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Compressive Strength and Leaching of Lead in Solidified Battery Waste Sludge using Calcium Carbide Waste and Rice Husk Ash

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ABSTRACT

Alternative uses of hazardous waste have been intensively studied. The aim of this research was to determine the compressive strength and amount of lead leached from solidified battery waste sludge using calcium carbide waste (CCW) and rice husk ash (RHA) as the cementitious binders in solidification. The CCW : RHA binder was tested at mixing ratios and curing times. Results indicated that the optimum ratio of CCW and RHA for the solidified sludge was 0.4:0.6. When the ratio of sludge of 0.25 was used in the solidification, increase of strength in solidified sludge significantly differed as the curing times increased ($p<0.05$). The linear relationship between the development of strength and curing time in solidified sludge was observed. The maximum compressive strength of solidified sludge exhibited at 23.58 ± 1.438 kg/cm^2 in 28-day curing. In addition, the highest leaching of lead in solidified sludge with ratio of sludge of 0.25 was found at 2.657 ± 0.036 mg/L in 21-day curing. The optimum ratio of CCW : RHA : sand : w/b ratio : sludge was (0.4:0.6):(2.75):(0.65):(0.25) which provided a compressive strength and the amount of lead leached that met the regulatory limit of Ministry of Industry, Thailand.

INTRODUCTION

Waste sludge from battery industries contains lead which requires to treat properly before discharging to the water sources. Currently, battery manufactures in the Samut Prakarn province, Thailand has used, at least, 400 tons/day of lead in the production processes and daily produced approximately 150 kg/day of sludge from wastewater treatment plant [1]. This wastewater sludge was contaminated with the lead and other harmful constituents. While, lead contaminated waste sludge is considered the hazardous substance as defined by Ministry of Industry, Thailand [2] and requires to treat properly as a non-toxic substance before the final disposal at the secured landfill.

Several technologies have been developed with a purpose to render a waste non-toxic or reduce the potential for the release of toxic species into the environment. Nevertheless, these technologies are not cost-effective due to their difficulties for construction and control [3]. Solidification and stabilization is an economical process and is a technology that is frequently use as a final treatment step prior to land disposal of hazardous wastes[4]. It accomplishes immobilization through the binding of hazardous constituents into a monolithic solid of high structural integrity that is resistant to leaching [4]. Solidification and stabilization processes can effectively immobilize harmful constituents in a waste and transform the waste into the form that will be beneficially reused such as a construction material [5-8].

In this study, the attempt to use calcium carbide waste (CCW), a by-product of the acetylene gas process, together with rice husk ash (RHA), a by-product of brick producing factory, as the alternative binders for solidification of battery waste sludge was undertaken. The results of the finding would be beneficial for the future treatment of heavy metal contaminated sludge with the binders and the proper disposal of the harmful substance.

MATERIALS AND METHODS

Preparation of materials

The battery wastewater sludge was obtained from wastewater treatment plant of battery factory in Samut Prakarn province, Thailand. The moisture of raw sludge was reduced by exposing to sunlight for a week. All sludge was then oven dried at 103-105ºC for 24 h and ground to particle size less than 50 mm for the subsequent use.

The cementitious binder of Elephant brand ASTM type – I Portland cement manufactured by The Siam Cement Company Ltd. was used in the study. Effective size of sand (0.2 mm) with uniformity coefficient of 3 mm and fineness modulus of 2.82 was used to mix cement with a tap water.

Calcium carbide waste (CCW), a by-product from producing acetylene gas, was supplied by the Chemical Department, Royal Thai army, Ministry of Defense. The moisture of CCW was primarily reduced by allowing to sun-dry for a week and then ground as a small particle. While, the rice husk ash (RHA), a by-product of burning rice husk, was obtained from a brick producing factory. The particle size of RHA was uniformly prepared using the grinder. In addition, tap water was used to mix the powder sludge and all binders at ratios in the solidification process.

Characteristics of Waste Sludge, CCW and RHA

The battery waste sludge properties and lead content in sludge (pH, moisture content, and total amount of lead in sludge) were determined as described in **Table 1.** The sludge properties appeared an alkalinity (pH of 9.91) with high moisture content (82.8%). Total amount of lead contained in the sludge was 55,330 mg/L per kg. of sludge dry wt. In addition the chemical compositions of CCW and RHA were determined using the X-ray diffraction analysis and are shown in **Table 2.** The compositions of CCW and RHA consisted of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, SO_3 and TiO_2. The highest compounds found in CCW were CaO (69.86%), followed by SiO_2(3.33%) and Al_2O_3(1.61%). While, the highest compounds found in the RHA were SiO_2 (84.83%), followed by K_2O (2.66%) and CaO (0.69%). Microstructure property of both cementitious binders and solidified sludge was observed under the Scanning Electron Microscope (SEM) using gold palladium coating.

Table 1. Properties of battery wastewater sludge from wastewater treatment plant of battery factory.

Characteristics of sludge	Average value/Method/Instrument appearance
Total lead content in 1.0 kg of sludge (dry wt.), mg/L	55,330 US.EPA. Method 3050B[6] / Atomic Absorption Spectrophotometer (AAS)
Moisture content,%	82.80 ASTM D2216-98[7] Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by mass. / Hot air oven
pH	9.91 ASTM D 4972-01 Standard Test Method for pH of Soils Electrometric method[8] / pH meter

Table 2. Characteristics of Cement, CCW and RHA.

Composition	CCW (%)	RHA (%)
Silicon dioxide, SiO_2	3.33	84.83
Aluminium oxide,Al_2O_3	1.61	0.30
Iron oxide, Fe_2O_3	0.37	0.18
Calcium oxide, CaO	69.86	0.69
Magnesium oxide, MgO	0.71	0.47
Potassium oxide, K_2O	<0.01	2.66
Sodium oxide, Na_2O	<0.01	0.16
Sulfur trioxide, SO_3	0.42	0.29
Titanium oxide, TiO_2	<0.01	<0.01

Preparation of solidified sludge and test methods

The solidified sludge was made of cement, sand, CCW, RHA, sludge and water at different ratios. Procedure for mixing solidified sludge was performed according to the steps outlined in C305-94 ASTM Standard [9].

The solidification test in this study involved three subsequent steps. First, the solidified sludge were prepared with different ratios of materials in six treatments. A treatment of mixing solidified sludge consisted of the cement and sand at ratio of 1:2.75 by wt., water to binder (w/b) ratio at 0.65, and sludge ratio at 0.2 remained as the control. Other five mixing solidified sludge were prepared from CCW and RHA at ratios of 0.3:0.7, 0.4:0.6, 0.5:0.5, 0.6:0.4 and 0.7:0.3. While, the portion of sand, water to binder ratio (w/b) and sludge were constant in each treatment at 2.75, 0.65 and 0.20, respectively. Each set of treatment was replicated four times.

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After curing time at 28 days, the solidified sludge were tested for compressive strength as outlined in C109/C109M-95 ASTM Standard [10] and amount of lead leachability done by the Leachate Extraction Method [2] (as described by the Standard Procedure from the Department of Industrial Works, Ministry of Industry, Thailand) to determine the optimized ratio of CCW and RHA. The amount of lead concentration in the test was analyzed using Atomic Absorption Spectrophotometer (AAS).

Second, the optimized ratio of CCW and RHA in the previous test was further used to determine the optimized ratio of sludge for the solidification The sludge to mix with CCW and RHA in the solidified sludge and curing times was tested at ratios of 0.05, 0.10, 0.15, 0.25 and curing times of 1, 7, 14, 21,28 days, respectively. The solidified sludge was used for compression test following C305-94 ASTM Standard [9] Results indicated that the strength of solidified sludge at sludge ratios and curing times could be detected up to the ratio of sludge at 0.25.

Third, the sludge ratio at 0.25 was therefore selected for further test with the binders (CCW:RHA,sand,w/b ratio,sludge at ratios of (0.4:0.6):(2.75):(0.65):(0.25) at curing times of 1, 7, 14, 21,28 days. The unconfined compressive strength of solidified sludge was then measured after curing for 1, 7, 14, 21,28 days. After that, the solidified sludge was measured for leaching of lead according to the Leachate Extraction Method[2]. The amount of lead concentration in the test was analyzed using Atomic Absorption Spectrophotometer (AAS). For each test, a set of four samples was used and the average was calculated.

Data analysis

Compressive strength and amount of lead leaching from the solidified sludge were analyzed as mean (¯) and standard deviation (SD). Mean comparison of compressive strength and amount of lead was carried out using the Least Significant Difference (LSD). The significant level was determined at α level of 0.05.

RESULTS

Microstructure of CCW and RHA

The observation of microstructure of CCW particle showed a corner, rough surface and porosity whereas those of RHA consisted of fine and high porosity **(Figure 1).**

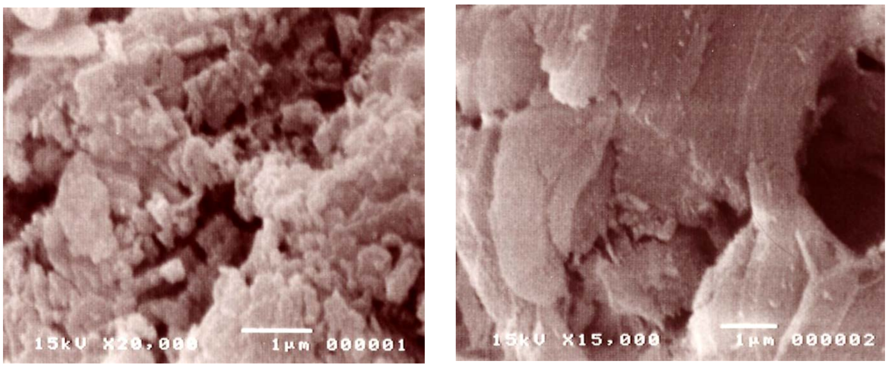

Figure 1. Microstructure of CCW at 20,000 X (a) CCW, and RHA at 15,000X (b) RHA.

Determination of the optimized ratio of CCW and RHA for solidified sludge

The highest compressive strength in this experiment was 7.73 ± 0.188 kg/cm^2 **(Table 3).** The amount of lead from all solidified sludge met the regulatory limit of hazardous waste of Industrial Ministry indicating that the amount of lead was not over than 5 mg/L. The optimized ratio of CCW and RHA in solidified sludge was 0.4:0.6 due to the highest compressive strength and required amount of lead specified by regulatory limit in Thailand. Therefore, the ratio of CCW and RHA at 0.4:0.6 was used for next test.

Table 3. Mean(± SD) of compressive strength and amount of lead in solidified waste ratios.

Treatment	Ratio					Mean(± SD) Compressive strength (kg/cm^2)	Mean(± SD) Amount of lead (mg/l)
	cement	sand	CCW:RHA	w/b ratio	sludge		
1	1	2.75	-	0.65	0.2	120.83 ± 8.315	4.431 ± 0.108
2	-	2.75	0.3:0.7	0.65	0.2	3.47 ± 0.188	0.547 ± 0.063
3	-	2.75	0.4:0.6	0.65	0.2	7.73 ± 0.188	1.336 ± 0.138
4	-	2.75	0.5:0.5	0.65	0.2	4.00 ± 1.423	0.795 ± 0.056
5	-	2.75	0.6:0.4	0.65	0.2	*	*
6	-	2.75	0.7:0.3	0.65	0.2	*	*

Remark : * = non-detectable : CCW = Calcium Carbide Waste ; RHA = Rice Husk Ash

Compressive strength of solidified sludge

The mean (± SD) compressive strength of solidified sludge at ratios of sludge at 0.05, 0.10, 0.15, 0.25 with CCW : RHA

: sand : water to binder (w/b) at 0.4:0.6, 2.75,0.65 was carried out with curing times and ratios of sludge. Preliminary results indicated that the observed strength of solidified sludge at sludge ratios and curing times could be detected up to the ratio of sludge at 0.25. When the observation of the microstructure of this solidified sludge was done, it showed the compacted and densed layer, few porosity and small size (gel pores) of matrix **(Figure 2).**

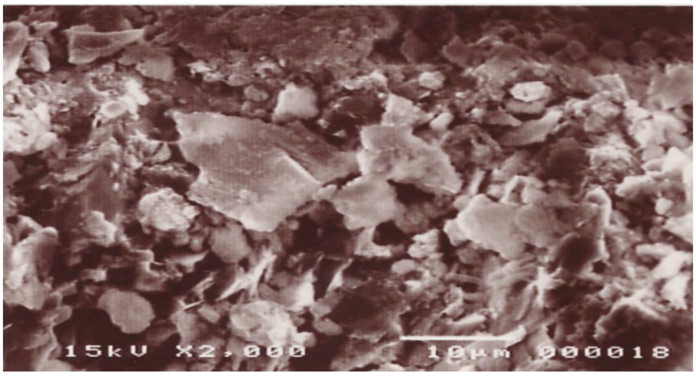

Figure 2. Microstructure of solidified sludge of ratio of CCW:RHA:sand:w/b ratio:sludge at (0.4:0.6) : (2.75) : (0.65) : (0.25) with curing 28 days at 2,000 X.

In addition, the results of further investigation of solidified sludge with ratio of sludge of 0.25 and curing times revealed that the increase of strength in solidified sludge significantly differed as the curing time increased from day 1 to day 28 ($p<0.05$). The linear relationship between the development of strength and curing time in solidified sludge was observed. Nevertheless, no significant difference in strength of solidified sludge was found in curing times between 21 days and 28 days ($p>0.05$) **(Table 4).** The compressive strength of solidified sludge with ratio of sludge at 0.25 maximized at 28-day curing (23.58 ± 1.438 kg/cm^{2}). At the curing times of 1, 7, 14 and 21 days, compressive strengths of the solidified sludge were 8.05 ± 1.420, 13.22 ± 1.486, 15.25 ± 1.687 and 21.20 ± 2.330 kg/cm^2, respectively.

Table 4. Mean (± SD) compressive strength of solidified sludge at curing times and ratio of sludge at 0.25.

Curing time (days)	Mean (± SD) Compressive strength (kg/cm^2)
1	8.05 ± 1.420 ^{a}
7	13.22 ± 1.486 ^{b}
14	15.25 ± 1.687 ^{c}
21	21.20 ± 2.330 ^{d}
28	23.58 ± 1.438 ^{d}

Remark: The same letter in the column was not significantly different at the α level of 0.05.

Leaching of lead in solidified sludge

As summarized in **Table 5**, the average(± SD) amount of lead from solidified sludge at mixing ratios of CCW : RHA : sand : w/b : sludge at (0.4:0.6):(2.75):(0.65):(0.25) was carried out with curing times. Significant increase of leaching of lead exhibited as the curing time developed from day 1 to day 21 ($p<0.05$). However, no significant difference in amount of lead of solidified sludge was detected between 21 days and 28 days of curing ($p >0.05$). The highest amount of lead (2.657 ± 0.036 mg/L) leached when the ratio of sludge and curing time were at 0.25 and 21 days. After that, significant decrease of lead leaching appeared in 28 days ($p<0.05$). The lowest amount of lead detected was 0.687 ± 0.035mg/L when the ratio of sludge and curing time were at 0.25 and 14 days. The amount of lead from the tested solidified sludge was not over the regulatory limit (5 mg/L) of Ministry of Industry [2].

Table 5. Mean (± SD) amount of lead from solidified sludge at curing times and ratio of sludge at 0.25.

Curing time (days)	Mean(± SD) Lead concentration (mg/L)
1	0.707 ± 0.087 ^{a}
7	0.838 ± 0.077 ^{b}
14	0.997 ± 0.035 ^{c}
21	2.657 ± 0.036 ^{d}
28	2.191 ± 0.106 ^{e}

Remark: The same letter in the column was not significantly different at the α level of 0.05.

DISCUSSION

Characteristics of wastewater sludge, CCW and RHA

Result indicated that the waste sludge from the battery factory contained a great amount of lead which was considered as hazardous substances. In this study, the solidification with cementitious binders as a replacement of ordinary Portland cement was, therefore, used to stabilize and solidify waste to make it immobilize prior to the final disposal in the secured landfill site.

Results of X-ray diffraction analysis indicated that CCW was contained the low percentage of SiO_2 + Al_2O_3 + Fe_2O_3 (5.31%

by wt.). The major content of CCW was a calcium oxide (CaO) at 69.86% by wt. and its amount was higher than the Portland cement [11]. Also, the amount of SiO_2 was higher in RHA (84.83% by wt.) as compared to the Portland cement [11]. Therefore, a previous study of compressive strength of mortar mixed with CCW and RHA suggested that both materials produced compressive strength of mortar high enough to use for some construction work without using any of cement [12]. In addition, the chemical characteristics of RHA was identified as Pozzolan class N according to ASTM C 618-05 [13,14]. This is because it contained high percentage of SiO_2 (85.31%) including SiO_2, Al_2O_3 and Fe_2O_3. The major content of mixture was a silicon dioxide (SiO_2) by 84.83% by wt. As shown in **Table 2**, it was found that the active silica content in RHA regarded as a good pozzolanic material. Pozzolan was defined as siliceous or siliceous and aluminous materials which in themselves possed little or no cementitious value. However, in presence of moisture it will chemically reacted with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. The use of natural pozzolans to replace cement ranged from 15 to 60%[11] which CCW:RHA at 0.4:0.6 in this experiment has the pozzolanic property to be an alternative cementtious binder in solidification process.

Compressive strength of solidified sludge

The compressive strength test reflects the amount of applied loading that the solidified sludge can withstand before failure in a secured landfill. Most of the tested samples detected met the regulatory limit of Department of Industrial Works, Ministry of Industry [2]. Many investigators found that the compressive strength of mortar decreased with the addition of waste sludge [15]. In this finding, however it was observed that the compressive strength of solidified sludge was observable at ratio of sludge up to 0.25. The occurrence of this phenomenon is possibly due to the mechanism of both binders (CCW and RHA) to form the hydration product in solidified matrix.

The increase of compressive strength with curing time of solidified sludge was observed as its strength at the sludge ratio of 0.25 and curing time at 28 days was higher than the early age. This occurs because the longer curing time of solidified matrix would allow the hydration process to occur continuously and completely[16]. The curing period provided the sludge matrix with a progressive hydration and subsequent reduction in the porosity and an increase in their compressive strength[17] .

Leaching of lead of solidified sludge

The leaching of lead in solidified sludge binded with CCW and RHA was not over the regulatory limit of Ministry of Industry [2] indicating that amount of lead was not over 5 mg/L. The occurrence of this phenomenon can be explained that the formation of hydration products of the solidified matrix would reduce the porosity and the leachabilty of lead.

It was also known that lead retarded the setting of cement. The retardation resulted in reduction of degree hydration and consequently increased the volume of capillary pore. Hence, the more sludge contained in solidified waste, the more lead was leached. As pointed out by Shively et al. [18], lead can be strongly complexed in the cement matrix in the form of insoluble silicates. At point of minimum leachability of each binder, the amount of lead in sludge may be chemically complexed with SiO_2 in cement pastes properly [19].

At the early curing time, the hydration reaction did not completely occur. Therefore, the product of complex compound containing calcium silicate hydrate was still not completely built up and not being built the strong bond to lead [20]. This allowed lead in the shorter curing time of specimen to be leached out at higher concentration than that of the specimen with longer curing time. At longer curing time, the hydration reaction completely occurred and the lead ions were strongly fixed with complex calcium silicate hydrate [11].

The results of previous research indicated that more hydration and reduction in the porosity and less permeability occurred over the curing time [21]. As a result, the binding effect of the cementitious binder matrix and heavy metals was increased. It is also known that abnormal settings, which can be traced to chemical reaction involving the aluminates such as tricalcium aluminate (C_3A), occur through hydrogen bonding of the hydroxyl group. The heavy metal sludge constituents used water in their hydroxide form and therefore could be adsorbed [22].

CONCLUSION

The compressive strength and leaching of lead from solidified battery waste sludge using calcium carbide waste (CCW) and rice husk ash (RHA) as the solidification binder was carried out. Results showed that the optimum ratio of CCW: RHA: sand: w/b: sludge for solidified sludge was (0.4:0.6) : (2.75) : (0.65):(0.25) with the curing time at 28 days. The maximum strength of solidified sludge (23.58 ± 1.438 kg/cm^2) was obtained at 28 days. The leaching of lead in solidified sludge was highest at day 21 (2.657 ± 0.036 mg/L) and it significantly decreased at day 28. Results of this finding suggest that the CCW and RHA can be an alternative binder for cement replacement in solidified battery waste sludge.

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