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Ternary blends containing demercurated lighting phosphor and MSWI fly ash as high-performance binders for stabilizing and recycling electroplating sludge

Wu-Jang Huang[a,*], Chia-Teng Wu[b], Chang-En Wu[a], Lin-Huey Hsieh[a],
Chang-Chien Li[a], Chi-Yuan Lain[a], Wei Chu[a]

[a] National Ping-Tun University of Science and Technology, Department of Environmental Science and Engineering, 91201 Ping-Tun, Taiwan
[b] Sustainable Environmental Research Center, National Cheng-Kung University, 709 Tainan City, TAIWAN

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Abstract

This paper describes the solidification and stabilization of electroplating sludge treated with a high-performance binder made from portland type-I cement, municipal solid waste incineration fly ash, and lighting phosphor powder (called as cement–fly ash–phosphor binder, CFP). The highest 28-day unconfined compressive strength of the CFP-treated paste was 816 kg/cm^2 at a ratio of cement to fly ash to lighting phosphor powder of 90:5:5; the strength of this composition also fulfilled the requirement of a high-strength concrete (>460 kg/cm^2 at 28 days). The CFP-stabilized sludge paste samples passed the Taiwanese EPA toxicity characteristic leaching procedure test and, therefore, could be used either as a building material or as a controlled low-strength material, depending on the sludge-to-CFP binder ratio.

Keywords: Electroplating sludge; Fly ash; Lighting phosphor; Stabilization

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1. Introduction

A quantity of 25,893 tonnes of electroplating sludge was produced in Taiwan in 2005, constituting 87.5% of the heavy metal-containing industrial sludges [1]. Most of the electroplating plants generating this sludge utilize the so-called “job shop” techniques. This electroplating sludge is usually treated through cement solidification and stabilization [2–7] processes. The binders that have been used for electroplating sludge include portland type-I cement (OPC) [4,6,7], lime fly ash [2,5], and high-temperature-treated sludge [3].

The Taiwanese EPA requires solidification/stabilization-treated wastes for use as building materials to have a compressive strength of >100 kg/cm^2. The unconfined compressive strength (UCS) of solidified sludge concrete is, however, usually much less than this value when the sludge replacement ratio is higher than 30% [5,6]. Therefore, our first goal in this study was to find a hard binder prepared from inorganic waste that would be suitable for manufacturing a high-strength electroplating sludge concrete. The UCS of solidified sludge concrete can reach higher than 100 kg/cm^2 when the sludge replacement ratio is 30%. The inorganic wastes that we selected were municipal solid waste incineration fly ash and demercurated lighting phosphor; the former requires stabilization with cement, but the behavior of the latter has yet to be determined and, thus, it has not currently subjected to recycling. Since 2002, the Taiwanese EPA has documented the recycling of waste lamps from municipal solid wastes [8]; the number of waste lamps was estimated to be 96 million pieces. The exciting species in these lamps is mostly mercury vapor; the lighting phosphor comprises mainly calcium phosphate [$Ca_3(PO_4)_2$] and CaClF. The total amounts of recycled lighting phosphor and liquid mercury are ca. 490 tonnes/year and 12–15 kg/year, respectively. The demercurated lighting phosphors have been stocked in four recycling plants for several years, waiting for a suitable recycling method to be developed. In a previous study [9], we found that demercurated lighting phosphor could be classified as a non-hazardous material because the leached concentrations of heavy metals were very low. There-

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* Corresponding author. Tel.: +886 8 7703202x7076; fax: +886 8 7740256.
E-mail address: wjhuang@mail.npust.edu.tw (W.-J. Huang).

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fore, our second goal for this study was to determine a method for recycling the recovered lighting phosphor powder.

2. Materials and methods

2.1. Sampling

(1) Chromium-containing wastewater sludge was generated at an electroplating plant in Tailain County. The Cr-containing wastewater was treated using a selective reduction precipitation process. $NaHSO_3$ and 40% NaOH(aq) were used as the reduction and alkali agents, respectively; polyaluminum chloride was used as the flocculant. The water content of the fresh sampled sludge was 66.9% (S.D. = 3.6%). The fresh sludge was oven-dried for 24 h and ground to pass through a 0.579-μm standard mesh.

(2) MSWI fly ash was sampled from the manhole of the baghouse of three incinerators in a large-scale MSW incineration plant in southern Taiwan [10]. The sampling was performed under normal operating conditions at least 2 h after the firing stage of the incinerators. Equal weights of the samples from the three incinerators were mixed together at room temperature and stored in HDPE bottles at 4 °C and relative humidity was <60%.

(3) demercurated lighting phosphor was sampled from the recycling process in a lamp treatment plant. The dry process developed by the Werec (Germany) and MRT (Sweden) companies was employed to treat the recycled lamps [8]. A subsequent heating treatment process was applied in the plant to remove any mercury from the phosphor powder.

2.2. Toxicity characteristic leaching procedure (TCLP) and unconfined compressive strength (UCS) tests

The TCLP test simulates the long-term leaching behavior prior to the co-disposal of a hazardous waste with general solid waste in a landfill. The TCLP test was performed following the US EPA's methods [11]. The ash sample was mixed with the acetic acid extractant at pH 2.88. The solid-to-liquid ratio was fixed at 1:20. The sample was then subjected to agitated extraction at a rate of 30 rpm for 18 h. The lead concentration in the final extracts was determined through flame atomic absorption spectrometry (Unicam Solar-969, USA) following the US EPA's methods. The concentrations of heavy metals in the TCLP extract were 46.3, 0.39, and 5.30 mg/L for copper, lead, and total chromium, respectively; all other ions (e.g., Ni, Cd, Zn, As, and Hg) were below the detection limit. The unconfined compressive strength (UCS) test was performed using the ASTM method [12].

2.3. Operation procedures for sludge stabilization

The sludge was stabilized by adding the CFP binder or OPC, and an appropriate amount of water; the solidified samples were then cured at room temperature for 7, 14, and 28 days.

2.4. Fourier-transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) measurements

XRD analysis was performed using a Shimadzu XRD-6000 diffractometer with irradiation from the Cu Kα line. The sweeping range was set from 5° to 75°, with a scanning rate of 2°/min, at room temperature. The FT-IR spectra of the samples were recorded using a Bruker Vector-22 FTIR spectrometer operated over a scanning range from 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}. Prior to recording the FTIR spectra, the solidified fly ash was mixed with a suitable amount of pre-dried KBr powder and then formed into a thin disc film using a hand compressor.

3. Results and discussion

3.1. Preparation of a high-performance sludge binder

Recycled solidified solid wastes and industrial sludge for use as construction materials (e.g., building materials or controlled low-strength materials) must pass the TCLP test and possess high strength. One of the key techniques for preparing such materials is to blend these wastes with high-performance binders. In this study, we prepared a novel waste-based high-performance binder from cement, MSWI fly ash, and demercurated phosphor (we call this blend the "CFP binder").

Table 1 lists the UCS values of the pure CFP paste solidified for 7, 14, and 28 days. The standard derivation of the UCS test was estimated to be 5 kg/cm^2. The data for the binary mixtures indicate that the highest value of the UCS (797 kg/cm^2) was that for the sample prepared at a cement-to-fly ash ratio of 90:10 (i.e., without addition of the phosphor); the value was 325 kg/cm^2 at a cement-to-phosphor ratio of 80:20 (i.e., without addition of the fly ash), and 5 kg/cm^2 at a fly ash-to-phosphor ratio of 80:20 (i.e., without the addition of the cement). For the ternary mixtures, the CFP binder exhibited its highest UCS value (816 kg/cm^2) at a ratio of cement to fly ash to phosphor of

Table 1
Strength of CFP binder[a]

Cement:fly ash:phosphor	UCS[b] (kg/cm^2)
100:0:0	373
90:10:0	797
80:20:0	425
70:30:0	340
60:40:0	277
90:0:10	220
80:0:20	325
70:0:30	165
90:8:2	571
90:5:5	816
90:3:7	628
0:90:10	4
0:80:20	5
0:100:0	3
0:0:100	0
Standard Concrete	210

Standard derivation = 5 kg.

[a] CFP means binder made from cement, fly ash and phosphor.

[b] UCS means unconfined compressive strength.

Table 2
TCLP[a] data of studied wastes

Wastes	Cu	Pb	Total Cr	Cd
Original phosphor	1.2	0.32	0.89	N.D.
Fly ash	2.87	12.83	N.D.	0.99
Cement	N.D.	N.D.	N.D.	N.D.
Original sludge	46.3	0.39	5.30	N.D.
Unsolidified CFP binder[b]	N.D.	1.33	1.02	N.D.
Regulation level from Taiwanese EPA	15.0	5.0	2.5	1.0

Unit: mg/kg.

[a] Toxicity characteristic leaching procedure from Taiwanese EPA.

[b] CFP means a mixture of cement:fly ash:phosphor = 90:5:5.

90:5:5. We used this optimized CFP composition in subsequent experiments for solidification of the Cr-containing sludge. The optimized UCS value is equivalent to that of high-performance concrete (>430 kg/cm^2 after 28 days); thus, we believe that our CFP binder is suitable for use as a high-performance binder for the solidification/stabilization of solid wastes and industrial sludge [13,14].

The value of the UCS (816 kg/cm^2) for the optimized CFP binder is 3.9 times higher than that of standard concrete prepared from cement and sand. The fine particles of the fly ash and phosphor powders might play the same role as sand in the CFP binder. X-ray diffraction and FT-IR spectroscopic studies of the solidified CFP binder indicated that the intensities of the peaks at 2θ values of 9.0°, 17.8° and 48.2° and at wavenumbers of 1200 and 1500 cm^{-1} increased upon increasing the values of the UCS (data not shown). We attribute the high strength of the CFP binder to the growth of an ettrignite phase [$Ca_6Al_2(SO_4)_3(OH)_2{\cdot}26H_2O$] in the solidified concrete [15,16].

3.2. *TCLP data of used wastes*

Table 2 lists the TCLP data of all of the wastes we employed in this study. The fly ash had a higher leaching concentration of lead and cadmium and the original electroplating sludge had a higher leaching concentration of copper and chromium. Therefore, both the fly ash and the sludge are classified as hazardous materials. The CFP binder, recycled phosphor, and cement leached very low concentrations of these ions; thus, they are classified as non-hazardous materials. Espinosa and Tenorio [17] treated electroplating sludge at 1250 °C and found that 99.6% of the chromium remained in the slag. This result suggests that Cr in the sludge is fixed very strongly, because Cr has quite a low-boiling point.

3.3. *Properties of cement and CFP binder-stabilized Cr-containing sludge*

In the following discussion, we compare the properties of the OPC and CFP binder-stabilized Cr-containing sludge samples. Tables 3 and 4 list the TCLP data of the CFP binder and cement-stabilized sludge concrete samples, respectively. It is clear that a decrease in the sludge-to-binder (or -cement) ratio led to an increase in the leaching concentrations of the four heavy metal ions that we monitored. The sludge concrete samples that formed were non-hazardous materials when the sludge-to-CFP and sludge-to-cement ratios were 90:0 and 40:60, respectively. Thus, these concrete samples can be reused as construction materials. The CFP binder exhibited a higher efficiency at stabilizing the leaching of Cr from the solidified sludge. This behavior might relate to the value of the UCS of the resulting concrete material. Park [7] improved the stabilization efficiency of $Cr(OH)_3$ even further when using clinker kiln dust-modified cement. Although the exact mechanism of stabilization of Cr species in cement paste remains unknown [7,18], our results indicate that a modified cement binder might indeed be required for stabilizing Cr-containing sludge samples [2,3,6].

Table 3
TCLP data of CFP–sludge waste forms

Sludge:CFP	Cu	Pb	Total Cr	Cd
0:100 (solidified binder)	N.D.	1.20	N.D.	N.D.
10:90	0.05	1.05	N.D.	N.D.
20:80	0.38	0.92	N.D.	N.D.
30:70	0.15	0.85	N.D.	N.D.
40:60	0.29	0.77	N.D.	N.D.
50:50	0.30	0.72	0.21	N.D.
60:40	1.05	0.66	0.57	N.D.
70:30	1.99	0.58	0.98	N.D.
80:20	4.75	0.51	1.42	N.D.
90:10	7.32	0.47	1.89	N.D.
100:0	46.3	0.39	5.30	N.D.
Regulation level from Taiwanese EPA	15.0	5.0	2.5	1.0

Unit: mg/kg.

Table 5 lists the values of UCS of the CFP binder- and cement-stabilized sludge concrete samples. Increasing the aging time increased the UCS of the concrete; in addition, an increase of the aging temperature decreased the UCS of the aged concrete. Stegemann and Burnfeld used neutral network analysis of literature data in an attempt to predict the values of UCS of cement pastes containing pure metal compounds; they found that the addition of Cr(III) can improve the value of the UCS of cement paste [19]. Roy and Eaton [2] found that lime-to-fly ash and sludge-to-binder ratios of 3:5 and 1:08, respectively, were optimal for stabilization of electroplating sludge samples. Guo et

Table 4
TCLP data of OPC[a]–sludge waste forms

Sludge:OPC	Cu	Pb	Total Cr	Cd
0:100	N.D.	N.D.	N.D.	N.D.
10:90	N.D.	N.D.	N.D.	N.D.
20:80	0.6	N.D.	0.11	N.D.
30:70	1.98	N.D.	0.54	N.D.
40:60	1.26	N.D.	1.03	N.D.
50:50	0.11	N.D.	1.57	N.D.
60:40	3.43	N.D.	2.11	N.D.
70:30	4.23	N.D.	2.58	N.D.
80:20	5.17	N.D.	3.02	N.D.
90:10	8.42	N.D.	3.53	N.D.
100:0	46.3	0.39	5.30	N.D.
Regulation level from Taiwanese EPA	15.0	5.0	2.5	1.0

Unit: mg/kg.

[a] OPC means portland type-I cement.

Table 5
Compression strength of binder–sludge waste forms

Binder:sludge	CFP			OPC	
	7 days (RT[a])	7 days (35 °C)	14 days (RT[a])	7 days (RT[a])	14 (RT[a])
0:100	0	–	0	0	0
10:90	0.62	–	0.35	1.53	3.4
20:80	1.86	–	1.27	3.17	8.5
30:70	2.48	–	4.81	3.71	7.8
40:60	15.0	–	4.39	12.69	23
50:50	39.78	–	8.98	25.44	32
60:40	79.28	–	22.9	41.08	35
70:30	109.85	50.1	55.9	57.86	53
80:20	220.4	168.5	163.9	113.0	77
90:10	376.0	208.3	365.9	173.68	195.0
100:0	816.0	484.8	605.0	373.0	339.7
Regulation level for landfill from Taiwanese EPA (kg/cm^2)					10
Regulation level for controlled low-strength materials from Taiwanese EPA (kg/cm^2)					>10 and <100
Regulation level for building materials from Taiwanese EPA (kg/cm^2)					>100

Unit: kg/cm^2.

[a] RT means room temperature.

al. studied the potential marine applications of phosphogypsum (PG) stabilized using C-class fly ash and portland type-II cement binder; they found that a composite of PG, fly ash, and cement at a percentage ratio of 55:35:10 exhibited a condensed layer structure [20]. Shehata and Thomas conformed that the addition of fly ash to concrete can reduce the percentage expansion [21].

Once a sludge concrete sample passes the TCLP test, it can be used as a construction material, e.g., a building material or a controlled low-strength material. The regulated values for the UCS of building materials and controlled low-strength materials (CLSMs) are >100 kg/cm^2 and within the range 10–100 kg/cm^2, respectively. Therefore, our CFP binder-stabilized sludge concrete sample prepared at binder-to-sludge ratios of 70:30, 80:20, and 90:10 can be used as building materials, while those prepared at 40:60 and 50:50 can be used as CLSMs. In contrast, the cement-stabilized sludge concrete samples prepared at binder-to-sludge ratios of 40:60, 50:50, and 60:40 can be used only as CLSMs.

4. Conclusions

In the past 8 years, the authors have paid much attention on the solidification of industrial sludge and municipal solid waste incineration fly ash. In this paper a high-performance binder (CFP binder) prepared from portland type-I cement, municipal solid waste incineration fly ash, and lighting phosphor powder was applied to the solidification of electroplating sludge. The highest 28-day unconfined compressive strength of the prepared binder pastes was 816 kg/cm^2, consistent with the regulated value for high-strength concrete (>460 kg/cm^2 after 28 days). The CFP-stabilized sludge paste samples passed the TCLP test and, therefore, could be used either as building materials or as controlled low-strength materials, depending on the ratio of sludge to CFP binder. In contrast, the Portland cement-stabilized sludge paste could be used only as a controlled low-strength material.

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