.26		CaO	61.74	
SiO_2	14.69		SiO_2	33.63		SiO_2	14.18	
Al_2O_3	5.84		Al_2O_3	0.48		Al_2O_3	5.12	
Fe_2O_3	3.05		Fe_2O_3	2.71		Fe_2O_3	3.34	
SO_3	4.50		SO_3	34.85		SO_3	4.64	
MgO	0.51		MgO	0.06		MgO	0.61	
K_2O	0.28		K_2O	0.00		K_2O	0.13	
ZnO	9.00		ZnO	0.00		ZnO	9.31	
Na_2O	0.91	a)	Na_2O	0.00	b)	Na_2O	0.93	c)

Figure 11. Chemical composition and physical appearance of CCR-BHA-based solidified wastes containing Na_2CO_3 at 28 days: (a) before soaking, (b) surface after soaking, and (c) core after soaking. [Color figure can be viewed at **wileyonlinelibrary.com**]

CNs4Ps50								
Before soaked			After soaked					
Chemical composition		Surface and core	Chemical composition		Surface	Chemical composition		Core
CaO	61.27		CaO	28.63		CaO	60.17	
SiO_2	13.87		SiO_2	32.63		SiO_2	15.18	
Al_2O_3	5.22		Al_2O_3	0.79		Al_2O_3	5.84	
Fe_2O_3	3.51		Fe_2O_3	3.15		Fe_2O_3	3.85	
SO_3	4.53		SO_3	34.75		SO_3	4.26	
MgO	0.62		MgO	0.05		MgO	0.51	
K_2O	0.48		K_2O	0.00		K_2O	0.13	
ZnO	9.57		ZnO	0.00		ZnO	9.11	
Na_2O	0.94	a)	Na_2O	0.00	b)	Na_2O	0.97	c)

Figure 12. Chemical composition and physical appearance of CCR-BHA-based solidified wastes containing Na_2SiO_3 at 28 days: (a) before soaking, (b) surface after soaking, and (c) core after soaking. [Color figure can be viewed at **wileyonlinelibrary.com**]

concentration (377 g/kg dry sludge). Fe and Cr are reported to exert less interference on the hydration reaction of the binder, but may promote the retardation effect of the Zn [28].

Metal Leaching from the Solidified Wastes

The metal concentrations and pH of the leachates after contact with the solidified wastes are shown in Table 5. The TCLP results show that pH of the leachates after contacting with the solidified wastes activated with 0, 2 and 4 wt % of Na_2O from Na_2SiO_3 and Na_2CO_3 increased from an initial pH of 3.0 to 13.29 and 13.39, respectively. This increase of leachate pH results from both the dissolution of unreacted CCR and the alkali activators in the solidified matrix. The metal concentration in the leachates after contacted with the solidified wastes (Table 5) indicated that the concentrations of Fe, Zn, and Cr are lower than the regulatory limit according to the Ministry of Industry, apart from chromium which in the case of the composite containing 50 wt % PS with and without Na_2SiO_3 and Na_2CO_3 exceeds the TCLP regulatory limit. The single exception is the composite prepared with 4 wt % from Na_2CO_3, which falls within the TCLP limits. Similar results have been reported for metals leached from solidified waste prepared with CCR-Fly ash cement binders [15,16]. The immobilization efficiency of Fe, Zn and Cr from PS by CCR-BHA cement binders is 97.18–98.43, 99.4–99.75, and 94.37–97.08%, respectively. Leaching results confirm that CCR-BHA cement is an effective solidification binder for the PS.

Durability of the Solidified Wastes

The resistance to acid corrosion of the solidified waste composites using CCR-BHA cement prepared with and without Na_2SiO_3 and Na_2CO_3 was determined after curing for 28 days (Figure 9). The total weight loss of solidified waste containing 50 wt % PS without activators was 70.2%, decreasing to 43.98 and 39.35% when Na_2CO_3 and Na_2SiO_3 were used as the activators. Apart from the role of both activators in the pozzolanic reaction between CCR and BHA, they may also reduce the interference of heavy metals present in the PS through the transformation of metal hydroxides into metal silicates and carbonates which are less soluble than metal hydroxides. As a result, the hydration reaction between CCR and BHA may be improved by comparison with samples without activators, thereby providing a less porous matrix, and as a consequence delaying the penetration of the acid solution into the sample [11,23].

The physical appearance of the CCR-BHA solidified wastes without activator after contacting with synthetic acid rain for 64 days was investigated by XRF (Figure 10a–c). The gray surface of the samples before contacting with synthetic acid rain (Figure 10a) is faded and turned white after the contact (Figure 10b,c). This was caused by the penetration of acid solution through the connected pores of the solidified matrix and the alkali nature of the matrix was used to neutralize the acid. As a result, the corroded surface and the core of the samples was observed. The CaO content at the surface and the core of the solidified wastes decreased from 61.43 wt % to around 29 wt %. Both calcium hydroxide (CH) and calcium silicate hydrate (CSH) gels are susceptible to decalcification, resulting in a low Ca/Si ratio. Consequently, a loss of cohesion and strength of the solidified matrix were obtained. In addition, the SO_3 content in both the core and surface of the solidified wastes was significantly increased to $\approx$ 39 wt % due to the formation of calcium sulfate thus, increasing the volume of the solidified wastes [34,35]. Approximately 9.51 wt % ZnO was present in the sample (Figure 10a) but disappeared after 64 days of contact with synthetic acid rain (Figure 10b,c), possibly reflecting the solubility of Zn in the synthetic acid rain during its penetration into the solidified matrix.

Figures 11 and 12a–c showed the chemical composition and physical appearance of the surface and core of the solidified wastes containing activators, before and after contact for 64 days with synthetic acid rain. After the contact, the surfaces of the samples containing Na_2CO_3 and Na_2SiO_3 were eroded to a distance of around 8–10 mm from the surface of the sample except the core. The addition of the activators increased the pH to $\approx$ 12.8–13.2. Corrosion depth of the CCR-BHA based solidified wastes containing Na_2SiO_3 was greater than the samples prepared with Na_2CO_3. The depth of acid corrosion has been reported to depend on the pore structure and water permeability of the matrix [34,35].

CONCLUSIONS

This research revealed that BHA and CCR which are waste residues can be used as solidification binder. The wastes-derived binder is effective in the encapsulation of heavy metals present in the electroplating sludge. The performance of the alkali-activated composites containing 50 wt % plating sludge was enhanced when used in combination with 4 wt % of Na_2SiO_3 and Na_2CO_3. Strength development, metal leaching characteristics and durability to corrosion by synthetic acid rain of the solidified wastes were also improved. These are the indication of successfully management of waste residues in the treatment of hazardous heavy metals to reduce negative environmental impacts.

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