Stabilize Ash Using Clemson's Sintering Process

(Part 1 – Phase I Results)

Mixed Waste Fly Ash Stabilization

OST Reference #2037

Mixed Waste Focus Area

MASTER

*Demonstrated at
Savannah River Site
Aiken, South Carolina*

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INNOVATIVE TECHNOLOGY

Summary Report

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

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SECTION 1

SUMMARY

Technology Summary

Incineration of applicable Department of Energy (DOE) mixed wastes has produced a secondary waste stream of radioactive and Resource Conservation and Recovery Act (RCRA) hazardous fly ash that also requires treatment before land disposal. Unlike bottom ash, fly ash usually contains constituents making efficient stabilization difficult. For example, fly ash from the DOE Waste Experimental Reduction Facility (WERF) incinerator at the Idaho National Engineering and Environmental Laboratory (INEEL) contains volatile metals, metal salts, high concentrations of zinc, and unburned organic residues. All of these constituents can effect the stabilization process. The Department of Energy, and in particular the Mixed Waste Focus Area (MWFA) of EM-50, has stated the need for "improved stabilization methods [that] would accept a higher ash waste loading (result in a smaller volume increase) while meeting waste form disposal criteria. These alternative stabilization technologies should include delivery systems to minimize worker exposure and minimize secondary waste generation, while maximizing operational flexibility and radionuclide containment." Currently, the standard practice for stabilizing ash is mixing with Portland cement at room temperature. This standard practice produces a significant increase of waste material volume or has difficulty in adequately stabilizing the components in the fly ash to ensure regulatory requirements are consistently satisfied. To address these fly ash stabilization shortcomings, the MWFA, a DOE/EM-50 program, invested in the development of several fly ash stabilization alternatives, including the Clemson University sintering method.

This sintering method stabilizes radioactive and hazardous fly ash and other mixed wastes and was patented by G. D. Crowe in 1992. The method involves a mixed waste stabilization/ immobilization process that uses a high iron/high potassium aluminosilicate material such as the rare, but naturally occurring, Red Roan Formation (RRF). If the RRF clay material is fired to at least 1,800°F (982°C) for 12 hours, a highly durable ceramic with low porosity, i.e., below 3.8%, can be made by slip casting.

A bench-scale treatability study was conducted at Clemson University in 1995 to determine whether or not this RRF material could be used to immobilize DOE waste. The technology development arm of DOE, EM-50, funded this project through a cooperative agreement with University Programs at the Savannah River Site (SRS). Results from this bench-scale effort revealed that the RRF material could be used successfully to stabilize certain DOE wastes into a durable form.

In this previous work, a surrogate mixed waste, derived from the Rocky Flats Plant wastewater treatment sludge, was combined with the RRF material and fired. The resulting pellets represented a 50% waste volume reduction and a 50 weight percent waste loading. These blocks were found to be highly durable based upon the toxicity characterization leaching procedure (TCLP) leachability test results evaluated under Land Disposal Restriction (LDR) limits imposed at that time. In addition, a surrogate of contaminated Fernald soil was also processed with RRF material into pellets with a 50 weight percent loading. The soil was spiked with 0.5% target species, including radionuclide surrogates and hazardous metals. These pellets were also found to be very durable, based on TCLP leach test results. These preliminary findings again suggested that mixed waste could be combined with this RRF material and fired to produce a durable waste form.

Two wastes were chosen for treatment in order to determine whether or not this ceramic stabilization technique could be scaled-up. The first waste chosen was a surrogate of the Silo #3 waste (S3S) from DOE's closed nuclear materials facility near Fernald, Ohio. This high salt bearing waste is not expected to be amenable to either vitrification or cementation due to its very high levels of phosphates, nitrates, and sulfates. Furthermore, two hazardous metals, As and Se, would likely volatilize during vitrification. The surrogate was readily formed and sintered into a stable waste form using RRF. This waste form product also passed TCLP leachability testing at up to a waste loading of 65 weight percent.

The other waste treated was a surrogate derived from the West End Treatment Facility, currently stored at the Y-12 area of the Oak Ridge Reservation. Fifty percent of the solids in this sludge waste stream are calcium carbonate, which proved difficult to sinter. However, bars were produced that passed TCLP leachability testing.

The past treatability study work described above successfully showed that rather difficult mixed waste streams could be stabilized using ceramic technology by a method that is scaleable to full production levels. The next step was to select an actual waste stream to be showcased in a full-scale demonstration of this Sintered Ceramic Stabilization (SCS) technology. Based on the DOE/ MWWFA assessment of problem waste streams, fly ash from the WERF Incinerator at the INEEL was selected as the demonstration waste stream.

The treatability and demonstration activities of the SCS process using WERF fly ash are to be accomplished in two phases. Phase I involved the bench-scale testing and support activities on a 5-gallon sample of the actual waste and was completed at the Clemson Environmental Technology Laboratory (CETL). Phase II will include a drum-scale demonstration of the process with approximately 100 kg of waste and will also take place at CETL. This ITSR addresses only the experimental approach and results pertaining to Phase I. Phase II results will be reported in a subsequent ITSR to be issued in FY 1999.

Demonstration Summary

The Phase I experimental protocol for evaluating the SCS method for WERF fly ash required statistically designed experiments (screening designs for identification of process factors and a response design for process optimization). The first screening experimental design selected was an eight factor, 16-run Box-Hunter Experimental design that tested the following factors at two levels: waste loading, RRF particle size distribution (psd) modulus, water content, phosphoric acid, premixing of RRF, mixing time, ramp rate of firing temperature, and top (soak) firing temperature. In a followup experiment, the eighth factor, firing temperature was retested using a higher temperature for the "low" level. This first set of experiments resulted in identifying that the three most significant factors are the waste loading, the RRF psd modulus, and the firing temperature.

The second set of experiments used the Box-Behnken Experimental design and tested the three most significant factors identified in the first screening experiment; waste loading, RRF psd modulus, and firing temperature at three different levels. A simple factorial design experiment was then set up to investigate three levels of waste loading and two levels of firing temperature.

Based on the statistically designed experimental activities described above for Phase I, stable, low porosity fly ash waste forms that meet the LDR limit of RCRA metal TCLP testing can be produced using the SCS process. The waste loading to achieve these goals (20% vol) was lower than originally anticipated. The resultant waste form volume is therefore larger than the original waste stream volume. Reduction of the waste form volume by further optimization of the processing variables may be possible. However, for the purposes of the larger scale demonstration planned in Phase II, it seems more appropriate to produce waste form products that consistently meet the LDR specification without the need to reprocess failed forms.

This study has successfully identified the appropriate mix particle size distribution needed to prepare an extrudable batch. The critical processing variables have been identified along with realistic upper boundaries for the waste loading. Empirical models have also been developed from the statistically designed experiments. These models predict the physical properties of the fired waste forms, including its resultant stability as determined by the TCLP leachability, as a function of the critical processing variables.

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SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

The SCS process consists of mixing sized fractions of a naturally occurring RRF material with the waste material (WERF fly ash) as well as with suitable dry and proprietary liquid plasticizers. The total mix is then formed into a shape by either pressing or extrusion, dried, and fired to produce a sintered ceramic waste form. Firing temperatures typically range from 1,050 to 1,150°C. The amount of mixed waste fly ash incorporated is restricted to a level at which the resultant waste form meets chemical durability requirements for RCRA landfill disposal limits (LDRs). During the firing process, the suite of minerals decompose at different temperatures and produce active glass forming constituents that may readily react with the waste stream constituents. These desired reactions are facilitated if the waste stream constituents are intimately mixed with the minerals. Both the minerals and the waste stream may evolve water vapor and other gases during the firing operation.

These gases may either promote or retard the reaction process. In some instances, the gas train may include reducing agents that cause accelerated reactions, early vitrification, and sintering. Early vitrification may result in deformation of fired ware or bloating. Both events may be undesirable and the firing conditions of the waste form treatment must be controlled to minimize these effects. It is possible to reduce or cause a plateau in the firing ramp rate to allow sufficient time for critical decomposition or oxidation reactions to take place.

When these offgases are innocuous, the primary concern is to allow them to escape without doing harm to the fired waste form. Other gases must be captured and condensed and made nonhazardous. In certain cases this can be accomplished by use of scrubbing systems. The condensed systems can be either treated further or may be recycled in the processing unit as makeup water for the subsequent waste form mix.

Another option available is to produce stable solid phases at temperatures below that used to stabilize the primary waste form. This alternative, although more complex, is a viable option in treating phases separated and concentrated during the initial firing process.

It is most desirable that the processing of waste forms is conducted so that none of the fired product fails to meet the RCRA Universal Treatment Standard (UTS) specified requirements (in regard to the leachability of hazardous heavy metals) for land disposal. The processing parameters to accomplish this must be developed in the early experimental work. The goal of this work is to define a processing model to predict leachability effects outside of the test envelope. In the event, however, that fired parts are found to be defective, these parts may be reground and introduced to the processing mix. This is usually accomplished by adding the failed waste form at a concentration constituting 10% of the raw unfired waste batch.

Various waste streams have been successfully treated with the ceramic stabilization process. The primary stabilization path appears to be the formation of a stable vitreous phase and stable crystalline phases that incorporate the active waste stream constituents. The vitreous phase may be uniform and several noncrystalline phases may coexist. The successful processing scenario results from the combination of processing parameters that provide the greatest reactivity between the waste stream constituents and the mineral mix with which they react. Optimization of the process to achieve final physical properties with the desired chemical inertness must be addressed through designed experiments and statistical analysis of the stabilization method.

System Operation

The SCS process is diagrammed in Figure 1. The raw material bins and dispensing equipment allow the waste ash and additive mixes to be dispensed volumetrically. The ash is preslurried with additives to enhance the plasticity and stability and then is dispensed with a positive displacement liquid pump under a controlled rate. The dry ingredients, consisting of a dry and sized RRF suite of minerals, have either been premixed or are dispensed in a desired combination to achieve a particular particle size distribution.

Figure 1. Diagram of SCS process.

The batch constituents are then blended in a mixer to achieve the desired consistency and to promote the distribution of ingredients. A further function of the mixer is to provide agglomeration and pelletization of the mix to promote flow of the mix to the forming machine, which is the next step in the process. Both pressing and extrusion have been successfully employed as forming machines in the processing of sintered ceramic waste forms.

Following the forming step is thermal processing. This step includes both the drying and firing operation. The drying step may be with air only or may incorporate a dryer. The firing is carried out in an electric kiln, which is regulated by a programmable controller. During firing, pyrometric cones are placed along with the dried-formed bars. The cones are used to confirm the degree of thermal heat treatment that the bars

actually receive. Usually some variability occurs within the kiln during the firing process and it is necessary to ensure that the variability is maintained within acceptable limits. Offgassing is controlled by a scrubbing system that will capture volatile species, including RCRA hazardous metals.

The next step in the process involves the testing of fired bars to ensure compliance with the desired waste form specifications. Specimens are statistically sampled from each fired lot for physical properties, including TCLP leachability and stability testing. Those lots passing the test proceed to the disposal step, while those that do not pass the process must be ground and reprocessed into disposal compliant waste forms.

SECTION 3

PERFORMANCE

Demonstration Plan

The goal of Phase I development was to determine the degree of success when using the SCS process to treat actual WERF incinerator mixed waste fly ash for compliant disposal. An additional objective consisted of identifying those SCS operating parameters necessary to ensure a successful large-scale demonstration in Phase II. The actual mixed waste WERF fly ash used in Phase I contained the RCRA hazardous metals of cadmium, chromium, and lead in the concentration ranges of 5000, 1000, and 35,000 ppm respectively. These levels are 4 to 6 orders of magnitude above acceptable land disposal concentrations.

One preliminary study and three statistically designed experiments comprised the scope of Phase I. The preliminary experiment was used to provide subjective information about the waste stream reactions in the SCS process and provide experience in designing an initial screening experiment. The three statistically designed experiments of Phase I had the following scope:

1. Experiment I was a screening experiment whose purpose was to yield an understanding of the manner in which eight process and mix variables affected the properties of the fired fly ash waste forms.
2. Experiment II was a response surface experiment, whose purpose was to predict the degree to which ash waste loading, RRF mix size distribution, and firing temperature affected the fly ash waste form density, porosity, and apparent specific gravity (ASG).
3. Experiment III was also a response surface experiment, whose purpose was to determine the effect of significant processing factors and their interactions with the waste loading of the WERF fly ash. Experiment III was also completed to yield the optimization of processing parameters to be used in the Phase II demonstration.

Experiment II focused on the interaction of the RRF blend size, waste loading, and temperature, where as Experiment III focused on the influence of the mixing and forming process variables on the waste form properties.

The development work of Phase I was carried out with bench-scale and/or laboratory-scale equipment. Equipment for the demonstration-scale size pilot plant was also purchased for Phase II, which is scheduled for early FY 1999.

The pilot plant for the demonstration has been assembled and approved for operation by the South Carolina Department of Health and Environmental Compliance. Mixing, forming, drying, firing, and scrubbing systems to be used in the actual demonstration have all been tested and successfully subjected to operational trials. The plan calls for verification testing of the empirical model using a sample ash consistent with the actual demonstration ash. The fired waste form from the verification test will be characterized for physical properties and leaching stability. The final demonstration will be used to prove that the SCS process will successfully stabilize WERF fly ash at production scale and will provide data to allow an economic assessment of the process for full-scale application to similar waste stream remediations.

Results

For the preliminary study, a 67 vol %, equivalent to 50 wt %, fly ash/RRF mixture was pressed under low pressure (5,000 psi) and high moisture content (18.1 wt % dry basis) and then fired (1,000°C) to produce ceramic waste-form samples for TCLP leachability testing. The waste form pellets were 1-inch diameter, 1-inch thick pressed and sintered pellets. See Figure 2. This test provided subjective information about the processing and waste loading requirements (or limitations) for the first statistically designed screening experiment, Experiment I.

Figure 2. Green (dried and unfired) and fired pellets.

Ten pellets were pressed and two were test fired on two schedules. A single pellet was test fired at 1,100°C, but slumped, necessitating a reduction in temperature and ramp rate. The second pellet, fired at 1,000°C, resulted in a dense, sintered specimen and the firing schedule was set for the following conditions: hold at 110°C for 5 hours, ramp at 2°C/min until soak temperature of 1,000°C is reached, hold for 1 hour and then cool at 5°C/min until furnace reaches 110°C. Four pellets were fired in Test Firing #3 and analyzed for TCLP. Of the remaining four pellets, one was measured and archived after drying, while the other three were fired, weighed, and measured. Of these, one was archived and two were analyzed for Archimedeian density data.

The TCLP specimens were sent to Maxim Technologies Laboratories, which tested the four samples for leachability. The results of those tests are shown in summary form in the Table 1 below.

Table 1. TCLP results from the preliminary experiment.

Metal Detected	Result mg/L	UTS/LDR limit	Over limit
Antimony	>.009	2.1	
Arsenic	0.294	5	
Barium	0.815	7.6	
Beryllium	>0.001	0.014	
Cadmium	21.4	0.19	*
Chromium	>0.004	0.86	
Lead	15.7	0.37	*
Mercury	>0.0001	0.025	
Nickel	0.036	5	
Selenium	0.016	0.16	
Silver	0.018	0.3	
Thallium	>0.007	0.078	
Vanadium	0.032	0.23	
Zinc	243	5.3	*

Statistical Experiment I was a screening experiment designed to evaluate the affects of the following eight factors on the physical properties of the final sintered fly ash waste form.

1. waste loading,
2. moisture content,
3. H₃PO₄ addition (water pH);
4. RRF PSD modulus,
5. premixed RRF,
6. mixing time,
7. ramp rate for burn,
8. firing temperature.

Sixteen mixes were batched separately and mixed in a Hobart 5-qt rotary mixer. The batch size in each case was approximately 270 grams. Since mixing was one variable, those batches that specified premixing were prepared by putting the RRF in the mixer and carrying out dry mixing with RRF before the water was added. The ash was added last. When not premixed, all the dry ingredients were batched into the mixer at the same time. The material was then pressed at 1,000 psi. The material for the pellets was preweighed to ensure consistent compaction. The pellets were then placed in the Lindbergh box furnace and ramped to 110°C and dried at that temperature for 6 hours. The pellets were then ramped to the soak temperature at 3°C/min and held for 1 hour. Because these experiments were statistically designed, an analysis of variance (ANOVA) was conducted to determine the effect of the factors. Table 2 shows the summary results of that analysis.

Table 2. Batch formulations and physical property data for Experiment I.

Batch Formulations							Physical Property Data			
Batch h	Wt % Waste loading	Wt % Moisture content	Wt % H ₃ PO 4 Amt.	RRF psd modulus	RRF pre Mixed (1) or not (0)	Min. Mixing time	°C Firing Temp	Apparent Specific Gravity	g/cc Bulk density	Apparent Specific Porosity
1	10	33	0	0.59	1	15	1,075	2.7	1.7	36.7
2	50	33	0	0.15	0	15	1,075	2.0	2.0	1.4
3	10	38	0	0.15	1	5	1,075	2.6	1.8	31.3
4	50	38	0	0.59	0	5	1,075	2.3	2.2	3.1
5	10	33	3	0.59	0	5	1,075	2.6	1.7	34.4
6	50	33	3	0.15	1	5	1,075	2.2	2.1	1.5
7	10	38	3	0.15	0	15	1,075	2.5	2.2	15.2
8	50	38	3	0.59	1	15	1,075	2.3	2.2	5.0
9	50	38	3	0.15	0	5	1,025	2.6	2.2	17.4
10	10	38	3	0.59	1	5	1,025	2.6	1.7	35.2
11	50	33	3	0.59	0	15	1,025	2.8	1.9	31.9
12	10	33	3	0.15	1	15	1,025	2.6	1.8	30.3
13	50	38	0	0.15	1	15	1,025	2.8	1.8	33.6
14	10	38	0	0.59	0	15	1,025	2.7	1.6	39.4
15	50	33	0	0.59	1	5	1,025	2.8	1.7	40.5
16	10	33	0	0.15	0	5	1,025	2.6	1.6	40.3

The low level firing temperature of 1,125°C was too low to achieve high-density pellets. An assumption was made that such low-density pellets would not achieve suitable TCLP stability. A decision was made to repeat Experiment I using a higher firing temperature for the low level. The results basically confirmed the results from the initial Experiment I. As the overall density increased, the porosity decreased, and the effect of the particle size distribution and mixing time were found to affect the porosity. From these data it was obvious that the firing temperature was a very critical factor and can have a remarkable influence on the waste form properties. As a result, the three most significant factors were waste loading, the RRF particle size distribution modulus, and firing temperature. These factors were therefore studied in more detail in Experiment II.

Experiment II was a response surface experiment designed to optimize the significant factors identified in Experiment I. The combination of factors and property data for specimens as well as TCLP results for Experiment II are shown in Tables 3 and 4 below.

Table 3. Experimental Factors and Physical Property Data for Experiment II.

Experimental Factors				Physical Property Data			
Batch	% Waste loading	RRF modulus	Firing Temp.	Dried density g/cc	Fired bulk density g/cc	Apparent porosity %	ASG
1	30	0.37	1,050	1.77	1.80	33.87%	2.72
2	50	0.37	1,025	1.78	1.75	37.89%	2.82
3	10	0.37	1,025	1.77	1.71	35.58%	2.65
4	10	0.59	1,050	1.76	1.69	36.62%	2.67
5	50	0.15	1,050	1.73	2.28	14.85%	2.67
6	50	0.37	1,075	1.85	2.30	0.00%	2.30
7	10	0.37	1,075	1.81	1.96	25.69%	2.64
8	30	0.37	1,050	1.82	1.79	33.66%	2.70
9	50	0.59	1,050	1.85	1.95	31.64%	2.85
10	30	0.59	1,075	1.8	2.17	16.17%	2.58
11	30	0.15	1,075	1.74	2.32	6.24%	2.48
12	30	0.15	1,025	1.78	1.63	39.93%	2.71
13	30	0.59	1,025	1.81	1.61	40.75%	2.71
14	10	0.15	1,050	1.75	1.83	30.46%	2.63
15	30	0.37	1,050	1.78	1.71	37.02%	2.72

Table 4. TCLP Results from Experiment II.

TCLP limit ppm	0.19	0.37	0.23	5.3
Batch	Cd	Pb	V	Zn
1	2.21	10.1	0.33	12.8
2	5.71	25.9	0.048	85.5
3	0.426	0.876	0.258	0.771
4	0.381	0.849	0.199	0.801
5	4.84	12.9	0.051	59.8
6	2.88	14.9	0.043	37.4
7	0.17	0.431	0.072	0.684
8	1.86	6.95	0.317	8.47
9	4.34	17.4	0.054	68.3
10	2.1	10.7	0.242	15.1
11	0.878	5.13	0.087	8.77
12	1.51	13.3	0.432	4.65
13	2.08	18.9	0.468	69.1
14	0.196	1.09	0.129	0.674
15	2.24	16.8	0.447	11.4

In order to investigate the effect of firing temperature and waste loading for lower waste levels, a simple factorial design was set up. The formulations were mixed in batches of about 500 grams of dry material. The distribution moduli was set at 0.37, and the other batching procedures used previously were employed again. Weighed and measured densities were obtained on the dried and fired pellets. The pellets were not tested for displacement density and porosity because the pellets were to be used for TCLP testing. The TCLP leach values increased for the fired waste forms with increased waste loading,

however, the increase was not linear. The leachability of the waste forms dramatically increased in specimens containing waste loading above 20 vol%. The leach rate decreased as the temperature increased.

Since the density measurements were obtained by weigh and measure techniques, it was not possible to correlate the leach rate with the apparent specific gravity for these specimens. There was an anomaly in the density data for specimens fired at 1,100°C. In this series, a density maximum occurred in specimens containing 20% waste loading. In all cases there was a statistically significant difference in the leachability

with increased waste loading. The TCLP values increased as the waste loading increased. One example plot of the TCLP leachability versus waste loading is shown in Figure 3.

Figure 3. TCLP versus waste loading for specimens fired to 1,100°C.

Experiment III was a response surface experiment designed to study the following four factors in 27 runs:

1. moisture content,
2. waste loading,
3. mixing time,
4. auger speed.

The physical properties and TCLP data for Experiment III are shown in Table 5.

Table 5. Physical property and TCLP data for Experiment III.

FACTORS				PHYSICAL PROPERTY DATA					
Run	Water grams	Mix time Min.	Waste Loading %	Dried Density g/cc	Bulk Density g/cc	Apparent porosity %	ASG	TCLP Cd ppm	TCLP Pb ppm
1	17.25	10	20	7.89	2.06	5.70	2.19	0.0876	0.111
2	16	5	20	7.89	2.08	4.57	2.18	0.0757	0.0946
3	18.5	15	20	7.89	2.05	7.03	2.21	0.13	0.131
4	18.5	10	15	7.89	2.08	8.08	2.27	0.1	0.122
5	17.25	5	20	10.52	2.08	5.41	2.20	0.264	0.211
6	18.5	5	20	7.89	2.08	6.51	2.23	0.172	0.176
7	17.25	10	15	10.52	2.06	4.03	2.15	0.25	0.195
8	17.25	15	20	10.52	2.03	3.10	2.10	0.184	0.196
9	16	10	20	10.52	2.03	2.94	2.10	0.151	0.167
10	18.5	10	25	7.89	2.08	7.01	2.24	0.101	0.102
11	17.25	10	15	5.26	2.08	11.93	2.36	0.0377	0.0957
12	17.25	15	20	5.26	2.06	12.74	2.36	0.0462	0.115
13	18.5	10	20	5.26	2.04	14.10	2.38	0.0278	0.0517
14	17.25	10	20	7.89	2.08	7.41	2.26	0.0768	0.114
15	16	10	25	7.89	2.08	5.87	2.21	0.0761	0.141
16	17.25	5	15	7.89	2.06	6.22	2.20	0.0721	0.152
17	17.25	15	15	7.89	2.05	7.40	2.22	0.0707	0.119
18	17.25	5	20	5.26	2.07	11.76	2.34	0.0188	0.0552
19	18.5	10	20	10.52	2.06	6.54	2.21	0.169	0.176
20	17.25	10	25	10.52	2.07	5.34	2.19	0.126	0.158
21	17.25	15	25	7.89	2.07	6.96	2.23	0.0937	0.119
22	17.25	5	25	7.89	2.07	9.41	2.29	0.0751	0.0862
23	16	10	20	5.26	2.07	9.57	2.29	0.0439	0.0879
24	17.25	10	25	5.26	2.05	13.06	2.37	0.0331	0.0674
25	16	15	20	7.89	2.05	10.72	2.30	0.0849	0.124
26	16	10	15	7.89	2.05	8.34	2.24	0.0666	0.108
27	17.25	10	20	7.89	2.05	9.03	2.26	0.0834	0.114

As represented by the graph of Figure 4, the test results show that all of the processing variables impact final TCLP content.

Figure 4. Plot showing the effects of each single process factor on the TCLP for Cd.

Single factor effects are shown by the example of Figure 5. Please note that the auger speed is not a significant factor by itself.

Figure 5. Response surface showing effect of water content and auger speed on TCLP of Cd.

The completed Phase II work conducted to date shows that stable, low porosity waste forms that meet the LDR limit of RCRA metals after TCLP testing can be produced using the SCS process. The waste loading to achieve these goals (20 % vol) was lower than originally anticipated. The resultant waste form volume is therefore larger than the original waste stream volume. It may be possible to reduce the waste form volume by further optimization of the processing variables; however, for the purposes of the demonstration in Phase II, it seems more appropriate to produce waste form products that consistently meet the LDR specification without the need to reprocess fired waste form.

This study has successfully identified the mix particle size distribution (psd) that could be used to prepare an extrudable batch. Empirical models have been developed from statistically designed experiments to predict both the physical properties of the fired waste forms and the resultant stability as determined by the TCLP leachability.

SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

SCS is one of three competing technologies being demonstrated for treatment of WERF fly ash generated at the INEEL. The process is relatively simple, easily scaled up to a larger capacity, and the raw feed materials required are relatively inexpensive and simple to prepare. Furthermore, the process could easily be compartmentalized for mobile transport to specific sites. The waste form block products are readily stacked to produce a dense and volume efficient disposal package, and there is little probability that waste products could escape from the processing system or cause a failure within the system that results in environmental contamination.

Phosphate bonded ceramic (PBC) stabilization, developed by Argonne National Laboratory-East, is one of two other WERF fly ash stabilization methods being specifically supported by the MWFA. The other being the RocTec™ sintering method. In the PBC process, calcined magnesium oxide is mixed with phosphoric acid or reactive phosphate compounds to form a paste or slurry. This is then mixed with waste for 20 to 30 minutes and allowed to cure for approximately 2 hours in a slightly exothermic process. The process occurs at room temperature, results in producing a ceramic magnesium oxide solid barrier, and converts soluble RCRA hazardous metal components into their less soluble phosphorous salts.

RocTec™ is another ceramic sintering process that can stabilize waste streams similar to those that are amenable to the PBC process and Clemson method. The waste to be stabilized is first calcined at approximately 500°C, depending on the amount of excess carbon. The waste is then ground and mixed with the reagents and additives. This mixture is then pressed into briquettes, air dried, and then sintered at approximately 1,100°C.

The advantage of the higher temperature sintering processes, including the Clemson SCS process, over that of the lower temperature PBC method is there potential to provide higher density, lower porosity waste forms. These attributes can lend to low overall waste volumes, compared to PBC. In addition, the introduction of the waste's hazardous constituents into an amorphous state tends to provide better long-term durability. However, the sintering methods require more costly processing equipment and produce secondary wastes that may require additional treatment.

Other technologies in use to stabilize various hazardous and radioactive wastes (including fly ash) in the DOE complex include, of course, cementation (grouting) and vitrification.

Grouting: This process consists fundamentally of hydraulic reactions between water and calcium silicate cement. Other cementitious blends may be used. The cementation reactions cause aggregate, waste and cement to solidify. The resultant solid form may develop very low permeability and has an inherent basicity that resists leaching by acidic agents. In some cases the grout may set slowly or may fail to set at all depending on the constituents within the waste stream.

Vitrification: This process relies on the ability to form a stable noncrystalline phase with the waste stream. In order to obtain a homogeneous and thoroughly mixed glassy phase, the reactants must be processed at high temperature for sufficient time to vitrify all of the batch constituents. The molten mixture should not separate or tend to crystallize on cooling. The properties of the vitrified phases are highly dependent upon the consistency of the composition of the batch. The processing temperatures

may be high and the times extended. Both of these features make processing highly volatile species challenging since they are difficult to retain in the vitreous phase.

The advantages of the SCS process are that it is simple and may accommodate both wet and dry waste streams without required drying. It forms stable vitrified phases that can be formed at temperatures lower than are typical for vitrification. Unlike the cementitious methods, it does not depend upon chemical or hydrating reactions to occur.

Technology Applicability

The Clemson SCS process is applicable to most inorganic homogeneous solids or sludges, including ash, dry particulate, incinerator blowdown residues, soils, and wet particulate. However it is not well suited for treating aqueous and organic liquids or unique mixed wastes, such as explosives or oxidizers. Heterogeneous debris waste is not recommended unless specifically sized.

The SCS method can handle waste containing most hazardous constituents, including the RCRA heavy metals as well as trace or small amounts of regulated organics. Large concentrations of volatile metals may pose problems of retention and will require development testing to ensure acceptable waste loadings and amounts of secondary wastes.

Patents/Commercialization/Sponsor

G. D. Crowe holds United States Patent number 5,302,565 in regards to the use of RRF clay and the SCS process in stabilizing mixed waste. The patent abstract statement reads as follows: " A leach-resistant vitrified composition, particularly suitable for long term encapsulation and disposal of nuclear wastes, comprises a high iron, high potassium aluminosilicate, fired a temperature of at least 1850°F for at least 12 h." The DOE's EM-50 technology development program is the only current known sponsor of this technology.

SECTION 5

COST

Methodology

No methodology has yet to be selected for evaluating costs associated with full-scale deployment of the Clemson SCS process. After completion of the Phase II demonstration, as well as the completion of demonstrations on alternative technologies such as PBC, a detailed cost analysis will be conducted. This cost analysis will contain all aspects of deploying a fly ash stabilization system at the INEEL WERF facility. Costs will be documented for development, design, equipment and operation. More important estimates of life-cycle cost, including volume dependent transportation and disposal costs, will be made for each of the three stabilization options currently being developed and evaluated for the INEEL WERF fly ash. This data will assist incinerator and waste managers in the DOE complex in selecting an effective ash stabilization process based on their unique situations.

Cost Analysis

The only cost data available to date consists of estimates to design and install the pilot sintering equipment necessary for the Phase II demonstration. Approximately \$200k has been spent to purchase and install the required mixers, extruders, and furnaces (along with the required radiological controls) to treat the 100 kg of Phase II WERF ash at a rate of 5 kg/hr. Additional and detailed cost data for operating, disposal and environmental compliance will be available in the ITSR to be issued after the completion of Phase II in FY 1999.

Cost Conclusions

The analysis to be completed after Phase II may indicate a cost advantage for the sintering method in comparison to both low-temperature (e.g., Portland cement and PBC) and vitrification stabilization alternatives. Sintering's cost competitiveness is a consequences of the high density, low porosity waste forms it produces, which lowers the overall disposal volume in contrast to the low-temperature techniques. Even though these waste forms will not exceed the volume reduction achievable through vitrification, the capital and operating cost of sintering is a fraction of that of melting. It is anticipated that future development data will indicate that the cost-effectiveness of the three general stabilization techniques (i.e., low temperature, sintering, and vitrification) will be dependent on the amounts of the homogeneous inorganic waste to be treated. As the mixed waste volume increases, sintering and vitrification become increasingly cost competitive. This trend is a result of sintering's and vitrification's lower disposal cost recovering and exceeding their higher capital and operating cost as the waste volume increases. However, the volume of waste needed to reach this advantage point may be in excess to that available and/or anticipated at many DOE complex sites.

SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

The regulatory goal of any end users considering deployment of the Clemson Sintering method is to produce stabilized waste forms that meet Environmental Protection Agency's (EPA's) 40 CFR 268.40 Land Disposal Restriction (LDR), including the UTSS for the burial of toxicity characteristic RCRA hazardous wastes that are otherwise prohibited from land disposal. For treating RCRA hazardous waste, any full-scale SCS treatment facility will require a RCRA permit or a modification to an existing RCRA permit.

In addition, Nuclear Regulatory Commission (NRC) 10 CFR 61 waste form testing will be necessary if disposal of the sintered waste form is to be in an NRC licensed facility. Additional requirements for applying the polysiloxane process at a federal facility include a National Environmental Policy Act (NEPA) review (a categorical exclusion is most likely to be applied), and any air emission considerations and/or permits as required under the National Environmental Standards for Hazardous Air Pollutants (NESHAPS) and Prevention of Significant Deterioration standards. Any commercial facility treating radiological waste must secure an NRC permit.

Any bench-scale testing and development of the Clemson SCS method must secure categorical treatability study exclusion. In addition, the cognizant RCRA regulatory authority must be notified 45 days before receiving treatability samples for testing.

Safety, Risks, Benefits, and Community Reaction

Even though greater than room temperature operations are involved, the Clemson sintering process is a relatively safe waste stabilization method. In addition to exposure to temperatures above 1,000°C volatile radioactive and toxic metal exposure is also possible. However, both of these hazards are easily controlled and exposures are negated with well established methods. These methods involve insulated furnaces, state-of-the art temperature controllers, and isolated offgas cleaning systems equipped with dust suppression, scrubbers, and high-efficiency particulate air (HEPA) filters.

The major environmental risk involves the release of volatile RCRA metals during firing of the waste-additive-RRF mix. This concern is easily mitigated with well-developed and established offgas treatment systems. This system condenses the radioactive and hazardous offgases into a circulating scrub system, which in turn is charged to the next waste/RRF feed batch. The method also eliminated the need to stabilize and manage a significant secondary waste stream.

Community and stakeholder reaction to deployment of the SCS process for mixed waste treatment would be overall favorable. The technology has many excellent attributes, including low volume increase waste forms and sufficient durability. However, stakeholder concerns will surface if methods to control emissions and manage secondary waste fail.

SECTION 7

LESSONS LEARNED

Implementation Considerations

In order to deploy the SCS process for a particular mixed waste stream, the potential users need to consider factors common to most waste treatment systems. The factors include the identification of the design requirements for the front-end waste feed sizing equipment and the back-end waste handling methods. Decisions also need to be made in regard to the need and type of dust and vapor handling and recycling methods that are required.

Because the primary hazard associated with the SCS process arises from the presence of dust and airborne contaminants, methods to control these risks must be implemented. The most suitable method is to feed the waste as a slurry or moist paste where possible. If used dry, the materials must be confined or personnel must be isolated from it.

Technology Limitations and Needs for Future Development

As mentioned previously, the SCS process is not suitable for highly volatile waste stream species like for example, Hg. Volatile species that are suitable for processing with the SCS process must be determined by experimentation for specific wastes. The mass balance of the process is yet to be completed. However, it is known that volatilization of certain species does occur, notably Cd and Pb. The plan to deal with these species is to recycle these constituents from the wet scrubber back into the next mix and waste form. The undesirable development of a secondary waste form composition requiring a lower firing temperature to stabilize these two specific waste constituents may require consideration.

Technology Selection Considerations

The potential end users and waste managers in the DOE complex need to consider many factors when selecting technologies for mixed waste ash. Those wastes that contain highly volatile species like mercury or particulate actinides may require special treatment of the offgases. Any process that requires elevated temperatures (a thermal process), as part of the processing steps will be sensitive to high vapor pressure species. The challenge is to reduce the processing temperature to the lowest practical level and to stabilize the species in a form that exhibits the lowest possible vapor pressure. The form or the state of the original waste will affect the viability of thermal and/or nonthermal processes. As such, pretreatment processes may be required to make a particular process a viable alternative. The following are general areas that require consideration in order to select technologies for development.

1. Form of the Waste

The SCS process relies on the direct reaction of particles or particulate/fluid systems. The waste constituents within the particles or particulate mass must be able to react with the mineral phase(s) upon which the process is based. This requirement means that the waste stream must be properly sized to enhance that reaction and reactivity with the RRF mineral material. Large sized waste debris must be reduced in size to enhance the reactivity; therefore, the ease with which it can be reduced is a consideration. The waste may occur in either a solid or fluid form and remain compatible with the SCS process. The solid content of wet or fluid based waste streams to be processed, ultimately will determine the maximum practical limit of waste addition to the mineral mix. This limit is directly related to the rheology of the mix formed when the waste stream is added to the RRF blend. If this

limit is below the maximum limit that the RRF system can stabilize, a concentration of the waste stream will be required.

2. Waste Composition and Characteristics

There is a wide range of compositions that can be treated using the SCS process. Most inorganic materials, excluding highly volatile species like mercury, would be appropriate. The limit of alkali halides that can be tolerated is fixed by the solubility of reaction products produced during the thermal processing that would contain RCRA metals. Waste streams containing significant organic content may be suitable feeds for the process. The oxidation rate can be controlled during the thermal processing to ensure thorough destruction of organic species. Furthermore, contaminants released from the organic vehicle, being in the vapor state could readily react with the RRF mineral to rapidly form condensed phase reaction products.

3. Secondary Waste Generation

The primary source of secondary waste generation results from volatilization during the thermal processing. The secondary waste stream can be captured and recycled in the system. Alternatively, treatment of the secondary waste stream using a modified waste form composition that allows processing at a lower temperature may be required.

4. Extent of Development

The SCS process is very similar to a well-developed industrial process for making ceramic ware. In fact, equipment to process the mineral mix with the variety of waste streams that have been successfully treated has been ceramic pilot-plant scale equipment. The technology needed to capture offgases via wet scrubbing is well developed and the technology needed to maintain consistent control of the materials processing is readily available from a variety of commercial sources.

The SCS process has been successfully tested on a variety of surrogate waste streams and used to treat WERF ash material in a feasibility trial for a larger demonstration scale process. The determination of the mass balance of the process and the parameters to clean up the offgas generated is currently under evaluation.

APPENDIX A

BIBLIOGRAPHY

1. H. D. Leigh, Final Report for "Scale-Up and On-Site Demonstration of a Sintered Ceramic Stabilization Process to Treat Actual DOE Low-Level Mixed Wastes, March 1998.
2. J. L. Resce, Final Report for "Bench-Scale Treatability Study on the Immobilization of Mixed Waste in a Brick-Like Ceramic Matrix," December, 1995.

APPENDIX B

TMS Data Elements

Funding Source

This section provides cross-reference information in regards to the EM-50 Mixed Waste Focus Area contract established for development of the Clemson Sintering Stabilization technology. The Department of Energy-Headquarters (DOE-HQ) Technology Management System (TMS) tracking number is provided as well as the specific Technical Task Plan (TTP).

TMS # 2037 Stabilize Ash Using Clemson's Sintering Process

TTP # SR16MW43 Phase II WERF Ash Demonstration and Treatability Study

APPENDIX C

ACRONYMS

ANOV	analysis of variance
ASG	apparent specific gravity
DOE	Department of Energy
DOE-HQ	Department of Energy-Headquarters
CETL	Clemson Environmental Technology Laboratory
CFR	Code of Federal Regulations
EPA	Environmental Protection Agency
EM	Environmental Restoration and Waste Management
HEPA	high-efficiency particulate air
INEEL	Idaho National Engineering and Environmental Laboratory
ITSR	Innovative Technology Summary Report
LDR	Land Disposal Restriction
MWFA	Mixed Waste Focus Area
NEPA	National Environmental Policy Act
NESHAPS	National Environmental Standards for Hazardous Air Pollutants
NRC	Nuclear Regulatory Commission
OST	Office of Science and Technology
PBC	phosphate bonded ceramic
Psd	particle size distribution
RCRA	Resource Conservation and Recovery Act
RRF	red roan formation
SCS	Sintered Ceramic Stabilization
SRS	Savannah River Site
TCLP	toxicity characterization leaching procedure
TMS	Technology Management System
TTP	Technical Task Plan
UTS	Universal Treatment Standard
WERF	Waste Experimental Reduction Facility