

# Development of a Cast Stone Formulation for Hanford Tank Wastes

Boyd A. Clark,<sup>1</sup> David G. Atteridge,<sup>2</sup> Marisol Avila,<sup>2</sup> Vicki R. Baca,<sup>2</sup> Kyle M. Bishop,<sup>3</sup>  
Gary A. Cooke,<sup>3</sup> Richard J. Lee,<sup>1</sup> Larry L. Lockrem,<sup>3</sup> Teo V. Rebagay,<sup>2</sup> Michael R.  
Silsbee,<sup>1</sup> Sandy R. Stephens,<sup>2</sup> and Richard A. Westberg<sup>2</sup>

## Abstract

The U.S. Department of Energy (DOE) Hanford Site, the location of plutonium production for the U.S. nuclear weapons program, is the focal point of a broad range of waste remediation efforts. This presentation will describe a test program to develop a "cast stone" formulation for the stabilization of certain Hanford tank wastes (Lockrem 2005). The program consisted of (1) a short series of tests with nonradioactive simulant to select preferred dry reagent formulations (DRF) and determine allowable liquid addition levels, (2) waste form performance testing on cast stone made from the DRF formulations using low-activity waste (LAW) simulant, (3) waste form performance testing on cast stone made from the preferred DRF using LAW, (4) waste form validation testing on a selected nominal cast stone formulation using the preferred DRF and LAW simulant, and (5) technetium "getter" testing with cast stone made with LAW simulant and with LAW.

In addition, nitrate leaching observations were drawn from nitrate leachability data obtained in the course of waste form performance testing. The nitrate leachability index results are presented along with data on other performance criteria. The results of this study led to the selection of a specific DRF. The key attributes of the DRF/waste loading combination considered were presence of "bleed" (or free) water, volume change on curing, compressive strength, maximum curing temperature, toxicity characteristic leaching testing, ANSI/ANS-16.1 (*Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure*) leachability, and hydraulic conductivity. Important considerations included that the monoliths could be produced using readily available, low-cost reagents. The key results from each of these testing and evaluation activity categories will be summarized.

## Introduction

Hanford DOE has approximately 53 million gallons of radioactive and chemical wastes now stored in 177 underground tanks. The wastes are a legacy from the 1940s through the 1970s efforts to produce plutonium for nuclear weapons.

Hanford DOE is presently building a vitrification plant [Waste Treatment and Immobilization Plant (WTP)] to turn much of the waste into glass for permanent burial in

---

<sup>1</sup> RJ Lee Group, Inc., Monroeville, Pennsylvania.

<sup>2</sup> Center for Laboratory Sciences, Pasco, Washington.

<sup>3</sup> CH2M HILL Hanford Group, Inc., Richland, Washington.

Yucca Mountain, Nevada. These efforts will produce glass logs of high-level radioactive waste. In an effort to minimize the amount of high-level radioactive waste processed and thus the volume required for storage, supplemental processes were envisioned to solidify LAW components. The paradigm was constructed so that the solidified LAW could then be stored in a separate location, which would require less stringent monitoring procedures due to the nature of the waste form. This paper describes the test program to develop a process for solidifying LAW, which would supplement the WTP processes.

The LAW simulant used for Parts 1 and 2 of this project was an aqueous solution with a nominal 5 M sodium content and was supplied by CH2M HILL Hanford Group, Inc. (CH2M HILL) for use in these studies. It was prepared and characterized by Pacific Northwest National Laboratory (PNNL), (Rassat et al., 2003). It was made to be representative of an actual dissolved saltcake waste stream and was designed to match the actual LAW sample prepared in parallel at the 222-S Laboratory (Callaway 2002).

Because the LAW simulant was prepared before the analytical data for the actual LAW were available, PNNL used a thermodynamic computer model to predict the concentrations of dissolved salts in the LAW. As input to the computer model, PNNL used the composition data for the composite saltcake sample used to prepare the actual LAW.

The test plan was divided into five generic testing schedules: (1) the selection of dry materials which when mixed with simulated liquid waste would form a suitable solid, (2) testing of various dry materials mixed with waste simulant to primarily determine suitability of leaching behavior, (3) selection of a preferred solid formulation (dry materials and liquid simulant waste loading) mixed with LAW to confirm leaching behavior, (4) validation of physical parameters and regulatory constraints for the preferred solid formulation using simulant, and (5) leaching tests of technetium-spiked simulants and LAW solid formulations containing “getters” to immobilize the technetium.

### **Part 1 - Selection of Dry Reagent Formulation**

Formulations were selected after a search of the open literature for mixtures that had been used to treat waste similar to the Hanford LAW (Lokken 1992, Langton 1998, Rebagay 1989). Each formulation was designated according to the dry mix components; as dry reagent formulations, or DRF. Four DRFs, assigned numbers DRF1, DRF2, DRF3, and DRF4, were selected as candidates on the basis of the cast stone mixture composition. DRF2 was a mixture of Portland cement, fly ash, and blast furnace slag. The other three DRFs were mixtures of Portland cement, fly ash, and one or two clays. The candidate DRF compositions are shown in Table 1.

**Table 1. Compositions of Dry Reagent Formulations.**

Components	DRF1 [wt%]	DRF2 [wt%]	DRF3 [wt%]	DRF4 [wt%]
Portland cement, type I, II	44.90	8.16	41.84	20
Fly ash, class F	42.86	44.90	39.78	66
Blast furnace slag, grade 120	0	46.94	0	0
Attapulgate clay	5.10	0	11.22	14
Indian red pottery clay	7.14	0	7.14	0

Initial testing revealed problems with excessive bleed water (>0.5%). This issue was solved by adjusting the total quantity of liquid added to the cast stone mixes. The waste loading was adjusted using evaporation or dilution of the simulant, as appropriate. The total quantity of liquid added to the cast stone mixes was adjusted until an acceptable level (negligible bleed water after 24 hours) was achieved. This adjusted liquid volume was about 35 ml for 90 g of dry components (DRF). A total of 71 cast stone specimens using various DRFs and liquid simulants (water requirements) were examined during DRF selection.

The leaching properties of the resulting cast stone samples were then evaluated using a "quick leach" procedure. The quick leach procedure is a modification of the *Toxicity Characteristic Leaching Procedure* (TCLP) [U.S. Environmental Protection Agency (EPA) SW-846, Method 1311] in which the 18-hour tumbling step is replaced with a less time-consuming leach step. In all cases, Extraction Fluid 2 was used. The TCLP procedure examines the leachate for various elemental metals.

After adjustments to the liquid volumes, none of the test conditions produced measurable bleed water. Quick leach results indicated very low levels of selenium and chromium in DRF2. Quick leach results were not as favorable for the other test conditions. Chromium results for DRF1 were between 6.2 to 8.8 mg/L, and results for DRF3 were between 5.4 to 6.7 mg/L; these levels are above the Federal Universal Treatment Standards (UTS). Selenium leach levels for both test conditions approached the Washington State standard of 1.0 mg/L. Results were slightly better for DRF4. Consequently DRF2 and DRF4 were chosen to continue through Part 2 testing.

### **Part 2 - Waste Form Performance Testing with Simulant**

Two waste formulations were selected from the testing in Part 1, DRF2 and DRF4. Twelve waste loading conditions using DRF2 and four waste loading conditions using DRF4 were selected for performance testing. For both DRF2 and DRF4, the waste loading was varied by at least a factor of three from low to high. Water was added to or evaporated from the simulant to obtain the selected waste loadings. Waste loadings are presented in Table 2. Ferrous sulfate monohydrate was added to all of the samples to aid in stabilizing chromium. Waste loadings are described in the table in terms of total dissolved solids (TDS) basis or in terms of the sodium content (Na<sub>2</sub>O Basis). For one of the twelve conditions, sodium perrhenate (NaReO<sub>4</sub>) was added to the simulant as a surrogate for technetium.

**Table 2. Part 2 Test Matrix.**

Condition	DRF	Waste Loading, TDS Basis (wt%)	Waste Loading, Na <sub>2</sub> O Basis (wt%)	Adjusted Simulant per 90 g DRF <sup>a</sup> (mL)	Initial Simulant Volume (mL)	Volume Reduction (Increase) (vol%)
1	2	24.2	9.87	40	95.2	58.0
2	2	21.8	8.89	40	84.6	52.7
3	2	18.8	7.67	35	69.0	49.3
4	2	16.1	6.57	35	58.3	40.0
5	2	14.7	6.00	35	52.8	33.7
6	2	13.2	5.38	35	47.1	25.7
7	2	11.6	4.73	35	41.2	15.0
8	2	10.0 (natural)	4.08	35	35	0
8 Replicate	2	10.0 (natural)	4.08	35	35	0
9	2	8.3	3.39	35	28.8	(21.5)
10	2	6.5	2.65	35	22.1	(58.4)
11	2	16.1	6.57	38.4	60.1	36.1
12	2	18.4	7.51	39.7	69.3	42.7
13	4	24.2	9.87	40	95.2	58.0
13FSX2 <sup>b</sup>	4	24.2	9.87	40	95.2	58.0
14	4	16.1	6.57	35	58.3	40.0
14FSX2 <sup>b</sup>	4	16.1	6.57	35	58.3	40.0
15	4	10.0 (natural)	4.08	35	35	0
15 Replicate		10.0 (natural)	4.08	35	35	0
16FSX2 <sup>b</sup>	4	8.0	3.26	30	26.6	(12.8)

<sup>a</sup> mL of simulant after evaporation or dilution to be added to 90 g of DRF.

<sup>b</sup> Ferrous sulfate monohydrate added at 2.2 g/100 mL of as-received simulant. For all other samples, ferrous sulfate monohydrate was added at 1.1 g per 100 mL of as-received simulant.

Performance testing included (on all or part of the waste loadings conditions) the following density measurements, bleed water measurements, compressive strength, volume change measurements, TCLP testing, and ANSI/ANS 16.1 (*Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure*) leaching testing. The density was determined on eight test conditions; density measurements were acquired through a probe and were approximately 2 g/mL for all of the samples. Bleed water, volume change, compressive strength, TCLP, and ANSI/ANS 16.1 testing were performed for all of the test conditions.

Bleed water was determined by ASTM method C940-98a, *Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory*, and is a measure of how much water remains on the top surface of a column of the hydrating waste form after 1 day of curing. Small amounts of bleed water were found for conditions 8, 9, 15, and 16 after 1 day of curing. No bleed water was found on any of the samples after 28 days of curing.

Volume change measurements were performed using ASTM method C 174/C 174M-97, *Standard Test Method for Measuring Thickness of Concrete Elements Using Drilled Concrete Cores*, which measures the length of a hardened waste form cylinder after the curing period. Condition 12 had a slight expansion (1.5 %), while condition 2 had no expansion or shrinkage. All of the other conditions show small shrinkage, <5.0 %. Condition 3 had shrinkage of 1.3 %.

Compressive strengths were determined for 7-day and 28-day cured samples and were carried out in accordance with ASTM C39/C 39M-99, *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*. All of the samples had compressive strengths greater than 500 psi, the strength requirement for the project.

The TCLP was determined on samples cured for 28 days and 118 days (28 + 90 days). The EPA SW-846, Method 1311, test was used to determine the TCLP from a crushed (minus 3/8 inch) sample (SW-846 1992). Analyses were carried out for antimony, arsenic, barium, beryllium, cadmium, chromium (total), lead, mercury, nickel, rhenium (condition 5 only), selenium, silver, vanadium, and zinc. Thallium concentration was not measured. The results for all of the samples were below the Washington State Department of Ecology Dangerous Waste Standards (Department of Ecology Standards), while all of the results, except chromium, were also below the more stringent UTS. All of the DRF4 samples except condition 16 did not meet the UTS for chromium. Condition 16 had twice the amount of ferrous sulfate monohydrate added to the mix. While the samples containing DRF2 meet the UTS for chromium except for condition 1, the highest waste loading, the measured value was 0.880 mg/L, while the standard is 0.6 mg/L. For DRF2, the highest chromium leaching levels in this study are associated with the lowest ratio of cement to waste content in the cast stone.

The leaching rates for nitrate, nitrite, chromium, and rhenium were measured on monolithic specimens using the method described in ANSI/ANS 16.1. The procedure describes a leachability index as determined by using a volume of demineralized water (in mL) that is 10X the surface area of a solid monolithic sample (in cm<sup>2</sup>). ANSI/ANS 16.1 leaching was performed for all of the test conditions and was carried out for 90 days. Analysis of the leachate for prescribed analytes is performed on leach solutions removed after 2 hours, 7 hours, 24 hours, 2 days, 3 days, 4 days, 5 days, 19 days, 47 days, and 90 days. Effective diffusivities for each leaching interval are calculated from each measured analyte concentration. The leaching index for that interval is the negative logarithm (base 10) of the effective diffusivity. The reported leaching index for a specific period of time (e.g., 19 days, 47 days, 90 days) is then the numerical average of the leaching indices of all the intervals included in that period of time. Higher numbers for the leachability index indicate reduced diffusion rate, for a given ionic species, through the cast stone matrix. Concentration measurements and the leaching index were determined for nitrate, nitrite, and chromium. For condition 5, the leaching index for rhenium was also determined.

ANSI/ANS 16.1 90-day leaching indices are presented in Table 3 for all of the test conditions. The results show that the DRF2 diffusivities are much lower (orders of magnitude for nitrate and nitrite leaching) than those for DRF4. For all of the samples, chromium leaching indices are >10.0 with many of the indices for the DRF2 conditions near 11.0. A leaching index of 12.1 was found for rhenium, the simulant surrogate for technetium.

**Table 3. 90-Day ANSI/ANS 16.1 Leach Test Results for Nitrate, Nitrite, Chromium, and Rhenium.**

Condition	DRF	Waste Loading (wt%) TDS Basis	Waste Loading (wt%) Na <sub>2</sub> O Basis	90-Day Leach Index			
				Nitrate	Nitrite	Chromium	Rhenium
1	2	24.2	9.87	7.2	7.1	>11.2	N/A
2	2	21.8	8.89	7.1	7.0	>11.1	N/A
3	2	18.8	7.67	7.7	7.4	>11.0	N/A
4	2	16.1	6.57	7.6	7.5	>10.9	N/A
5 <sup>a</sup>	2	14.7	6.00	7.8	7.6	>10.9	12.1
6	2	13.2	5.38	8.1	8.0	>10.7	N/A
7	2	11.6	4.73	8.3	8.2	>10.6	N/A
8	2	10.0	4.08	8.5	8.3	>10.6	N/A
8 Replicate	2	10.0	4.08	8.3	8.2	>10.5	N/A
9	2	8.3	3.39	8.2	8.1	>10.4	N/A
10	2	6.5	2.65	8.5	8.4	>10.2	N/A
11	2	16.1	6.57	7.9	7.9	>10.9	N/A
12	2	18.4	7.51	7.5	7.4	>11.0	N/A
13	4	24.2	9.87	6.1	6.0	>10.5	N/A
13FSX2 <sup>b</sup>	4	24.2	9.87	6.1 <sup>c</sup>	6.0 <sup>c</sup>	>11.0 <sup>c</sup>	N/A
14	4	16.1	6.57	6.4	6.2	>10.7	N/A
14FSX2 <sup>b</sup>	4	16.1	6.57	6.4 <sup>c</sup>	6.3 <sup>c</sup>	>10.8 <sup>c</sup>	N/A
15	4	10.0	4.08	7.5	7.4	>10.4	N/A
15 Replicate	4	10.0	4.08	7.5	7.3	>10.3	N/A
16FSX2 <sup>b</sup>	4	8.0	3.26	7.5 <sup>c</sup>	8.4 <sup>c</sup>	>10.1 <sup>c</sup>	N/A

<sup>a</sup> NaReO<sub>4</sub> was added to the condition 5 sample at a level of 4.9 mg/L of as-received simulant.

<sup>b</sup> Ferrous sulfate monohydrate added at 2.2 g/100 mL of as-received simulant. For all other samples, ferrous sulfate monohydrate was added at 1.1 g/100 mL of as-received simulant.

<sup>c</sup> 47-day results only.

After the 19-day ANSI/ANS 16.1 leaching results were measured, a “nominal” waste loading, condition 3, of 18.8 wt% (TDS basis), or 7.67 wt% (Na<sub>2</sub>O basis) was determined to have provided satisfactory results and was selected for further analysis in Part 3 of the project. The factors that aided in this selection included (1) nitrate, nitrite, and chromium leaching behavior was superior in DRF2 to DRF4, (2) nitrate and nitrite diffusivities had not changed dramatically between condition 3 and condition 4, (3) chromium diffusivity was low in DRF2 samples, (4) in condition 3, the waste loading was almost double that for the condition with no evaporation, and (5) the use of evaporation to reduce liquid waste volume by up to 50 % was possible (a specification that could be achieved in the field). This condition therefore became the nominal formulation and was included in the

Part 3 test matrix. Five additional Part 2 conditions were also selected for Part 3. All of the chosen conditions used DRF2, and work with test conditions containing DRF4 was discontinued.

### **Part 3 - Waste Form Performance Testing with LAW**

For Part 3 all experimental studies were carried out at the 222-S Laboratory at the Hanford Site. The LAW with a nominal sodium content of 5 M was supplied by CH2M HILL for use in these studies. One dry reagent formulation (DRF2) was used based on the results of the Part 1 and Part 2 tests.

The LAW was prepared at the 222-S Laboratory by dissolving a composite sample in water. The composite sample was made by blending saltcake from seven single-shell tanks (Callaway 2003). The resulting solution, containing nominally 5 M sodium, was shipped to the 325 Laboratory where it was treated by ion exchange to remove <sup>137</sup>Cs. The <sup>137</sup>Cs-depleted LAW was thoroughly characterized at the PNNL 325 Laboratory, and then a portion of it was shipped back to the 222-S Laboratory to perform the cast stone testing.

Both the LAW simulant and the actual LAW were characterized at PNNL using the same instrumentation and procedures. The overall agreement between the actual waste and the simulant is shown in Table 4. The agreement was better than 10% for most of the concentrated analytes, including sodium, nitrate, hydroxide, carbonate, and nitrite. Larger differences resulted for less concentrated species, including aluminum, chromium, fluoride, potassium, and total organic carbon. In general, these differences were judged to have minimal impact on the cast stone process testing. The chromium difference (concentration in simulant 48% lower than in actual LAW) may have had some impact on the cast stone leach test results.

Six waste loading conditions using DRF2 were selected. The Part 2 conditions included in the Part 3 matrix were numbers 1, 2, 3, 4, 8, and 12. The nominal condition (condition 3) with a waste loading of 18.8 wt% (TDS basis) or 7.60 wt% (Na<sub>2</sub>O basis) was run in duplicate. The waste loading was varied by more than a factor of two from low to high. Water was evaporated from the supplied LAW to obtain the selected waste loadings.

All conditions were tested after 28-day curing, similar to Part 2 testing, using ANSI/ANS 16.1, TCLP, and bleed water measurements. Table 5 shows the test matrix used for the Part 3 waste performance tests using radioactive LAW material. In addition, total organic volatiles and semivolatile organic analysis (SVOA) of the TCLP solutions were performed. No analytes of interest were detected by the SVOA and volatile organic analysis (VOA).

Calculations utilized a LAW density of 1.2585 g/mL and a LAW dissolved solids content of 31.06 wt%. Ferrous sulfate monohydrate (1.1 g per 100 mL of as-received LAW) was added to all samples.

**Table 4. Comparison of Simulant and Actual LAW Composition.**<sup>(a,b)</sup>

Analyte	LAW Simulant (M)	Actual LAW (M)	Difference (%)
Al	0.058	0.208	-72
B	N/A	0.0021	N/A
C <sub>2</sub> O <sub>4</sub>	0.0097	0.0105	-7.4
CO <sub>3</sub> (TIC)	0.484	0.533	-9.1
Ca	N/A	0.0014	N/A
Cl	0.0430	0.0415	3.6
Cr	0.0097	0.0186	-48
F	0.030	0.018	63
K	0.0118	0.0090	30
Na	4.75	5.10	6.9
NO <sub>2</sub>	0.414	0.414	0
NO <sub>3</sub>	2.34	2.44	-4.4
Free OH	0.52	0.51	2.2
PO <sub>4</sub>	0.0461	0.0515	-11
Si	N/A	0.0039	N/A
SO <sub>4</sub>	0.0891	0.0932	-4.5
Other soluble TOC (e.g. acetate)	0.36	N/A	N/A
TOC	0.285	0.233	22.6

<sup>a</sup> From Rassat et al. 2003.<sup>b</sup> Concentrations in molarity.

Water was evaporated from the supplied LAW to obtain the waste loadings given in Table 5. The exception was condition 8, labeled “natural,” for which no evaporation was needed. Table 5 shows the volume of LAW before evaporation (“Initial Volume LAW”) and after evaporation (“Adjusted Volume LAW”).

The TCLP procedure tested for metals of antimony, arsenic, barium, beryllium, cadmium, chromium (Cr, total), lead, mercury, nickel, selenium, silver, thallium, vanadium, and zinc. The measured leaching results were compared with the values given in the Washington State Department of Ecology (Ecology) standards and with the more stringent UTS. All results met Ecology standards. With the possible exception of thallium, all results also met the UTS. For thallium, the method detection limit (MDL) was greater than the UTS value.

The ANSI/ANS 16.1 leaching procedure was used to determine the concentration and to calculate the leach rate for technetium, uranium, iodine, nitrate, nitrite, chromium, and cesium. Uranium and cesium leach indices could not be calculated due to uncertainties in the LAW source terms and barium interference with the inductively coupled plasma spectrometer/mass spectroscopy analysis of the leach liquids. Leaching indices were similar to those found with simulant testing in Part 2; indices for nitrate and nitrite were between 7.5 and 8.6, for chromium between 12.6 and 13.3, and for technetium between 9.4 and 10.1 (technetium results were lower than the 12.1 index found for rhenium). The leaching index for <sup>129</sup>I was also measured and a leaching index >8.0 estimated.

**Table 5. Part 3 Test Matrix.**

Condition	Waste Loading, TDS Basis (wt%) <sup>a,b</sup>	Waste Loading, Na <sub>2</sub> O Basis (wt%) <sup>c</sup>	Adjusted LAW per 90 g DRF (mL) <sup>d</sup>	Initial Volume LAW Actually Used (mL)	Adjusted Volume LAW Actually Used (mL)	Volume Reduction (%)	Actual DRF Used (g)
1	24.2	9.79	40	35.1	15.0	57.3	33.75
2	21.8	8.82	40	31.3	15.0	52.1	33.75
3-1	18.8	7.60	35	29.1	15.0	48.5	38.55
3-2 (dup)	18.8	7.60	35	29.1	15.0	48.5	38.55
4	16.1	6.51	35	24.5	15.0	38.8	38.55
8	10.2 (natural)	4.12	35	15.0	15.0	0	38.55
12	19.2	7.76	35	29.8	15.0	49.7	38.55

<sup>a</sup> Waste loading on a total dissolved solids (TDS) basis, 100 % times grams of TDS in the simulant divided by grams of cast stone.

<sup>b</sup> DRF2 was used for all conditions.

<sup>c</sup> To convert from a TDS basis to a Na<sub>2</sub>O basis, multiply by 0.4044.

<sup>d</sup> Milliliters of simulant after evaporation or dilution to be added to 90 g of DRF.

#### Part 4 - Waste Form Validation Testing

Four tests were performed for the Part 4 analyses: maximum curing temperature, curing heat evolution and modeling, hydraulic conductivity, and thermal conductivity. All work was done with samples prepared from DRF2 and simulant. The waste loading was 18.8 wt% (TDS basis) or 7.67 wt% (Na<sub>2</sub>O basis).

##### Maximum Curing Temperature Testing

Five samples, approximately 1-in. diameter x 2-in.-long cylinders, were cast in PVC containers, sealed and then immediately cured for 28 days at five distinct, elevated temperatures of 60, 70, 75, 80, and 85 °C. Five additional samples were also cured at room temperature during the same time period. This temperature range was determined after the initial waste loading confirmation tests during which no substantial temperature rise was noted. A study by Langton (1998) also indicated that a similar grout waste form showed no deleterious effect up to a temperature of 70 °C but did exhibit deterioration effects at 90 °C.

After the samples were cured for 28 days, they were immersed in accordance with the ANSI/ANS 16.1 procedure for a 19-day time period. Visual observations were made and recorded at 1, 5, and 19 days. Visual observations included but were not limited to cracking, scaling, and delamination. After the 19-day time period, compression tests in accordance with ASTM method C39/C39M were made. Using the visual observations and compression test data, an assessment was prepared for the maximum curing temperature. Cracking, scaling, and delamination were not observed for any of the specimens, regardless of curing temperature or time, suggesting the maximum curing

temperature could reach 85° C with no ill effects. After the 19-day immersion period, all of the final compressive strengths were at least three times the acceptance criteria of 500 psi.

### **Curing Heat Evolution and Modeling**

The hydration of a cementitious formulation (DRF2) is an exothermic process. During the hydration process, a significant amount of heat is generated.

Testing was performed to determine the heat output during the curing process. The tests performed used a semiadiabatic mold setup and embedded thermocouples cast into the sample. Freshly mixed cast stone slurry, using an 18.8% simulant waste loading, was placed into a 1-gallon mold surrounded by R-30 insulation (a separate plastic container kept the insulation in place). Thermocouples within the mold were kept stationary by a 1/16-in. steel rod. Three thermocouples were placed inside the 1-gallon mold, in the middle of the pour, at one-quarter the distance to the container side and on the edge of the thermos container. Thermocouples were also placed on the outside of the thermos container (directly opposite the thermocouple inside the container), below the thermos and insulation, and above the thermos and insulation. Another thermocouple measured room temperature. The temperature rise (and decrease) was monitored for a 2-week period. Appreciable heat generation was observed only during the first week of hydration.

A similar experiment was conducted prior to the 1-gallon test using a 5-gallon mold and a waste loading of only 9 wt%. The experimental setup was nearly identical. Thermocouples were embedded into a freshly mixed cast stone and the temperature was measured for 11 days.

The highest temperature achieved was 54.0 °C with a temperature differential (difference between room temperature and the maximum recorded cast stone temperature) of 30.2 °C. These results from both the heat of hydration and the heat dissipation experiments were used in calculations performed by Service d'expertise en matériaux (S.E.M. Inc). Numerical modeling using the experimental results indicated the maximum temperature differential in the final waste container would be 50° C. The results overall indicate that the temperature rise will not be a significant factor in causing cracking or in reducing cast stone durability.

### **Thermal Conductivity**

The hydration of the cementitious system in the presence of liquid LAW is an exothermic process. The heat generated during this process needs to be dissipated relatively quickly through the material.

The thermal conductivity of the cast stone was determined by the thermal transmission of flat cast stone slab specimens that had been cured for 7 days. The test was conducted using ASTM method C 177-97, *Test Method for Steady-State Heat Flux Measurements*

*and Thermal Transmission Properties by Means of the Guarded-hot-plate Apparatus.* Flat plate specimens of 6-in. x 6-in. x 0.5-in. thick were prepared inside form-wood molds and immediately placed inside a sealed plastic container with moist burlap. The form-wood is coated so that all of the moisture is retained within the mold (i.e., water is not absorbed by the wood mold). The specimens were cast and allowed to hydrate for 4 days before transportation (inside the moist plastic container) to Geoscience LTD where the C 177-97 test was performed. Thermal transmission was measured between 75 °F and 90 °F. A decrease in the thermal conductivity was observed from the first to the last day indicating the thermal conductivity is greatest during the early stages of hydration. Thermal conductivity during curing was measured as 0.785 to 0.316 Btu/hr f °F.

### **Hydraulic Conductivity**

Hydraulic conductivity was measured to determine the permeability, a direct consequence on the rate of leaching of various chemical species from the cast stone. The hydraulic conductivity of cementitious materials is expected to be lower than  $1 \times 10^{-7}$  cm/s. ASTM test method D6527, *Test Method for Determining Unsaturated and Saturated Hydraulic Conductivity in Porous Media by Steady-State Centrifugation*, measures hydraulic conductivity between  $10^{-4}$  cm/s and  $10^{-11}$  cm/s. The method uses steady-state centrifugation and a steady solution flow to measure the conductivity.

ASTM D6527 testing was performed on 1-in.- x 2-in.-long cylinders. Three test specimens were produced for the tests. The samples were cured at room temperature for 28 days and surrounded (embedded) within a liquid aluminum epoxy to form the cylindrical mold for the centrifuge. The top and bottom of the cylinder were ground to ensure that no epoxy obstructed flow into and out of the cast stone. The specimens were then sent to UFA Ventures, Inc. for ASTM D6527 testing. Tap water was used as the centrifuge flow fluid.

Results indicate cast stone samples had such low hydraulic conductivities that only the transient initial saturated hydraulic conductivity could be measured, and this only as an upper limit. The estimated saturated hydraulic conductivities were between  $<1.41 \times 10^{-10}$  and  $<3.57 \times 10^{-10}$  cm/s. The actual hydraulic conductivity will be lower; the calculated values act as an upper bound. These data (and the experimental experience) indicate cast stone is nearly impervious to hydraulic fluid flow. The cast stone samples never saturated over the 3-week experimental period, indicating extremely low hydraulic conductivities or perhaps diffusion-control.

### **Part 5 - Technetium Getter Testing**

One of the critical properties under investigation is the capacity of cast stone to bind or sequester technetium and prevent this chemical element from leaching into the environment. As part of the investigation of technetium leaching, a number of materials were investigated to determine their capacity to immobilize technetium.

A test plan was written (Cooke 2003) to govern testing of technetium getter materials. This test plan involved three steps. The first step was to acquire as many different potential technetium getters as possible and determine their ability to bind with nonradioactive rhenium (an element that has similar chemical properties to technetium) mixed with LAW simulant in solution. These fall into two general categories. First are those materials that reduce the radionuclide or toxic metal to a less oxidized and less soluble form. Second are inorganic materials that bind the normally soluble species in the oxidation state that they normally occur in with a less soluble substance.

After determining which getters showed the greatest potential for binding with rhenium, these getters were combined with simulant spiked with rhenium, mixed with DRF2 to form cast stone, cured for 10 days, and subjected to the quick leach procedure previously used in the Part 1 studies. The four candidate getter materials selected for testing in cast stone samples were (1) Cosmic Black<sup>4</sup> bone char, (2) Will Form synthetic apatite, (3) zero valent iron, and (4) hydrotalcite. The leachate was analyzed for rhenium. A sample with no technetium getter was prepared from LAW and DRF2 and leached as a control. Finally, these same getters were combined with LAW containing technetium, mixed with the DRF2 to form cast stone, cured for 9 days, and subjected to the quick leach procedure. The leachate was analyzed for technetium.

The Cosmic Black bone char gave the best performance. For the sample containing Cosmic Black, the technetium concentration in the leachate was 62 % of the technetium concentration in the leachate for a sample with no getter added. The next best getter was the Will Form synthetic apatite, with its leachate containing about 70 % of the technetium contained in the sample with no getter added.

## Conclusions

### Part 1 – Selection of Dry Reagent Formulation

- a. Based on results from an approximation of the TCLP, a Portland cement/fly ash/blast furnace slag formulation is superior to formulations based on Portland cement, fly ash, and clays.
- b. Chromium leaching can be reduced by adding ferrous sulfate to the formulation.
- c. To achieve waste loadings of greater than about 10 wt% (TDS basis), or 4 wt% (Na<sub>2</sub>O basis), evaporation of the LAW is needed.
- d. Bleed water formation can be avoided by using a formulation that involves adding no more than about 30 to 40 ml of liquid waste, after evaporation or dilution, to 90 g of DRF.

---

<sup>4</sup> Cosmic Black is a trade name of Ebonex Corporation, Melvindale, Michigan.

## **Part 2 – Waste Form Performance Testing with Simulant**

- a. The use of DRF2 results in cast stone with compressive strengths well above the requirement of 500 psi. This is for samples cured at room temperature.
- b. For most conditions studied, a slight reduction in volume can be expected during the curing of the cast stone samples prepared from DRF2 and simulant.
- c. For samples prepared from DRF2 and simulant ANSI/ANS 16.1 leaching indices are between 7.1 to 8.5 for nitrate, 7.0 to 8.4 for nitrite, and greater than about 10 to 11 for chromium.
- d. A formulation condition with a waste loading of 18.8wt % (TDS basis) or 7.67 wt% (Na<sub>2</sub>O basis) provides satisfactory waste form testing results and can be obtained by use of evaporation to reduce the simulant volume by slightly less than 50%.

## **Part 3 – Waste Form Performance Testing with Radioactive (LAW-based) Samples**

- a. With the possible exception of thallium, samples prepared from DRF2 and LAW do not exceed the leaching requirements of Ecology standards and the UTS for all conditions studied. For thallium, the MDL for the analysis was greater than the UTS standard. VOAs and SVOAs are not present at levels of interest.
- b. For samples prepared from DRF2 and LAW ANSI/ANS 16.1, leaching indices are between 7.4 to 8.5 for nitrate, 7.5 to 8.6 for nitrite, are greater than about 8 to 9 for iodide, are greater than about 12.4 to 13.2 for chromium, and are 9.4 to 10.3 for technetium. Iodine leach indices appear to be greater than 7.9, although <sup>129</sup>I concentrations in the leach liquids were below the quantification limit.
- c. ANSI/ANS 16.1 leaching indices for nitrate, nitrite, and technetium increase as waste loadings decrease.

## **Part 4 – Waste Form Validation Testing with a Selected Nominal Formulation Using Simulant-Based Samples**

- a. The adiabatic temperature rise during curing of cast stone with the nominal formulation and prepared from simulant is approximately 30 °C.
- b. Providing the effective average temperature of the LAW and DRF being blended to produce cast stone is maintained at or below 40 °C, the maximum temperature achieved during curing is 70°C or less.
- c. Curing at elevated temperatures of 60 to 85 °C as opposed to room temperature reduces compressive strength. Samples cured at elevated temperatures still have exceptionally high compressive strength, three to four times the required level.
- d. Cast stone is extremely nonpermeable with a saturated hydraulic conductivity of about 10 E-10 cm/s.

- e. It may not be possible to measure the unsaturated hydraulic conductivity of cast stone due to its impermeable nature.

### **Part 5 – Technetium Getter Testing**

All potential getter materials that were tested showed the ability to sequester rhenium, a surrogate for technetium. Of the nine candidate technetium getters tested, Cosmic Black bone char produced the best results, with a technetium leachate concentration at 62 % of the technetium leached from a sample with no getter added.

### **Nitrate Leaching Observations**

- a. Values measured for ANSI/ANS 16.1 nitrate leaching indices in Part 2 and Part 3 testing were very similar. This also held true for nitrite. In both the Part 2 and Part 3 studies, the nitrate ANSI/ANS 16.1 leaching indices decreased as waste loadings increased. This also held true for nitrite.
- b. Very similar nitrate and nitrite results were obtained with simulant and with LAW.
- c. Crystal formation during evaporation to increase waste loading does not appear to influence nitrate leaching.

### **References**

- ANSI/ANS-16.1, 1986, *Measurement of the Leachability of Solidified Low Level Radioactive Wastes by a Short-Term Test Procedure*, American National Standards Institute/American Nuclear Society, La Grange Park, Illinois.
- ASTM C39/C 39M-99, 1999, *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*, American Society for Testing and Materials, Easton, Maryland.
- ASTM C 174/C 174M-97, 1997, *Standard Test Method for Measuring Thickness of Concrete Elements Using Drilled Concrete Cores*, American Society for Testing and Materials, Easton, Maryland.
- ASTM C 177-97, *Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded-hot-plate Apparatus*, 1997, American Society for Testing and Materials, Easton, Maryland.
- ASTM C 940-98a, 1998, *Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory*, American Society for Testing and Materials, Easton, Maryland.
- ASTM D6527, 2001, *Test Method for Determining Unsaturated and Saturated Hydraulic Conductivity in Porous Media by Steady-State Centrifugation*, American Society for Testing and Materials, Easton, Maryland.

- Callaway, W. S., 2002, *222-S Laboratory Test Plan for Preparation of Ex-Situ Vitrification Test Solution*, RPP-13046, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Cooke, G. A., 2003, *Test Plan for the Evaluation of Grout Additives to Enhance the Sequestration of Radioactive and Toxic Metals*, HNF-16346, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Langton, C. A., 1998, *Direct Grout Stabilization of High Cesium Salt Waste: Salt Waste Alternative Phase III Feasibility Study (U)*, WSRC-TR-98-003337, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina.
- Lokken, R. O., et al., 1992, *Durability of Double-Shell Tank Waste Grouts*, PNL-7835, Battelle Pacific Northwest National Laboratory, Richland, Washington.
- Lockrem, L. L., 2005, *Hanford Containerized Cast Stone Facility Task 1 - Process Testing and Development Final Test Report*, RPP-RPT-26742, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.
- Rassat, S. D., et al., 2003, *Cold Dissolved Saltcake Waste Simulant Development, Preparation, and Analysis*, PNNL-14194, Pacific Northwest National Laboratory, Richland, Washington.
- Rebagay, T. V., and D. A. Dodd, 1989, *Leach Characterization of Phosphate-Sulfate Grouts*, WHC-SA-0466-FP, March 1989 paper presented at the Annual Meeting of the American Chemical Society, Dallas, Texas.
- SW-846, Method 1311, 1992, *Toxicity Characteristic Leaching Procedure*, Rev. 0, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

#### **Bibliography**

- Brown, P., September 14, 1994, *US Patent #5,678,233, Method of Immobilizing Toxic or Radioactive Inorganic Wastes and Associated Products*.
- Center for Laboratory Sciences SOP Manual*, Rev. 1, Center for Laboratory Sciences, Columbia Basin College, Pasco, Washington.
- Center for Laboratory Science Quality Assurance Manual*, CLS QAM, CLS-QAM-001, Rev. 1, Center for Laboratory Sciences, Columbia Basin College, Pasco, Washington.
- Conca, J. L., and Wright, J., April 17, 2001, *US Patent #6,217,775, Treatment of Metal-contaminated Leachates Using Fish Bones and Hard Parts*.

- Cooke, G. A., 2003, Test Procedure for Cast Stone, Part 3 Radioactive Sample Laboratory Experiment, HNF-N-70-3, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Fluor Hanford, Inc., 2002, *222-S Laboratory Quality Assurance Plan (QAP)*, HNF-SD-CP-QAPP-016, Rev. 6, Fluor Hanford, Inc., Richland, Washington.
- Fluor Hanford, Inc., 2003, *Test Plan for the Evaluation of Grout Additives to Enhance the Sequestration of Radioactive and Toxic Metals*, HNF-16346, Rev. 0, Richland, Washington.
- Fluor Hanford Inc., 2003, *Hanford Containerized Cast Stone Facility Phase I Testing and Demonstration Activities Interim Process Development Testing Report*, Richland, Washington.
- Kanezaki, E., August 2001, *Intercalation of Anionic Species at the Interlayer Gallery Region of Layered Double Hydroxides with Hydrotalcite-like Structure*, 222<sup>nd</sup> American Chemical Society Annual Meeting, Chicago, Illinois.