ELSEVIER

Journal of Hazardous Materials 37 (1994) 277–283

JOURNAL OF HAZARDOUS MATERIALS

Long-term stability of superplasticized monoliths of a solidified electroplating sludge

Gordon C.C. Yang*, Chia-Fan Chang

Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC

(Received 16 October 1993; accepted in revised form 4 January 1994)

Abstract

In this work, physicochemical durability of superplasticized monoliths, solidified from an electroplating sludge, were investigated. Two categories of superplasticizer, namely modified lignosulphonates and sulphonated naphthalene formaldehyde condensates, were employed in this study. Each was used as an auxiliary binding agent or as a modifier to ordinary portland cement, which was the major binder for solidification. The solidified monoliths were then subjected to various physical and chemical tests. Tests carried out included measurements of the unconfined compressive strength (UCS), the leaching toxicity by the TCLP method, the physical durability test (i.e., freezing and thawing test and wetting and drying test), and the chemical durability test (i.e., multiple TCLP test). It was found that superplasticized, solidified monoliths outperformed the corresponding control monoliths (without addition of any superplasticizer) in terms of various physical and chemical properties. Generally, the performance of both superplasticizers was found to be comparable in this study. Experimental results indicated that the physical durability test only resulted in less than one percent of corrected, cumulative weight loss for solidified monoliths modified by any type of superplasticizer. However, results of UCS measurements have shown that these very solidified specimens have been deteriorated to some degree after physical weathering tests. As for the resistance of solidified monoliths against the leaching of contaminants due to repetitive precipitation of a synthetic acid rain, the multiple TCLP test results have shown that the employment of either superplasticizer will be satisfactory.

1. Introduction

The demands for high durability solidified wastes have greatly increased. This is due to the problem associated with the long-term stability of solidified monoliths. It has been found in many instances that a few years after the solidification the solidified

* Corresponding author.

0304-3894/94/$07.00
SSDI 0304-3894(94)00005-2

monoliths deteriorated physically and chemically. Therefore, attempts have been made to improve the durability of solidified monoliths [1–3]. One way to achieve this goal is by adding polymers to the cement paste. It is known that addition of polymer dispersions improves adhesion to substrates in the cement paste [3,4]. Although limited investigations in this regard have been carried out in the field of waste solidification, a number of research findings can be adopted from the field of cement and concrete [5–7].

The objective of this study was to investigate the influence of polymer modification on physical and chemical durability of a solidified electroplating sludge. Two commercially available polymers, known as superplasticizers, were used in this investigation. Measurements of the unconfined compressive strength (UCS) and the leaching toxicity by the TCLP method were also conducted before and after various weathering tests whenever applicable. The physical durability test conducted in this study includes the freezing and thawing test and the wetting and drying test. The chemical durability test employed is the multiple TCLP (MTCLP). The MTCLP method has been successfully used for studying the long-term stability or leachability of solidified hazardous wastes by the first author of this work elsewhere [2, 8].

2. Experimental

2.1. Materials

In this work, an electroplating sludge was obtained from a local factory having electroplating activities. ASTM Type I portland cement was used as a major binding agent for sludge solidification. In addition, two commercially available polymers were employed as additives to the major binding agent. These two polymers are also known as superplasticizers, namely a sulphonated naphthalene formaldehyde condensate (designated SPF in this study) and a modified lignosulphonate (designated SP). Both belong to ASTM C 494-86 Type F chemical admixtures. These two superplasticizers were generously provided by a local, anonymous supplier.

All chemicals used in this investigation were reagent grades as specified in various standard methods adopted by R.O.C. EPA and/or U.S. EPA for evaluating solid wastes. Water used in this work was ASTM Type I deionized water.

2.2. Methods

The sludge sample was characterized by various standard methods for evaluating solid wastes recommended by R.O.C. EPA and U.S. EPA [9, 10]. The determined properties included moisture content, ash content, combustible content, total contents of heavy metals of interest, and heavy metal concentrations of the leachate resulting from the toxicity characteristic leaching procedure (known as TCLP test). In addition, loss on ignition was determined according to ASTM C 114.

To simultaneously take into account the effects of all major experimental factors and to obtain the optimal experimental conditions for solidification, an experimental

Table 1
Solidification recipes based on a modified Taguchi method

Monolith No.	Solidification recipe			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1
Level No.	**Solidification recipe**			
	A (wt%)	B (g)	C	D
1	0.4	300	0.9	2
2	0.8	500	0.8	3
3	1.5	700	0.7	4

Notes: (1) A denotes the amount of superplasticizer added based on the weight of cement. (2) B denotes the weight of portland cement. (3) C denotes the weight ratio of water to cement. (4) D denotes the weight ratio of cement to electroplating sludge.

design established by the Taguchi method [11] with a minor modification was adopted in this work. The L_9 (3^4) orthogonal arrays with three levels of variation were employed using the following as the experimental facors: (1) weight percent of the polymer used, (2) weight of ASTM Type I portland cement used, (3) weight ratio of water to cement, and (4) weight ratio of cement to sludge. Details are shown in Table 1.

Sludge solidification was conducted in the following manner: (1) mixing the dried sludge and cement thoroughly in a Hobart-like mixer for a few minutes, (2) adding the well-mixed water dispersion of polymer into the mixer for further mixing, (3) pouring the mortar into an adequate size of PVC molds of cylindrical shape, (4) curing under ambient conditions for one day, (5) demolding, (6) curing in an environmental chamber maintaining 23 °C and 98% relative humidity for a desired length of time. After this stage, the solidified monoliths were tested for a variety of purposes. In this study, solidification was conducted according to CNS 1230 A3043; unconfined compressive strength, CNS 1232 A3045; freezing and thawing test, ASTM D 4842-90; wetting and drying test, ASTM D 4843-88; leaching toxicity, TCLP test; chemical durability, multiple TCLP test [2]; and heavy metal concentration, flame atomic absorption spectroscopy (AAS).

3. Results and discussion

3.1. Characterization of the electroplating sludge

Characterization results for the electroplating sludge used in this work are shown as follows: moisture content, 64.5%; ash content, 27.7%; pH, 8.17; and loss on ignition, 39.66%. The total contents of heavy metals (mg/l) were found to be: Zn, 1293; Cd, 35.25; Pb, < 0.2; Cu, < 0.09; As, < 0.15; and Cr, 34.10. On the other hand, the heavy metal concentrations (mg/l) of the TCLP leachate were found to be 168.63, 28.80, 0.01, and 0.042 for zinc, cadmium, arsenic, and chromium, respectively. The TCLP result indicates that both zinc and cadmium concentrations are greater than the current R.O.C. EPA regulatory thresholds of 25 mg/l for Zn and 0.5 mg/l for Cd. Thus, the sludge sample obtained in this study is classified as a hazardous waste. A proper treatment/disposal method is inevitably needed.

3.2. Measurements of unconfined compressive strength (UCS)

For the solidification recipes used, the values of UCS_{28} (i.e., UCS measured when the solidified monolith is 28 days old) for the control group (i.e., specimens without polymer modification) ranged from 10.61–29.62 kg/cm^2. The specimen with the greatest UCS value was solidified with water to cement ratio of 0.7 and cement to sludge ratio of 2. The reason for low UCS values of control specimens is ascribed to a high content of organic materials (as evidenced by a high value of loss on ignition), which would impede the hydration of portland cement.

Experimental results have indicated that polymer addition gave rise to different degrees of influence on UCS of the solidified monoliths with different solidification recipes. Generally, for the same solidification recipes except the polymer type, these two superplasticizers (SP and SPF) yielded solidified monoliths with a comparable performance in terms of UCS. For monoliths solidified with either of the superplasticizers, their UCS_{28} values have been greatly increased comparing the control specimens (see Table 2). Values of UCS_{28} for monoliths solidified with superplasticizer SP were found to be in the range of 45.58 and 146.68 kg/cm^2. The specimen with the greatest UCS value was solidified with water to cement ratio of 0.7, cement to sludge ratio of 3, and 1.5 wt% of polymer addition. For superplasticizer SPF, the UCS_{28} values ranged from 57.65–130.79 kg/cm^2. Similarly, the specimen with the greatest UCS value was solidified with water to cement ratio of 0.7, cement to sludge ratio of 3, and 1.5 wt% of polymer addition.

According to Abrams' law (also known as water/cement ratio law) [12], the smaller the water/cement ratio is, the greater the compressive strength of concrete will be. The same law is also applicable to cement pastes and mortars. Keeping this law in mind would help explaining the superior performance of both superplasticizers (SP and SPF) used in this work.

As indicated above, the superplasticizers used in this investigation are ASTM C 494-86 Type F chemical admixtures. In fact, the chemical admixtures in this category are known as high-range water-reducing admixtures. It is self-explanatory

Table 2
Effects of superplasticized solidification on unconfined compressive strengths of monoliths

Monolith No.	UCS_{28} (kg/cm^2)		
	Control group	SP group	SPF group
1	20.03	45.58	62.95
2	20.29	70.89	67.07
3	20.88	84.44	69.52
4	13.07	75.89	60.96
5	29.62	68.40	83.12
6	16.64	68.76	65.45
7	25.30	146.67	130.79
8	10.61	46.09	57.65
9	24.36	55.26	74.10

Notes: (1) Control group denotes monoliths solidified by portland cement alone. (2) SP group denotes monoliths solidified by Type I portland cement with an addition of a modified lignosulphonate. (3) SPF group denotes monoliths solidified by Type I portland cement with an addition of a sulphonated naphthalene formaldehyde condensate.

that high-range water-reducing admixtures are capable of reducing the amount of water required while maintaining excellent concrete properties. The employment of this type of chemical admixtures would reduce the water/cement ratio, thereby increasing the compressive strengths of concrete, cement mortars, and cement pastes. This would explain why specimens solidified with the addition of ASTM C 494-86 Type F chemical admixtures (e.g., SP and SPF used in this study) had much higher UCS_{28} values than that of control specimens.

3.3. TCLP leaching toxicity

Comparing the experimental results of TCLP test, no reduction of leaching toxicity could be obtained through the superplasticized solidification in this study. For the solidification recipes used, the leached concentration (mg/l) ranges were found to be: (1) Zn (0.021–0.575) and Cd (0.048–0.057) for the control group, (2) Zn (0.140–0.730) and Cd (0.067–0.075) for the SP group, and (3) Zn (0.328–1.100) and Cd (0.050–0.060) for the SPF group. The above data are all based on 28-day-old solidified specimens. Although no improvement in leaching toxicity can be obtained, the above concentrations of TCLP leachates are all far below the current R.O.C. EPA regulatory requirements that have been indicated above.

3.4. Chemical durability test

Based on the same design principles of multiple extraction procedure (MEP) [10], multiple TCLP (MTCLP) is designed to simulate the leaching that a solidified monolith will undergo from repetitive precipitation of acid rain. The first sequence in MTCLP test is indeed the traditional TCLP test.

In this study, only those solidified specimens having the greatest UCS values in each of the polymer types (i.e., SP_7 and SPF_7) were subjected to MTCLP test. It was found that solidification greatly reduced the leaching toxicity of the sludge no matter what type of polymer was used. Concentrations (mg/l) of heavy metals for the TCLP leachates were found to be: Zn (0.730) and Cd (0.073) for SP; and Zn (0.618) and Cd (0.066) for SPF. After ten extraction sequences, the cumulative weights (mg) of leached heavy metals based on 100 g of dry sludge were found to be: (1) Zn (6.400) and Cd (1.200) for SP; (2) Zn (6.962) and Cd (1.306) for SPF; and (3) Zn (346.05) and Cd (66.46) for the sludge without solidification treatment. Therefore, the tested specimens are considered to be highly durable in a chemical sense.

3.5. Physical durability test

Again, only those solidified monoliths having the greatest UCS values in each of the polymer types were subjected to the wetting and drying test and freezing and thawing test, respectively. After testing, all solidified monoliths were not broken up. Experimental results also indicated that either test only resulted in less than one percent of corrected, cumulative weight loss for any specimen tested. According to ASTM 4842-90 and ASTM 4843-88, tested specimens are of failure when their corrected, cumulative weight losses are greater than 30%. Thus, the solidified monoliths tested in this study are considered to be highly durable in a physical sense.

In addition to the determination of mass loss of a solidified waste, the influence of the physical durability test on UCS was also investigated. Note that the dimensions of solidified monoliths for the physical durability test (i.e., 44 mm × 74 mm; $d \times h$) and for standard UCS measurements (i.e., 50 mm × 100 mm; $d \times h$) are different. The values of UCS for these two sizes of monoliths must be different. One must also keep in mind that each of the corresponding monoliths of the sample group and the control group have exactly the same solidification recipe but subjecting to different environmental conditions during the physical durability test. By comparing the monoliths with a solidification recipe of No. 7, the values of UCS have reduced from 52.93 kg/cm^2 (the SP control specimen) to 30.38 kg/cm^2 and 45.21 kg/cm^2 (the SP sample specimens) after the freeze–thaw test and the wet–dry test, respectively. More specifically, a decrease of 22.55 kg/cm^2 in UCS after the freezing and thawing test; but only 7.72 kg/cm^2 after the wetting and drying test. Again, it was found that the freezing and thawing test had a stronger attack on solidified wastes (SPF_7) than did the wetting and drying test. The values of UCS have reduced from 63.30 kg/cm^2 to 33.77 kg/cm^2 and 52.00 kg/cm^2 after the freeze–thaw test and the wet–dry test, respectively.

4. Conclusions

In this work, properties of an electroplating sludge solidified by ASTM Type I portland cement with polymer modification were studied. An experimental design following the Taguchi method was employed to set up the L_9 orthogonal arrays and to determine the solidification recipes. The polymers used in this investigation were two superplasticizers (SP and SPF). Effects of polymer modification on physical and chemical durability of solidified monoliths were investigated. The physical durability test included wetting and drying test and freezing and thawing test. The chemical durability test carried out was multiple TCLP test.

Experimental results indicate that superplasticized solidification would yield a better quality monolith in terms of unconfined compressive strength, but not TCLP leaching toxicity. For the solidification recipes used, SP and SPF yielded comparable results in terms of unconfined compressive strength and TCLP leaching toxicity.

Results of physical and chemical durability tests show that the electroplating sludge solidified by ASTM Type I portland cement with the modification of either superplasticizer tested would yield a long-term durable monolith. This is evidenced by their structure integrity and low cumulative weight loss after the physical durability test, and low cumulative concentrations of leached heavy metals after the repetitive leaching of a synthetic acid rain.

Acknowledgement

This study was sponsored by the R.O.C. National Science Council under project No. NSC 81-0421-E110-536-Z.

References

[1] D. Kirk and P.L. Bishop, Long-term durability of solidified/stabilized materials, Abstract Proc. 18th Ann. RREL Res. Symp., pp. 67–71, U.S. EPA/600/R-92/028, 1992.
[2] G.C.C. Yang, Durability study of a solidified mercury-containing sludge, J. Hazardous Mater., 34 (1993) 217.
[3] G.C.C. Yang, C.H. Lee and G.H. Hsiue, Properties of a mercury-containing sludge solidified by polymer latex modified cementitious materials, Hazardous Waste Hazardous Mater., 10 (1993) 453.
[4] Z. Su, J.M.J.M. Bijen and J.A. Larbi, The influence of polymer modification on the adhesion of cement pastes to aggregates, Cement Concr. Res., 21 (1991) 169.
[5] V.K. Bhattacharya, K.R. Kirtania, M.M. Maiti and S. Maiti, Durability tests on polymer-cement mortar, Cement Concr. Res., 13 (1983) 287.
[6] Z. Su, J.M.J.M. Bijen and J.A. Larbi, Influence of polymer modification on the hydration of portland cement, Cement Concr. Res., 21 (1991) 242.
[7] S. Chandra and P. Flodin, Interactions of polymers and organic admixtures on portland cement, Cement Concr. Res., 17 (1987) 875.
[8] G.C.C. Yang and K.L. Kao, Feasibility of using a mixture of an electroplating sludge and a calcium carbonate sludge as a binder for sludge solidification, J. Hazardous Mater., 36 (1994) 81.
[9] R.O.C. Environmental Protection Administration, Analytical Methods for Solid Wastes, Environmental Communication Service, Taipei, 1990 (in Chinese).
[10] U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, SW-846, 3rd edn., Washington, DC, 1986.
[11] C.N. Chang et al. (translators), Introduction to Quality Engineering by Taguchi Method, Quality Control Institute, Taipei, 1991 (in Chinese).
[12] I. Soroka, Portland Cement Paste and Concrete, Chemical Publishing Co., New York, 1980.