STABILIZATION OF MIXED WASTE AT THE IDAHO NATIONAL ENGINEERING LABORATORY[a]

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ABSTRACT

EG&G Idaho, Inc. has initiated a program to develop safe, efficient, cost-effective treatment methods for the stabilization of some of the hazardous and mixed wastes generated at the Idaho National Engineering Laboratory. Lab-scale testing has shown that Extraction Procedure toxic wastes can be successfully stabilized by solidification, using various binders to produce nontoxic, stable waste forms for safe, long-term disposal as either landfill waste or low-level radioactive waste, depending upon the radioactivity content.

This paper presents the results of drum-scale solidification testing conducted on hazardous, low-level incinerator flyash generated at the Waste Experimental Reduction Facility. The drum-scale test program was conducted to verify that lab-scale results could be successfully adapted into a production operation.

INTRODUCTION

Radioactive waste which is also hazardous [as defined by the Resource Conservation and Recovery Act (RCRA) in 40 CFR 261], is considered a radioactive mixed waste (RMW). The Department of Energy-Idaho Operations (DOE-ID) Office has decided that the Radioactive Waste Management Complex (RWMC), which is the INEL's low-level waste disposal facility, shall not accept RMW. Proper disposition of a hazardous waste (HW) requires that the HW be sent to an Environmental Protection Agency (EPA) permitted disposal facility. Existing EPA-permitted disposal facilities will not accept radioactively contaminated hazardous waste since they do not have an NRC license and are not designed to handle radioactivity.

There are two other options for dealing with RMW: to treat it so that it is no longer hazardous or radioactive, or to store it until it can be treated or legally disposed of. Treatment and storage of a RMW also require an EPA permit.

The INEL has applied to the EPA for a RCRA Part B permit. The permit application includes a storage facility for HW, a storage facility for RMW, incineration of HW and RMW, and stabilization of HW and RMW. This paper describes the stabilization development activities conducted at the INEL by EG&G Idaho, Inc., for the DOE.

There are two primary purposes for stabilizing a RMW. One is to enhance the waste form for optimum storage conditions; the second is to treat the waste so that hazardous characteristics are eliminated and the waste can then be disposed of as a low-level waste.

The stabilization development plan consists of four primary activities: (a) characterize the HW and RMW at the INEL to determine volumes, levels of radioactivity, and which wastes can be stabilized; (b) conduct lab-scale stabilization tests to evaluate stabilization binders and processes and to determine the optimum binder-to-waste ratios; (c) conduct drum-scale tests to ensure that 55-gal (208-L) drums of waste can be successfully stabilized and to obtain the necessary test data to support the RCRA permit application; and (d) provide a production stabilization capability at the Waste Experimental Reduction Facility (WERF).

The first activity, waste characterization, has been completed for existing identified HW and RMW at the INEL. However, this will be a continuing activity as new wastes are identified and/or changes to the regulations add chemicals or materials to the list of regulated wastes. Also included in this activity was a determination of which wastes might be candidates for stabilization. Detailed waste characterization information is contained in Reference 1.

Wastes which are hazardous due to toxicity, as determined by the Toxicity Characteristic Leaching Procedure (TCLP), are prime candidates for stabilization. Proper stabilization of these wastes, so that they will pass the TCLP test, will allow them to be disposed of as LLRW. Stabilization development activities at the INEL have concentrated on these wastes.

The second activity, lab-scale development, was conducted on flyash from incineration of low-level waste, photochemical wastes, aqueous potassium

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chromate solutions, and lead refining dross. Binders that were economical and easy to use were chosen for testing. These included cement, combinations of cement and sodium silicate, and ENVIROSTONE. Recipes were developed for binder-to-waste ratios which resulted in successful stabilization of each waste, as demonstrated by success in passing the TCLP test. Reference 2 provides detailed information on the lab-scale development.

The third activity in stabilization development is the drum-scale testing required to ensure that 55-gal (208-L) quantities can be successfully stabilized and pass the TCLP test, and to obtain the data required to support the RCRA Part B permit application. The only waste to be tested to date in drum-scale quantities is the flyash generated from incineration of LLRW at WERF. The WERF flyash is considered a RMW due to leachable lead and cadmium levels detected by the TCLP test. This flyash is collected in 55-gal drums.

To support drum-scale development, a stabilization development facility was installed in the Waste Engineering Development Facility (WEDF, the deactivated SPERT II Reactor building). The facility consists of a drum-tumbler for mixing the waste and binders; a HEPA-filtered air-exhaust system; a scale for weighing the waste, water, and binder additions; a water supply system; and miscellaneous support equipment.

Drum-scale testing evolved through four phases before an acceptable process was settled on to yield consistently successful results. The flyash was sampled before and after solidification, and samples were submitted to two independent laboratories for analysis, using the TCLP to verify binding of the hazardous constituents. Eight (8) drums of flyash were solidified. Two of the first five drums did not pass the leach tests on all samples submitted. The final three drums passed the leach tests on all samples submitted.

Statistical evaluation of the data obtained from the final three drums showed that the number of samples analyzed from these drums was sufficiently large to determine that cadmium and lead are not present in the solidified flyash in hazardous concentrations.

Following the successful completion of the drum-scale testing on WERF flyash, conducted at the WEDF, a production solidification system was installed at WERF. The equipment and procedures to be used for the production solidification system for flyash were evaluated for operability and completeness during the system checkout test. Flyash Drum No. 9 was solidified during the checkout test. All the samples of solidified flyash from this drum passed the leach test (these results are included in this paper).

Based on the data presented in this paper, the production solidification system which has been installed at WERF will produce a stabilized waste monolith that contains no free liquids, no leachable metal levels in excess of EPA limits, and can therefore be disposed of as a low-level radioactive waste.

DESCRIPTION OF OPERATION

The existing drums of flyash contain solid liners with lids which provide no access for the addition of binder materials. Consequently, all of the existing liner lids will be replaced with modified lids. The modified lids for the first two drums contained three bungs to allow for drum ventilation and the addition of cement and water separately. The lid configuration was changed to two bungs for the last six drums, one for ventilation and the other for material addition. Changeout of the first two liner lids was conducted in the WERF incinerator ash collection system glovebox. The liner lids on the remaining six drums were changed out in the WEDF solidification room after it was determined that the operation, properly conducted, did not result in flyash dispersion.

The flyash was sampled during the lid changeout operation to provide baseline data for leach tests. Samples were taken at various depths in each drum, using a grain probe (thief) sampler, and combined to provide a composite sample for each drum.

Solidification mixture sampling was accomplished for all drums using a core sampler inserted to the bottom of the drum at two radial locations. This yielded a good cross section of samples to give an indication of homogeneity.

The actual development of the stabilization process was conducted in four phases (described in the following paragraphs), using the same ingredients, (with the exception of the addition of one gallon of liquid sodium silicate to Drum No. 8), but with variations in recipe, sequence, method of addition, and method of mixing. These phases and their variations are detailed in Table I.

Drum No. 1 (Phase A) used the initial recipe developed in the lab-scale program, with an additional amount of water intended to facilitate thorough mixing, but the mixture proved to be too wet. After 24 hours, the mixture remained in slurry form under a 6-inch (15.24-cm) water layer. Additional dry cement was then added and the drum retumbled. A slurry mixture under a 4-inch (10.2-cm) water layer still remained. At this point, additional lab-scale testing was performed on the mixture to determine the amount of dry cement needed to set up the slurry. The water layer on top of the mixture was removed, and, using additional dry cement, the slurry was set up into a monolith with no free liquid. All samples of this monolith passed the leach test.

The water layer that was removed was sampled and the samples sent for analysis. The results of this analysis showed that the water contained a cadmium level of 108 mg/L, which is in excess of the EPA limit of 1.0 mg/L. The other seven toxic metals levels were below the EPA limits (from 40 CFR 261). The water was placed into a 30-gallon (113.6-L) drum and solidified with cement. Analysis of a sample of the solidified water/cement mixture showed a leachable cadmium content of <0.01 mg/L, which is below the limit. This drum will therefore be disposed of as a low-level radioactive waste.

The recipe, based on additional lab-scale tests, was adjusted for Drum No. 2 (Phase B). However, the flyash in this drum had been compacted during drumming so that it contained 50% more flyash by weight than Drum No. 1, even though the fill level was only slightly higher. As a consequence, the drum became so full with the basic recipe ingredients that there was not sufficient headspace to allow proper mixing. Samples of this drum, prior to setup, showed

TABLE I

Stabilization Development Phase Description

Phase	A	B	C	D	Operations
Drum	Number 1	Number 2	Numbers 3-5	Numbers 6-8	Number 9
Lid Configuration	Lid with 3 bungs, threaded fittings	Lid with 3 bungs, threaded fittings	Lid with 2 bungs, slip fittings	Lid with 2 bungs, slip fittings	Lid with 2 bungs, slip fittings
Ash Weight (lb/kg)	106/48	150/68	87/39.5, 98/44.5, 97/44	88/40, 89/40.4, 97/44	100/45.4
Step 1	Slurry ash at a water-to-ash ratio of 2.25:1[a] by tumbling with mixing bars	Slurry ash at a ratio of 1.5:1[a] by tumbling with mixing bars	Same as drum No. 2	Slurry ash at a ratio of 1.25:1[a] by tumbling with mixing bars	Same as phase D
Step 2	Add dry cement at 0.72:1[a] and water at 0.75:1;[a] tumble again	Add dry cement at 2:1[a] and water at 0.5:1;[a] tumble again	Same as drum No. 2	Slurry cement in mixer. Cement-to-ash ratio of 2:1,[a] water-to-ash ratio of 1:1[a]	Same as phase D
Step 3	Measure void space and fill with equal parts dry cement and water; tumble again	Would have been the same as drum No. 1 but was omitted due to full drum	Sample mixture	Pour cement slurry into drum. Mix with motorized mixing paddle	Same as phase D
Step 4	Add additional dry cement to thicken mixture; tumble again	Sample mixture		Add dry cement to adjust consistency for best sampling, and mix with mixing paddle	Same as phase D
Step 5	Skim off surface water			Sample mixture	Sample mixture
Step 6	Sample mixture				
Comments	Mixture too wet	Drum too full	Inconsistent Mixing	No problems	No problems
Leach test	Passed	Failed	No. 3 and 4 passed; No. 5 failed	All passed	Passed

a. All ratios shown are of the ingredient mentioned to ash, by weight.

layers of wet and dry ingredients, indicating nonhomogeneity.

The quantity of ash per drum was limited to 100 pounds (45.4 kg) for all subsequent operations. Drums No. 3, 4, and 5 (Phase C) were solidified with the same recipe as that used for Drum No. 2. Sampling of these drums showed inconsistent mixing from drum to drum, indicating that the tumbling process was not adequate, particularly when using dry cement.

During the processing of Drums No. 3, 4, and 5, the decision was made not to fill the void space remaining after mixing the basic ingredients because it was felt that this should be accomplished in a separate operation after mixture setup. It was also determined that at the time the void space was filled, another visual inspection for the presence of free liquid would be conducted.

The initial inspection for free liquid is conducted during the solidification processing. The operators inspect the surface of the monolith during the sampling operation, and, if free liquids are present, they would also be observed when the sample is extruded from the sample probe.

No free liquids have been observed in any of the solidified monoliths to date, and none are expected, but the visual inspections will be conducted as a verification. The void space in the drum will be filled with sand or dry cement. The void space is filled only to minimize future subsidence in the disposal facility and will not alter the leaching characteristics of the monolith in any way.

The final three drums, No. 6, 7, and 8 (Phase D), were stabilized by adding cement (slurried in a cement mixer) to the slurried ash and mixing with a motorized paddle inside the drum. Dry cement was then mixed in, using the paddle mixer, to obtain the desired consistency for sampling, and probe samples of the mixture were removed.

Following the completion of the production solidification facility installation at WERF, Drum No. 9 was stabilized using the production system equipment. The procedure used contained the final 2:2.25:1 cement-to-water-to-ash recipe, and the mixing of slurried cement and slurried ash with the paddle mixer, as was done for Drums No. 6, 7, and 8.

RESULTS

The testing conducted during this development activity to identify the leachable levels of hazardous metals in the flyash, solidified flyash, and quality control samples was completed using the TCLP. This procedure is being developed by the EPA as a replacement for the Extraction Procedure (EP) toxicity leach test.

The TCLP test differs from the EP toxicity leach test in that the TCLP requires: elimination of the structural integrity procedure; tumbling method of agitation only; change of leaching solution; and crushing of the sample so that it passes through a 3/8-in. (.95-cm) sieve before leaching. These changes make the TCLP a more stringent test; it was therefore used as a worst-case procedure for sample leachable toxic metals evaluation. The TCLP was also used to ensure that the process will provide a waste form which will meet the requirements of the new method and will be in compliance with anticipated EPA regulations.

Results of the drum-scale testing are contained in the following sections.

Flyash Analytical Results

The TCLP was the first test conducted on the flyash and was used: to verify that the flyash was hazardous, to give an indication of the homogeneity of the leachable levels of metals in the flyash, and to provide a basis for comparison of the leachable metal levels before and after solidification.

As shown by the data presented in Table II, the flyash was definitely above the EPA toxicity limits for cadmium and lead, 1.0 and 5.0 mg/L respectively, thus verifying that the flyash was a hazardous waste.

Multiple samples of flyash from Drum No. 2, taken from 5 different levels in the drum, were analyzed to determine the homogenity of the leachable metals in the flyash. The data from Lab 1 tests on Drum No. 2, indicated good homogeneity of the leachable metals throughout the drum. The data from all 5 levels of Drum No. 2, as well as that from the composite sample, are fairly consistent. Based on the results of this analysis, it was decided that analysis of composite samples of unsolidified flyash from the remaining test drums would provide the required data.

The data obtained from Lab 2 analyses are reported, but are not used in the evaluation because of incorrectly performed procedures. Lab 2 used mineral acid digestion of part of the solid samples, in addition to the TCLP, to obtain the results. This would not be an indication of leachable levels of metals, but rather an indication of the total amounts of metals in the sample, which is substantially higher.

The flyash samples were also analyzed for radionuclide content. Major isotopes found consistently in the flyash are cobalt-60, cesium-137, cesium-134, and antimony-125. Silver-110m, zinc-65, and manganese-54 were also found (in lesser amounts) in some of the drums of flyash.

Analyses of flyash samples have been conducted on a random basis since the incinerator began contaminated operations. These analyses were done to provide an indication of the composition of the ash. The results of spectrochemical analyses have been relatively consistent in identifying the principal constituents of the flyash. These results are summarized in Table III.

Moisture content was also evaluated and found to be consistently low, ranging from 0.5 to 4.1 percent, and averaging about 2 percent. No correlation was found between the moisture content of the flyash and the variation in the amount of water required to stabilize the flyash.

From the relative consistency of the flyash composition analytical results, it seems reasonable to conclude that large variations in waste feed makeup have not occurred, or have not negatively affected flyash composition. The waste feed makeup is administratively controlled and randomly checked

TABLE II

Flyash TCLP Results

Sample Number[a]	Lab Number	Analyte Concentration Detected (mg/L) Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver
D1T1	1	<0.01	0.8	155	<0.01	34.6	0.0016	0.02	0.11
D1T2	1	<0.01	0.8	138	<0.01	29.8	0.0011	0.01	0.10
D1T3	1	0.06	0.5	149	0.01	13.0	<0.0004	0.03	0.06
D1T4	2	0.80	1.1	310	1.8	420	0.047	<0.01	0.61
D2C1	1	<0.01	0.2	283	0.19	82.1	0.0007	0.03	0.02
D2C2	2	0.76	7.1	260	8.3	1400	0.012	0.028	0.58
D2P1	1	<0.01	0.2	273	0.17	61.1	0.0006	0.01	0.02
D2P2	1	<0.01	0.1	287	0.15	88.5	0.0004	0.03	0.03
D2P3	1	<0.01	0.2	297	0.14	73.1	0.0005	0.05	0.02
D2P4	1	<0.01	0.2	282	0.18	75.0	0.0004	0.05	0.02
D2P5	1	<0.01	0.2	280	0.17	71.2	0.0006	0.04	0.02
D2SP1	2	0.078	0.9	260	1.4	350	<0.002	<0.01	0.23
D2SP3	2	<0.01	<0.5	300	<0.1	120	<0.002	<0.01	0.08
D2SP5	2	0.33	2.8	290	3.4	740	0.012	0.018	0.34
D3C1	1	0.03	0.3	136	0.3	28.0	0.0092	0.06	0.09
D4C1	1	0.02	<0.1	169	<0.1	212	<0.0004	0.05	0.19
D5C1	1	<0.01	<0.1	438	<0.1	130	<0.0004	0.05	0.14
D6C1	1	<0.01	0.4	77.2	0.1	33.5	0.0037	0.04	0.13
D6C2	3	0.16	0.9	69	0.71	26	0.0052	<0.02	0.22
D7C1	1	<0.01	<0.1	366	<0.1	125	<0.0004	0.03	0.14
D7C2	3	<0.001	<0.1	340	<0.01	120	<0.0002	<0.04	0.32
D8C1	1	<0.01	<0.1	305	0.5	168	<0.0004	0.02	0.13
D8C2	3	<0.001	<0.1	280	0.02	94	0.0004	<0.04	0.27
D9C1	1	<0.01	0.2	187	0.05	59.0	<0.0004	0.04	0.51
D9C2	1	<0.01	0.2	202	0.05	57.3	<0.0004	0.03	0.68

a. D_ = drum number
T_ = top sample
C = composite sample
P_ = first probe sample and level in drum, 1=top to 5=bottom
SP_ = second probe and level in drum, 1=top to 5=bottom

to minimize inclusion of prohibited materials, (chlorinated materials, free liquids, large metal objects, etc.), but it is impractical to attempt to quantify the specific waste feed makeup. It is therefore not possible to relate flyash composition to waste feed makeup.

The WERF incinerator was designed to operate with a minimum combustion efficiency of 99.9 percent and a minimum destruction efficiency of 99.99 percent. Operation at these efficiencies ensures that the flyash will be relatively inert with respect to reactivity and organic content, regardless of the waste feed mix. The absence of significant quantities of organic compounds increases the efficiency of cement as a binder in the solidification process.

Solidified Flyash Analytical Results

The results of the TCLP testing were used to verify that the solidified monolith did not contain leachable metal levels in excess of EPA limits and to give an indication of the homogeneity of the monolith. As shown by the data presented in Table IV, Drum No. 1 did not contain leachable levels of metals in excess of EPA limits, with the exception of one sample analyzed by Lab 2. As stated previously, the data from Lab 2 are considered invalid because of improper procedures.

The data obtained from the analysis of Drum No. 2 samples show leachable levels of metals in excess of EPA limits in some sections of the drum; the contents of this drum must therefore still be considered a mixed waste. These results were the

TABLE III

Principal Ash Constituents

Constituent	Concentration Range ~% Weight
Carbon (fixed)	11 - 37
Calcium	0.1 - 5
Cadmium	0.1 - 0.6
Chromium	<0.1 - <5
Iron	0.8 - 4.9
Potassium	1.0 - 2.1
Sodium	<0.1 - 3.1
Phosphorus	0.4 - 3.1
Lead	0.1 - 9.6
Sulfur	1.3 - 2.0
Zinc	4.9 - >30
Chlorides	1.7 - 21.6
Sulphates	1.6 - 3.4
H_2O	0.5 - 4.1

first indication of a lack of homogeneity, resulting from poor mixing within the drum. The poor mixing was a result of insufficient headspace, caused by too much flyash in the drum. Addition of the binder and water required for stabilization filled all of the headspace, preventing the agitation required for good mixing.

As a result of these findings, the weight of ash in the drums was limited to 100 pounds (45.4 kg) per drum, and solidification of Drums No. 3, 4, and 5 was initiated.

The data obtained from Drums No. 3 and 4 sample analysis showed no leachable levels of metals in excess of EPA limits. However, the sampling operations revealed inconsistent mixing within the drums. As shown by the leach test results obtained from Drum No. 5, the inconsistent mixing caused a lack of homogeneity in the solidified flyash. Therefore, Drum No. 5 did not pass the leach test and remains a mixed waste. Homogeneity of the drum contents is required to ensure that the chemical reactions are adequate to bind the metallic ions and prevent leaching. It became apparent that tumbling as a mixing method, and/or addition of dry cement were inadequate to produce homogeneous drum mixtures. Therefore, the decision was made for future drums, to slurry the cement with water prior to adding it to the drum, and to mix the drum contents with a paddle mixer in the drum and not rely on tumbling for final mixing. Solidification of Drums No. 6, 7, and 8 was then initiated using these changes.

In the solidification of Drum No. 6, 75 pounds (34.1 kg) of dry cement were added and mixed into the drum mixture following the addition and mixing of the slurried ash and slurried cement. This cement was

TABLE IV

Solidified Flyash TCLP Results

		Analyte Concentration Detected (mg/L)	
Sample Number[a]	Lab Number	Cadmium	Lead
Phase A			
D1C1	1	<0.001	0.3
D1C2	2	23	80
D1R1	2	0.05	0.4
D1R2T	1	<0.001	0.2
D1R2M	1	<0.01	0.3
D1R2B	1	<0.001	0.2
Phase B			
D2C1B	2	240	14
D2C2T	1	0.4	<0.01
D2C2M	1	<0.001	2.3
D2C2B	1	<0.001	2.4
D2C3T	1	25.8	2.4
D2C3M	1	<0.001	6.0
D2C3B	1	<0.001	1.4
D2R1	2	30	5.9
D2R2T	2	360	55
D2R2B	1	24.9	2.8
D2R3T	1	46.2	37.5
D2R3M	1	48.3	16.1
D2R3B	1	<0.001	0.3
Phase C			
D31T	1	<0.001	2.2
D31B	1	<0.001	2.0
D32T	1	<0.001	1.9
D32B	3	<0.005	0.52
D33T	3	<0.005	0.46
D33B	3	<0.005	0.35
D41SA	1	<0.001	2.0
D41SB	1	<0.001	1.7
D42T	3	<0.005	0.66
D42B	3	<0.005	0.67
D51T	1	66.4	12.0
D51B	3	59	10
D52T	3	56	8.2
D52B	3	63	12
D53T	1	68.4	9.7
D53B-C[b]	1	<0.001	1.5
Phase D			
D61T	1	<0.001	1.7
D61M	1	<0.001	1.8
D61B	1	<0.001	2.0
D62T	3	<0.005	1.5
D62M	3	<0.005	1.2
D62B	3	<0.005	1.2
D63T	3	<0.005	1.5
D63B	1	<0.001	1.3
D71T	3	<0.005	1.0
D71M	3	<0.005	1.1
D71B	3	<0.005	1.2
D72T	1	<0.001	<0.01
D72M	1	<0.001	<0.01
D72B	1	<0.001	0.05

TABLE IV

(continued)

Sample Number[a]	Lab Number	Analyte Concentration Detected (mg/L) Cadmium	Lead
D82SA	3	<0.005	0.08
D82SB	1	<0.001	0.04
D83SA	3	<0.005	0.06
D83SB	1	<0.001	0.04
D84SSA	3	<0.005	0.04
D84SSB	1	<0.001	<0.01
D85SSA	3	<0.005	<0.03
D85SSB	1	<0.001	<0.01
Operations			
D9C1T	1	0.03	1.2
D9C1B	1	0.02	1.5
D9R1T	1	0.02	1.0
D9R1B	1	<0.01	1.5

a. D = Drum number
C = probe sample taken from center bung of drum
R = probe sample taken from a radial bung in drum
1,2,3,4 = probe numbers in order taken from drum
T = top of probe sample
M = middle of probe sample
B = bottom of probe sample
S = split sample
SS = split sample after silicate addition

b. This sample was a chunk of material, mostly cement, which came out in the bottom of the probe from the layer of material on the bottom of the drum.

added to provide a mixture viscous enough to permit immediate removal of probe samples. In Drum No. 7, a small amount [22 pounds 10 kg)] of dry cement was added and mixed into the drum after mixing of the cement and flyash slurries. This amount of cement was not enough to provide a consistency sufficient to permit immediate sampling. The drum mixture was allowed to set for 20 minutes, at which time sampling was performed.

Drum No. 8 was solidified using only the slurried ash and slurried cement mixtures. Samples D82SA&B and D83SA&B were then taken from the drum. One gallon of liquid sodium silicate was then mixed into the drum contents and samples D84SSA&B and D85SSA&B were taken.

The data obtained from the analysis of the solidified samples of Drums No. 6, 7, and 8 show that this method of solidification (adding slurried cement to slurried ash and mixing with the paddle mixer) provides a monolith which does not contain leachable levels of toxic metals in excess of EPA limits. The results also show a very good homogeneity of the drum contents. The results of Drum No. 6 in particular show an excellent consistency throughout the drum and also between the two laboratories. The additional dry cement which was added to Drums No. 6 and 7 appears to have had little or no effect on the leachable levels of lead in the monolith. The sodium silicate which was added to Drum No. 8 had no effect on the consistency of the drum mixture and showed little effect on the leachable lead levels. Sodium silicate used in the lab-scale testing caused an almost instantaneous set of the flyash mixture and did reduce the amounts of leachable lead. The quantities of silicate used in the lab-scale testing were in a greater ratio than the one gallon used in Drum No. 8, thus explaining why the addition of sodium silicate reduced leachable lead levels in lab-scale tests but not in drum scale.

Homogeneity of the drum mixture is verified in two ways. First, the sample probe extracts a full-length core sample of the drum mixture. A visual inspection of the sample as it is extruded from the probe gives an indication of homogeneity. The sample of a nonhomogeneous drum will show layers or spots of cement intermixed with the flyash, whereas a homogeneous drum sample is a single color and does not break apart when extruded.

These observations have been supported by the second way of verifying homogeneity, i.e., analytical results. Drum No. 1 samples appeared to be quite homogeneous, and all passed the leach test. Some layering was observed in Drum No. 2 samples, and some of the samples passed, but others did not. Drums No. 3 and 4 showed a fairly homogeneous sample. Some very small cement pockets were observed, but these samples did pass the leach test. Drum No. 5 samples showed considerable layering, and the samples from this drum failed to pass the leach test. Samples from Drums No. 6, 7, 8, and 9 appeared homogeneous, and all of these samples passed the leach tests with consistent results.

The results from Drums No. 6, 7, 8, and 9 were also evaluated with respect to what effect dilution would have had. In earlier lab-scale testing, samples of the flyash were solidified using only water. The water does set up the flyash, but, as shown in sample numbers 1 and 2 in Table V, it does not affect the leachable levels of either cadmium or lead. Therefore, the water has no dilution effect on the leachable metals levels.

The cement was added at a 2:1 ratio with the flyash, thereby cutting nondiluted leachable levels in half. Therefore, doubling the final results would account for any dilution resulting from the process. As shown in Table V, the results from the drums, even when doubled, are still below EPA limits.

Statistical evaluation of the data obtained for Drums No. 6, 7, and 8 was performed per EPA-SW-846 (see Reference 3). The statistical evaluation was conducted only on the leachable lead levels because all the leachable cadmium levels were below the detectable limits.

Stratified random sampling was appropriate for analyzing the lead concentrations in the solidified flyash from Drums No. 6, 7, and 8. Because the drums were solidified using slightly different methods for each drum, it was known that nonrandom chemical heterogeneity could have existed. Each drum is thus considered a stratum and samples are drawn from each drum. Stratified random sampling results in greater precision than simple random sampling when it is evident that the population can be efficiently divided into strata that maximize the variability among strata and minimize the variability *within* each stratum.

Drum	Stratum (k)	n_k	$\bar{X}_k$	S_k^2	$W_k = n_k/N$
6	1	8	1.525	.085	0.364
7	2	6	0.562	.352	0.272
8	3	8	0.039	.001	0.364

where

n_k = number of samples from the stratum

TABLE V

Dilution Effect Evaluation

	Average Analyte Concentration Detected (mg/L)				Accounting for the Dilution Effect
	Before Solidification		After Solidification		
Sample Number	Cd	Pb	Cd	Pb	Pb[a]
1 (D1A)	32	443	46	407	--[b]
2 (D2A)	37	332	29	399	--[b]
D6	73.1	29.8	<0.005	1.5	3.0[c]
D7	353	122.5	<0.005	0.8	1.6[c]
D8	292.5	131	<0.005	0.05	0.10[c]
D9	194.5	58.2	0.02	1.3	2.6[c]

a. The results for cadmium are below the detectable limits; therefore, the dilution effect is considered negligible.

b. These are the lab-scale samples solidified using water only, which has no dilution effect as demonstrated by these results.

c. Cement was added at a ratio of 2 to 1, so the results were doubled to account for dilution.

$\bar{X}_k$ = sample mean from the stratum

S_k^2 = variance of the sample from the stratum

W_k = fraction of the population represented by the stratum

N = total number of samples

SW-846 Box 2. Strategy for Determining if Chemical Contaminants of Solid Waste are Present at Hazardous Levels - Stratified Random Sampling of Wastes (Strategies section, page 19) outlines the method for

Calculating $\bar{X}$ and S^2:

$$\bar{X} = \sum_{k=1}^{3} W_k \bar{X}_k = 0.722$$

$$S^2 = \sum_{k=1}^{3} W_k S_k^2 = 0.127$$

The appropriate number of samples, n, is determined by:

$$n = \frac{t_{.20}^2 \, S^2}{\Delta^2}$$

Where

$t_{.20,\text{degrees of freedom } 21} = 1.323$

$\Delta^2 = (RT - \bar{X})^2 = (5 - 0.722)^2 = 18.301$

this yields n = 0.1. This shows that the samples of size 8, 6, and 8 from the three drums were greater than the appropriate number of samples, n = 0.1, and were sufficiently large to draw the following conclusion.

An 80% confidence interval (the level is specified in EPA-SW-846) is determined by:

$CI = \bar{X} \pm t_{.20} S_{\bar{X}} = 0.722 \pm 0.101 = 0.621, 0.823.$

The upper limit of the confidence interval (0.823 mg/L) is well below the regulatory threshold of 5.0. It can therefore be concluded that lead is not present in the solidified flyash at a hazardous concentration.

Following the successful completion of the drum-scale testing at the WEDF, a production solidification system was installed at WERF. This system duplicated the hardware/equipment used in the solidification of Drums No. 6, 7, and 8. The operating procedures which will be used for the production operations were used to solidify Drum No. 9 at WERF during the system checkout testing.

The results of the analysis of solidified samples from Drum No. 9 showed that the production method to be used for stabilization of the WERF flyash produces a homogeneous monolith which contains no free liquids, and does not contain leachable levels of toxic metals in excess of EPA limits.

QUALITY ASSURANCE/QUALITY CONTROL

Quality Assurance/Quality Control (QA/QC) of the sample gathering and analysis was considered important to ensure that the methods used would provide valid, reliable, consistent, and representative analytical results. Therefore, a formal QA/QC plan was prepared for each phase of development. Appendix A contains the final QA/QC plan, "QAPP3-Sampling and Analysis Program Plan for Flyash Stabilization Operations," which will be used for QA/QC control during production stabilization operations.

Each laboratory used for sample analysis also has its own QA/QC plan, which includes procedural controls, specifications, and standard methods for performing analysis, verifying results, performing instrument calibration, instrument maintenance procedures and internal quality control. All analyte concentration analyses were performed using EPA-approved or laboratory standard procedures. Each of the laboratories used for analysis uses blanks periodically in analytical procedures for background data and quality control.

The procedure used for leaching the samples, to provide the extract for metals analysis, was the TCLP. EG&G personnel were familiar with the development and intent of this procedure and provided resolution to questions the laboratories had regarding this method. However, Lab 2 did not question EG&G personnel before using an acid digestion of solids that passed through the filter during their analyses of samples. The mineral acid digestion would have released metals from the solids which would not have leached under normal test procedure, thereby accounting for the higher lead levels reported by Lab 2. Because this procedure was not properly performed, the results from Lab 2 were considered invalid. A contract was then negotiated with Lab 3, so that there would still be two independent laboratories performing analysis.

The data in Table VI are the results of the standards and blanks submitted to the laboratories for analysis. These samples were submitted blind to provide a check of lab accuracy, and were analyzed simultaneously with the samples of flyash and solidified flyash.

The sample series labeled WEDSS1 and WEDSS2 were standard solutions, prepared by EG&G Chemical Sciences personnel, and contained 1.0 mg/L cadmium and 5.0 mg/L lead. Samples WEDSS3 and WEDSS4 were a standard solution, purchased from a chemical supply company, which contained 1000 mg/L lead. As shown by the analytical results, all labs performed very well.

The sample series labeled SPC consisted of solidified blanks, prepared by WED personnel, which contained only cement and demineralized water. These samples were used to determine if any bias existed in the lab procedures for specific metals, or if any tramp metals were present in the cement used in the solidification tests. The data obtained from all the labs are consistent, and indicate no bias for any metal, nor the presence of any tramp metals in the cement used.

The sample series labeled WEDFAS consisted of flyash standards, purchased from the National Bureau of Standards. The leachable levels content of the flyash standards was not known initially; however, with the small amounts of total metals present in the standard as compared to the total metal levels in the WERF flyash, the leachable levels in the standards were assumed to be very low. The intent of the analysis of flyash standards was to develop a leachable levels standard of a medium similar to that of the WERF flyash. The analytical results of the flyash standards are fairly consistent and will be evaluated over a period of time (as more samples are analyzed) to provide an average leachable level as a basis for future analyses.

In addition to the standards and blanks used as quality control samples, the flyash and solidified flyash samples also contained quality control samples.

The flyash samples for all the drums were splits of a composite sample that was drawn from levels throughout the drum and tumbled together to provide a representative sample of the drum population. The results of the analysis of these samples show a good consistency within and between laboratories, with the exception of Lab 2 results which are considered invalid because of improper procedure. The probe samples of flyash analyzed from the individual levels throughout Drum No. 2 were collocated samples which were used to give an indication of the homogeneity of the leachable metal levels throughout the drum and to determine that a composite sample drawn form all levels throughout the drum was a representative sample of the drum population.

The solidified flyash samples were collocated samples, drawn in the same method at the same time from the drum; these gave an indication of the homogeneity of the solidified mixture. In addition, the samples from a single probe were split into two or three separate samples to provide further indication of the homogeneity of the drum and consistency between and within the laboratories. The results of this analysis showed Drums No. 1, 3, 4, 6, 7, 8, and 9 to be homogeneous and also showed a good consistency of analytical between and within the laboratories.

The data obtained for this program have been shown to be valid, reliable, consistent, and representative of the sample population by the consistency and accuracy of the analysis results both between and within the laboratories.

CONCLUSIONS

The primary goal of the drum-scale stabilization development was to verify that the successful results obtained in the lab-scale program could be adapted into a production-scale operation. The result of the production-scale will be a stabilized waste monolith that contains no free liquids, no leachable metal levels in excess of EPA limits, and can therefore be disposed of as a general or low-level radioactive waste. The objectives set for meeting this goal were:

- Verification of the lab-scale binder-to-waste ratios (recipes) at a drum-scale level
- Development of mixing and sampling methods to ensure and verify homogeneity of the mixture in the drum
- Verification that the monolith leachable metal levels are below EPA toxicity leaching criteria
- Development of procedures for production-scale solidification.

As discussed in the text, the lab-scale recipe was adjusted for Drum No. 1 processing; the resulting mixture was too wet. Additional cement was added, and samples of the resulting monolith did pass the leach test. Drum No. 1 contained no free liquids after solidification was completed. The recipe was adjusted and Drum No. 2 was processed. The weight of flyash in Drum No. 2 was too great to allow sufficient headspace for mixing once the recipe ingredients were added. Samples of this monolith did not pass the leach test. The weight of flyash in the drums was limited to 100 pounds (45.4 kg) and processing of Drums No. 3, 4, and 5 was initiated.

TABLE VI

QA/QC Sample Analytical Results

Sample Number	Lab Number	Analyte Concentration Detected (mg/L)							
		Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver
WEDSS1A	1	--[a]	--[a]	1.1	--[a]	5.6	--[a]	--[a]	--[a]
WEDSS1B	2	--[a]	--[a]	0.95	--[a]	4.6	--[a]	--[a]	--[a]
WEDSS1C	3	--[a]	--[a]	0.99	--[a]	4.6	--[a]	--[a]	--[a]
WEDSS2A	2	--[a]	--[a]	1.2	--[a]	5.2	--[a]	--[a]	--[a]
WEDSS2B	1	--[a]	--[a]	1.03	--[a]	5.8	--[a]	--[a]	--[a]
WEDSS2C	1	--[a]	--[a]	1.1	--[a]	5.0	--[a]	--[a]	--[a]
WEDSS3A	1	--[b]	--[b]	--[b]	--[b]	984	--[b]	--[b]	--[b]
WEDSS3B	3	--[b]	--[b]	--[b]	--[b]	1000	--[b]	--[b]	--[b]
WEDSS3C	1	--[b]	--[b]	--[b]	--[b]	1002	--[b]	--[b]	--[b]
WEDSS4A	1	--[b]	--[b]	--[b]	--[b]	974	--[b]	--[b]	--[b]
SPC1	1	<0.01	1.7	<0.001	0.01	<0.01	<0.0004	<0.01	<0.01
SPC2	2	<0.01	1.9	<0.04	0.1	<0.01	<0.002	<0.01	0.35
SPC3	1	<0.01	1.9	<0.001	<0.01	<0.01	<0.0004	<0.01	<0.01
SPC4	2	0.065	3.2	<0.04	0.5	0.26	<0.002	<0.01	0.06
SPC5	1	<0.01	2.4	<0.001	0.01	<0.01	<0.0004	<0.01	<0.01
SPC6	2	<0.01	1.5	<0.04	<0.1	<0.1	<0.002	<0.01	0.04
SPC7	3	<0.001	1.5	<0.005	0.01	<0.03	<0.0002	<0.004	<0.01
SPC8	1	<0.01	2.4	<0.001	<0.1	<0.1	<0.0004	<0.01	<0.01
SPC9	3	<0.001	2.1	<0.005	<0.01	<0.03	<0.0002	<0.004	0.03
SPC10	1	<0.01	1.9	<0.001	<0.1	0.06	<0.0004	<0.01	<0.01
SPC11	1	<0.01	2.0	<0.03	0.3	0.01	<0.0004	0.01	<0.01
WEDFAS1	1	0.22	0.2	0.007	0.14	<0.01	<0.0004	0.01	<0.01
WEDFAS2	3	0.13	0.4	<0.005	0.23	<0.03	<0.0002	0.044	<0.01
WEDFAS3	1	0.06	0.2	0.008	<0.1	0.19	<0.0004	0.02	<0.01

a. Standard solution of 1.0 mg/L cadmium and 5.0 mg/L lead only; therefore, the sample was not analyzed for this element.

b. Standard solution of 1000 mg/L lead only; therefore, the sample was not analyzed for this element.

Since processing of these drums showed mixing problems, the mixing method was changed to incorporate use of a paddle mixer. The processing of Drums No. 6, 7, 8, and 9 involved using the final recipe of 2:2.25:1 cement-to-water-to-flyash, addition of cement in slurry form, and mixing with the paddle mixer. This process produced satisfactory monoliths of the WERF flyash; however, testing will be required for each new waste stream.

The homogeneity of the drum mixture is initially determined by visual inspection of samples taken from the drum mixture after mixing, but before final setup of the monolith. Homogeneity is verified by the analysis of the drum mixture samples. The visual inspection and analyses from the last four drums have shown the monoliths to be homogeneous.

The final drum of flyash was solidified using the production facility and operation procedures. The samples from this drum passed the leach test and provided verification of the operating procedures and production facility equipment.

The results obtained from the final four drums processed show, through both analytical and statistical evaluations, that the monolith resulting from the solidification process does not contain leachable toxic metal levels in excess of EPA limits and can be disposed of as a low-level radioactive waste.

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