

**Cementation and Solidification of Miscellaneous Mixed
Wastes at the Rocky Flats Environmental Technology Site**

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ABSTRACT

The Rocky Flats Environmental Technology Site produces a variety of wastes which are amenable to micro-encapsulation in cement. Portland cement is an inexpensive and readily available material for this application. The Waste Projects (WP) group at Rocky Flats evaluated cementation to determine its effectiveness in encapsulating several wastes. These included waste analytical laboratory solutions, incinerator ash, hydroxide precipitation sludge, and an acidic solution from the Delphi process (a chemical oxidation technology being evaluated as an alternative to incineration). WP prepared surrogate wastes and conducted designed experiments to optimize the cement formulation for the waste streams. These experiments used a Taguchi or factorial experimental design; interactions between the variables were also considered in the testing. Surrogate waste samples were spiked with various levels of each of six Resource Conservation and Recovery Act (RCRA) listed metals (Cd, Cr, Ba, Pb, Ni, and Ag), cemented using the optimized formulation, and analyzed for leach resistance using the Toxicity Characteristic Leaching Procedure (TCLP). The metal spike levels chosen were based on characterization data, and also based on an estimate of the highest levels of contaminants suspected in the waste.

This paper includes laboratory test results for each waste studied. These include qualitative observations as well as quantitative data from TCLP analyses and environmental cycling studies. The results from these experiments show that cement stabilization of the different wastes can produce final waste forms which meet the current RCRA Land Disposal Restriction (LDR) requirements. Formulations that resulted in LDR compliant waste forms are provided. The volume increases associated with cementation are also lower than anticipated. Future work will include verification studies with actual mixed radioactive waste as well as additional formulation development studies on other waste streams.

INTRODUCTION

The Rocky Flats Environmental Technology Site (Rocky Flats) currently generates and/or stores mixed wastes which are subject to Resource Conservation and Recovery Act (RCRA) Land Disposal Restriction (LDR) treatment requirements. Cementation is a technically viable, economic solidification treatment process for some of these wastes and is a widely accepted waste management method.^[1] It is one of several solidification technologies proposed to bring these wastes into compliance with RCRA-LDR requirements. Cement is inexpensive, readily available, solidifies under ambient conditions, and is capable of immobilizing RCRA hazardous metals in the wastes. Cements have been used for approximately 2000 years and show good durability to weathering^[2-4] making this an attractive technology for waste encapsulation. Cementation of low-level radioactive and mixed waste forms (wastes containing both chemically hazardous and radioactive constituents) offers long term stability at low cost. This technology has been proven for several waste streams at the Rocky Flats Site including a spray dried salt/brine waste and multiple analytical laboratory waste solutions. These low level mixed wastes (< 100 pCi/g) are currently being cemented at a production scale to produce certifiable waste forms. This report summarizes cementation studies performed on five waste streams at the Rocky Flats Environmental Technology Site in Fiscal Year 1994.

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DISCUSSION

Cementation development activities focused on five waste streams: analytical laboratory solutions, silver nitrate solutions, fluidized bed incinerator (FBI) ash, hydroxide precipitation sludge, and an acidic solution from the Delphi process. Activities on each of these wastes are discussed separately below. Please note that the term "percent" or "%" refers to weight percent unless noted otherwise.

Analytical Laboratory Solutions

The analytical laboratory waste solutions at Rocky Flats are generally acidic and consist of an aqueous solution of salts and with a low level of plutonium (< 100 pCi/g). They also contain various RCRA listed toxic metals including silver (Ag), nickel (Ni), cadmium (Cd), chromium (Cr), barium (Ba), and lead (Pb). The waste must be neutralized prior to cementation; the neutralization process causes the dissolved metals to precipitate as oxides or oxyhydroxides^[5] which reduces the solubility and mobility of the metals in the alkaline cement matrix.^[6] The treated waste must be RCRA-LDR compliant and pass the Toxicity Characteristic Leaching Procedure (TCLP) test. The cement's alkalinity further neutralizes acidic solutions which could degrade the cement structure and increase the leachability of these RCRA constituents. After the waste is neutralized, the solution is poured into a 55-gallon drum two-thirds full of type I/II cement and Ramcote® 1200 and is manually stirred in a production-scale operation. Each drum is capable of treating approximately 80 to 90 liters of waste solution.

Waste Projects conducted two sets of bench-scale experiments to evaluate the effectiveness of the process. The first experiment was a TCLP evaluation of the cemented waste form prepared using a spiked surrogate waste solution. The surrogate waste was a mixture of water, sodium chloride, potassium nitrate, heavy metal compounds (Ag = 5 mg/L; Ni = 10 mg/L; Cd = 50 mg/L; Cr = 300 mg/L; Ba = 300 mg/L; and Pb = 400 mg/L), and sodium hydroxide. The surrogate composition was based on characterization data from the actual waste. The surrogate solution was prepared by dissolving appropriate quantities of the heavy metal compounds in 500.0 grams of distilled water. Sodium chloride (90.0 grams) and potassium nitrate (80.0 grams) were then added, followed by sodium hydroxide (2.0 grams). The temperature and pH were measured at each stage. The solution was then divided into five lots and added to the cement/Ramcote® mixture.

These samples were prepared using surrogate waste spiked with "worst case" levels of the metals based on characterization data from actual waste laboratory solutions. This testing was used to confirm that the production-scale process produced a waste form with adequate leach resistance.^[7] A second series of experiments investigated the capability of the production-scale process to treat wastes contaminated with the six RCRA listed heavy metals but at significantly higher levels. The surrogate waste solution was spiked with Ag, Ni, Cd, Cr, Ba, and Pb at levels of 1,000, 5,000, and 10,000 mg/L each, and mixed with the cement/Ramcote® mixture as before.

The samples were mixed by repeatedly inserting and withdrawing a metal spatula to simulate the production process mixing. The samples were cured for 24 hours in an oven heated to 50°C, and then transferred to the Environmental Technologies (ET) group within Rocky Flats Technology Development for TCLP testing. ET prepared the samples per standard TCLP requirements with leach levels of metals measured with an Inductively Coupled Plasma (ICP) spectrometer. The numeric average (x_{avg}) and standard deviation (σ) or pooled standard deviation (s_p) of the leachability for each element were calculated to determine the upper confidence limit (UCL) of the leachability at a 90% confidence level using the following equations:^[8,9]

$$x_{avg} = \sum x_{leachability} / n, \quad (1)$$

where, n = number of data points,

$$90\% \text{ UCL} = x_{avg} + (1.2804 \times \sigma), \quad \text{or} \quad (2)$$

$$90\% \text{ UCL} = x_{avg} + (1.2804 \times s_p). \quad (3)$$

The 90% UCL defines the upper leachability limit assuming the leachability follows a normal distribution. The numeric average and upper limit can be directly compared to the maximum allowable limits established by the Environmental Protection Agency (EPA).^[10] The Colorado Department of Public Health and the Environment (CDPHE) is responsible for enforcing RCRA in Colorado. CDPHE expects Rocky Flats to

adopt the Universal Treatment Standards (UTS) as established by the EPA.

The TCLP results from the 1,000 ppm spike, 5,000 ppm spike, and 10,000 ppm spike are shown in Table I. These results show excellent leach resistance for all metals tested up to 10,000 ppm with the 90% UCL being below the treatment standard for all three experiments. Data from the initial experiment also passed the TCLP testing but have not been included.

Silver Nitrate Studies

At Rocky Flats, silver nitrate is a small volume waste stream which is difficult to treat. This waste consists of several bottles of radioactively contaminated solutions with silver concentrations as high as 368,000 ppm. Recovery of the silver is not feasible due to radioactive contamination. This waste is scheduled to be processed in the previously described production process for treating analytical laboratory solutions. Surrogate solutions with a similar composition as the analytical laboratory solution were prepared. These solutions were spiked solely with silver in the form of AgNO_3 at concentrations of 100, 1,000, 10,000, 50,000, 100,000, and 500,000 mg/L, respectively. The required quantities of silver nitrate were dissolved in 500.0 grams of distilled water after which 90.0 grams of NaCl and 80.0 grams of KNO_3 were added. Finally, 2.0 grams of NaOH were added to neutralize the solution. Each solution was added to the cement/Ramcote® mixture, mixed, cured at 50°C for 24 hours, and transferred to ET for TCLP testing.

The results of this TCLP testing are shown in Table II. Analysis of the data shows all samples to pass the UTS for Ag at levels up to 100,000 ppm. Samples spiked with 500,000 ppm Ag, however, failed the TCLP test. These samples had a brown interior and a metallic-like coating which was presumably silver metal from a reduction of Ag^+ ions to Ag^0 . It is believed that the NaCl reacted with AgNO_3 to form AgCl which is generally less soluble.^[11] As the amount of AgNO_3 was increased to the higher levels, however, there was insufficient NaCl available in solution to form AgCl. This resulted in excess Ag being available in the 500,000 ppm spike (as a metal or soluble compound) and resulted in this sample failing the TCLP test. The 90% UCL was also noted to be unusually high for samples spiked from 100 to 100,000 ppm. This was due to excessive scatter in the TCLP data which skewed the pooled standard deviation.

Fluidized Bed Incinerator (FBI) Ash

Rocky Flats produced a Fluidized Bed Incinerator (FBI) ash from the fluid bed incineration of compressor oils, crankcase oils, office trash, solid waste, and diesel fuel. This ash also contains a significant amount of sodium carbonate (Na_2CO_3), which was used as an acid sorbent in the bed, and spent chromia-alumina ($\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$) oxidation catalyst.

For the cementation of incinerator ash, a Taguchi experiment was designed to evaluate fly ash loading (0%, ≈12%, and ≈23%), waste loading level (20%, 25%, or 30%), water/cement ratio (0.5, 0.6, or 0.7), and cement type (type I/II or type V). These levels were based on preliminary testing with a surrogate ash which had similar physical properties to the actual ash waste. Attributes to be analyzed were mix viscosity, waste form density, waste volume increase, and resistance to degradation after freeze-thaw cycling. This experiment did not consider interactions between the variables. Nine experimental runs were required to complete this test phase.

A "best case" (low catalyst-high carbonate) and "worst case" (high catalyst-low carbonate) surrogate ash samples were prepared by the Technology Development/Waste Projects group based on process knowledge. These formulations are shown in Tables III and IV. Samples of each were prepared and spiked with heavy metal compounds of Ag, Ba, Cd, Pb, and Ni; the spike level for each was 1,000 ppm of each heavy metal. Cr was spiked into the surrogate in the form of the chromia-alumina catalyst. These surrogate wastes were mixed into cement using a 30% waste loading, cured at 50°C, and submitted for TCLP analysis. The results from these tests showed all heavy metal concentrations, except for Cr, to be below the treatment standard limits (refer to Table V). Additional samples were prepared with only the catalyst and cemented using waste loadings of 20% and 30%. The results from these tests showed the 20% waste loading yielded a waste form which met the treatment standard of 5.0 ppm for Cr (refer to Table V). The 30% waste loading sample again failed the TCLP test for Cr. The cause for this is still being investigated. In future studies, ash will be mixed with cement using a 20% waste loading and a water/cement ratio of approximately 0.6. This work is scheduled to be conducted in mid-1995.

Hydroxide Precipitation Sludge

The hydroxide precipitation sludge was created from a process in Building 374 which consisted of adding magnesium sulfate, calcium chloride, iron(III) sulfate, and diatomaceous earth to an aqueous waste stream entering the building. The waste stream originated from several diverse locations such as storm water runoff and the analytical laboratories' process aqueous waste. Potassium hydroxide was added to the waste until the pH was greater than 10.5 which created a precipitation of magnesium, calcium, and iron ions along with most other metallic cations in the waste stream. The sludge was produced at a rate of approximately 18.5 m³ per year when the process was operational (pre-1990). Because the sludge is a mixed waste, it must be treated to meet RCRA-LDR standards. Process knowledge indicated that the waste stream had no appreciable concentrations of ions except for the various nitrate salts. Therefore, a surrogate waste was developed which was based almost entirely on the chemical additions to the waste stream and represents the composition of the waste prior to any pre-treatment. The composition of the surrogate waste is shown in Table VI.

For cementing the sludge, a Taguchi experiment was designed to evaluate the effect of the following independent variables: class F fly ash loading (0% or ≈23%), waste loading (20% or 30%), water/cement ratio (0.5 or 0.6), and cement type (type I/II or type V). Interactions between specific variables (fly ash loading-waste loading, fly ash loading-water/cement ratio, and waste loading-water/cement ratio) were also considered. Waste loading considered the waste as a dry powder. The attributes tested were mix viscosity, waste form density, waste volume increase, and sample weight change after 12 freeze-thaw cycles. Determining the effect of changing the independent variables on the attributes requires calculating the degrees of freedom (DF), response total (RT), correction factor (CF), total sum of squares (SS_{Total}), individual factor sum of squares (SS_{Factor}), and mean square (MS). These are defined below:

$$DF = n - 1 \text{ (DF= 2 for each factor and } n = \text{ number of trials),} \quad (4)$$

$$RT = \text{Summation } (\Sigma) \text{ of the individual responses,} \quad (5)$$

$$CF = (RT)^2/n, \quad (6)$$

$$SS_{\text{Total}} = \Sigma (\text{Response}^2) - CF, \quad (7)$$

$$SS_{\text{Factor}} = (\Sigma \text{ Factor at level 1} - \Sigma \text{ Factor at level 2})^2 / \text{Number of responses,} \quad (8)$$

$$MS_{\text{Factor}} = SS_{\text{Factor}} / DF \quad (9)$$

The pooled error is used to calculate the F-Ratio per the following equation:

$$\text{F-Ratio} = MS_{\text{Factor}} / DF_{\text{Pooled error}} \quad (10)$$

F-Table values were chosen at a pre-determined 95% confidence level.^[8]

Analysis of variance (ANOVA) tables were prepared to analyze these attributes to determine the significance of the independent variables and the interactions. For viscosity, the viscometer reading at 300 revolutions per minute (rpm) was selected as the point of reference as the cement tends to gel at lower viscometer settings thus increasing the measurement error. Freeze-thaw cycling consisted of freezing the samples at -30°C for 24 hours followed by thawing the samples at 50°C for 24 hours to complete one freeze-thaw cycle. This process was completed for 12 cycles for the samples. The sample weight percent change chosen as the parameter to be evaluated during freeze-thaw cycling because the samples were kept in the plastic vials during the tests. Any dimension changes in the samples would be masked by the presence of the plastic shell. ANOVA tables for cement density, waste percent volume increase, and final percent weight change (12 completed freeze-thaw cycles) are shown in Tables VII-IX.

Statistical analysis showed that none of the independent variables had a significant effect on the cement mix viscosity. The variation in the viscosity was insufficient to produce a significant variable. Observations indicated that batches with higher waste loadings and lower water/cement ratios yielded a more fluid mix when fly ash was incorporated. This is due to the lubricating properties of the fly ash particles. As expected, additional water in the mix made it less viscous, while higher waste loadings caused the mixture to thicken. The only batch which did not yield a workable mixture was the mixture with a low water/cement

ratio and a high waste loading. This produced a tacky viscous mixture which had poor flow characteristics.

Some variables, while not significant with respect to mix viscosity, are known to improve the mixing consistency. The water/cement ratio will be important during scaled mixing using conventional mixing equipment. The Hobart mixer used in laboratory studies is capable of adequately mixing all batches with little or no problem since it is a robust mixer which can tolerate wide ranges of viscosities. Scaling the process to a larger mixer may require compositional adjustments as the larger mixers are not usually as rugged as the Hobart. Poor mixing would result in a non-homogeneous waste form; therefore, a minimum water/cement ratio of 0.6 is recommended for future testing.

The statistical analysis of the waste form density showed three variables to be significant (refer to Table VII). These variables were fly ash addition (A), waste loading (B), and water/cement ratio (C). Cement type (D) was not significant. These results allow one to estimate and predict the waste form density based on these results. This is accomplished by averaging the density obtained for a given level 1 value and also at the level 2 value. For example, the level 1 average for the 0% fly ash was 1.91 gm/cc whereas the average value for the level 2 experiments (\approx 23% class F fly ash) was 1.83 gm/cc. These results are shown graphically in Figure 1. One drawback to this modeling approach is that there are only two data points; therefore only linear relationships are considered. A confirmation test showed moderate agreement with the experimental results (refer to Figure 1).

For waste loading, the average density obtained for a 20% waste loading was 1.84 gm/cc, while the average density at a 30% waste loading was 1.90 gm/cc. These results are shown graphically in Figure 2. Confirmation test results show a linear relationship and excellent agreement between the two sets of data. Increasing the waste loading increases the waste form density, the packing efficiency, and the final weight of the waste container. The differences observed would result in a minimal increase in weight for a 55-gallon waste drum. Finally, the additional water causes the cement mix density to decrease. The average density obtained at a water/cement ratio of 0.5 was 1.91 gm/cc while the average density at a water/cement ratio of 0.6 was 1.83 gm/cc.

For waste volume, the statistical analysis of the data showed only one variable, waste loading (B), to be a significant (refer to Table VIII). Volumes were extrapolated from known quantities or calculated using density and mass measurements. These calculations were made using the following equations:

$$\text{Volume} = \text{Total Mass}/\text{Average Waste Form Density, and} \quad (11)$$

$$\% \text{ Volume Change} = (\text{Final Volume} - \text{Initial Volume})/\text{Initial Volume} \times 100. \quad (12)$$

Increasing the waste loading from 20% to 30% substantially decreased the volume of the cemented waste form. The average volume increase at a 20% waste loading was 133% when considering the volume of the waste as a slurry (waste plus the addition of 40% water) while a 30% dry waste loading resulted in a volume increase of only 50% (refer to Figure 3). Data obtained during confirmation tests showed excellent confirmation of these results. These predictions can be used to minimize the volume increase of the final waste form to maximize storage space without sacrificing the durability of the waste form. The volume increases observed in this testing are sufficiently low to make cementation a viable waste stabilization technology for the sludge waste.

The statistical analysis of the waste form weight change after 12 freeze-thaw cycles showed two variables to be significant at a 95% confidence level (refer to Table IX). These variables were waste loading (B) and water/cement ratio (C). The results predict that increasing the dry powder waste loading from 20% to 30% decreases the weight loss. Data obtained during this experiment showed the weight loss to decrease from 2.76% to 1.45%. This is shown graphically in Figure 4. The reduced weight loss is due to the reduced moisture content that results from increasing the waste loading; the weight loss was attributed primarily to evaporation from the sample and not sample degradation. Likewise, increasing the water/cement ratio caused the weight loss to increase which again was due to evaporation from the material even though efforts were made to keep the vials sealed during testing. The data obtained during this experiment showed the weight loss to increase from 1.83% to 2.53% by increasing the water/cement ratio from 0.5 to 0.6.

Visual examination of the freeze-thaw samples showed no noticeable physical degradation. These freeze-thaw samples were sealed in plastic vials during cycling to minimize evaporation. Visual examination of samples exposed to the atmosphere showed minor surface cracking on samples containing class F fly ash and a 20% dry powder waste loading. It was possible to fracture these samples by hand with some effort. This was not possible on samples prepared using cement only. This is probably due to the high fly ash loading level which lowered the cement hydration and decreased the strength of the samples. The exposure cracking should not present a problem based on current LDR requirements with the waste form sealed in a drum or crate.^[12] There was also significant salt migration to the top and side surfaces of samples not containing fly ash. The presence of the fly ash in the mix tends to reduce the pore pressure within the samples and thereby decrease the migration of salt and moisture to the outer surface.

As part of the evaluation of the sludge, specimens were prepared and submitted for TCLP analysis. Heavy metals (Cd, Cr, Ba, Pb, Ni, and Ag) were spiked at a level of 1,000 ppm based on an aqueous sludge waste (sludge powder with 40% added water). This represents an extreme value as no appreciable heavy metal ions are in the waste based on process knowledge. An initial set of five samples was prepared and mixed by hand using a 30% dry powder waste loading and a water/cement ratio of 0.55. The higher water/cement ratio was used to yield a more fluid mix. The results (refer to Table X) show good leach resistance for all metals but lead. Five of the six TCLP data points for lead were well below the established treatment standard for lead. It was believed that the one non-compliant point was an anomaly, so the test was repeated and all data points were well below the treatment standard value. This test was repeated using a 20% waste loading and a 30% waste loading with fly ash partially substituted for cement (refer to Table X). When the standard deviation was pooled and the isolated data point for lead was excluded, the leachability for lead was below the allowable limit of 0.37 ppm.

Samples of the cemented surrogate bypass sludge waste were analyzed by x-ray diffraction (XRD) and scanning electron microscopy (SEM) to detect the possible presence of expansive crystalline phases in the cemented waste. These analyses were conducted approximately 6 months after the experiment had been completed since these phases typically require significant time to form. XRD detected the presence of a small amount of ettringite ($6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_4\cdot 32\text{H}_2\text{O}$) which could be problematic if present in sufficient quantities. The use of a type V cement could minimize the expansion problems associated with the presence of this crystal phase. The quantity of the crystalline phase in the waste was determined to be insignificant at this time.^[12] Samples will be routinely examined (approximately every two months) so that corrective measures can be taken if the amount of ettringite increases with time.

DETOX Solution from the DELPHI Process

The final waste stream studied is a strong acidic solution used in a chemical oxidation process being developed by Delphi, Inc., of Albuquerque, NM. This technology is being tested as an alternative to incineration for the destruction of organics in various wastes. The solution, known as the DETOX solution, is prepared by adding 60% anhydrous ferric chloride (FeCl_3) to a 1.5 M hydrochloric acid solution. This strong acid, in the presence of a platinum-palladium-ruthenium catalyst, oxidizes combustible waste and reduces the waste volume. This acid must be neutralized and treated as a secondary waste prior to disposal. Since it is an aqueous waste, cementation is an appropriate technology to evaluate for stabilizing and immobilizing the RCRA listed species which may be present in the waste solution.

The phase I cementation evaluation was conducted using a factorial experimental design evaluating fly ash loading (0%, $\approx 14.4\%$, and $\approx 28.8\%$) and waste loading (35% and 50%). The attributes tested were mix viscosity, waste form density, waste volume increase, and freeze-thaw cycling. The DETOX solution was mixed according to instructions provided by Delphi, Inc. This yielded a highly acidic solution ($\text{pH} < 0$) which was neutralized with 1.5 N NaOH solution to a pH of 7-10. The neutralized solution was estimated to have a specific gravity slightly greater than water. During neutralization, the solution generated considerable heat; in fact, the solution boiled when attempting to neutralize the solution with 5 N and 10 N NaOH. The gas coming off the solution was a mixture of HCl and water which will require a scrubber in the production process. The use of the mildly basic solution resulted in a large volume increase as approximately 3-liters of NaOH solution were required to neutralize 250 ml of DETOX (volume increase of 1200%). Cement was added to the solution and mixed using a Hobart mixer and the samples were cured

in an oven at 50°C for 24 hours. The results from this experiment show the waste loading to be significant for each attribute evaluated. This is not surprising as the neutralized waste was mostly water with NaOH and solids precipitated from the DETOX solution.

The phase II cement evaluation was conducted to test the leach resistance of a cemented spiked solution. A sample of DETOX solution was spiked with Cd (50 ppm), Cr (150 ppm), Ba (250 ppm), Pb (2,500 ppm), Ni (150 ppm), and Hg (50 ppm). These levels were based on the anticipated waste reduction factor of 300:1 provided by Delphi. Samples were mixed with cement and cement/fly ash using a waste loading of 50%. These results have been completed on all elements but mercury but have not yet been received. All elements tested were below the EPA treatment standard limits.^[13]

Experimental Conclusions/Recommended Formulations

- 1) Based on the tests conducted with the surrogate waste, the analytical laboratory solution waste can be cemented into a monolith using the following: 42.3% type I/II cement, 22.8% Ramcote®, and 35% waste solution. The waste form produced has excellent leach resistance to Ni, Ba, Cd, Cr, and Pb at concentrations up to 10,000 ppm.
- 2) Based on the tests conducted with the silver nitrate waste, these solutions can be cemented into a monolith using the following: 42.3% type I/II cement, 22.8% Ramcote®, and 35% waste solution. This waste form has excellent leach resistance to Ag spike levels up to 100,000 ppm, but failed TCLP testing at 500,000 ppm.
- 3) Cementation of the incinerator ash produces an LDR compliant waste using a formulation of 20% waste, 53.3% cement, and 26.7% water based on the tests conducted with the surrogate waste and the older treatment standard which was applicable at the time of testing. Additional tests are required to further optimize the cement formulation for this waste stream.
- 4) Based on the tests conducted with the hydroxide precipitation sludge surrogate waste, the sludge should be cemented into a mixture consisting of the following: 30% dried sludge (50% in slurry form), 21.8% type I/II cement, 21.8% class F fly ash, and 26.25% water (water/cement ratio of 0.6). This can be mixed using standard mixing equipment and has adequate resistance to freeze-thaw cycling. This waste product has leach resistance to Cd, Cr, Ba, Pb, Ag, and Ni at concentrations up to 1000 ppm.
- 5) A waste loading of 30% of the sludge in cement produces a waste form which meets pertinent waste acceptance criteria. The volume increase of the waste form is only 50%, making cementation a practical waste stabilization technology for this waste stream. Increasing the waste loading to 33% further reduces the volume increase to approximately 35%.
- 6) Class F fly ash, partially substituted for cement in the sludge waste formulation, improves the fluidity of the cement-waste mixture and can be used to reduce the water loading requirements. The substitution of fly ash for 50% of the cement (total loading of ~23% class F fly ash) showed no noticeable degradation on the sample after 12 freeze-thaw cycling tests. The presence of fly ash in the mix also reduced salt migration to the exterior surface of the samples due to a reduced internal pore pressure.
- 7) In tests conducted with the surrogate sludge waste, the presence of ettringite may require the use of type V cement (versus type I/II) to improve the resistance of the waste form to sulfate degradation.
- 8) Based on the initial tests conducted on the surrogate DETOX waste solution, cementation appears to be an effective stabilization technology for this waste. Initial tests with the neutralized acid have demonstrated waste loadings of 50% (from a neutralized acidic waste) can be cemented to produce an acceptable waste form. Samples have been submitted for TCLP analysis to confirm this. Additional refinements in the processing (i.e., neutralizing and drying the waste) will result in a reduced overall volume increase and produce a waste similar to the hydroxide precipitation sludge.

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**Table I: TCLP Data from Analytical Laboratory Solution Testing
Expressed in Parts per Million**

Sample	Cd	Cr	Ba	Pb	Ag	Ni
1,000 ppm						
X_{avg}	0.041	0.212	1.990	< 0.250	< 0.050	< 0.025
90% UCL	0.047	0.183	2.750	< 0.250	0.072	< 0.025
5,000 ppm						
X_{avg}	0.033	0.128	2.460	< 0.250	< 0.050	< 0.025
90% UCL	0.039	0.168	1.940	< 0.250	< 0.050	< 0.025
10,000 ppm						
X_{avg}	0.033	0.231	2.635	0.250	0.071	0.025
90% UCL	0.042	0.279	4.253	0.263	0.191	0.035
UTS[10]	0.19	0.86	7.6	0.37	0.30	5.0

UTS - Universal Treatment Standard

**Table II: TCLP Data of Silver Nitrate Solution Testing
Expressed in Parts per Million**

	100 ppm	1,000 ppm	10,000 ppm	100,000 ppm	500,000 ppm
X_{avg}	0.050	0.067	0.067	0.052	0.763
90% UCL	0.170	0.187	0.187	0.172	0.883
UTS[10]	0.30				

Table III: "Best Case" Ash Composition

<u>Material</u>	<u>Weight Percent</u>
Catalyst - Cr ₂ O ₃ /Al ₂ O ₃	20.70
Sodium Carbonate - Na ₂ CO ₃	24.10
Sodium Chloride - NaCl	14.80
Sodium Sulfate - Na ₂ SO ₄	4.60
Coconut Charcoal - Ground Carbon	6.90
<u>Class F Fly Ash</u>	<u>28.90</u>
Total	100.00

Table IV: "Worst Case" Ash Composition

<u>Material</u>	<u>Weight Percent</u>
Catalyst - Cr ₂ O ₃ /Al ₂ O ₃	32.00
Sodium Carbonate - Na ₂ CO ₃	5.70
Sodium Chloride - NaCl	19.90
Sodium Sulfate - Na ₂ SO ₄	4.00
Coconut Charcoal - Ground Carbon	5.00
<u>Class F Fly Ash</u>	<u>33.40</u>
Total	100.00

**Table V: TCLP Data from "Best Case" Ash, "Worst Case" Ash,
20% Waste Loading, and 30% Waste Loading
Expressed in Parts per Million**

Sample	Cd	Cr	Ba	Pb	Ag	Ni
Best Case						
x_{avg}	0.027	14.10	0.311	0.250	0.050	0.025
90% UCL	0.032	16.61	0.345	0.250	0.050	0.025
Worst Case						
x_{avg}	0.032	13.60	0.806	0.250	0.050	0.025
90% UCL	0.043	15.58	0.904	0.250	0.050	0.025
*20% Waste						
x_{avg}		1.902				
90% UCL		2.637				
*30% Waste						
x_{avg}		10.93				
90% UCL		13.18				
UTS	1.0	5.0	100	5.0	5.0	5.0

* - Spiked only with Cr_2O_3/Al_2O_3 Catalyst

Table VI: Bypass Surrogate Sludge Composition

<u>Material</u>	<u>Weight Percent</u>
Iron Oxide - Fe_2O_3	16.50
Magnesium Hydroxide - $Mg(OH)_2$	8.03
Calcium Sulfate - $CaSO_4 \cdot 2H_2O$	14.34
Calcium Hydroxide - $Ca(OH)_2$	24.34
Potassium Nitrate - KNO_3	28.53
<u>Diatomaceous Earth</u>	<u>8.26</u>
Total	100.00

Table VII: ANOVA Table for Waste Form Density

Source	SS	DF	MS	F-Ratio	F-Table
A	0.0889	1	0.0889	18.88	7.71
B	0.0522	1	0.0522	11.09	7.71
AxB	0.0072	1	0.0072		
C	0.0910	1	0.0910	19.32	7.71
AxC	0.0003	1	0.0003		
BxC	0.0036	1	0.0036		
D	0.0078	1	0.0078		
Error	0.0100	56			
Pooled Error	0.0188	4	0.0047		

Table VIII: ANOVA Table for Waste Percent Volume Increase

Source	SS	DF	MS	F-Ratio	F-Table
A	0.0135	1	0.0135	7.45	7.71
B	1.3572	1	1.3572	748.93	7.71
AxB	0.0032	1	0.0032		
C	0.0133	1	0.0133	7.36	7.71
AxC	0.0003	1	0.0033		
BxC	0.0023	1	0.0023		
D	0.0013	1	0.0013		
Error	0				
Pooled Error	0.0072	4	0.0018		

Table IX: ANOVA Table for Percent Weight Change After 12 Freeze-Thaw Cycles

Source	SS	DF	MS	F-Ratio	F-Table
A	0.2873	1	0.2873		
B	3.3996	1	3.3996	19.22	6.61
AxB	0.1141	1	0.1141		
C	1.4145	1	1.4145	8.00	6.61
AxC	0.1554	1	0.1554		
BxC	0.1671	1	0.1671		
D	0.1604	1	0.1604		
Error	0				
Pooled Error	0.8842	5	0.1768		

Table X: TCLP Data of Spiked Surrogate Bypass Sludge Expressed in Parts per Million

Sample	Cd	Cr	Ba	Pb	Ag	Ni
30% Waste						
x_{avg}	0.041	0.249	0.709	0.335	0.087	0.025
90% UCL	0.051	0.298	1.105	0.455	0.155	0.025
20% Waste						
x_{avg}	0.049	0.211	1.638	0.250	0.079	0.025
90% UCL	0.059	0.260	2.034	0.371	0.147	0.025
30% Waste 11% Fly Ash						
x_{avg}	0.036	0.177	2.87	0.251	0.119	0.025
90% UCL	0.046	0.226	3.27	0.371	0.187	0.025
30% Waste 23% Fly Ash						
x_{avg}	0.047	0.173	1.52	0.250	0.051	0.025
90% UCL	0.046	0.226	3.27	0.371	0.118	0.025
UTS^[10]	0.19	0.86	7.6	0.37	0.30	5.0

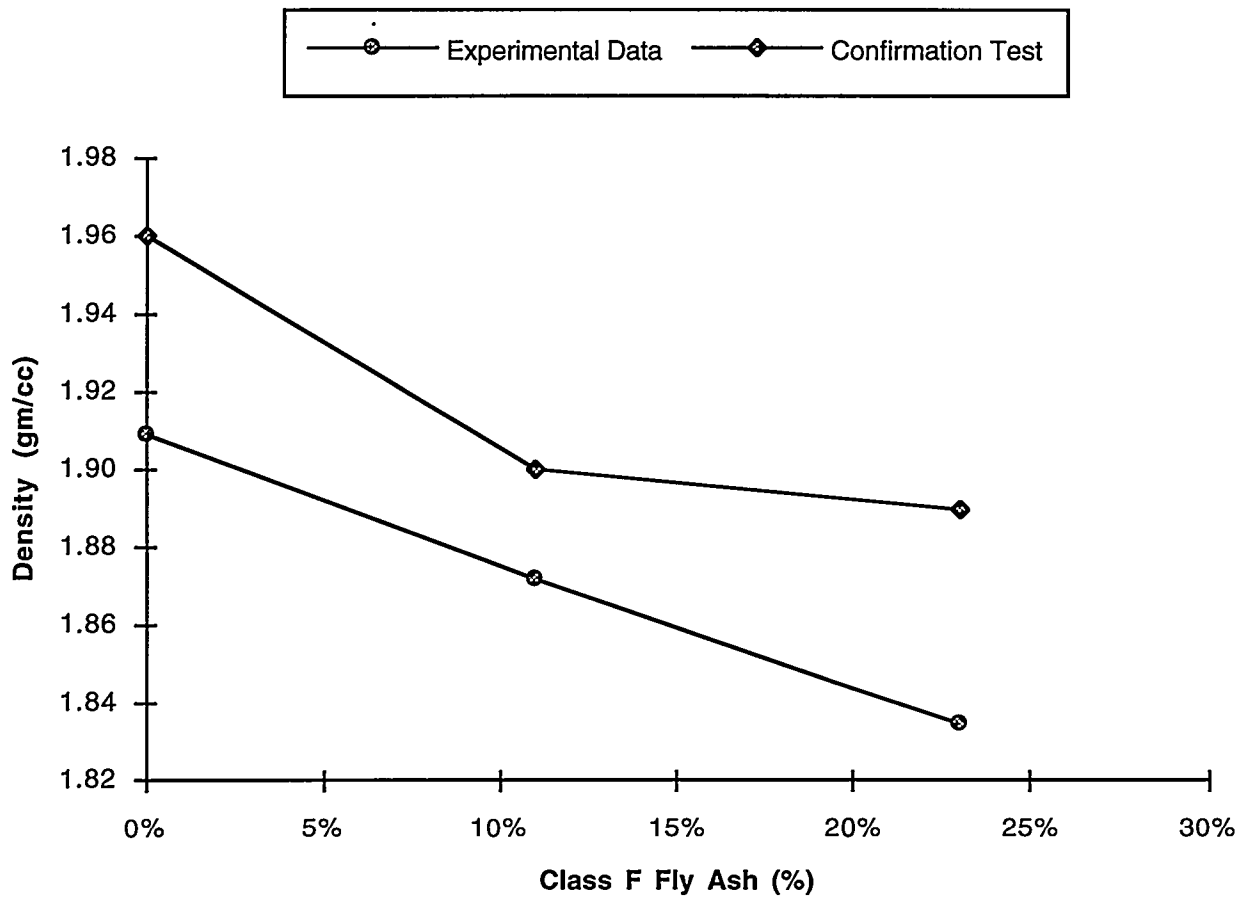


Figure 1: Cemented Sludge Waste Form Density as a Function of Class F Fly Ash Loading.

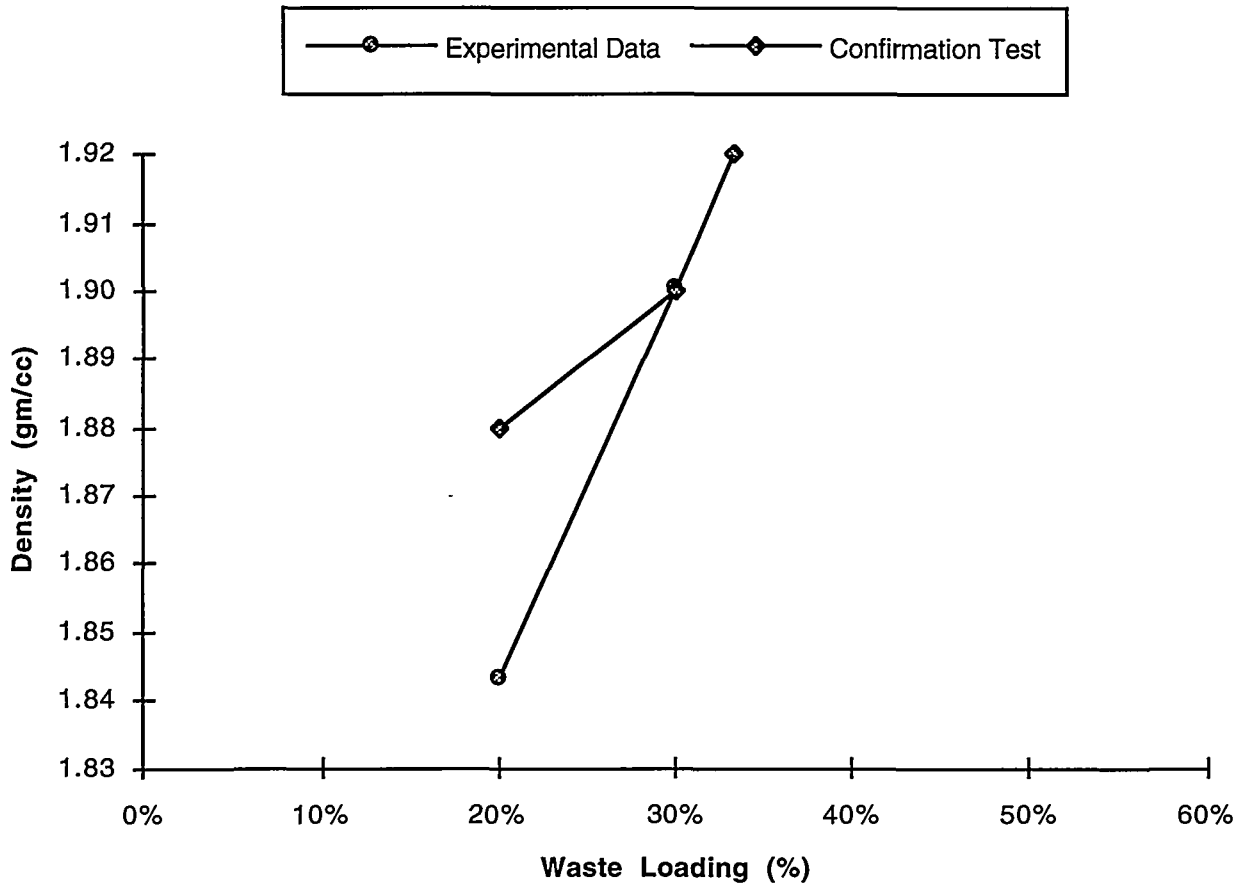


Figure 2: Cemented Sludge Waste Form Density as a Function of Sludge Waste Loading.

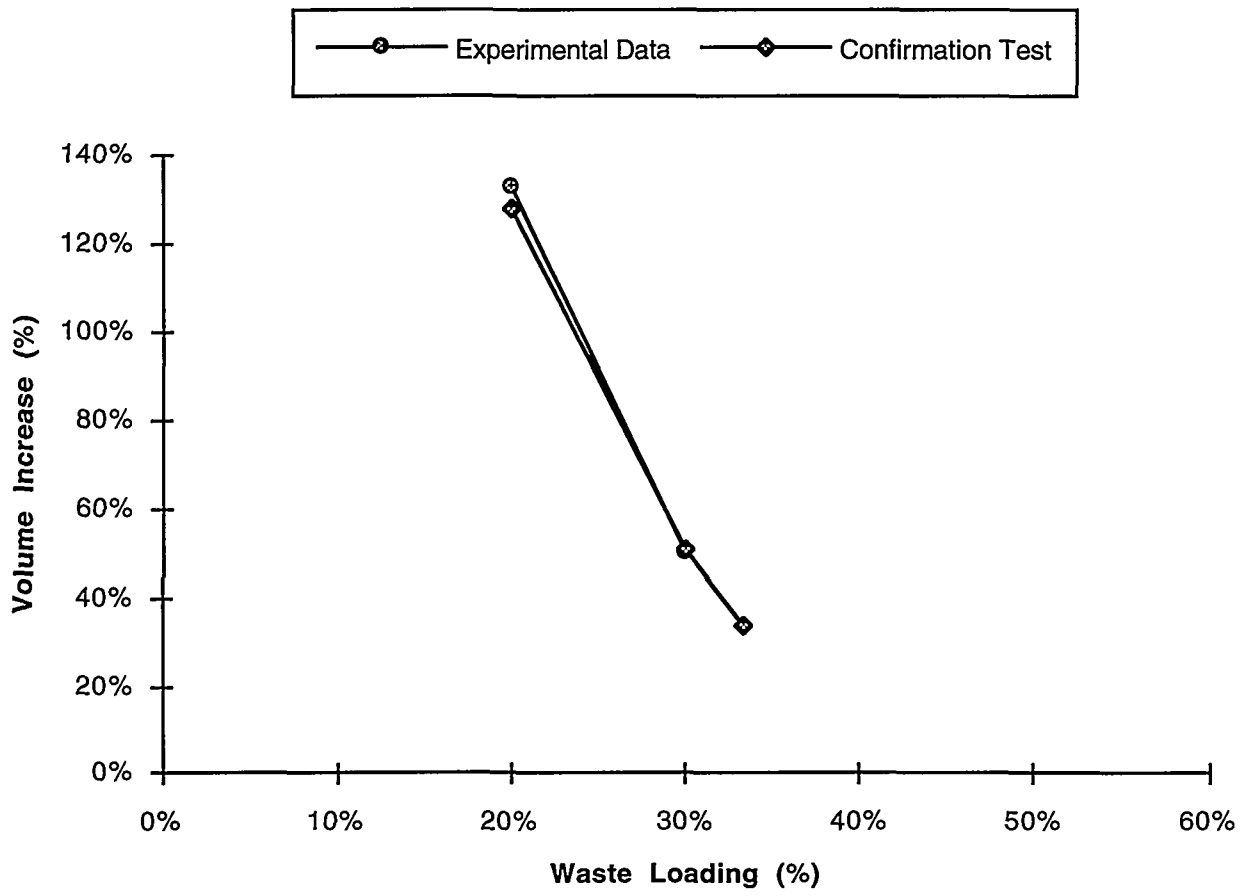


Figure 3: Cemented Sludge Waste Form Volume Increase as a Function of Sludge Waste Loading.

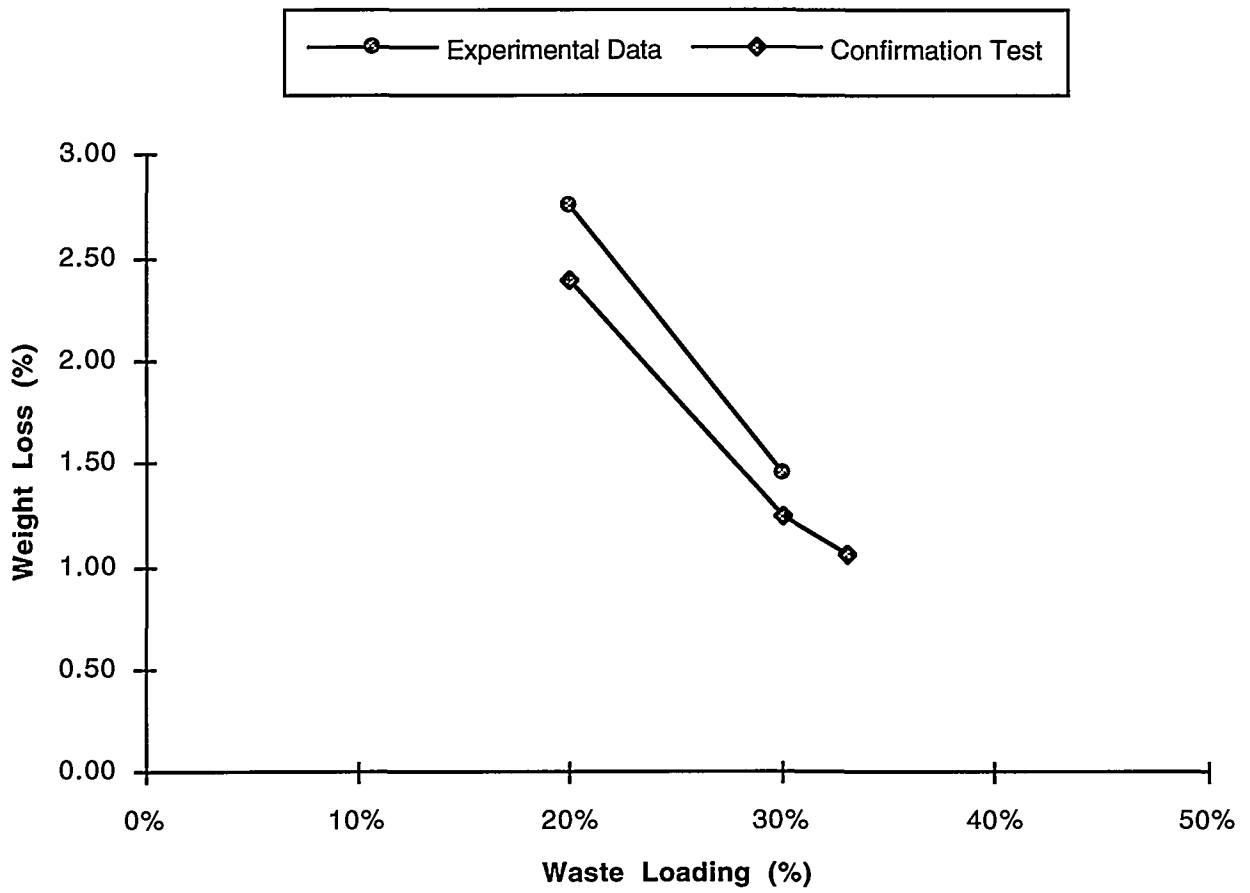


Figure 4: Cemented Sludge Waste Form Weight Loss as a Function of Sludge Waste Loading After 12 Freeze-Thaw Cycles.