Journal of Hazardous Materials, 34 (1993) 217–223
Elsevier Science Publishers B.V., Amsterdam

Durability study of a solidified mercury-containing sludge

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(Received June 12, 1992; accepted October 12, 1992)

Abstract

To more efficiently dispose of hazardous wastes, the durability of a solidified mercury-containing sludge was studied. A sludge sample was obtained from a chloro-alkali plant and solidified using a commercially available sludge treatment agent (STA II). The solidified monoliths were then subjected to physical and chemical durability tests. The physical durability tests (the freezing and thawing test and the wetting and drying test) were followed by the measurements of unconfined compressive strength and mercury concentration resulting from the toxicity characteristic leaching procedure (TCLP), if possible. The multiple TCLP (MTCLP), developed by this author, was employed for the chemical durability test. It was found that the smaller the sludge-to-binder ratio (S/B) was, the better the physical and chemical properties of a solidified monolith would have. This conclusion was a result of the various durability tests, unconfined compressive strength measurements, and TCLP test. All solidified specimens were broken during the freezing and thawing test except the one with S/B = 0.5, which was found to be degraded in terms of compressive strength and leaching toxicity as well. Results of the wetting and drying test also showed that all solidified specimens were degraded as evidenced by the compressive strength and TCLP leachate concentration measurements. The multiple TCLP test was carried out to determine the long-term stability of the solidified specimens subjected to cyclic erosion and leaching by acid precipitation. The test results in this study showed that solidification with the binder STA II has reduced the cumulative amount of mercury leached from 10.57% to less than 0.66% by weight.

1. Introduction

Mercury is the only metal in liquid form at ambient temperatures. Generally, mercury can exist in any of the following three forms: zero valence (elemental mercury), positive monovalence, and positive bivalence. Mercury is a very toxic heavy metal. When mercury is in an organic form, it would give rise to the greatest toxicity comparing the inorganic and metallic forms. Mercury can easily enter the human bodies via the bioconcentration and foodchain.

The content of mercury is very low in the natural environment. For example, the average content of mercury ranges from 0.06 to 0.08 μg/g for soils; 0.3–0.41 μg/g for freshwater, estuarine and marine sediments; and 0.01–0.05 μg/g for water [1, 2].

In Taiwan, there used to be eight chloro-alkali plants employing the mercury process to generate chlorine gas, hydrogen gas and caustic soda. The residue from the following reactions in the mercury process is the so-called "mercury-containing sludge" employed in this study:

$$NaCl + xHg \rightarrow NaHg_x + \tfrac{1}{2}Cl_2(g)$$

$$NaHg_x + H_2O \rightarrow NaOH + \tfrac{1}{2}H_2(g) + xHg$$

Approximately 30,000 metric tons of mercury-containing sludge were generated by the chloro-alkali plants in Taiwan. Although no longer used after August 1989, this waste still remains to be managed in a proper manner or it will pose severe threats on the environment and human health.

The objective of this work was to determine whether the chemical solidification of the aforementioned mercury-containing sludge would yield a durable monolith. The durability of the solidified monolith was evaluated by the freezing and thawing test, the wetting and drying test, and a cyclic leaching test.

2. Experimental

2.1 Materials

A composite sample of mercury-containing sludge was obtained from a chloro-alkali plant, which has stopped generating such waste when it began using an ion exchange membrane (IEM) process instead. In this work, a commercially available sludge treatment agent (STA II) was used as the binder for sludge solidification. STA II, a cement-based binder with some proprietary additives, is a product of the Taiwan Cement Company.

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

2.2 Methods

The original sample was characterized by various standard methods for evaluating solid wastes recommended by the U.S. EPA and R.O.C. EPA [3, 4]. The measured properties included moisture content, ash content, combustible content, density, 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).

Sludge solidification was carried out by: (1) mixing the sludge, binder and water in a Hobart mixer for a few minutes; (2) pouring the mortar into an adequate size of PVC molds of cylindrical shape; (3) curing under the ambient conditions for one day; (4) demolding; (5) curing in an environmental chamber maintaining 20 °C and 90% relative humidity for a desired length of time. After curing, the solidified specimens were tested for a variety of purposes. In this work, solidification was conducted according to CNS 1230 A3043; unconfined compressive strength measurement, CNS 1232 A3045; wetting and drying test, ASTM D4843-88; freezing and thawing test, ASTM B553-79; leaching toxicity, TCLP test; heavy metals concentration, atomic absorption spectroscopy (AAS); and mercury concentration, a cold-vapor atomic absorption method (Method 7471, SW-846, U.S. EPA) [3].

Multiple TCLP (designated MTCLP), developed by this author, was the repetitive leaching test employed in this work. This test basically is a combined technique of TCLP and Multiple Extraction Procedure (MEP; Method 1320, SW-846, U.S. EPA) [3]. In MTCLP, the first leaching test is exactly the same as the conventional TCLP test, which uses glacial acetic acid as the extraction fluid. The solid portions of the sample that remain after the first leaching are generally re-extracted nine times using a synthetic acid rain extraction fluid (sulfuric acid/nitric acid = 60/40 wt% mixture).

3. Results and discussion

3.1 Characterization of the mercury-containing sludge

Characterization results for the composite sample of the mercury-containing sludge are given as follows: moisture content, 41.24%; ash content, 37.18%; combustible content, 21.58%; true density, 2.39; and pH, 9.9. The total contents of heavy metals (μg/g) were found to be: Hg, 174.4; Zn, 192.5; Pb, 202.3; Cd, 11.5; Cr, 40.2; Cu, 108.6; and Ni, 89.6. On the other hand, the heavy metal concentrations (mg/l) of the TCLP leachate were: Hg, 0.81; Zn, 0.15; Pb, <0.2; Cd, <0.03; Cr, <0.2; Cu, <0.1; and Ni, 0.53. The result of TCLP test indicates that the mercury concentration is greater than the R.O.C. regulatory threshold of 0.25 mg/l. Thus, the sludge sample studied is classified as a hazardous waste.

3.2 Characterization of solidified monolith prior to durability tests

As expected, an increase in the quantity of binder in the solidified monolith would increase its unconfined compressive strength. The smaller the weight ratio of sludge to binder (S/B), the greater the compressive strength (see Table 1). In the case of S/B = 0.5 and weight ratio of water to binder of 0.5, the compressive strength for the specimen 28 days old was 124.5 kg/cm^2.

Solidification indeed decreased the leaching toxicity of mercury in the sludge. Prior to solidification, the mercury concentration of the TCLP leachate for the sludge specimen was 810 ppb. After solidification, such as S/B = 0.5, the mercury concentration of the TCLP leachate was found to be 3.4 μg/L.

The effect of the binder quantity on the TCLP leaching toxicity was clearly shown in Table 2. A specimen solidified with a greater amount of binder would give rise to a greater compressive strength, which in turn would result in a lower leached concentration for each hazardous constituent. Besides,

TABLE 1

Effects of physical durability tests on unconfined compressive strength of a mercury-containing sludge solidified with the binder STA II

Sludge-to-binder ratio (wt%)	Unconfined compressive strength (kg/cm^2)		
	No durability test	Freezing and thawing test	Wetting and drying test
0.5	124.5	70.2	64.5
1.0	57.2	N.A.	24.5
1.5	24.6	N.A.	14.6
2.0	20.5	N.A.	10.5
3.0	18.7	N.A.	8.7

Note: N.A. means the solidified monolith has failed in the test.

TABLE 2

Effects of physical durability tests on leaching toxicity of a mercury-containing sludge solidified by the binder STA II

Sludge-to-binder ratio (wt%)	Mercury concentration of the TCLP leachate (μg/L)		
	No durability test	Freezing and thawing test	Wetting and drying test
0.5	3.4	34.3	8.5
1.0	8.9	59.5	17.9
1.5	10.8	73.4	34.7
2.0	17.4	85.7	58.2
3.0	30.6	99.4	69.1

a greater quantity of a cementitious binder would indeed reduce the leaching capability of the extraction fluid due to a partial neutralization resulting from a rather high pH of the binder.

3.3 Freezing and thawing test

Effects of the freezing and thawing test on unconfined compressive strength of solidified specimens are shown in Table 1. Except for the case of S/B = 0.5, all solidified specimens were cracked or broken into smaller pieces during the test. This makes the compressive strength measurement impossible (see Table 1).

The negative effect of the freezing and thawing test on leaching toxicity is depicted in Table 2. In this work, the leached mercury concentration compared with the sample subjected to this test has been found to be three to ten folds after the freezing and thawing test.

3.4 Wetting and drying test

Table 1 shows also the results of the compressive strength measurement for the sludge solidified with the binder STA II and then subjected to the wetting and drying test. From this table, it is clear that the wetting and drying test would lower the compressive strength of a solidified specimen. But the degradation of the solidified monolith due to the weathering effect of this test was found to be less than that of the freezing and thawing test.

The influence of the wetting and drying test on the leaching toxicity of the solidified specimen is shown in Table 2. As indicated above, this test would cause the degradation of the solidified monolith, which in turn would make the extraction of hazardous constituents easier. Again, in terms of leaching toxicity, the weathering effect of the wetting and drying test is not as significant as the freezing and thawing test.

3.5 MTCLP test

Based on the same design principles of Multiple Extraction Procedure (MEP), this author has combined TCLP and MEP tests to develop a new leaching test designated Multiple TCLP (MTCLP). Since MTCLP is a modification of MEP, its design function should be very similar to, if not the same as, that of MEP. MEP is designed to simulate the leaching that a solid waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill [3]. In a similar manner, MTCLP should reveal the highest concentration of each hazardous constituent that is likely to leach in a harsh, natural environment.

TABLE 3

Results of multiple TCLP test for a mercury-containing sludge and its solidified monolith

Sequence no. of MTCLP	Mercury-containing sludge unsolidified			Solidified specimen		
	Hg conc. (μg/L)	Wt of Hg leached (mg)	% of Hg leached (wt%)	Hg conc. (μg/L)	Wt of Hg leached (mg)	% of Hg leached (wt%)
1	810	1.620	9.31	30.6	0.061	0.47
2	21.90	0.044	0.25	0.63	0.001	0.01
3	8.95	0.018	0.10	1.13	0.002	0.02
4	11.30	0.023	0.13	0.84	0.002	0.02
5	9.74	0.019	0.11	0.91	0.002	0.02
6	12.60	0.025	0.14	2.09	0.004	0.03
7	10.60	0.021	0.12	2.41	0.005	0.04
8	6.51	0.013	0.07	0.63	0.001	0.01
9	27.90	0.056	0.32	1.69	0.003	0.02
10	1.51	0.003	0.02	1.25	0.003	0.02

Note: All calculations were based on 100 g of solid sample in 2000 ml of extraction fluid.

Table 3 shows the results of MTCLP for a mercury-containing sludge before and after solidifying with the binder STA II. For ease of comparison, the weight of mercury leached has been determined on the same basis that 100 g of solid sample is leached in 2000 ml of extraction fluid. As shown in Table 3, for both unsolidified and solidified specimens, the first leaching (Sequence No. 1) of MTCLP yielded the highest concentration of mercury. Starting from the Sequence No. 2 towards the end of the test, each leaching sequence gave only a very small increment (less than 0.3 wt%) of mercury leached. The cumulative amounts of mercury leached were found to be 10.57% and 0.66% by weight for unsolidified and solidified (S/B = 3) specimens, respectively. Thus, it is evident that solidification of the mercury-containing sludge with the binder STA II is capable of providing long-term stability for the waste disposed in this manner. A further study for the same sludge solidified with the same binder (S/B = 0.5) and 1 wt% (S + B) of a styrene–butadiene rubber (SBR) has indicated that the cumulative amount of mercury leached is reduced to 0.20 wt%.

4. Conclusions

In this work, properties of a mercury-containing sludge solidified by a commercially available binder STA II were characterized. The effects of physical and chemical durability tests on solidified monoliths were investigated as well. The former durability tests include the freezing and thawing test and the wetting and drying test, whereas the latter is a newly developed Multiple TCLP (MTCLP).

Experimental results indicate that physical durability tests would degrade the solidified monolith when their degradation was measured by unconfined compressive strength and TCLP leachate concentration of mercury. Except for the case of S/B = 0.5, all solidified monoliths were cracked or broken during the freezing and thawing test. The weathering effect of the wetting and drying test is not as strong as that of the freezing and thawing test.

Results of MTCLP show that the first leaching (the conventional TCLP) is the most significant step in the entire MTCLP test. In this leaching step, approximately 70–90 wt% of total leached mercury would be extracted. Only a rather small increment of leached mercury will be obtained for each of the subsequent leaching steps. For the unsolidified sludge specimen, the cumulative amount of mercury leached is 10.57%. Solidification of the same sludge with the binder STA II would reduce the cumulative amount of mercury leached to 0.66% by weight, or even smaller depending on the solidification conditions.

As indicated above, Sequence No. 1 leaching dominates the overall leaching of MTCLP. Whether this finding is applicable to other wastes solidified with other binders still remains uncertain. Further studies in this regard are therefore needed.

Acknowledgements

This study was sponsored by the R.O.C. EPA under project No. EPA-80-E3H1-09-23 (Report No. EPA 044800557). The author wishes to extend his sincere appreciation to Messrs S.C. Wang, C.M. Lin and W.S. Yang, and Misses S.L. Fan and R.C. Liu of Energy & Resources Laboratories, ITRI and Miss L.C. Huang of Tsing Hua University for the experimental assistance. The author also is indebted to Professor G.H. Hsiue of Tsing Hua University in Taiwan for his advice and discussions in the course of this work.

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