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Project Summary

Evaluation of Solidification/ Stabilization Treatment Processes for Municipal Waste Combustion Residues

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The investigations described in this report were carried out to compare and evaluate the effectiveness of solidification/stabilization (S/S) processes as treatment technologies for residues from municipal waste combustion (MWC). A full, factorial, experimental design was used to evaluate five S/S processes. The two experimental factors were the residue type to be treated and the S/S process. The three experimental levels within the residue type factor were (1) bottom ash, (2) air pollution control (APC) residue, and (3) combined ash. The six experimental levels within the S/S process factor were the untreated residue, a Portland-cement-only control process, and four selected vendor processes. Thus, 2 experimental factors at 3 and 6 experimental levels, respectively, resulted in the evaluation of 18 experimental cases.

Evaluation of each experimental case included analysis of chemical composition, physical properties, durability, and leaching characteristics. The testing included moisture content, loss on ignition, bulk density, modified Proctor density, particle size distribution, permeability, specific surface area, porosity, cone penetrometer, unconfined compressive strength, pozzolanic activity, unconfined compressive strength after immersion, wet/dry, freeze/thaw, toxicity characteristic leaching procedure (TCLP), availability leach test (ALT), distilled water leach test (DWLT), acid neutralization capacity (ANC), and the monolithic leach test (MLT).

Based on comparison of untreated residues with treated residues, the S/S processes evaluated generally did not decrease the potential for the release of target contaminants. A phosphate process did, however, reduce the potential for lead to be released. Whether treated or not, the typical release potential for metals was a small fraction of the total metal concentration present in the residues.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The proper management of MWC residues is necessary to ensure that the use of combustion as a solid waste management method protects human health and the environment. Although recent Federal regulations for municipal solid waste (MSW) and landfills (Federal Register, Oct. 9, 1991) address the disposal of MWC residues, regulations specific to ash disposal generally remain the responsibility of individual states. Recently, the U.S. Congress has considered legislation that would require the U.S. Environmental Protection Agency (EPA) to develop comprehensive national ash disposal, treatment, and utilization standards. To have the scientific data available to support possible future legislative requirements to promulgate technical guidance and/or regulations for the proper management of MWC residues, the EPA initiated studies on MWC ash characteristics, ash disposal facilities, and ash management practices. This study adds to that database.

Specific Objectives and Approach

The investigations described in this report were carried out to compare and evaluate the effectiveness of S/S processes as treatment technologies for bottom ash, APC residue, and combined ash. Rather than determine how ash characteristics are affected by municipal waste combustor designs, operating conditions, and waste input, the program emphasized the evaluation of S/S treatment technologies. Therefore, the residues included in the study were limited to those from a single, modern, waste-to-energy facility. The specific objectives of this study were to:

1. define residue sampling, preparation, and characterization protocols to permit bench and pilot-scale demonstrations of S/S treatment processes with representative residues;
2. carry out MWC residue S/S treatment process demonstrations under carefully controlled and monitored conditions;
3. determine how the S/S treatment process affects the fundamental physical and chemical properties of the MWC residues;
4. compare the effects of the S/S processes on leaching properties of MWC residues through laboratory procedures, which include the TCLP and other tests that can estimate contaminant release potential and release rate over a prolonged period of time and under diverse environmental conditions; and,
5. evaluate the physical durability of the treated MWC residues during aggressive environmental cycling tests.

A full factorial design was used to evaluate five S/S processes for treating MWC residues. The two experimental factors were the residue type to be treated and the S/S process. Residue types tested were (1) bottom ash, (2) APC residue, and (3) combined ash. The six experimental levels within the S/S process factors were the untreated residue, the Waterways Experiment Station (WES) Control (Portland cement only) S/S process, and four selected vendor S/S processes. Thus, 18 experimental cases were evaluated in triplicate.

The three residue types were obtained during a single composite sampling taken from a typical, state-of-the-art, mass-burn municipal waste combustor. The facility has a lime-slurry spray drier (wet-dry), an acid gas scrubber, and a fabric filter particulate removal system. Bulk residue samples were dried, size reduced, screened, and homogenized before use in this program. Thus all process demonstrations, testing, and evaluations were carried out on preprocessed residues to facilitate laboratory-scale testing and the comparisons of treatment effects.

Five S/S processes were evaluated. Four of the processes were proprietary modifications of four different generic S/S processes. The four proprietary processes evaluated were:

- Portland cement and polymeric additives or other proprietary additives (Process 1);
- Portland cement and soluble silicates (Process 2);
- Cement kiln dust and proprietary additives (Process 3);
- Addition of soluble phosphates (Process 4).

The fifth process (WES) used Type 1 Portland cement only (control process). The Type 1 Portland-cement-only process was selected to provide a baseline comparison of the treatment effects of Portland cement without vendor additives.

All vendors demonstrated their specifically designed S/S processes on each residue type. The vendors were provided approximately 50 lb of each residue type to develop optimum formulas before the process demonstrations. They were also provided a list of test and program objectives that would be used to evaluate each process. The vendors were not provided specific performance criteria to which the residue should be treated; performance criteria were left to the vendor's discretion. Based on analysis of results, vendor process optimization may have focused on minimizing contaminant release based on TCLP, concurrent with minimizing cost, and not on maximizing the physical properties of the treated residue.

Demonstrations were conducted under the observation of EPA representatives and U.S. Army Corps of Engineers personnel. Each demonstration, done in triplicate, consisted of the vendor carrying out the specified process to produce approximately 100 lb of treated residue. Each experimental case was analyzed for chemical composition and tested for physical properties, physical durability, and leaching characteristics with the use of the following tests: moisture content, loss on ignition, bulk density, modified Proctor density, particle size distribution, permeability, specific surface area and porosity, cone penetrometer, unconfined compressive strength, pozzolanic activity, unconfined compressive strength after immersion, wet/dry, freeze/thaw, TCLP, ALT, DWLT, ANC test, and MLT.

Summary of Leaching Tests

The leaching tests were selected to provide a broad understanding of contaminant release under a variety of potential environmental conditions. The primary objective was to evaluate fundamental leaching properties rather than to simulate specific environmental exposure scenarios. These fundamental leaching properties were (1) release potential, (2) elemental solubility as a function of pH, and (3) release rate under diffusion-controlled conditions. This approach permits the use of leaching data to estimate contaminant release for a variety of environmental conditions instead of only the particular exposure scenario tested. TCLP also was carried out on untreated and treated residues for comparison purposes. Untreated residue samples were tested after mechanical processing steps, which included screening, size reduction, and homogenization. Therefore, results from testing the untreated residues may not be indicative of the behavior of "as disposed" residues, which have not been mechanically processed. The leaching tests and the basis for selecting each are discussed in the following paragraphs.

The TCLP was selected to allow these results to be compared with a broad database of results from tests of other materials. The TCLP was carried out in accordance with the method outlined in the U.S. Code of Federal Regulations, Title 40, Part 268, Appendix I.1988. In this test, a solid sample is crushed to a sample size less than 9.5 mm and is extracted with dilute acetic acid at a 20:1 liquid-to-solid ratio. The extraction solution is either buffered or unbuffered depending on the alkalinity of the material to be tested. Only a fixed quantity of acid is used for the extraction, and therefore, the final pH of the extract may vary widely. Thus, metals concentrations observed in the extract often reflect the pH-dependent solubility constraints of the specific element. The contaminant concentrations in the test leachate are compared with a published list of limits that apply to hazardous wastes (not MWC residues).

The ALT was selected to assess the maximum amount of specific elements or species that could be released under an assumed "worst case" environmental scenario. This test, originally developed by the Netherlands Energy Research Center, is carried out on a sample size reduced to less than 300 μm. Two serial extractions are carried out, each at a 100:1 liquid-to-solid ratio, with the use of distilled water. The pH is controlled to pH 7 during the first extraction and to pH 4 during the second extraction by using an automatic pH controller that delivers dilute nitric acid. Thus, the final extraction pH is controlled rather than the amount of acid used. The first and second extracts are combined for analysis. The very large liquid-to-solid ratio ensures that the contaminant release is not constrained by its solubility at the final pH and that the amount of contaminant extracted is the maximum amount that would be available at that pH. This test generally extracts all species not tightly bound in a mineral or glassy matrix. The test does not provide information on the rate of contaminant release.

The DWLT was selected to assess the amount of specific elements or species that might be released under continued exposure to rainfall or to clean water percolation. Synthetic acid rain solutions were not selected because the very high natural alkalinity of the residues would significantly limit the effects of acid rain acidity. The DWLT was carried out in accordance with procedures of the sequential batch leaching test used at the Environmental Laboratory, U.S. Army Corps of Engineers. A sample, crushed in size to less than 2.0 mm, is extracted four times in succession, each at a 10:1 liquid-to-solid ratio with the use of distilled water as the extractant. Acid is not added nor is pH controlled. Thus, the natural buffering capacity of the material controls the final extract pH, which was typically between pH 10 and 12 for the materials tested. The first and second extracts were combined for analysis, as were the third and fourth extracts. Results are used to estimate the amount of contaminant released over prolonged exposure to the leachant and to provide limited information on the rate of contaminant release.

The ANC test assesses the solubility of specific metals over a broad pH range. The test was carried out on a residue sample crushed and size reduced to less than 300 μm. Eleven separate extractions are performed using separate samples at a liquid-to-solid ratio of 5:1. The low liquid-to-solid ratio results in the extraction being solubility-constrained for some analytes. Each extraction receives a different amount of dilute nitric acid, varying from 0 to 12 meq/g dry residue, resulting in a range of final pHs. A titration curve also is obtained for each material tested.

The MLT was used to assess the release rate of specific elements and species from the untreated and treated residues under diffusion controlled conditions. This would be the case under field conditions where the flow of infiltration or contacting water is predominantly around monolithic structures (e.g., blocks, other forms, or low permeability, compacted fill). The MLT was carried out based on a modification of the American Nuclear Society (ANS), American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure (ANSI-16.1,1986). A 4-cm diameter by 4-cm long cylindrical, monolithic sample was tested instead of the specified size test specimen. The monolithic samples were extracted by contacting them with 8.47 L distilled water for up to 64 days. Contacting water was replaced with fresh distilled water at 1, 2, 4, 8, 16, 32, and 64 days and analyzed for metals and other species.

A new test method was developed for evaluating compacted granular materials. Release rate data were obtained for untreated bottom ash and combined ash by compacting each ash at optimum moisture content, using modified Proctor compactive effort, in 4" diameter by 4" long cylindrical polyethylene molds. Specimens were cured in the mold for 28 days at 24°C and 98% relative humidity. The exposed face of the specimen in each mold was covered with a 22-mm-thick layer of 3-mm-diameter glass beads and contacted with 8.47 L distilled water. Contacting water was replaced with fresh distilled water at 6 hr and at 1, 2, 4, 8, 16, and 32 days.

Modeling of the release data in conjunction with the results of the availability leach test was used to determine effective diffusion coefficients, tortuosity, and chemical retention factors for estimating long-term release rates for selected species. The full report provides the results of each of these determinations for each element assayed and for each S/S process and residue type evaluated.

Test Results

When the extracts from laboratory leach tests are chemically analyzed, the concentration in the aqueous phase can be determined. However, transforming the concentration data into element or species release (e.g., the mass of an element or species emitted from the solid matrix into the extract per unit mass of solid extracted) permits normalization and the comparison of data obtained from different leach tests. The TCLP, DWLT, and ALT are all intended to assess the potential for (or the maximum extent of) species release under different extremes of leaching conditions. Each test, however, employs different liquid-to-solid ratios and extraction conditions. Only the TCLP has a defined concentration basis for interpretation of resulting extract concentrations. Thus, data interpretation on an extract concentration basis is of limited value. Using additives for each treatment process and varying treated residue moisture contents may result in dilution effects, further confounding direct comparison of extract concentration data. To provide more uniform data interpretation from these leaching tests, extract concentration data were transformed to a basis of release per mass of residue extracted. Results are based on a comparison of treated residues with the untreated results. The typical release potential for metals was a small fraction of the total metal concentration present in the residues. Detailed results for each element assayed for each process and residue type are provided in the full report.

The TCLP, DWLT, and the ALT leaching data are interpreted on a release basis because these test results most frequently are viewed as the potential for release under the extreme conditions represented by the testing procedures. The ANC test is the principal exception to leaching data interpretation on a release basis. The ANC test was performed at a low liquid-to-solid ratio (5:1) to facilitate determining pH titration curves and saturated solution concentrations of a variety of elements as a function of pH. Therefore, it was most useful to present ANC data on a concentration basis. In addition, extract data also have been presented on a concentration basis for cadmium, copper, lead, and zinc from TCLP extractions.

Table 1 summarizes the levels of immobilization achieved by each process for each of the target elements in all three residues, as obtained by the most aggressive of all leaching procedures used, the ALT. These levels ranged from total immobilization of aluminum in APC residue by Process 4 to no immobilization at all of cadmium in the same residue by Processes 1, 2, 3, and WES control. No one

Table 1. *Fractions of Elements Released in the Availability Leach Test after Treatment*

	Total* Concentration (mg/kg ash)	Process 1 (%)	Process 2 (%)	Process 3 (%)	Process 4 (%)	WES Control (%)
APC Residue						
Aluminum	25,586	16	31	33	1	
Cadmium	137	≥100†	≥100†	≥100†	87	≥100†
Calcium	290,725	≥100†	95	≥100†	85	≥100†
Chloride	90,325	≥100†	≥100†	≥100†	≥100†	≥100†
Copper	515	30	55	76	25	≥100†
Lead	2,969	40	72	76	0.1	≥100†
Sodium	20,467	≥100†	≥100†	≥100†	94	≥100†
Potassium	15,598	≥100†	≥100†	≥100†	≥100†	≥100†
Zinc	17,453	38	62	69	38	
Bottom Ash						
Aluminum	51,749	5	10	11	1	9
Cadmium	35	23	29	46	49	51
Calcium	113,087	53	≥100†	≥100†	78	92
Chloride	24,301	61	≥100†	≥100†	71	≥100†
Copper	1,477	5	18	13	15	10
Lead	1,563	9	10	20	3	21
Sodium	19,777	17	≥100†	38	17	23
Potassium	9,510	21	48	≥100†	24	47
Zinc	6,793	10	≥100†	24	27	31
Combined Ash						
Aluminum	56,083	11	27	21	1	9
Cadmium	32	≥100†	63	63	81	75
Calcium	123,357	≥100†	≥100†	≥100†	85	≥100†
Chloride	28,922	55	≥100†	≥100†	≥100†	≥100†
Copper	1,734	14	23	22	14	19
Lead	1,054	24	47	≥100†	4	32
Sodium	21,678	32	≥100†	34	24	24
Potassium	13,245	52	57	≥100†	36	43
Zinc	6,172	27	21	32	35	34

* *All total element concentrations are based on NAA results except lead, which is based on SW-846 results.*
† *Values nominally greater than 100% were calculated because of either contributions from process additives or correction for process dilution.*

process demonstrated superiority over other processes for all elements. Note, however, that Process 4 retained lead in all the treated residue types significantly better than did the other processes.

Data from the other leaching tests, although not given in this Project Summary, are presented in detail in the full report. No clear pattern could be noted other than that no single process demonstrated clear superiority over the other processes for all target elements as was noted with the ALT, except for lead in Process 4.

Another measure of immobilization used in this study is the level of total dissolved solids (TDS) released during the DWLT. Data obtained from this test showed that all processes were comparable to one another with releases ranging from 4% to 32%. Significantly more TDS were released from the APC residue compared to the other ash types. Many of the treatments resulted in increased release of TDS when compared to the untreated residues. Table 2 shows the releases from all three residues by each of the processes as well as the control and the untreated samples.

Conclusions

Based on the results presented in the full report of all the testing conducted on the untreated and treated residues, the key findings and conclusions are as follows:

- The S/S processes evaluated generally did not decrease the potential for release of target contaminants based on comparison of untreated residues with treated residues. The phosphate process, however, did reduce the potential for lead to be released.
- Whether the MWC residues were treated or not, the typical release potential for metals (lead, cadmium, zinc, etc.) was a small fraction of the total concentration present in the residues. Release rates of the elements were very low for compacted, granular, untreated bottom ash and combined ash. Release rates also were very low for bottom ash and combined ash treated by processes that produced physically durable specimens.
- The S/S processes evaluated did not successfully treat the residues to reduce the potential for release of TDS and soluble salts. Whether the MWC residues were treated or not, the release potential and release rates were high for TDS and the salts of calcium, sodium, potassium, chloride, and sulfate. The total amounts of these constituents released typically approached the total concentration in the MWC residues. In the case of the APC residues, the treatment

Table 2. Comparison of Total Dissolved Solids Released for the Distilled Water Leach Test (g release/kg ash, dry solid), and the Weight % of the Material Released (in parenthesis).

Sample source	Bottom Ash	APC Residue	Combined Ash
Untreated	58 (6%)	289 (29%)	60 (6%)
Process 1	53 (4%)	640 (32%)	54 (4%)
Process 2	187 (12%)	565 (26%)	208 (13%)
Process 3	126 (7%)	578 (24%)	144 (8%)
Process 4	47 (4%)	194 (15%)	56 (5%)
WES control	59 (5%)	671 (30%)	79 (6%)

processes increased the release potential of the salts.

- The high concentration and ultimate fate of soluble salts in MWC residues should be carefully considered in the design of treatment processes and the use and disposal of the residues.
- Based on results from the program, APC residues have the least potential for use in applications requiring structurally durable products. The physical retention values for the treated APC residues indicated limited or no physical retention. The major contaminant release from the APC residue was salts. In excess of 30% of the total mass was released in the form of sodium, calcium, chloride, and sulfate salts.
- The use of proprietary additives in the evaluated S/S processes did not enhance the strength of the treated residues. The Portland-cement-only (WES control) process produced test specimens with unconfined compressive strengths greater than or equal to those of all the processes with proprietary additives. It should be noted, however, that high strength probably was not an objective of the vendor's processes. Process 4 developed a granular product.
- Evaluation of S/S process design, performance, and treatment efficiency should be based on a matrix of several testing protocols. No single test, such as TCLP, can provide all the information required to evaluate contaminant release potential, contaminant release rate, and physical durability. An appropriate test matrix to evaluate S/S processes should include tests that will address these factors.
- Formulas for most processes evaluated in this study were probably developed on a limited number of testing procedures. Variations in Portland-cement-based and other S/S technologies will influence the degree of durability and chemical leaching potential. Therefore, substantial improvements in S/S process optimization may be obtainable by optimizing process design based on results of multiple test criteria.
- The Portland-cement-based processes can be formulated to produce S/S test specimens of MWC bottom and combined residues with high structural integrity and increased resistance to weathering. These types of processes, if properly designed, are likely to be successful in producing monolithic products with physical properties acceptable for various uses. This does not mean, however, that the chemical characteristics would also be acceptable. Physical durability or possessing a monolithic structure does not ensure acceptable performance with respect to contaminant release.
- The release rate of most potentially toxic metals will be very slow to negligible for S/S-treated MWC residues, at least those that have minimal leachability in the raw state.
- The unconsolidated, granular nature of the ash material required that a method for estimating diffusion-controlled release from compacted granular materials be developed. Such a method was developed for this evaluation, and the application of a modified MLT to determine intrinsic leaching properties for granular materials has proven very consistent. The data are comparable with results from other types of diffusion measurements. The tortuosity data obtained in the experimental setup are consistent with diffusion measurements using radiotracers.
- TCLP was not a good indicator of release from untreated and treated residues for several reasons. Variable end-point pH for the extraction resulted in wide variation in estimated metals release because of pH-dependent solubility constraints. The low liquid-to-solid ratio for the TCLP (20:1) also may have resulted in solubility limitations for many elements of concern. Finally, TCLP does not provide for determination of the total release of soluble salts and anions.
- The most durable test specimens to the cyclic weathering tests and the immersion tests were those with the highest unconfined compression strength (UCS). Thus, UCS may be useful as a preliminary indicator of physical durability.
- The MLT for construction materials and stabilized products provides intrinsic information on long-term leaching effects and usefulness in relation to product quality. The MLT also provides useful information for improving product quality. By focusing on the controlling parameter requiring adjustment, initial estimates of release rates and fluxes for varied application scenarios can be obtained. The distinction between physical retention and chemical retention and the release mechanisms (dissolution, wash-off, and diffusion) can be made. Existing regulatory tests do not provide such useful information.
- Physical retention was directly correlated with the compacted, dry densities of the material for the bottom and combined ashes. The test specimens with the greater densities had more physical retention.
- The EPA-recommended methods of chemical analysis (SW-846) were not comparable in many cases to the neutron activation chemical analysis (NAA) for total elemental concentrations in the raw and treated residues. The EPA method results indicated significantly lower elemental concentrations than did the NAA methods; this suggests that only partial analytical recoveries occurred. This discrepancy warrants further investigation into the chemical analysis methods to investigate and develop more applicable methods for similar type solid matrices.

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The complete report, entitled "Evaluation of Solidification/Stabilization Treatment Processes for Municipal Waste Combustion Residues," (Order No. PB93-229 870/AS; Cost: $61.00, subject to change) will be available only from:
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