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Further study on properties of a solidified electroplating sludge using a mixture of an electroplating sludge and a calcium carbonate sludge as a binder

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Abstract

Using a waste mixture as a binder to yield solidified monoliths of good physical and chemical properties is the objective of this study. The incentive of this recycling attempt is to further verify the concept of using wastes to treat wastes. It has previously been reported that it is feasible to use a heat-treated mixture of an electroplating sludge and a calcium carbonate sludge as a binder for sludge solidification. In this work (Part II of the research), a further study on various properties of a solidified electroplating sludge using the above waste mixture binder was carried out. Properties studied include the resistance to wetting and drying cycling, resistance to freezing and thawing cycling, acid neutralization capacity (ANC), and generalized acid neutralization capacity (GANC) of selected solidified specimens. For the purpose of comparison, the same properties were also tested for monoliths solidified by ordinary portland cement with partial replacements of a water-quenched blast-furnace (BF) slag.

It was found that BF slag performed slightly better than the heat-treated waste mixture only in ANC and GANC tests, but did not in others. The heat-treated waste mixture, however, still showed its capability to yield solidified monoliths of outstanding physical and chemical properties. In this study, a modified Taguchi method with the L_9 orthogonal arrays was employed for the experimental design of solidification. The heat-treated waste mixture or BF slag was used to partially replace (10 wt%, 20 wt%, or 40 wt% replacement) the ordinary portland cement as a binder. Selected solidified monoliths were then tested to determine their physicochemical properties for comparisons between two binder systems. Results of the wetting and drying test showed that the cumulated, corrected relative mass losses were all less than one percent with one exception for the tested specimens of both binder systems. On the other hand, results of the freezing and thawing test showed that some specimens were broken up, whereas others still remained their physical integrity macroscopically or had very little mass losses for both binder systems. Regarding the acid neutralization capacity, monoliths solidified by either binder system outperformed the sludge specimen without solidification. A similar observation was obtained for the above systems in terms of generalized acid neutralization capacity. Overall, the heat-treated waste mixture has been proved to be an excellent binding material for sludge solidification.

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1. Introduction

This work is Part II of the research concerning the use of a mixture of an electroplating sludge and a calcium carbonate sludge as a binder for sludge solidification. In Part I of this research [1], it has been reported that it is technically feasible to use the above waste mixture as a binder for sludge solidification. In other words, an emerging technology for recycling the above waste mixture as a substitute of ordinary portland cement (OPC) for sludge solidification was developed by the authors. In Part I of this research, an amount up to 40 wt% of the heat-treated waste mixture was used to substitute OPC as a binding material in a solidification treatment of the original, hazardous electroplating sludge. The solidified monoliths were found to have satisfactory unconfined compressive strengths, TCLP leaching toxicity, and long-term chemical durability. In the present study (Part II), solidified monoliths of the same solidification recipes were further tested for their resistance to freezing and thawing cycling, resistance to wetting and drying cycling, acid neutralization capacities, and generalized acid neutralization capacities. The objective of this work is to determine whether the heat-treated waste mixture was able to yield solidified monoliths of satisfactory physicochemical properties, especially long-term durability.

In a separate work, these authors have reported the effects of cement replacement by slag on various properties of a solidified electroplating sludge including the physical durability [2]. Solidified monoliths with 20 wt% OPC replaced by BF slag were found to be capable of passing the wetting and drying test and the freezing and thawing test. However, solidified monoliths with 40 wt% replacement failed in the freezing and thawing test. These findings and other experimental results will be used for comparing the relevant properties of the solidified monoliths resulting from partial OPC replacement by the heat-treated waste mixture.

2. Experimental

2.1. Materials

In Part II of this research, the same heat-treated waste mixture that has previously been reported [1] was used as an ordinary portland cement substitute in a solidification treatment of an electroplating sludge. The electroplating sludge has been identified as a hazardous waste according to the ROC EPA regulations. Its TCLP leachate was found to have concentrations of 168.63 and 28.80 mg/l for zinc and cadmium, respectively. The heat-treated waste mixture was prepared by mixing an electroplating sludge and a calcium carbonate sludge and heating at 1000 °C for four hours. Details of the preparation method can be found elsewhere [1]. As for the specifications of all chemicals and water used, they remain the same as in the previous report.

A water-quenched blast furnace (BF) slag was also used as a cement substitute in this work for comparison. The ground BF slag was generously provided by China Hi-Ment Corporation with which China Steel Corporation is holding 50% of shares.

2.2. Methods

Characterization tests conducted for the electroplating sludge and calcium carbonate sludge were the same as in the previous report [1]. Regarding the characteristics of the BF slag, they were provided by the supplier. No additional testing was carried out.

In this study, the same experimental methods and conditions are applicable for both binder systems (i.e., cement substituted by the heat-treated waste mixture and by the BF slag). The solidification recipes were followed the same L_9 orthogonal arrays adopted in the Taguchi method that has been reported earlier [1]. The solidification procedure and curing conditions also remained the same. Unless otherwise specified, all relevant tests for solidified monoliths were not different from those in the previous report [1]. New tests included the wetting and drying test (ASTM D4843-88), freezing and thawing test (ASTM D4842-90), standard acid neutralization capacity (ANC) test [3], and generalized acid neutralization capacity (GANC) test [4].

3. Results and discussion

Characterization results for the electroplating sludge and the calcium carbonate sludge have been reported elsewhere [1]. They will not be repeated here.

3.1. Characterization of the water-quenched blast furnace slag

Characterization results shown below were provided by the supplier. The chemical composition of the BF slag used are given as follows (wt%): SiO_2, 32.79; Al_2O_3, 13.29; Fe_2O_3, 0.35; CaO, 41.64; MgO, 6.94; SO_3, 0.88; Na_2O, 0.14; and K_2O, 0.50. The characterization results also provided include: (1) loss on ignition: 2.18 wt%, (2) specific gravity: 2.93, (3) fineness: 5000 Blaine, and (4) hardness: 5–7 in Mohs scale.

3.2. Unconfined compressive strength (UCS)

For solidified monoliths of 28-day old, the heat-treated waste mixture was found to be superior to the BF slag in terms of UCS. As previously reported [1], the UCS ranged from 23.46 to 76.43 kg/cm^2 for the former binder system. For the latter binder system, it yielded monoliths with a UCS range of 10.57 to 29.62 kg/cm^2. For monoliths solidified using a cement-based technique, these UCS values are too low in a general sense. But, they are still in compliance with the current ROC EPA regulatory requirement for landfilling of solidified monoliths (i.e., 10 kg/cm^2). Nonetheless, this UCS range is slightly lower than the corresponding “control group” monoliths that are solidified with straight OPC by definition. A possible reason for such low UCS ranges for “control group” and “sample group” monoliths resulting from either binder system might be due to a high loss on ignition (LOI) of the electroplating sludge (i.e., 39.66%). A high LOI is an indication of a high organic content in the electroplating sludge. A waste with a high organic content is not suitable for solidification by a cement-based technique because organic materials would interfere the hydration of cement [5]. If so, apparently, the heat-treated waste mixture binder system is capable of overcoming this interference to a greater extent than does the BF slag.

It was noted that the highest and the lowest UCS values were associated with monolith Nos. 5 and 8, respectively for both binder systems. Further examination of the experimental results and solidification recipes, one would find that monolith Nos. 5 and 8 represented cases of 20 wt% and 40 wt% of OPC replacement, respectively. For the ease of discussion, only these two solidified monoliths will be selected for comparing their physical durability and acid neutralization capacities, unless otherwise specified.

3.3. TCLP leaching toxicity

Regarding the TCLP leaching toxicity, both binder systems yielded comparable results for solidified wastes with an age of 28 days. The leached concentrations of zinc and cadmium are all much smaller than the current ROC EPA regulatory thresholds. The leached concentrations of zinc and cadmium (mg/l) were: (1) < 0.483 and < 0.080, respectively for the heat-treated waste mixture binder system, and (2) < 0.742 and < 0.082, respectively for the BF slag binder system.

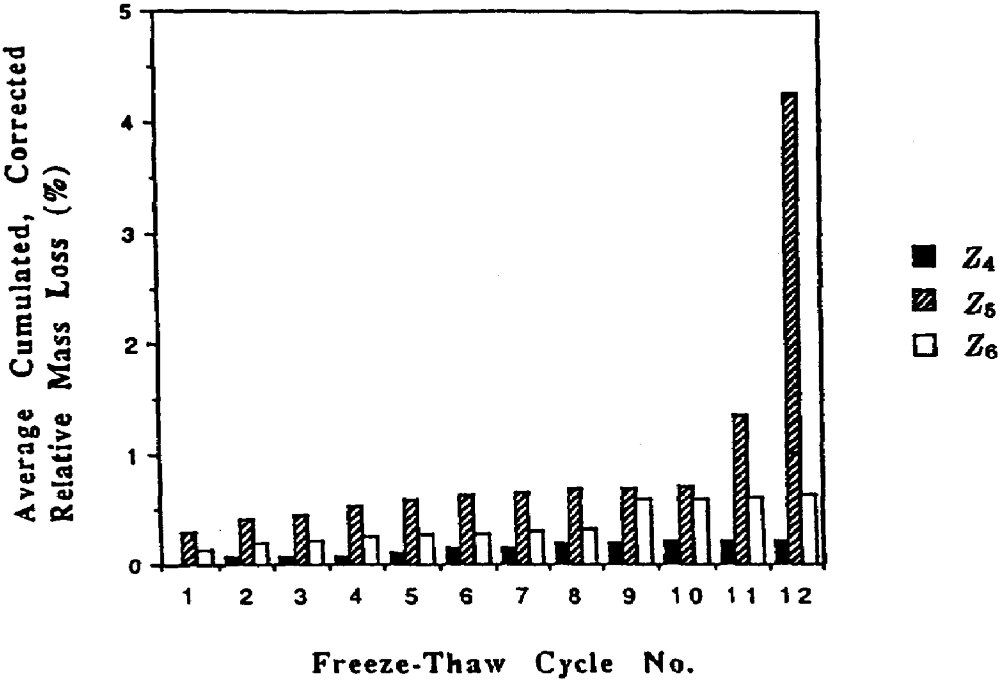


Fig. 1. Freezing–thawing durability of selected monoliths (i.e., Z_4, Z_5, and Z_6) solidified by a cement-based technique with a 20 wt% cement replacement by water-quenched BF slag.

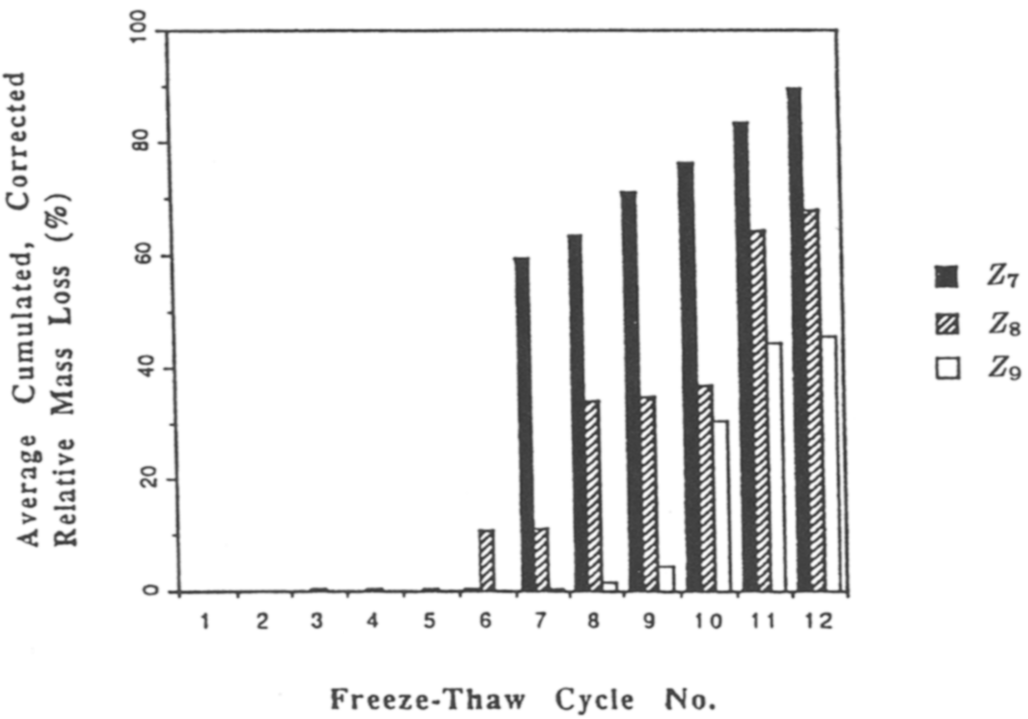


Fig. 2. Freezing–thawing durability of selected monoliths (i.e., Z_7, Z_8, and Z_9) solidified by a cement-based technique with a 40 wt% cement replacement by water-quenched BF slag.

3.4. Freezing–thawing durability

Experimental results showed that the heat-treated waste mixture binder system outperformed the BF slag binder system in terms of the resistance to freezing and thawing cycling, if only monolith Nos. 5 and 8 were compared. For the former binder system, the cumulated, corrected relative mass losses for monolith Nos. 5 and 8 were 1.96% and 43.72%, respectively; whereas the latter binder system, 4.26% and 68.13%, respectively. It was found that No. 8 monoliths (i.e., 40 wt% cement replaced) for both binder systems did not pass the test because their cumulated, corrected relative mass losses were greater than the threshold value of 30%.

One should not jump to a conclusion that monoliths of 20 wt% cement replacement would always pass the freezing and thawing test and that monoliths of 40 wt% cement replacement would always fail the test. Results of additional tests have shown that the above statement is true for the BF slag binder system (see Figs. 1 and 2), but not true for the other binder system (see Figs. 3 and 4). For instance, monolith No. 6 (also 20 wt% cement replacement by the heat-treated waste mixture) had a cumulated, corrected relative mass loss of 36.65% and monolith No. 7 (also 40 wt% cement replacement by the heat-treated waste mixture) had a value 15.72%. Accordingly, monolith No. 6 failed in the freezing and thawing test, whereas monolith No. 7 passed the test.

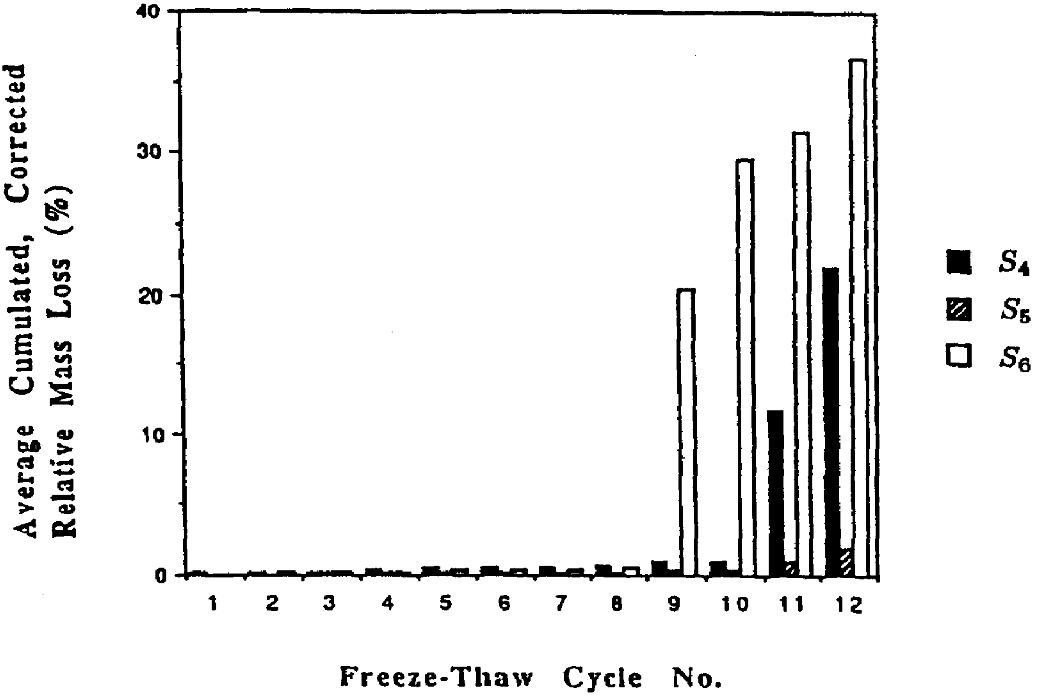


Fig. 3. Freezing–thawing durability of selected monoliths (i.e., S_4, S_5, and S_6) solidified by a cement-based technique with a 20 wt% cement replacement by the heat-treated waste mixture.

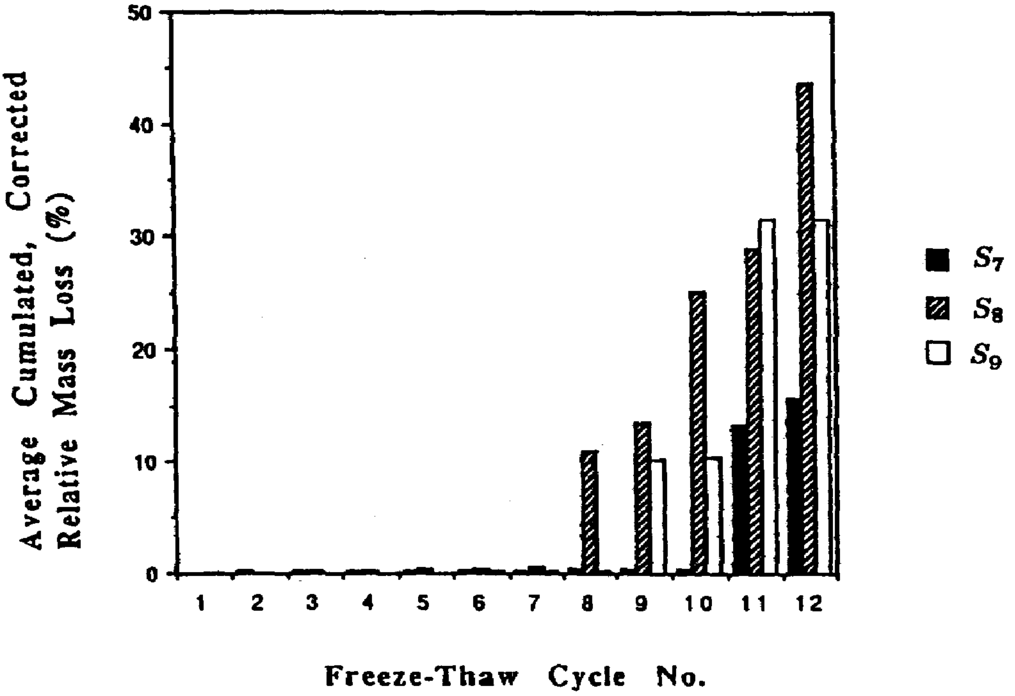


Fig. 4. Freezing–thawing durability of selected monoliths (i.e., S_7, S_8, and S_9) solidified by a cement-based technique with a 40 wt% cement replacement by the heat-treated waste mixture.

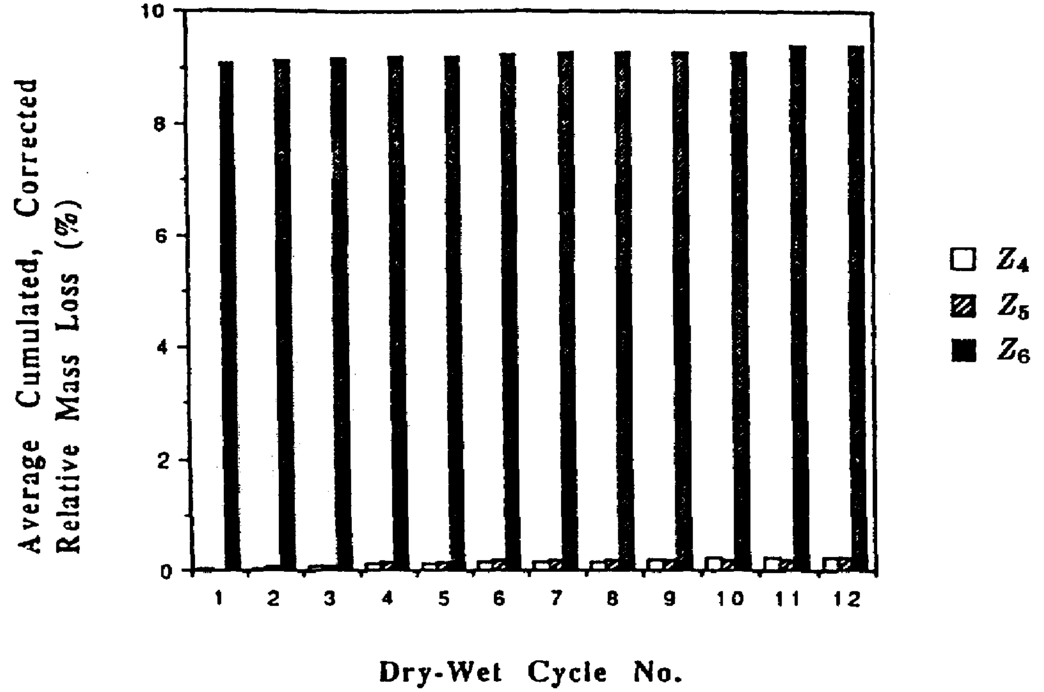


Fig. 5. Wetting–drying durability of selected monoliths (i.e., Z_4, Z_5, and Z_6) solidified by a cement-based technique with a 20 wt% cement replacement by water-quenched BF slag.

3.5. Wetting–drying durability

Experimental results showed that both binder systems yielded a strong, comparable resistance to wetting and drying cycling. According to ASTM D4843-88, the threshold value of the cumulated, corrected relative mass loss is 30%. For the BF slag binder system, monolith Nos. 5 and 8 had cumulated, corrected relative mass losses of 0.23% and 0.14%, respectively; whereas for the heat-treated waste mixture binder system, 0.27% and 0.45%, respectively.

Results of additional tests also showed that for both binder systems all solidified monoliths with an OPC replacement up to 40 wt% passed the wetting and drying test. Their cumulated, corrected relative mass losses were all less than one percent except monolith No. 6 of the BF slag binder system. This is evidenced by Figs. 5–8.

3.6. Acid neutralization capacity (ANC, by the standard method)

Results of the standard ANC test showed that the BF slag binder system had a greater resistance to pH reduction by exposure to an acidic solution (e.g., nitric acid solution) than did the heat-treated waste mixture binder system (see Fig. 9). In general, pH 7 is selected as the reference level for ANC comparison. From Fig. 9, it is apparent that monoliths solidified with either binder system would have much greater acid

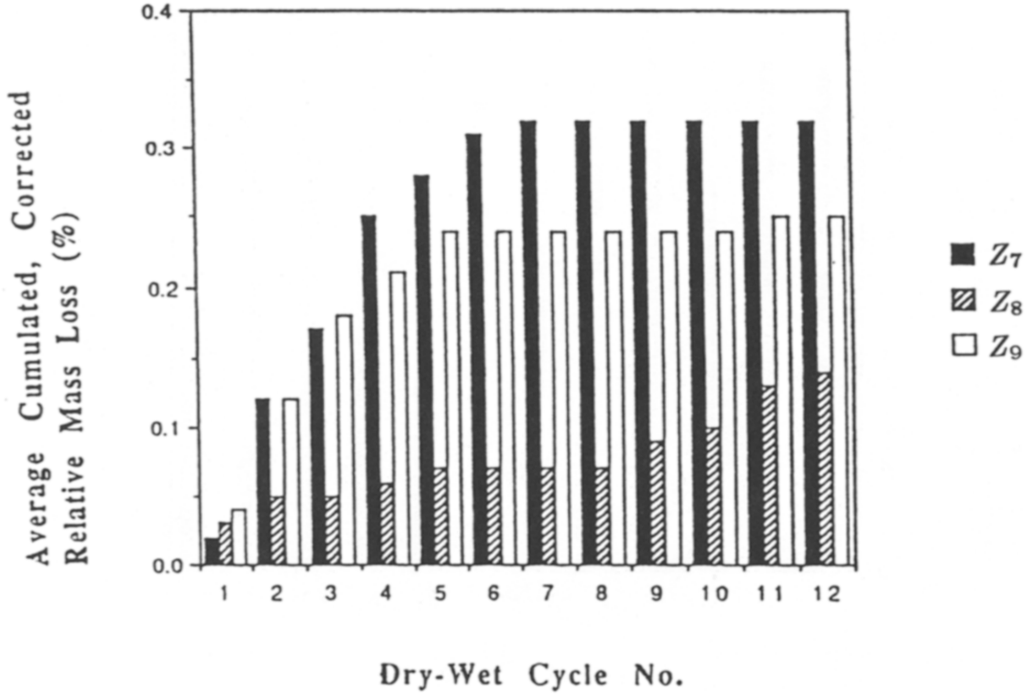


Fig. 6. Wetting–drying durability of selected monoliths (i.e., Z_7, Z_8, and Z_9) solidified by a cement-based technique with a 40 wt% cement replacement by water-quenched BF slag.

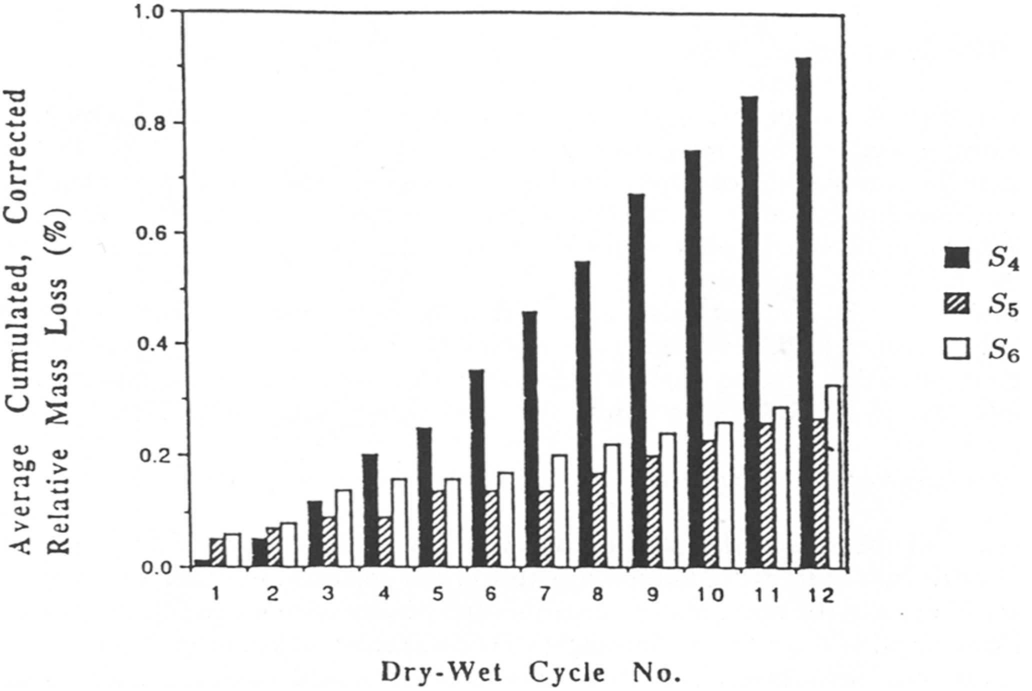


Fig. 7. Wetting–drying durability of selected monoliths (i.e., S_4, S_5, and S_6) solidified by a cement-based technique with a 20 wt% cement replacement by the heat-treated waste mixture.

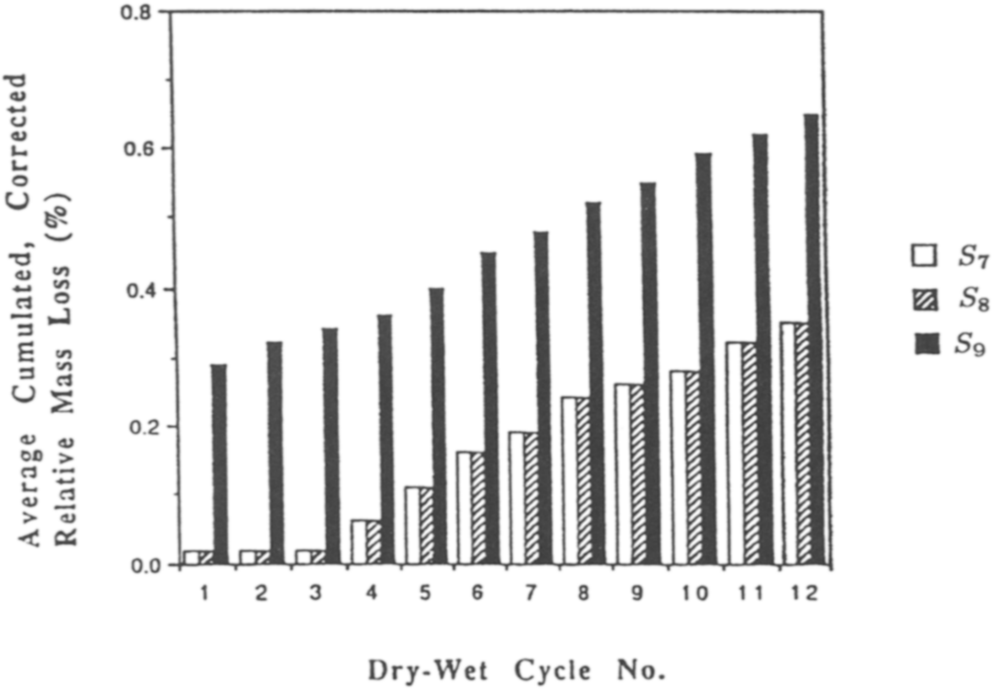


Fig. 8. Wetting–drying durability of selected monoliths (i.e., S_7, S_8, and S_9) solidified by a cement-based technique with a 40 wt% cement replacement by the heat-treated waste mixture.

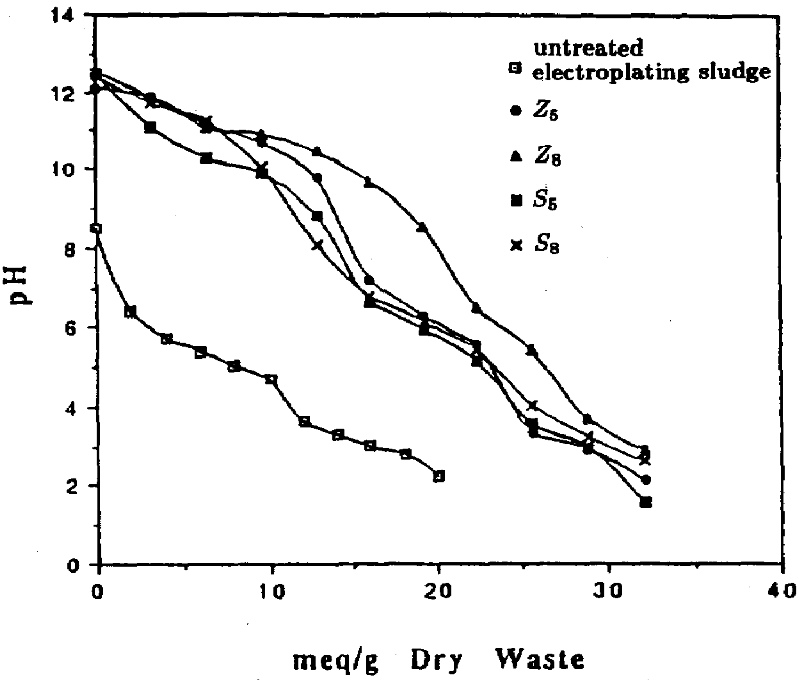


Fig. 9. Comparisons of acid neutralization capacity among the untreated electroplating sludge and selected monoliths solidified by BF slag binder system (i.e., Z_5 and Z_8) and by the heat-treated waste mixture binder system (i.e., S_5 and S_8).

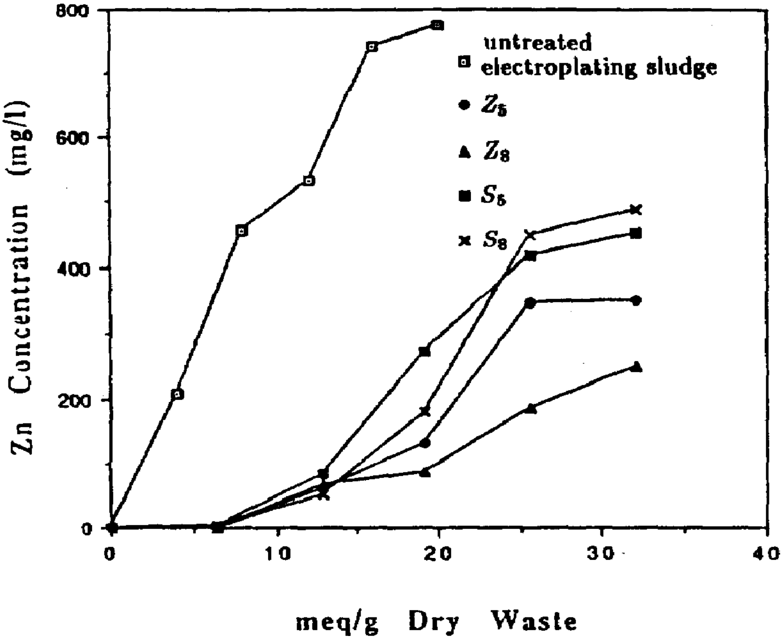


Fig. 10. Comparisons of leached zinc concentration in the ANC test among the untreated electroplating sludge and selected monoliths solidified by BF slag binder system (i.e., Z_5 and Z_8) and by the heat-treated waste mixture binder system (i.e., S_5 and S_8).

neutralization capacities than that of the untreated electroplating sludge. For the untreated electroplating sludge, it needs only 2 milli-equivalent (meq) of 2 *N* HNO_3/g of dry waste to reduce its pH value to a point below 7. For monolith Nos. 5 and 8 resulting from either binder system, it needs more than 16 meq/g dry waste to reach the same pH level.

Additional tests were carried out to determine the relationship of the leached heavy metal concentrations and the amount of nitric acid added in the ANC test. Figs. 10 and 11 show the results of the untreated electroplating sludge and monolith Nos. 5 and 8 resulting from both binder systems for leached zinc and cadmium, respectively. Not surprisingly, much greater leached heavy metal concentrations were obtained for the untreated electroplating sludge than that of solidified monoliths. This is understandable because the former has a pH of 8.17; whereas the latter, pH > 12 as shown in Fig. 9.

3.7. Generalized acid neutralization capacity (GANC)

The GANC test developed by the US EPA laboratory at Center Hill, Cincinnati intended to correlate the standard methods ANC and TCLP and to combine them into one test. In this new test, 2 *N* nitric acid used in the original ANC test is replaced by 2 *N* acetic acid. Thus, a condition of the TCLP test will be incorporated into the GANC test. Detailed objectives of this new test can be found elsewhere [4].

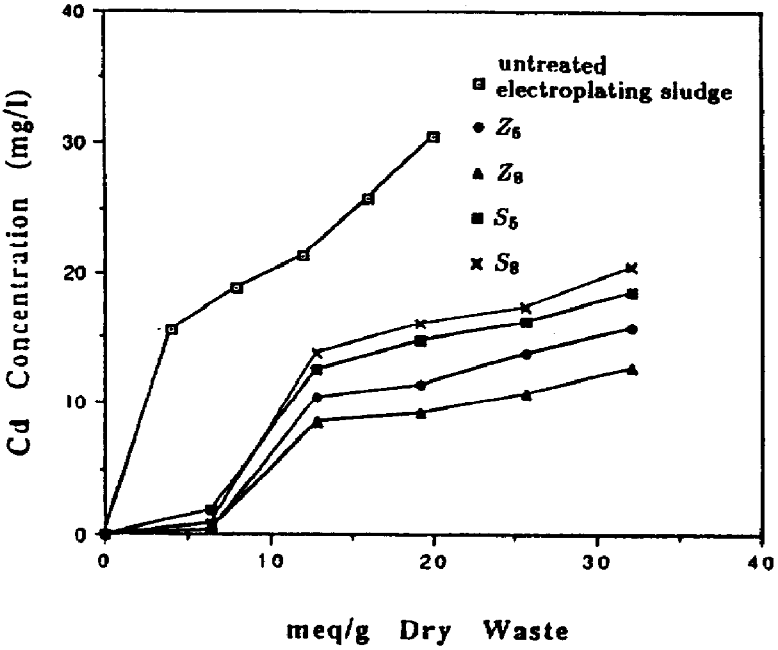


Fig. 11. Comparisons of leached cadmium concentration in the ANC test among the untreated electroplating sludge and selected monoliths solidified by BF slag binder system (i.e., Z_5 and Z_8) and by the heat-treated waste mixture binder system (i.e., S_5 and S_8).

As in the ANC test, any of the tested monoliths had a much greater generalized acid neutralization capacity than did the untreated electroplating sludge. An addition of 2 equivalent of 2 *N* acetic acid per kilogram of dry waste would lower its pH to a level of below 7, while a minimum of 12 equivalent of acetic acid per kilogram of dry waste would be needed for tested monoliths. By comparing No. 8 monoliths resulting from different binder systems, it was found that the BF slag binder system gave rise to a greater GANC than did the other binder system (see Fig. 12). As for No. 5 monoliths, both binder systems yielded a comparable GANC.

Figs. 13 and 14 show the relationship between the leached heavy metal concentrations and the amount of acetic acid added in the GANC test. Again, for the same amount of acetic acid added, it was found that much greater leached heavy metal concentrations were obtained for the untreated electroplating sludge than for solidified monoliths.

3.8. Comparison of ANC and GANC results

From the experimental results obtained, it is clear that the ANC test and GANC test would give rise to a similar trend of findings. However, their results will be different because these two tests differ in many aspects.

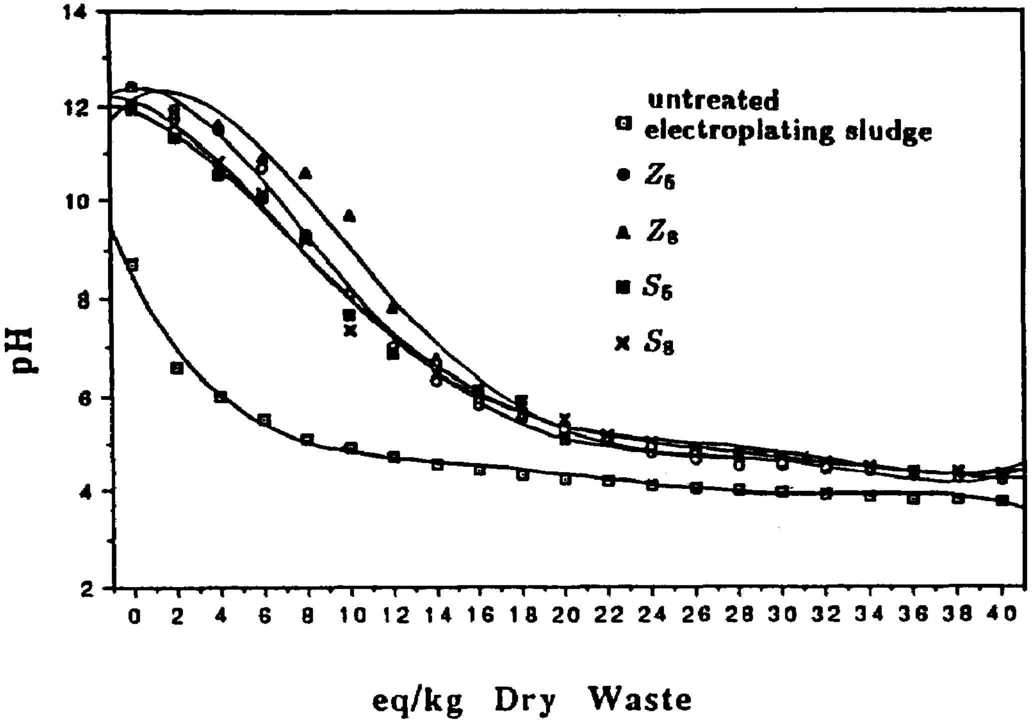
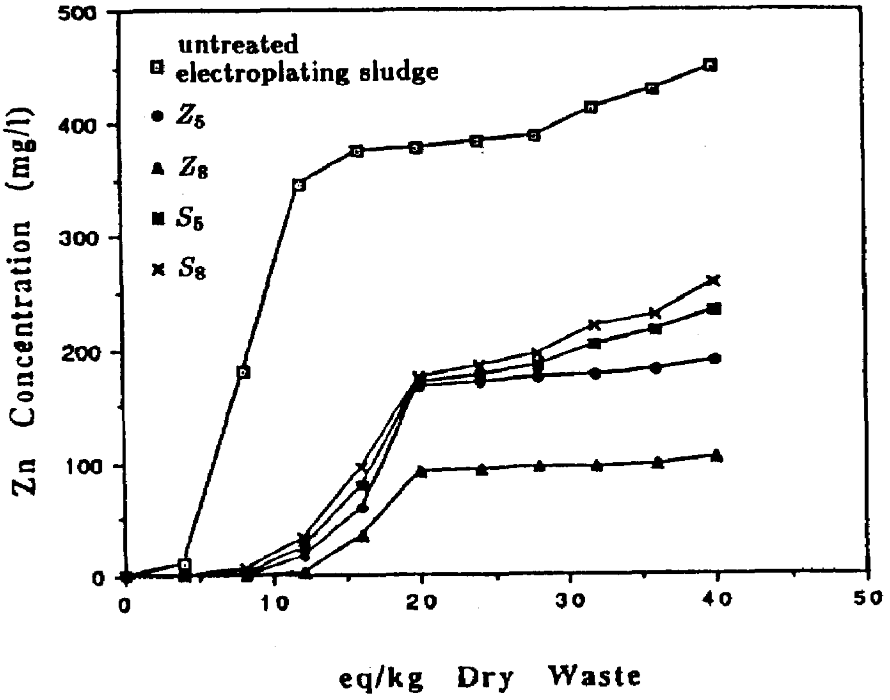


Fig. 12. Comparisons of generalized acid neutralization capacity among the untreated electroplating sludge and selected monoliths solidified by BF slag binder system (i.e., Z_5 and Z_8) and by the heat-treated waste mixture binder system (i.e., S_5 and S_8).



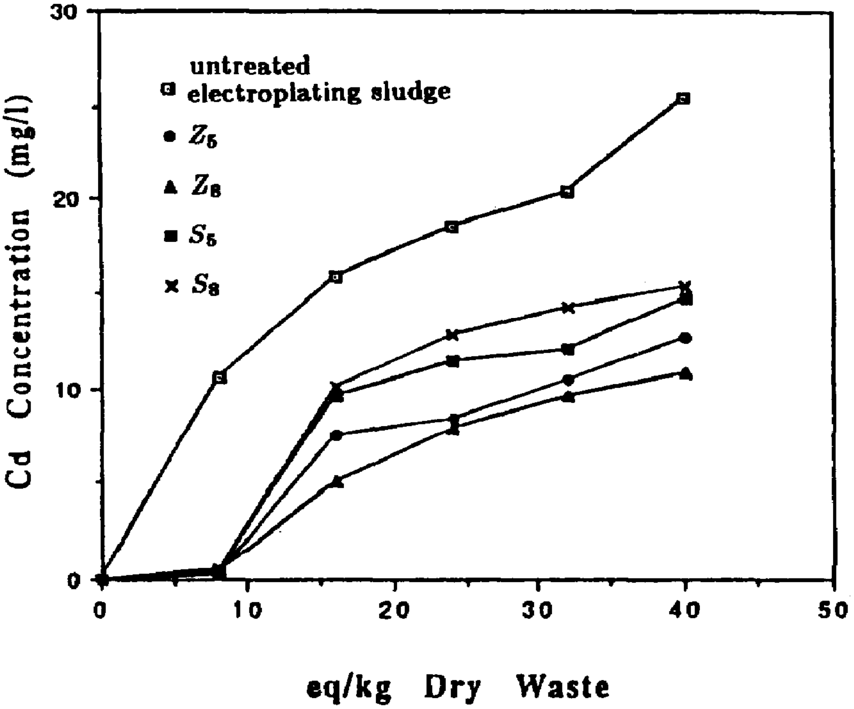


Fig. 14. Comparisons of leached cadmium concentration in the GANC test among the untreated electroplating sludge and selected monoliths solidified by BF slag binder system (i.e., Z_5 and Z_8) and by the heat-treated waste mixture binder system (i.e., S_5 and S_8).

A comparison of ANC and GANC results obtained in this work is presented in Table 1. It is obvious that for the same specimen greater heavy metal concentrations will be leached in the ANC test than does the GANC test. Roughly speaking, the difference is about two-fold. This is because that nitric acid is a much stronger acid than acetic acid, thereby resulting in a greater leaching capability in the former test.

4. Conclusions

This work is a further investigation on the performance of a heat-treated waste mixture as a binding material for a solidification treatment of a hazardous electroplating sludge. It has previously been reported by these authors that it is feasible to use a heat-treated mixture of an electroplating sludge and a calcium carbonate sludge as a binder for sludge solidification. Therefore, in Part II of this research, solidified

Fig. 13. Comparisons of leached zinc concentration in the GANC test among the untreated electroplating sludge and selected monoliths solidified by BF slag binder system (i.e., Z_5 and Z_8) and by the heat-treated waste mixture binder system (i.e., S_5 and S_8).

Table 1
Comparison of ANC and GANC results of the untreated electroplating sludge and its monoliths solidified by a cement-based technique with a partial replacement of cement by BF slag or a heat-treated waste mixture

Tested specimen, and type and amount (meq/g) of extraction fluid added	Leached heavy metal concentration (mg/l)	
	Zinc	Cadmium
1. *Untreated Sludge*		
a. Nitric acid (20)	775.0	30.5
b. Acetic acid (20)	377.4	18.0
2. *Monolith No. 8 (BF slag binder)*		
a. Nitric acid (32)	489.5	20.5
b. Acetic acid (32)	200.5	14.3
3. *Monolith No. 8 (Waste mix. binder)*		
a. Nitric acid (32)	249.0	12.6
b. Acetic acid (32)	96.5	9.6

electroplating sludge specimens were subjected to additional tests to determine their other properties such as freezing–thawing durability, wetting–drying durability, acid neutralization capacity, and generalized acid neutralization capacity. For comparison, the same tests were also conducted for a second group of monolithic solids that were solidified with the same mix formulations except using a BF slag instead of the heat-treated waste mixture .

Experimental results have proved that the heat-treated waste mixture is an excellent material to partially replace ordinary portland cement for sludge solidification. By proper selection of a solidification recipe, it is possible to prepare a solidified monolith of good physicochemical properties. Solidified monoliths of this kind would present satisfactory values of unconfined compressive strength, TCLP leaching toxicity, chemical durability, physical durability, and acid neutralization capacity. Experimental results have indicated that these solidified monoliths are not inferior to those solidified by the BF slag binder system. The set objective of this study is thus fulfilled. The concept of using wastes to treat wastes once again is realized and verified in this work.

Acknowledgement

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