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WASTE-FORM DEVELOPMENT FOR CONVERSION TO PORTLAND CEMENT AT LOS ALAMOS NATIONAL LABORATORY (LANL) TECHNICAL AREA 55 (TA-55)

by

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ABSTRACT

The process used at TA-55 to cement transuranic (TRU) waste has experienced several problems with the gypsum-based cement currently being used. Specifically, the waste form could not reliably pass the Waste Isolation Pilot Plant (WIPP) prohibition for free liquid and the Environmental Protection Agency (EPA)-Toxicity Characteristic Leaching Procedure (TCLP) standard for chromium. This report describes the project to develop a Portland cement-based waste form that ensures compliance to these standards, as well as other performance standards consisting of homogeneous mixing, moderate hydration temperature, timely initial set, and structural durability. Testing was conducted using the two most common waste streams requiring cementation as of February 1994, lean residue (LR)- and oxalate filtrate (OX)-based evaporator bottoms (EV). A formulation with a pH of 10.3 to 12.1 and a minimum cement-to-liquid (C/L) ratio* of 0.80 kg/l for OX-based EV and 0.94 kg/l for LR-based EV was found to pass the performance standards chosen for this project. The implementation of the Portland process should result in a yearly cost savings for raw materials of approximately $27,000 over the gypsum process.

INTRODUCTION

TA-55 houses a variety of operations related to plutonium processing. The intended destination of the TRU wastes generated from these operations is the WIPP repository. Accordingly, these wastes must be in compliance with the WIPP-Waste Acceptance Criteria (WAC).[1] The majority of the wastes at TA-55 meet the WIPP-WAC in their initial state. However, particulates# and free liquids (aqueous and nonpolar organic) require further treatment to meet the WIPP criteria designed to reduce respirability and dispersibility of these wastes. The purpose of the TA-55 cementation operation is to convert these particulate and liquid wastes to a solid, cohesive form that meets the WIPP-WAC.

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* The C/L ratio is used in this report to express the relationship between the cement weight and total liquid volume. The liquid includes the water and ionic components used to prepare the surrogate waste and the NaOH solution used for pH adjustment. In order to remain historically consistent with TA-55 operations, this ratio is used instead of the dimensionless water-to-cement ratio commonly used in the cement industry.

This work was performed under Revision 4 of the WIPP-WAC, which required the immobilization of particulates. Since then, Revision 5 of the WIPP-WAC has been issued. Revision 5 does not require the immobilization of particulates although it does not prohibit their immobilization.

Initially, Portland cement was used as the fixation agent in the TA-55 process, but in 1983 a gypsum/polymer-based cement named Envirostone* was substituted. Envirostone's setting reaction involves the hydration of hemihydrated calcium sulfate ($CaSO_4 \cdot 1/2H_2O$) to the dihydrated form ($CaSO_4 \cdot 2H_2O$). The polymer component serves to reduce permeability within the solidified waste form.[2] There were three reasons for the conversion to Envirostone. First, Envirostone was more compatible with TA-55's nonpolar organic liquid waste. Second, while Portland's setting reaction required an alkaline pH, Envirostone's was compatible with an acidic pH. Since the EV waste is highly acidic, less caustic solution was therefore needed with Envirostone for pH adjustment. Third, the lower pH required for Envirostone reduced the ammonia-based fumes that had previously obscured visibility for the process operator.#

Envirostone served TA-55's cementation needs well until the cementation operation came under the jurisdiction of the more stringent WIPP-WAC and the EPA-Resource Conservation and Recovery Act (RCRA) regulations concerning characteristic toxicity.[3] It then became apparent that Envirostone exhibited several deficiencies that outweighed the benefits of its use. These deficiencies related to free-liquid generation in violation of the WIPP-WAC restriction on such and failure to meet the EPA-RCRA standard for leaching resistance for chromium. Portland cement was found to be a superior performer in both of these areas.[4,5] This report will review the investigation into the performance of Portland cement and describe the development of a Portland cement waste form to address the problems associated with Envirostone.

RATIONALE FOR PURSUING PORTLAND CONVERSION

Radiolytic Free-Liquid Generation: The first inadequacy with Envirostone became apparent in 1989 with the discovery that Envirostone cemented waste forms were generating free liquid several weeks after cementation.[6,7] This liquid generation resulted in the decertification of the TA-55 cementation process to produce waste forms acceptable for WIPP. A significant effort was subsequently initiated to find the cause of and arrest the phenomenon.[7-12] Several mechanisms capable of producing liquid were investigated and discarded.[9,12,13] These included the occurrence of a polymerization reaction having H_2O as a by-product and reversal of the calcium sulfate hydration reaction+. Polymerization was eliminated when Envirostone without the polymer component (plaster of Paris) was found to likewise generate free liquid. Dehydration was eliminated when x-ray powder diffraction analysis found no change in the $CaSO_4$ molecule following free-liquid generation.

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* Envirostone is a trademark of the United States Gypsum Company.

The NH_4 content of the waste streams has decreased since the previous Portland operation to the extent that fuming should no longer be excessive at a high pH.

\+ The type of polymerization reaction taking place in Envirostone was unknown because the identity of the polymer component was proprietary. However, if the reaction was a condensation-type polymerization, H_2O would be generated as a by-product. If the cement had already hardened when the polymerization took place, the H_2O may have be seen as free liquid.

The free-liquid mechanism was ultimately shown to be irradiation-induced when it was found that cemented surrogate-waste samples subjected to gamma irradiation produced free liquid, while unirradiated samples did not.[7,12,13] A phenomenon that is compatible with this finding was radiolysis of the water in the pores of the cement structure to produce H_2.[14-16] It was conceivable the H_2 built up sufficient internal pressure to force residual liquid to the surface. This mechanism was investigated at Hanford[17-20] and LANL for its potential to generate free liquid in cemented waste forms. Hanford workers showed that free-liquid generation is related to the waste form's compressive strength and permeability.[19] Work was also done at Hanford to develop a computer model to predict the occurrence of radiolytic free liquid based on a waste form's permeability, gas generation rate, and internal pressurization.[20] Work at LANL with actual waste showed that increasing either the C/L ratio or mixing time reduced the occurrence and volume of free liquid,[9,11,12] presumably because of a resulting reduction in pore size and therefore in permeability.[21] Very good results were achieved in the LANL full-scale operation by extending the mix time into the setting stage until the mixer began to lose its ability to generate a surface vortex.[9,10,22] However, because a few waste forms still generated free liquid,[11,22] the extended-mix technique was not considered to have entirely solved the problem.

A study was conducted to investigate the differences between Portland and Envirostone cements in their susceptibility to radiolytic free-liquid generation.[23] The study was also intended to determine if the Portland waste form would generate free liquid when produced under conditions conducive to high permeability, namely a low C/L ratio and low-energy mixing.* A 590 rad/min ^{60}Co gamma source was used to simulate the radiolytic effects of alpha irradiation in the actual waste. In this study, the Envirostone sample generated liquid after 2.5×10^6 rads in 3 days. The testing was continued to 8.1×10^7 rads (95 days) with the Portland sample producing no free liquid during this time. These results demonstrated the superiority of the Portland waste form in suppressing radiolytic free-liquid generation, even when produced under substandard conditions.

Leaching Resistance: In 1992, the Envirostone waste form was found to be unable to meet the nonhazardous limit for chromium as defined by the EPA. This inadequacy was first indicated in leaching studies using surrogate EV waste[25] and later confirmed with actual EV waste studies.[26] Both tests also showed Portland waste forms had at least an order of magnitude higher leaching resistance for total chromium (Cr^{+3}/Cr^{+6}) in the TCLP. Portland cement also showed superior leaching resistance for cadmium and lead, two other metals found to have elevated concentrations in the EV waste. The graphical comparisons of TCLP performance in the surrogate- and actual waste tests using Envirostone and Portland cement are shown in Figures 1 and 2.

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* The ability of Portland waste forms to suppress radiolytic free-liquid generation completely had previously been questioned after the discovery in 1992 of free liquid in some Portland drums produced before the conversion to Envirostone in 1983.[24] However, the quality of these waste forms was considered poor because very low-energy (manual) mixing was used to produce them. In addition, no records were available that documented the C/L ratio used to produce these waste forms. Substandard conditions may have resulted in excessive bleed-water formation and/or an increase in permeability that allowed radiolytic free-liquid generation.

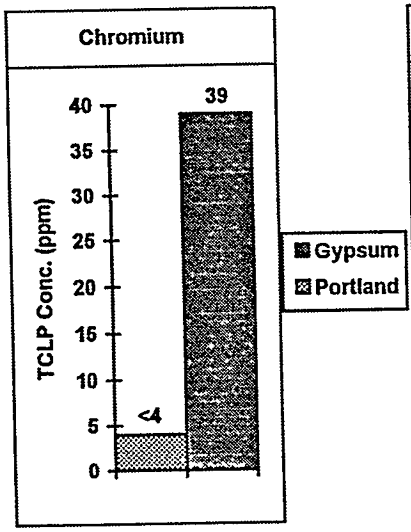

Fig. 1. TCLP performance with surrogate EV. Initial Cr conc. = 1000 ppm. Cr leach resistance* = >92% in Portland, 22% in gypsum.

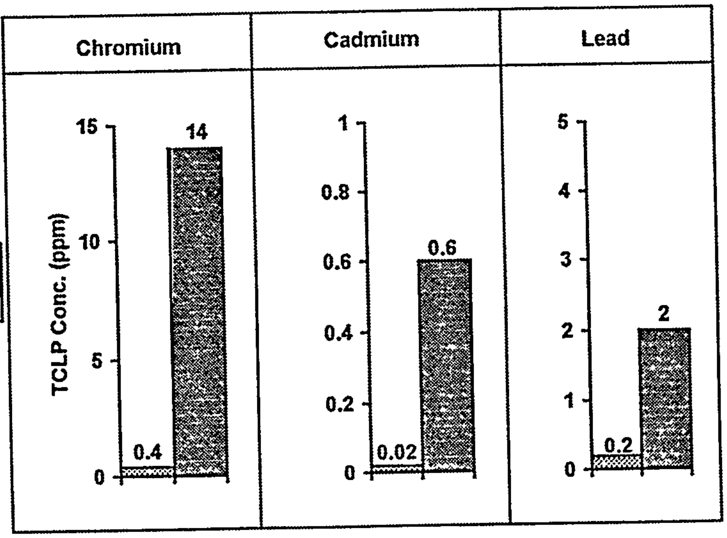

Fig. 2. TCLP performance with actual EV. Initial conc.# ≅ 1201 ppm Cr, 32 ppm Cd, 166 ppm Pb. Cr leach resistance = 99.3% in Portland, 78.5% in gypsum; Cd leach resistance = 98.6% in Portland, 64.7% in gypsum; Pb leach resistance = 97.5% in Portland, 76.9% in gypsum.

DEVELOPMENT OF THE PORTLAND WASTE FORM

Waste stream characterization: The surrogate waste used in this project consisted of only EV waste because of its predominance in TA-55's waste streams that require cementation. In order to prepare surrogate mixtures that accurately reflect current conditions, a characterization study of the EV waste streams was conducted.[27] For this study, all EV waste batches produced from April 1992 to February 1994 were analyzed for historically-present cations and anions, RCRA metals, and other components that can interfere with the Portland setting reaction. The results were sorted into the three major categories of EV waste: LR-based, OX-based, and hot distillate-based EV streams. The primary difference between the first two categories was that the LR-based EV had a high concentration of calcium and magnesium, while the OX-based EV had a high concentration of sodium and oxalate. The composition of the hot distillate-based waste+ was similar to the LR-based waste composition. Because of this similarity, testing with hot distillate-based surrogate was not included in this project. The data defining these waste streams are listed in Appendix 1.

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* Leach resistance indicates the ability of the cement to retain the RCRA metals during the TCLP and can be defined as the percentage of the initial metal concentration that remains in the waste form after the TCLP. The equation used to calculate the leach resistance is as follows (initial concentration is expressed in terms of the volume of the waste form):

$$\text{Leach Resistance} = \frac{\text{Initial conc.} - (\text{TCLP conc.} \times 20)}{\text{Initial conc.}} \times 100$$

\# Actual concentrations are higher in Envirostone waste forms and lower in Portland waste forms than these average values because of dilution differences arising from pH adjustment, cement type, and C/L ratio.

\+ Hot distillate is evaporator distillate that has not met the TA-55 plutonium concentration limit for discharge to the off-site treatment facility. The original source for this material (before evaporation) can be from the LR, OX, or any other process stream.

Waste Form Performance Standards: The following standards were devised to define satisfactory performance of the final waste form. These include the regulatory-based standards to meet the EPA TCLP limits to produce a non-mixed waste form and the WIPP-WAC restrictions on free liquid and particulates. Operational-based standards were included to ensure homogeneous mixing, timely setting for efficient process throughput, and an operating temperature low enough to prevent thermal damage of the drum packaging.

1) Adequate mixability

To ensure that the recommendations of this work will provide consistent results, the mixing must be thorough enough to yield a homogeneous paste. Therefore, the viscosity of the cement paste must not be above the maximum viscosity at which the mixing equipment can provide thorough mixing. This limiting viscosity was defined as the maximum viscosity at which center-to-edge mixing of the cement paste could still occur.* Dilution with water was necessary for samples with viscosities above this limit.

2) No free liquid at ≥24 hours following cementation

The requirement for absence of free liquid was necessary to meet the WIPP-WAC restriction on free liquid.[1] The 24-hour limit was considered desirable to ensure a reasonable throughput efficiency. The free liquid could be due to initial bleed water not reabsorbed or delayed generation of free liquid resulting from radiolysis. Adequate performance related to radiolysis would be defined by no generation of free liquid during a 10^8-rad exposure to a ^{60}Co gamma source.

3) Moderate hydration temperature

The objective of this standard was to prevent the failure of the vinyl drum bag as a result of excessive heat from the hydration reaction of the cement. The conservative estimate by the bag manufacturer for the failure temperature was 145°F.[28] Since the temperature of the cement monolith reached during hydration in a drum-scale sample would be higher than in the bench-scale tests, an assumption had to be made on what temperature ceiling to select for the bench-scale tests. Using the industry standard of an increase of 15°F per 100 lb of Portland cement,[29] the assumption was made that an increase of as much as 45°F could be seen on scale-up to the drum scale. This led to the range of acceptable temperatures being set at ≤100°F for the bench-scale experiments. All temperatures were taken at the center of the waste form. The actual full-scale temperature increase would be determined in a full-scale test.

4) Penetration resistance of ≥500 psi at 24 hours following cementation

To ensure a reasonable throughput efficiency, it was considered desirable that indication of a successful setting reaction should be seen within 24 hours after the start of cement addition. The condition used to indicate a successful set was 500 psi penetration resistance. This indicator was adopted from the American Society for Testing and Materials (ASTM) standard for determining the initial set of a cement sample.[30]

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* Center-to-edge mixing is defined as rotational movement of the cement surface extending to the point of contact with the wall of the mixing container.

5) Sustained compressive strength of ≥ 500 psi at 28 days following cementation

Minimum compressive strength was not needed to meet WIPP or EPA requirements. It was incorporated as a means to ensure the waste form was cohesive enough to resist breakdown to a particulate size prohibited by the Revision 4 WIPP-WAC. A minimum compressive strength of 500 psi was adopted for this study from the Nuclear Regulatory Commission's use of this level of strength as the best indicator of general physical durability for cemented waste.[31] The compressive strength data were collected according to the ASTM standard test method for compressive strength determination.[32] An additional requirement was included after the start of this work that there be no significant decline in compressive strength during the 28-day monitoring period. This was done after an expansive phase phenomenon was discovered that resulted in complete strength failure in a sample after satisfactory early development (see below). The objective was to identify and reject any samples undergoing this phenomenon that still had a 28-day compressive strength above 500 psi, but would have failed at a later time.

6) Pass EPA leaching standards for RCRA metals

The EPA has jurisdiction over the on-site storage of mixed waste. Since mixed waste is much more costly to store than nonhazardous TRU waste, it is advantageous for a waste form be classified as nonhazardous TRU (non-mixed) waste. In the case of TA-55 cemented waste, the major obstacle to achieving non-mixed status is meeting the chromium concentration limits in the TCLP extractant. Performance in this area was determined by TCLP testing on selected samples according to the EPA procedure.[33]

EXPERIMENTAL EVALUATION

The goal of this project was to develop a simple cement formulation using only Type I/II Portland cement. Type I/II is the most readily available type of Portland cement, and its sole use would simplify the procurement of the raw materials. Another advantage to a one-component formulation would be the prevention of segregation problems that can occur with multicomponent formulations in vibrating silos such as the one at TA-55. Other cement types and additives would be investigated only if required to address significant problems in areas such as slow setting, inadequate leaching resistance, or excessive temperature rise. This project was conducted according to the LANL/TA-55 Quality Management Plan: Documents and Records Control Section, procedure number SS-TA-55-110-0-03.1-1.

Surrogate preparation: The surrogates of the LR- and OX-based waste streams were prepared to approximate the median concentrations found in the waste stream characterization study listed in Appendix 1. The OX-based surrogate was prepared with selected RCRA metals to evaluate the TCLP performance of the cemented waste form. The LR-based surrogate was prepared without RCRA metals. The concentrations of the LR- and OX-based surrogates are listed in Table 1.

Test Conditions: It was not the intention of this project to establish the failure boundary of all process parameters. Rather, it was to define a set of target parameters whose performance had been shown to be successful. To that end, this project varied the process parameters of pH, C/L ratio, and water dilution to collect data regarding their influence on waste form performance. The equipment used for preparation of the samples and data acquisition is described in Appendix 2. Bench-scale testing was completed with LR-based surrogate before OX testing was begun. Conditions found to be unsatisfactory in the LR tests were not included in the OX tests. The pHs evaluated were 8.5, 9.6, 10.5, and 12.1 for the tests involving LR surrogate. The tests with OX-based surrogate were performed at a more limited range of 9.5, 10.5 and 11.5 as a result of pHs 8.5 and 12.1 being eliminated in the LR tests (see below). All pH adjustment was achieved using 10 molar NaOH solution. The pH, C/L ratio, and dilution values for the bench-scale tests are listed in Table 2.

A full-scale test was performed under conditions similar to a specific bench-scale sample (LR16) to ascertain how scale-up would affect bench-scale results. A full-scale test was necessary because there are several areas in which bench-scale testing may not predict performance on the full scale. Bench-scale samples often do not show bleed water when full-scale samples would.[34] Also, larger-scale samples exhibit a higher temperature rise during hydration that can produce cracks in the cement monolith. This damage can compromise performance in compressive strength development and leaching resistance.[34] In our case, the temperature was also a concern because of its potential to cause thermal damage to the vinyl drum bag.

Table 1: Composition of Surrogates
(in g/l except as noted)++

Ion	LR-based	OX-based	Ion	LR-based	OX-based
Fe	9.03	8.56	SO_4	1.55	1.00
Ca	58.39	16.88	C_2O_4	3.2	33.8
K	18.51	6.38	F	6.0	1.7
Mg	54.77	21.40	Cd	0	0.0028
Na	6.85	26.98	Cr	0	2.45
Al	4.75	1.75	Pb	0	0.056
NH_4	0.028	0.09	Ag	0	0.0014
H^+ (M)	1.40	4.55	Ba	0	0.0355
Cl	1.02	0.27	Ni	0	1.205
NO_3	630	398			

++Based on quantity of chemicals used to prepare surrogate instead of analysis.

RESULTS AND DISCUSSION

All bench-scale samples were evaluated for mixability, bleed-water generation, initial set time, setting-temperature characteristics, and compressive strength. Evaluations of TCLP performance and radiolytic free-liquid generation were conducted only on OX samples. The performance in each category is discussed below. The results of the full-scale test follow those of the bench-scale tests.

The LR samples were used for the dilution study in which the pH and water dilution values were varied concurrently with each sample (see mixability section). Consequently, pH and water dilution must be considered together when determining their influence on LR samples in the following performance categories. The OX tests were conducted with only one of these process parameters being varied at one time. Subsequently, the OX tests are more useful in determining the individual influence of pH and water dilution.

Table 2: Parameters and Results

Sample No.	pH	C/L Ratio (kg/l)	Waste / NaOH / H_2O (vol%)[a]	Initial Set Time (hr.)	Compressive Strength (psi) 7-day	14-day	28-day
LR15	8.5	0.80	58.1 / 28.9 / 13.0	58	450	0	0
LR11	9.6	0.94	67.3 / 32.7 / 0	26	1200	1550	1775
LR18	9.6	0.80	45.0 / 32.0 / 23.2	28	650	825	750[e]
LR16	10.5	0.80	41.4 / 27.8 / 30.8	20	750	700	850
LR14	12.1	0.80	35.1 / 30.6 / 34.3	18	688	925	1075
OX1	9.5	0.94	57.9 / 42.1 / 0	30.6	687	775	975
OX2	9.5	0.94	57.2 / 42.8 / 0	33	650	825[d]	950
OX9	9.5	0.94	56.3 / 38.7 / 5	ND[b]	875	1100	1250
OX12	9.5	0.94	51.4 / 38.6 / 10	24.6	1525	1000	1250
OX19	9.5	0.94	51.4 / 38.6 / 10	24.2	600	875	1000
OX16	9.5	0.80	51.4 / 38.6 / 10	29.8	375	450	650[e]
OX5	10.5	0.99	62.3 / 37.7 / 0	ND[b]	975	1150	1325
OX6	10.5	0.94	55.2 / 39.8 / 5	23.1	800	2125	1300
OX17	10.5	0.94	55.2 / 39.8 / 5	26.7	700	825	1100[e]
OX4	10.5	0.94	52.3 / 37.7 / 10	21.8	725	925	1150
OX10	10.5	0.94	54.2 / 35.8 / 10	25.4	750	850	1100
OX13	10.5	0.94	54.2 / 35.8 / 10	17.7	800	1000	1150
OX18	10.5	0.94	54.2 / 35.8 / 10	22.3	875[c]	1000	1150[e]
OX3	10.5	0.84	58.1 / 41.9 / 0	<24	650[c]	800	1100
OX14	10.5	0.80	54.2 / 35.8 / 10	26.9	300	500	700
OX7	11.5	0.94	56.0 / 39.0 / 5	26.8	850	1100	1275
OX8	11.5	0.94	53.1 / 36.9 / 10	22.6	825	950	1275
OX11	11.5	0.94	53.1 / 36.9 / 10	24.6	950	1025	1150
OX15	11.5	0.80	53.1 / 36.9 / 10	28.4	375	525	675
OX20[f]	4	1.80	79.1 / 20.9 / 0	<24	1000	925	800
OX21[g]	4	1.80	79.1 / 20.9 / 0	<24	1200	1175	1000

[a] Vol% of total liquid volume; [b] Not determined; [c] Determined at 9 days; [d] Determined at 15 days; [e] Determined at 29 days; [f] Envirostone short mix; [g] Envirostone long mix

Bench-Scale Experiments

Mixability. The mixability limit was defined as the paste viscosity above which the mixing equipment lost its ability to achieve center-to-edge mixing. It was found that all pH-adjusted LR samples exceeded this limit after the addition of the cement required for a C/L ratio of 0.80 kg/l. Besides the dilution provided by the NaOH solution used for pH adjustment, additional dilution of these samples with water was required to meet the mixability limit. As a result of increased salt precipitation, samples at a higher pH exhibited a higher viscosity and therefore required more dilution. To quantitatively establish the effect of dilution on waste loading as the pH was increased, the 0.80 kg/l LR samples were prepared at the same viscosity. In this dilution study the viscosity was established at what was necessary to attain a 0.1-watt power demand by the mixer while mixing the pH-adjusted, precemented surrogate at 250 rpm. This viscosity was found to result in a paste that was as viscous as possible without exceeding the mixability limit at 0.80 kg/l . The water, NaOH solution, and waste values as a percentage of the total liquid volume of each LR sample before concentration are reported in Table 2.

The same type of study was not conducted on OX samples. Instead, the water dilutions in the OX samples were fixed at 0%, 5%, and 10%. Although the viscosity of the OX samples with 0% dilution was considered excessive, no difficulty in mixing was observed in any sample at 5% or 10% dilution. This lower dilution requirement for the OX samples is due to the lower salt content of the OX-based surrogate, as reflected in the lower total dissolved solids (TDS) value of the OX waste stream reported in Appendix 1. All dilution and waste percentages for the OX samples are reported in Table 2.

Free Liquid from Bleed-Water Generation. Although several samples initially generated bleed water, all bleed water was reabsorbed before 24 hours in all LR and OX samples.

Initial Set Time. The LR tests showed a definite relationship between each sample's initial set time and the pH and dilution values. This can be seen in Figure 3a, which shows the initial set time decreasing as the pH and dilution values increase. The samples prepared at pH 8.5 and pH 9.6 had initial set times exceeding 24 hours. Because the pH 8.5 sample greatly exceeded the 24-hour limit, it was eliminated from further consideration.

The OX samples presented in Figure 3b show a somewhat different effect of pH on initial set time in that the lowest initial set time occurred at pH 10.5. Nevertheless, the results were consistent with the LR tests in that no sample prepared at a pH $\leq$9.6 met the 24-hour standard. This finding further cast doubt on the acceptability of the samples prepared in the pH 9.6 region. Figure 3b also shows a definite relationship between C/L ratio and initial set time in that the set time increased as the C/L ratio decreased. This increase was enough to prevent all 0.80 kg/l OX samples from meeting the 24-hour standard. Dilution was also found to effect initial set time in that the initial set time decreased as the dilution increased. This decrease is presumably a result of the decrease in the concentrations of set-retarding constituents of the waste. Figure 3c shows this relationship between dilution and initial set time for the 0.94 kg/l OX samples at each pH. This relationship should also have had an increasingly significant effect on the initial set times of the LR samples as the pH was increased.

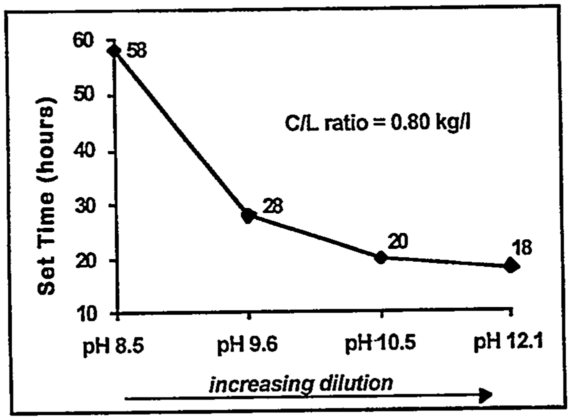

Fig. 3a. Effect of pH/dilution on initial set time for LR samples. (see Table 2 for dilution values)

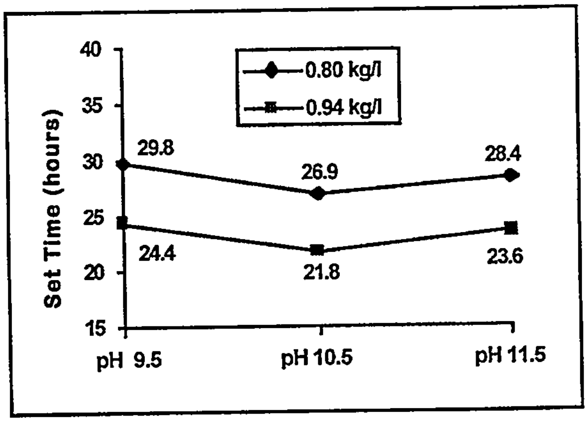

Fig. 3b. Effect of pH and C/L ratio on initial set time for OX samples. (avg. of samples w/ 10% water dilution).

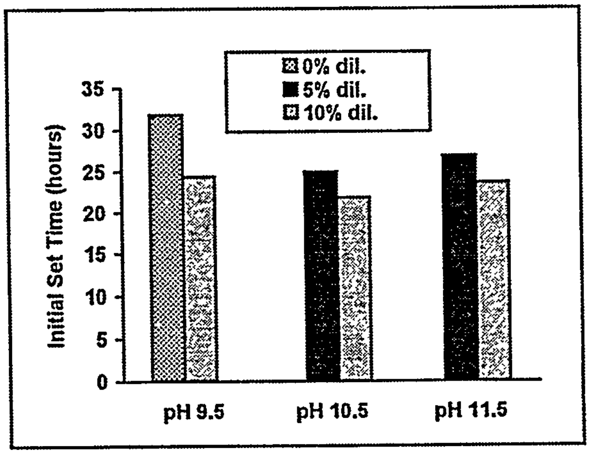

Fig. 3c. Effect of water dilution on initial set time for OX samples (avg. of samples w/ C/L ratio of 0.94 kg/l).

Temperature. The LR tests showed a definite relationship between the pH and dilution values of each sample and the maximum hydration temperature and the elapsed time to maximum temperature. As the pH and dilution values increased, the maximum temperature increased and the elapsed time generally decreased. This can be seen in Figure 4a. The maximum temperature of 107°F reached by the LR14 sample exceeded the 100°F temperature ceiling, thus causing a failure of this sample to meet the bench-scale temperature standard.

The OX samples presented in Figure 4b showed no significant change in temperature behavior as the pH was varied. The temperature profile of all OX pHs looked similar, with a peak temperature of approximately 860° F at 24 hours. Since the water dilution values of these OX samples were held relatively constant, this may indicate that the changing temperature profiles of the LR samples in Figure 4a were significantly influenced by the changing dilutions of these samples. However, differences in chemical composition of the two EV types can not be ruled out as being a factor.

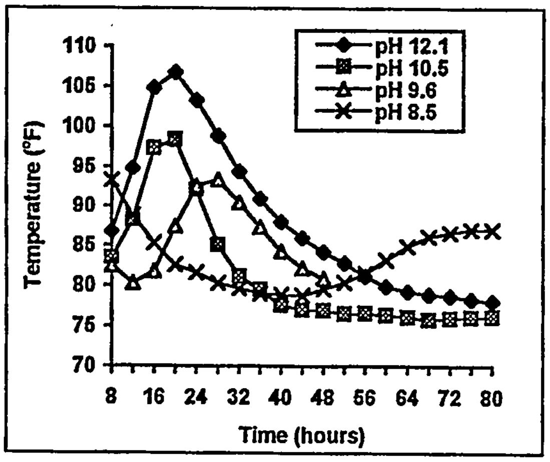

Fig. 4a. Temperature profile for LR samples LR14, LR15, LR16, & LR18. (C/L ratio = 0.80 kg/l, see Table 2 for dilution values).

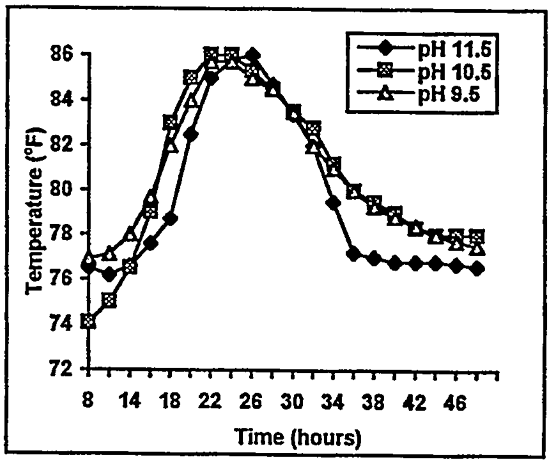

Fig. 4b. Temperature profile for OX samples OX4, OX8, & OX19. (C/L ratio = 0.94 kg/l, water dilution = 10%).

Compressive Strength. As expected, the compressive strength increased as the C/L ratio was increased. This relationship is shown for selected LR and OX samples in Figures 5a and 5b, respectively. The relationship of pH to compressive strength is shown for selected LR and OX samples in Figures 6a and 6b, respectively. In the LR samples a higher pH resulted in a higher 28-day compressive strength. However, this trend is likely to have been promoted by the increased dilution at the higher pHs of the LR samples. This statement is supported by the fact that no consistent trend was seen in OX samples at the same pH with a constant dilution percentage (see Figure 6b and Table 2). Table 2 also shows that the average 28-day compressive strength values for the OX samples with 0% water dilution (OX1 and OX2) were less than those at 5% and 10%. This was expected because of a higher ionic concentration in the 0% samples. However, the 5% average values in all pH categories were greater than those at 10%. The reason for this apparent anomaly is not known although it may be a statistical artifact resulting from the small number of samples.

The compressive strength of each sample generally increased with time, but this was not always the case. An exception occurred in the pH 8.5 LR sample. A phenomenon was observed in this sample that allowed satisfactory early strength development, but resulted in cube expansion and complete structural failure (compressive strength = 0 psi) at the 14- and 28-day strength determinations (see Figure 6a). It is possible that the LR sample prepared at pH 9.6 and 0.80 kg/l also exhibited some effects of this phenomenon (see Figure 6a). Although the pH 9.6 sample still had a compressive strength above 500 psi at 28 days, the compressive strength at 28 days was lower than at 14 days. This may indicate that the waste form would have self destructed at a later time.

This concern, along with the marginal initial-set-time performance of samples at this pH, prompted the removal of pH 9.6 from further consideration. The OX samples did not experience this delayed expansion phenomenon at the tested pHs of 9.5, 10.5, and 11.5. The explanation for this phenomenon in the LR samples is not certain. Since this occurred only in the LR samples with the lowest dilutions, the effect may be linked to a high concentration of one or more of the ions that are not as concentrated in the OX surrogate.

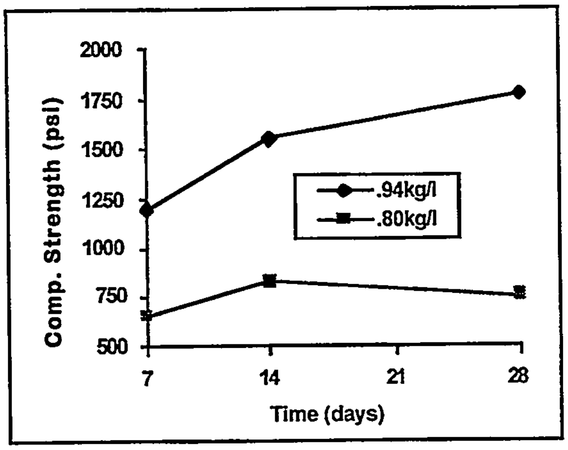

Fig. 5a. Effect of C/L ratio on compressive strength of LR samples LR11 & LR18. (pH = 9.6, see Table 2 for dilution values).

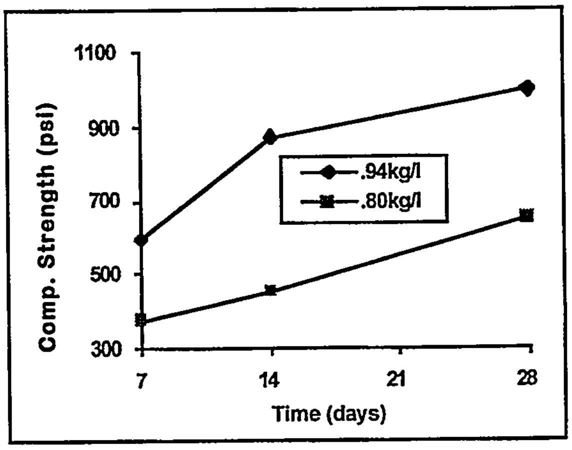

Fig. 5b. Effect of C/L ratio on compressive strength of OX samples OX16 & OX19. (pH = 9.5, water dilution = 10%).

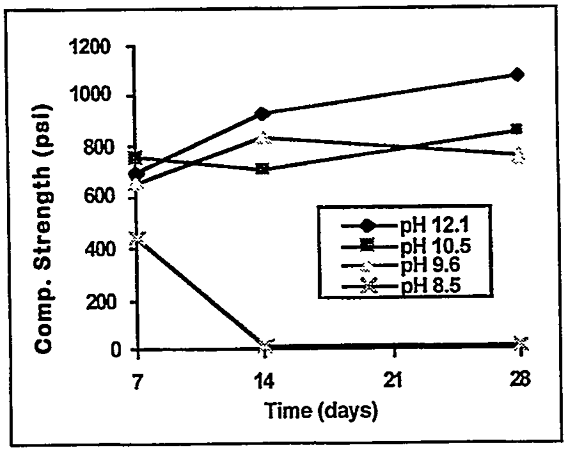

Fig. 6a. Compressive strength of LR samples LR14, LR15, LR16, & LR18. (C/L ratio = 0.80 kg/l, see Table 2 for dilution values).

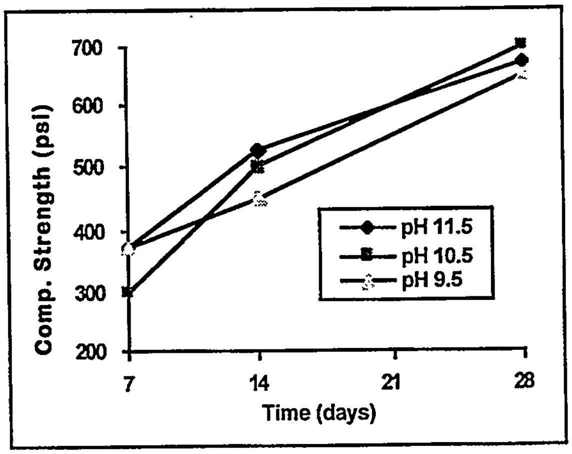

Fig. 6b. Compressive strength of OX samples OX14, OX15, & OX16. (C/L ratio = 0.80 kg/l, water dilution = 10%).

TCLP Results. TCLP testing was done on selected OX samples. The OX samples were analyzed for the RCRA metals Cr, Cd, Pb, Ba, and Ni. The RCRA metals not included in the TCLP testing were present in concentrations that would be well below the TCLP limit even if 100% of each metal leached out in the TCLP. The samples for TCLP analysis were taken from the pH categories of

9.5, 10.5, and 11.5 and included the sample with the lowest compressive strength in each category. The sample with the lowest compressive strength was considered the worst-case condition for leaching resistance because of the connection of compressive strength to leaching resistance through a common dependency on permeability.[21] The analytical results in Table 3 show that all samples passed the TCLP standards for nonhazardous waste.

Table 3: TCLP Results for Oxalate Surrogate Samples
(all concentrations in ppm)

Sample ID	Cr	Cd	Pb	Ba	Ni
OX7	0.11	<0.003	<0.011	2.6	0.01
OX8	0.12	<0.003	<0.011	2.4	0.01
OX9	0.12	<0.003	<0.011	3.0	<0.01
OX14	0.10	<0.003	<0.011	2.7	0.01
OX15	0.13	<0.003	<0.011	2.6	<0.01
OX16	0.11	<0.003	<0.011	2.7	<0.01
OX17	0.14	<0.003	<0.011	2.7	0.01
OX18	0.11	<0.003	<0.011	2.9	0.01
OX19	0.17	<0.003	<0.011	2.8	0.05
Leach Resistance++	99.9%	>97.9%	>99.6%	69.0%	99.9%

++These values represent the lowest leach resistance for each metal calculated from the TCLP results in Table 3. The definition and the calculation of leach resistance is presented in Figure 1.

Radiolytic Free-Liquid Generation. The testing for susceptibility to radiolytic free-liquid generation was conducted with OX samples. Gamma irradiation was used to simulate the radiolytic degradation caused by alpha irradiation in the actual wastes.* To achieve 10^8 rads quickly, the test was conducted using a 380 rad/sec ^{60}Co gamma source at Sandia National Laboratories. The samples were taken from the pH categories of 9.5, 10.5, and 11.5 and included the sample with the lowest compressive strength in each category. Compressive strength was again used as the worst-case indicator because of its common dependency with free-liquid generation on permeability. The test results, presented in Table 4, show that no Portland cement sample produced free liquid during the irradiation test.

Two Envirostone-cemented samples were also included in this test, a short-mixed (OX20) and a long-mixed (OX21) sample. These were included to investigate a correlation found in previous work between longer mixes and suppression of radiolytic free-liquid generation in Envirostone cemented waste forms.[9,10,22] During the irradiation test, free liquid was found in both samples, the short-mix sample at 1.7×10^7 rads and the long-mix sample at 4.4×10^7 rads. The liquid generated by the long-mix sample was actually greater in volume than that of the short-mix sample (see Table 4).

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* Gamma irradiation is less efficient than alpha irradiation in the production of radiolytic H_2. The G value (H_2 molecules produced per 100 eV of energy absorbed) from gamma radiolysis has been reported to be approximately 33% lower than that from alpha radiolysis.[14]

Based on these results, it can be concluded that the long-mix technique cannot be consistently relied upon to suppress radiolytic free-liquid generation in Envirostone cemented waste forms.

Table 4: Gamma Irradiation

Cumulative Dose: (rad)	$8.3\text{x}10^6$	$1.7\text{x}10^7$	$4.4\text{x}10^7$	$5.3\text{x}10^7$	$7.2\text{x}10^7$	$9.8\text{x}10^7$
Sample ID	Liquid?	Liquid?	Liquid?	Liquid?	Liquid?	Liquid?
OX14	no	no	no	no	no	no
OX15	no	no	no	no	no	no
OX16	no	no	no	no	no	no
OX17	no	no	no	no	no	no
OX18	no	no	no	no	no	no
OX19	no	no	no	no	no	no
OX20 short-mix Envirostone	no	Yes (damp[++])	Yes (1.55g)	Yes (3.35g)	no	no
OX21 long-mix Envirostone	no	no	Yes (3.59g)	Yes (4.91g)	no	no

[++] Weights in parentheses are totals from the start of free-liquid generation.

Full-Scale Testing: The full-scale test was conducted with LR-based surrogate and was designed to simulate the bench-scale sample LR16. The full-scale sample had a pre-cement pH of 10.3 and a C/L ratio of 0.80 kg/l, which corresponded to 220 lb of Portland cement. The EV, NaOH, and water volume percentages in the full-scale sample were 41%, 28%, and 31%, respectively. All performance standards were monitored in the full-scale test except RCRA-metal leaching resistance and radiolytic generation of free liquid. Compressive strength was used as an indicator of performance in these nonmonitored areas because of its common dependence with them on permeability. The results relative to each performance standard are reported below.

Mixability. The mixing equipment had no difficulty in providing center-to-edge mixing of the cement paste.

Free Liquid. No bleed water was present at any time after cementation.

Initial Set Time. Initial set occurred at 20.6 hours after cementation, approximating the 20-hour initial set time of LR16. The profile of the penetration resistance is shown in Figure 7.

Temperature. The full-scale test was useful in illuminating several areas of uncertainty concerning temperature behavior. The temperature was monitored approximately halfway down at the center and edge (1 inch in) of the cement monolith and between the rigid liner and bag. The temperature reached a maximum of 163°F at the center, 150°F at the edge, and 103°F at the bag. The full-scale temperature profile at the center of the monolith is shown in Figure 8.

The maximum center temperature of the full-scale sample was 66°F higher than that of LR16. This corresponds to an increase of 30°F per 100 lb of Portland cement ([66°F / 220 lb] x 100). This is twice as high as the industry standard of 15°F per 100 lb used to establish the temperature ceiling for the bench-scale tests. This difference is likely a result of the industry standard being based on concrete, in which the aggregate would act as a heat sink. Another meaningful finding was that the temperature at the bag location was 60°F lower than at the center of the monolith. This resulted in a temperature significantly below the bag-failure temperature of 145°F even though the center temperature was higher than expected. These data can now be used to back-calculate a revised temperature ceiling of 139°F for the bench-scale tests (145°F + 60°F - 66°F). At this higher ceiling, the pH 12.1 LR sample, previously rejected with a maximum temperature of 107°F, falls within in the acceptable temperature range.

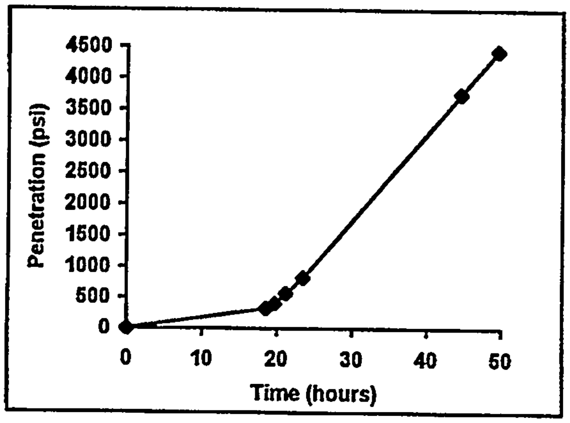

Fig. 7. Penetration resistance of full-scale test.

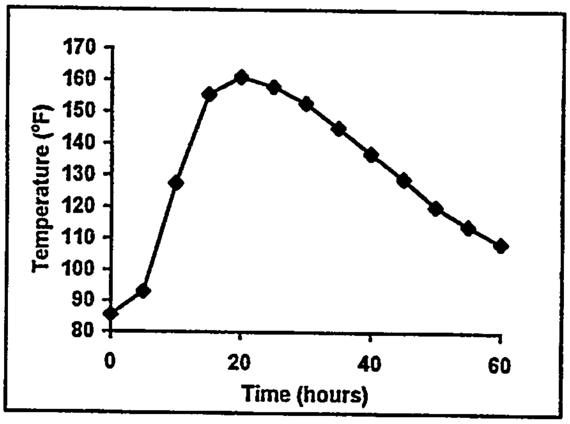

Fig. 8. Temperature profile of full-scale test (center).

Compressive strength. The compressive strength values of the full-scale sample exceeded those of LR16 after the first week of the 28-day monitoring period. This indicates no damage to the monolith occurred as a result of increased hydration temperature from scale-up. The compressive strength profiles of the full-scale sample and LR16 are shown in Figure 9.

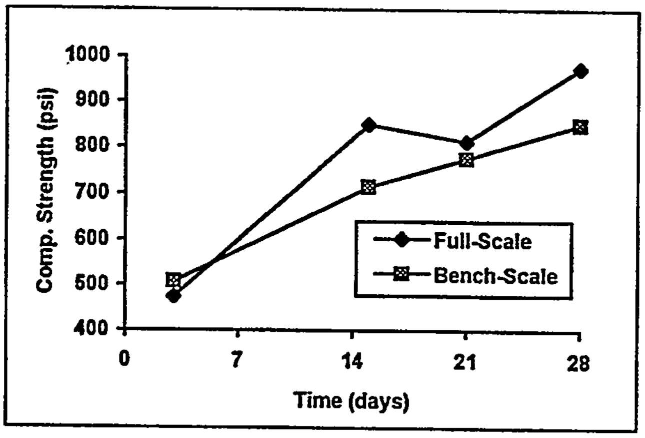

Fig. 9. Compressive strength comparison of full- and-bench-scale (LR16) samples. (Full-scale data taken at 3, 15, 21, and 28 days. LR16 data at 3, 15, and 21 days were extrapolated from Table 2 values).

TCLP. The LR surrogate used for the full-scale test did not contain RCRA metals so a TCLP analysis was not performed on the full-scale sample. However, two considerations indicate the TCLP-extractant values for the RCRA metals would be lower than that of the OX-based sample (OX14) prepared at the same pH and C/L ratio, which easily passed the TCLP standards. First, the higher compressive strength of the full-scale sample (975 psi vs. 700 psi at 28 days) indicates the permeability should be less than of OX14[21]. Since leachability is dependent on permeability, the resistance to TCLP leaching should be greater for the full-scale sample than for OX14. Second, because the dilution percentage of the full-scale sample was greater than that of OX14, the concentration of the RCRA metals would be less in the full-scale sample.

Radiolytic Free-Liquid Generation. Testing for radiolytic free-liquid generation was not performed on the full-scale sample, but a conclusion can be drawn from the compressive strength data. The work at Hanford showed that the susceptibility of a waste form to radiolytic free-liquid generation decreased as the compressive strength increased.[18,19] Since the compressive strength of the full-scale sample was higher than the OX sample prepared at the same pH and C/L ratio (OX14), resistance to radiolytic free-liquid generation should also be greater.

CONCLUSIONS

The above results define a range of operability that can be used to produce a Portland-based waste form meeting the performance standards identified in this project. The performance standards of principal importance were those used in addressing the inadequacies of Envirostone cement regarding free-liquid generation and failure to meet the TCLP limit for chromium. The Portland waste form was shown to be superior to both the short-mix and long-mix Envirostone waste forms in resisting gamma-induced free-liquid generation. The 9.8×10^7-rad dose at which the Portland sample still suppressed free liquid exceeded the dose at which the short-mix and long-mix Envirostone samples began to generate free liquid by 5.8 and 2.2 times, respectively (see Table 4). The earlier TCLP studies presented in Figures 1 and 2 had demonstrated that the Portland waste form was superior to Envirostone waste forms in chromium TCLP performance by at least an order of magnitude. The TCLP evaluation of the OX-based Portland samples in the present work (see Table 3) showed TCLP performance similar to these earlier studies, as can be seen by a comparison of the leach resistance values in each study.

The bench-scale results were successfully conducted at a C/L ratio as low as 0.80 kg/l for LR-based EV surrogate and 0.94 kg/l for OX-based EV surrogate. The OX-based EV waste required a C/L ratio of 0.94 kg/l solely because of a failure to meet the 24-hour initial set standard at 0.80 kg/l. The bench-scale tests established the acceptable pH range for the liquid (EV, NaOH, and dilution water) at 10.5 to 11.5. The full-scale test, conducted with LR surrogate at pH 10.3 and 0.80 kg/l, demonstrated the pH range could be lowered to 10.3. The full-scale test also provided revised temperature data that reinstated pH 12.1 as an acceptable pH, thus extending the final pH range to 10.3 to 12.1.

Actual operations will present some areas for flexibility. First, the C/L ratio may be increased to the limit of the mixing equipment's ability to achieve adequate mixability. An increased C/L ratio will improve performance in leaching resistance, set time, and compressive strength development. Second, to simplify operations, it is recommended that the water dilution not be readjusted for the viscosity or chemical composition of each EV batch. Instead, a dilution percentage should be based on the more highly concentrated batches so that the dilution will be adequate for all routine EV batches. The additional dilution will also reduce the initial set time for the typically less-concentrated OX-based waste streams, which may allow the OX waste forms prepared at 0.80 kg/l to meet the 24-hour set time standard.

Waste loading will depend on how much drum volume is required by the other components making up the final waste form. The highest waste loading will be achieved by operating at the lowest acceptable C/L ratio and pH. The amount of reduction in waste loading as a result of the increased dilution at higher pHs was shown in the dilution study conducted with the LR samples (see bench-scale mixability section). A waste loading of 33.5 vol% was achieved in this project's full-scale test.* This waste loading is approximately equal to that of the Envirostone-based operation. The lower C/L ratio of the full-scale Portland sample compared to the Envirostone-based operation (0.80 kg/l vs. 1.75 kg/l) did not result in a higher waste loading because it was offset by the higher water and NaOH dilution required by Portland's higher pH. However, increased waste loading can be expected in actual operations if the EV waste contains less salts than the LR surrogate used in this project. On the other hand, if the EV waste contains more salts, increased water dilution will be necessary to offset the higher viscosity, and lower waste loading will result. Additional dilution may also be necessary in the case of an increased or altered salt content to offset an increased chemical interference with the Portland setting reaction.

The amount of cement needed to produce a full drum will be approximately 275 lb.# The cement addition rate should be as high as possible in the TA-55 operation. Mixing should be continuous during the time of addition and the mixer rpm ramped up as the paste viscosity requires to maintain adequate mixing. To prevent overmixing, the paste should be mixed for only 4 minutes after the end of cement addition. Overmixing is to be avoided because it is known to interfere with an initial stage of the setting reaction, causing delayed set, slow curing, and even loss of final physical properties.[34] The presence of bleed water after completion of mixing is acceptable as long as reabsorption occurs within a reasonable time frame. The 24-hour standard for free-liquid reabsorption was selected as a *desired* standard to ensure a reasonable throughput for the cementation operation and is not related to the physical integrity of the waste form. The 24-hour standard for initial set time was likewise established as a *desired* standard to achieve a reasonable process throughput and may also be extended without jeopardizing the physical integrity of the waste form.

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* Calculated as percentage of the volume of the cemented waste form.

The amount of cement is higher than the 220 lb. used in the surrogate full-scale test because the surrogate test did not utilize the full capacity of the drum. A full drum is considered to be 3 inches below the top of the drum liner.

Quality Assurance: Some care must be taken in procuring the Type I/II cement for the TA-55 cementation operation. Type I/II Portland cement is defined by a range for each of its chemical, mineralogical, and physical properties. The ranges are broad enough that variations in setting characteristics and sensitivity to chemical interferences are sometimes observed between Type I/II cements from different sources. It is recommended, therefore, that the QA program for this operation assure that procurement be from a source offering a Type I/II cement with similar composition to that used in this development project. The particular cement used in this project is a low-alkali Type I/II cement. The source of the cement was Rio Grande Portland Cement Corporation in Tijeras, New Mexico. The chemical and mineralogical composition and other pertinent physical characteristics for this cement are listed in Appendix 3.

Costs: For a production rate of 3 cement drums per week, the Portland cement required for operating the TA-55 cement process will be approximately 20.6 tons per year.* The current delivered cost from Rio Grande Portland Cement Corporation is $77.20 per bulk ton, resulting in a yearly cost of $1,592. This compares to $1,300 per ton and $33,627 per year for Envirostone cement.# The resulting savings in cement cost with the use of Portland cement will be approximately $32,035 per year. The increased volume of NaOH solution required by the Portland operation should result in an increased cost for NaOH of no more than $5,000 per year. This results in a net savings in raw materials of approximately $27,000 per year. The cost for Portland cement from Rio Grande Portland Cement Corporation is for bulk powder cement. Bulk delivery is less costly and has the advantage of allowing pneumatic delivery into the TA-55 cement silo. Pneumatic delivery will also reduce the number of person-hours required to load the silo from approximately 20 hours for the current manual technique to 1 hour per year.

Other Wastes: The recommendations of this report should be compatible with the addition of dry, non-reactive particulate wastes. In the present TA-55 operation, this type of waste is added to a pre-established cement paste to prevent the solids from settling during mixing. The primary effect of using this technique will be an increase in paste viscosity, which can be addressed by additional dilution with water if necessary. Slurries (wet particulates) with a pH outside the range recommended in this report should be pretreated to properly adjust the pH before addition to the cement paste. Low-density slurries that do not require addition to a pre-established paste can be added to the EV waste and their pHs adjusted with the EV waste before cement is added. Ion-exchange resins present an additional concern in that they have been reported to cause setting and free-liquid problems under certain conditions.[35,36] Non-EV aqueous wastes may also cause chemical interferences with the Portland setting reaction. Thus, it is recommended further studies be conducted before ion-exchange resins or non-EV aqueous wastes are incorporated into the cementation operation.

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* Calculated at 150 drums per year at 275 lb of Portland cement per drum.

\# Calculated at 150 drums per year at 340 lb of Envirostone cement per drum.

No testing was done with organic wastes in this development project. Portland cement is not as efficient as Envirostone in treating nonpolar organics, but methods exist that permit satisfactory treatment of some organics with Portland cement.[37] It generally is adequate for limited volumes of nonpolar organics if they are prepared in a well-dispersed, oil-in-water emulsion. It does not perform well with inverse emulsions (water-in-oil) or pure solvents.[34] Organics with high solubility (polar) generally are not immobilized well by Portland cement.[34] It is recommended additional development be conducted before organic wastes are incorporated into the cementation operation.

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Appendix 1

Analysis of Evaporator Bottoms[a]

(in g/l except as noted)

	Lean Residue	Oxalate Filtrate	Hot Distillate
Fe	17.0	7.9	16.9
Ca	61	10.5	39.1
K	17.6	4.8	14.6
Mg	58.7	13.3	41.9
Na	7.4	23.9	9.4
Al	4.6	2.3	4.7
NH_4	0.025	0.090	0.035
Cl	1.1	0.265	1.35
NO_3	457	398	419
SO_4	1.6	<1	1.57
C_2O_4	3.3	33.8	11.3
F	5.4	1.7	5.1
H^+ (molar)	1.0	4.6	1.75
TDS[b]	629	330	600
Ag	<0.005	<0.001	<0.002
As	<0.015	<0.005	0.010
Ba	0.035	0.018	0.029
Cd	0.014	0.003	0.014
Cr	3.0	1.94	2.35
Hg	<0.025	<0.005	0.010
Ni	1.8	1.205	1.60
Pb	0.19	0.056	.125
Se	<0.008	<0.008	0.009
Tl	<0.060	<0.020	<0.060

[a]Median values of all analyzed EV samples; [b]Total dissolved solids

Appendix 2

Equipment for Sample Preparation & Data Acquisition

The bench-scale equipment was assembled to match the design and proportions of the TA-55 full-scale process as much as possible. A programmable laboratory mixer (Lightnin Labmaster TSM2510) was used as the mixing device. The mixing profile was matched to the TA-55 process with the rpm being ramped up from 250 rpm to 400 rpm to maintain adequate mixing during cement addition. A program was written for the laboratory mixer that automatically and continuously recorded the mixer power, mixer rpm, and mixing time for each bench-scale test. For the full-scale test, the mixing container consisted of a 1/4-inch thick polyvinyl chloride rigid liner, inside a 12-mil vinyl bag, inside a 55-gallon drum (DOT 17-C). This configuration was identical to that used in the TA-55 operations minus the lead between the bag and drum. The mixer (Lightnin XJ350), mixer shaft, and propellers (12.4-inch diameter Lightnin A100) were identical to those used in the TA-55 process. The two propellers were separated on the shaft by one propeller diameter with the lower propeller being one-half diameter above the bottom of the liner. The full-scale test had a mixing rpm of 400 during the entire test.

The following equipment was used for data acquisition in the bench- and full-scale tests. The bench-scale mixing profiles were recorded by a Compac Model M84 personal computer through an RS-232 interface with the mixer. Temperature was monitored using a Yokogawa Model LR4120 strip chart recorder and a type-K, Omega thermocouple (5TC-TT-K-24-36). The thermocouple was Teflon-coated to ease its removal from the hardened cement monoliths. The compressive strength of all waste forms was determined using a model C, 12-ton hydraulic press from the Carver Laboratory Press Company. The compressive strength data were taken on 2-inch cubes cast in Humboldt H-2810 cube molds. Penetration resistance was determined using a Humboldt model H-3143 hydraulic penetrometer. The gamma irradiation data for the bench-scale samples were collected with the use of a 380 rad/sec ^{60}Co gamma source located at Sandia National Laboratories.

Appendix 3

Composition of Type I/II Portland Cement Used in Tests

(in %, except where noted)

	#1 1/1/93 - 12/12/93[a] Average	 (Std. Dev.)	#2 5/13/94 Bin 9 - Test 114	#3 7/1/94 - 10/31/94 Average	#4 9/1/94 - 1/18/95 Average
SiO_2	20.9	(0.22)	20.9	21.1	21.1
Al_2O_3	4.3	(0.087)	4.3	4.3	4.3
Fe_2O_3	3.1	(0.082)	3.1	3.0	3.1
CaO	63.3	(0.55)	63.3	63.6	63.6
MgO	2.8	(0.51)	2.4	2.5	2.6
SO_3	2.9	(0.08)	3.0	3.0	2.0
Na_2O	0.18	(0.023)	0.21	0.19	0.21
K_2O	0.52	(0.029)	0.52	0.55	0.52
Loss On Ignition	1.5	(0.12)	1.2	1.4	1.40
Insoluble residue	0.24	(0.022)	0.22	0.23	0.24
C_3S[b]	57.8	(2.48)	57	57	57
C_2S[c]	16.3	(2.1)	17	17	18
C_3A[d]	6.1	(0.24)	6.3	6.3	6.0
C_4AF[e]	9.5	(0.24)	9	8	10
Alkalies (Na_2O equiv.)	0.52	(0.033)	0.57	0.55	0.55
Blaine, (sq. M / kg.)	353	(8.0)	349	359	361
-325 mesh fineness	93.3	(1.19)	92.7	93.3	95.2
Autoclave expansion	0.05		0.03	0.05	0.05
Air content	8.5		8.9	8.2	8.1

[a] Dates are date of manufacture; [b] C = CaO; [c] S = SiO_2; [d] A = Al_2O_3; [e] F = Fe_2O_3