# Low Temperature Waste Form for Supplemental Immobilization of Hanford Low Activity Waste – 14232

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## ABSTRACT

The Hanford Site has approximately 56 million gallons of radioactive waste stored in 177 underground storage tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is being constructed to treat all of the high-level waste (HLW) in the tank farms but will not have sufficient capacity to treat all of the low-activity waste (LAW) within the anticipated time frame for completion of the waste treatment mission. The LAW vitrification facility will need to be supplemented with a second LAW vitrification facility or an alternate LAW immobilization technology.

In this work, tests were conducted on a low-temperature waste form for immobilization of Hanford LAW. A statistically designed matrix of Cast Stone formulations were prepared and characterized for key processing and waste form performance properties. The results were analyzed to identify effects of formulation parameters including LAW composition, LAW concentration, sources of blast furnace slag and fly ash, and water to dry mix ratio on Cast Stone properties. Of the five main variables, the mix ratio, fly ash source, and blast furnace slag source were the most significant variables affecting the Cast Stone properties. Effects of LAW composition and concentration were less important indicating that Cast Stone is robust with respect to LAW composition and that higher waste loadings may be possible. All Cast Stone formulations easily met Universal Treatment Standards (UTS) for hazardous metals in the Toxicity Characteristic Leaching Procedure (TCLP). This work provides a firm basis for further development to optimize Cast Stone for immobilization of Hanford LAW.

### **INTRODUCTION**

More than 56 million gallons of radioactive and hazardous waste are stored in 177 underground storage tanks at the U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed to treat the wastes and immobilize them in a glass waste form. The WTP includes a pretreatment facility to separate the wastes into a small volume of high-level waste (HLW) containing most of the radioactivity and a larger volume of low-activity waste (LAW) containing most of the nonradioactive chemicals. The HLW will be converted to glass in the HLW vitrification facility for ultimate disposal at an offsite federal repository. At least a portion (~35%) of the LAW will be converted to glass in the LAW vitrification facility and will be disposed of onsite at the Integrated Disposal Facility (IDF). The pretreatment and HLW vitrification facilities will have the capacity to treat and immobilize the wastes destined for each facility. However, a supplemental LAW treatment facility will be needed for the expected volume of LAW requiring immobilization.

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A cementitious waste form known as Cast Stone is being evaluated to provide the required additional LAW immobilization capacity. The Cast Stone waste form and immobilization process must be tested to demonstrate that the final Cast Stone waste form can comply with the waste acceptance criteria for the disposal facility and that the immobilization processes can be controlled to consistently provide an acceptable waste form product. Further, the waste form must be tested to provide the technical basis for understanding the long-term performance of the waste form in the disposal environment. These waste form performance data are needed to support risk assessment and performance assessment (PA) analyses of the long-term environmental impact of the waste disposal in the IDF. The PA is needed to satisfy DOE Order 435.1 requirements.

Cast Stone has been selected for solidification of radioactive wastes including WTP liquid secondary wastes treated at Hanford's Effluent Treatment Facility (ETF). This selection was based in part on recent test data that showed improved performance of Cast Stone for immobilization of contaminants such as Tc-99 [1]. Further, it was noted that WTP liquid secondary waste simulants had similar concentrations of major constituents to the LAW simulant compositions selected for this work.

Cast Stone was previously evaluated for supplemental immobilization of Hanford LAW in the early 2000s [2]. That work involved limited formulation development and focused on a single LAW composition that represented an average of much of the salt cake in Hanford Tank Waste.

The objectives of the current program to evaluate the suitability of Cast Stone for supplemental LAW immobilization are as follows:

- Determine an acceptable formulation for the LAW Cast Stone waste form.
- Evaluate sources of dry materials for preparing the LAW Cast Stone.
- Demonstrate the robustness of the waste form for a range of LAW compositions.
- Demonstrate the robustness of the formulation for variability in the Cast Stone process.
- Provide Cast Stone contaminant release data for PA and risk assessment evaluations.

The first step in determining an acceptable formulation for the LAW Cast Stone waste form was to conduct screening tests to evaluate the impact of key parameters including ranges in waste composition, waste stream concentrations, sources of dry materials, and mix ratios of waste (free water basis) to dry blend. A statistically designed test matrix was used to evaluate the effects of these key parameters on the properties of the Cast Stone as it is initially prepared and after curing.

### METHODS AND MATERIALS

The tests were performed by investigators at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) with technical direction and oversight by Washington River Protection Solutions (WRPS), the current Hanford Tank Operations Contractor to the US Department of Energy, Office or River Protection (DOE/ORP).

#### **Screening Test Matrix**

Screening tests were performed to evaluate the effects of key parameters on the properties of the

Cast Stone as it is initially prepared and after curing. The test parameters and their ranges that were investigated in the screening tests included:

- Simulants representing a range of LAW compositions (Average, SST Blend, High Al, and High SO<sub>4</sub>)
- Waste concentration (5 M and 7.8 M Na)
- Class F fly ash source (NW = High Ca, SE = Low Ca)
- Blast furnace slag source (NW, SE)
- Free-water-to-dry-blend solids mix ratio (0.4, 0.6).

The four simulants are discussed below. The Na concentrations of 5 M and 7.8 M were selected to represent a range of possible waste concentrations for processing. The Class F fly ash included a relatively high Ca content material available in the Pacific Northwest (designated NW) and a lower Ca content material available in the southeastern (designated SE) part of the country. Blast furnace slags (BFSs) from the northwest (NW) and southeast (SE) were also selected for the screening tests. The 0.4 and 0.6 values of the water-to-dry-blend solids mix ratio (henceforth referred to as "mix ratio") were selected based on the range (0.35 to 0.41 grams of water per gram dry blend solids) used for the secondary waste Cast Stone formulation work [2] and 0.60 grams of water per gram of dry blend solids used at the Saltstone Production Facility at the Savannah River Site. The different combinations of simulants, Na concentrations, and mix ratios yielded waste loadings ranging from 9.5 wt% to 20.3 wt% total waste solids in the final Cast Stone waste form.

The dry blend mix ratio was held constant at 8 wt% portland Type I/II cement, 45 wt% Class F fly ash, and 47 wt% Grade 100-120 BFS [3]. A single source of portland cement was used for all of the testing because the variability in the cement was not expected to be significant among the possible sources.

The original test matrix for the screening tests was composed of 26 test conditions. The matrix was developed using statistical optimal experimental design (OED) methods and software and included two blocks of tests. The first block consisted of 14 tests including 12 distinct parameter combinations and 2 replicates to assess the effects of the individual test parameters. The second block consisted of 12 tests including 10 distinct parameter combinations and 2 replicates. The second block of tests augmented the first block of tests to assess the individual parameter effects as well as selected two-parameter interactions and to determine if there was a "block" effect. A fifth replicate pair included one test in each block. The replicate tests provide for quantifying the experimental and measurement uncertainties in performing tests and measuring properties and also provide for statistically assessing the significance of individual parameter and two-parameter interaction effects [3].

During preparation of the matrix samples, one of the laboratories discovered that the BFS source in 12 of the mixes had been inadvertently transposed (NW vs. SE). As a corrective measure, those mixes were repeated with the correct dry blend material. The mis-batched samples were retained, re-designated as Mix No.s 27 through 38. The augmented matrix with the additional samples identified appears in Figure 1.

#### **Simulant Compositions**

Four simulants were selected to represent a range of possible LAW compositions to be solidified in the Cast Stone waste form. They included a dissolved saltcake simulant used in previous testing of LAW immobilization technologies and three chemical simulants based on the Hanford Tank Waste Operations Simulator (HTWOS) flowsheet modeling of the LAW feed that is anticipated to be sent to a Supplemental LAW immobilization facility. A detailed description of the simulant development work is provided by Russell et al. [4].

Saltcake waste is a predominant form of the wastes in a large fraction of the Single Shell Tanks (SSTs) at Hanford. To support an evaluation of supplemental treatment alternatives for Hanford LAW, a saltcake waste simulant was developed based on a blend of real waste samples from SSTs S-101, S-109, S-110, S-111, U-106, and U-109 [5]. This simulant has been used in previous Cast Stone testing with Hanford LAW stimulants and real waste. The composition matches the average composition of saltcake from 68 Hanford SSTs representing 85 percent of the total saltcake inventory in all Hanford SSTs and DSTs at that time [6].

	Fly Ash Source/Blast Furnace Slag Source (Northwest or Southeast USA)							
Waste Composition	NW/NW	NW/SE	SE/NW	SE/SE	NW/NW	NW/SE	SE/NW	SE/SE
Average 5M	35	20						13 2
High SO₄ 5M			1		10	31		
High Al 5M	28	4			24	37		17
SST Blend 5M			8		32	12		
Average 7.8M	5	29	6		27 36	3 22		
High SO₄ 7.8M	15 25	33 38		14 7			26 21	
High Al 7.8M			19		30	9	11	
SST Blend 7.8M	16	34		18			23	
Mix Ratio (w/dm)	0.4	0.4	0.4	0.4	0.6	0.6	0.6	0.6
Original Mix No.								
Additional Mix No.			Test Combination			Replicate		

Figure 1. Cast Stone Screening Test Matrix

Three additional simulants representing a range of LAW tank waste compositions were developed based on output from the Hanford Tank Waste Operations Simulator (HTWOS)

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supporting the *River Protection Project System Plan*, Revision 6 [7]. The HTWOS model is used to track the tank waste as it moves from storage through retrieval, feed staging, and multiple treatment and immobilization processes over the life of the WTP mission. The HTWOS model can be used to forecast the quantities and compositions of primary and secondary waste streams as a result of various proposed operating scenarios. As one of the outputs, the HTWOS model provides the projected compositions of LAW feed to a supplemental immobilization facility over the course of the tank waste cleanup mission.

The first simulant was an overall average of the 1046 weeks of LAW immobilization waste feed compositions modeled over a 20-year mission, henceforth referred to as the "Average" simulant. The second simulant was the "High Al" corresponding to the highest concentration of dissolved aluminum relative to Na. Elevated Al could lead to faster cure and higher strength. The third simulant, referred to as the "High SO<sub>4</sub>" simulant, was selected because sulfate and fluoride were at relatively high concentrations relative to sodium and phosphate was near its maximum. High phosphate and fluoride could result in sodium fluorophosphate precipitation at the high pH levels of the LAW and elevated sulfate could cause ettringite formation in the Cast Stone product. In fact, fluorophosphate precipitation was observed in initial the simulant preparations. The simulant compositions were subsequently adjusted to reflect the concentrations that would actually be present in the LAW solution after filtration. The actual simulant compositions selected for testing appear in Table I.

Waste Constituent	SST Blend Saltcake	HTWOS Average	HTWOS High Al	HTWOS High SO4		
	Concentration (moles/mole Na) <sup>(a)</sup>					
Na	1.000	1.000	1.000	1.000		
К	0.002	0.007	0.028	-		
Al	0.013	0.061	0.112	0.047		
Cl	0.009	0.008	0.018	0.007		
F	0.006	0.006 <sup>(b)</sup>	0.010	0.012 <sup>(b)</sup>		
$SO_4$	0.018	0.017	0.004	0.030		
$PO_4$	0.010	0.010 <sup>(b)</sup>	0.005	0.010 <sup>(b)</sup>		
$NO_2$	0.085	0.113	0.194	0.098		
NO <sub>3</sub>	0.502	0.324	0.287	0.367		
CO <sub>3</sub>	0.095	0.055	0.040	0.035		
TOC Total	0.057	0.015	0.021	0.007		
Free OH	0.097	0.312	0.293	0.306		
(a) $\Delta$ fter charge halancing						

TABLE I. Hanford LAW Simulant Compositions

(a) After charge balancing.

(b) Concentration of F and  $PO_4^{3-}$  reduced from HTWOS values because of solids formation observed in preliminary simulants.

constituent not included

#### **Spike Levels for Constituents of Concern**

The simulants used to make Cast Stone waste forms for contaminant release testing were spiked with hazardous chemicals and/or radionuclides to determine how well the Cast Stone waste form controls the release of these constituents of concern (COCs). Results in the Final Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland Washington [9] showed that only  $^{99}$ Tc,  $^{129}$ I, Cr, and NO<sub>3</sub> had non-negligible projected groundwater concentrations from Cast Stone disposed at the IDF.

An initial feed vector for the RCRA metals was selected by taking the maximum weekly batch values from the HTWOS modeling for System Plan 6 [8] for the feed to Supplemental LAW immobilization. An initial screen of these values showed that levels As, Ba, Se, Ag, Sb, Be, and Ni in the Cast Stone would be below Universal Treatment Standards (UTSs) by total analysis (i.e. TCLP leachate concentrations would be below the UTS even if 100% of the COC leached). The list of RCRA metals added and their spike levels appears in Table II. None of the COCs that fell below UTS by total analysis were added to the simulants with the exception of Ni. Nickel was included because it contributes a significant mass to the RCRA metals vector. Mercury was excluded because it forms highly insoluble compounds with iodine which would decrease the ability of iodine to leach from the waste form. Thallium was not included because the secondary waste Cast Stone program showed satisfactory performance for thallium in TCLP

Waste Constituent	HTWOS Average	HTWOS Maximum	Other Considerations	
RCRA Metals and UHCs <sup>(d)</sup>	moles/mole Na	moles/mole Na	moles/mole Na	
Cd	2.78E-06	3.19E-05	_	
Cr	2.42E-03	9.99E-03	4.30E-03 <sup>(a)</sup>	
Pb	1.16E-05	5.13E-05	-	
Ni	6.41E-05	6.61E-04	_	
Radionuclides	Ci/mole Na	Ci/mole Na	Ci/mole Na	
<sup>99</sup> Tc	1.13E-05	4.13E-05	-	
<sup>99</sup> Tc <sup>(c)</sup>	(6.65E+02 µg/mole Na)	(2.43E+03 µg/mole Na)	-	
<sup>129</sup> I	1.44E-08	8.01E-08	3.54E-06 <sup>(b)</sup>	
<sup>127</sup> I (stable) <sup>(c)</sup>	(8.14E+01 µg/mole Na)	(4.53E+02 µg/mole Na)	(2.00E+04 µg/mole Na)	
<sup>232+233+234+235+236+238</sup> U	1.59E-08	5.63E-08		
Natural or depleted U <sup>(c)</sup>	-	(3.56+04 µg/mole Na)	-	

TABLE II. Spike Levels for Hazardous Constituents and Radionuclides

(a) Cr concentration adjusted based on review of best basis inventory and previous simulant work

(b) Iodine concentration increased to address possible detection limit issues in waste form leach tests.

(c) These COCs were added to simulants based on mass (as shown).

(d) UHCs = underlying hazardous constituents

leach testing [1]. Thallium was also very close to the UTS value by total analysis (0.36 mg/L versus 0.2 mg/L) and thus would require minimal attenuation in TCLP leach testing to meet the UTS. The Cr spike level of  $4.3 \times 10^{-3}$  M/M Na represents the 95th percentile of HTWOS modeled compositions and is comparable to levels tested in previous work with Cast Stone for both LAW [9] and WTP liquid secondary waste [1].

To measure the retention and release of radionuclides of concern, spikes of <sup>99</sup>Tc, <sup>129</sup>I (substituted with nonradioactive <sup>127</sup>I), and U were added to Cast Stone batches prepared for EPA Method 1315 leach testing studies. Table II shows the spike levels for these radionuclides. The <sup>99</sup>Tc was spiked in all samples at the HTWOS maximum concentration. To increase the probability of being able to detect iodine in as many of the leachates as possible and at various leach intervals, the stable iodine (<sup>127</sup>I) concentration in the simulants was increased to 100 mg/L for the 5 M Na simulants and 156 mg/L for the 7.8 M simulants. These concentrations of stable iodine are 245 times larger than the average mass concentration of <sup>129</sup>I and 44 times larger than the maximum mass concentration of <sup>129</sup>I projected by the HTWOS model to be present in LAW.

# **Cast Stone Sample Preparation**

The Cast Stone monoliths were prepared by mixing aliquots of the simulant batches and the dry blend mixes and then casting the slurry into plastic molds to cure. Batches of each of the four simulants were prepared ahead of time and 1.75-kg batches of the dry blend mixes were prepared ahead of time by weighing the cement, fly ash, and BFS at a ratio of 8:45:47. To minimize the effects of inter-laboratory variation due to sample preparation, a mixing method developed at SRNL for fresh properties was used at both SRNL and PNNL for sample preparation. Simulants were aliquoted for each respective batch into a 2-L plastic beaker. A Caframo model BDC1850 overhead mixer with a 3.5–in. outer diameter (OD) elliptical impeller was used to mix the simulants and blend the Cast Stone mixture (see Figure 2). The



Figure 2. Cast Stone Sample Preparation

beaker was positioned such that the impeller was 0.5 in. from the front of the beaker and 1 in. off the bottom. The mixer was started with an agitator speed of 200 rpm. The pre-mixed dry material was then added over a time period of 2 to 7 minutes. The agitation speed was adjusted to maintain a slight vortex and the wet slurry was stirred for 15 minutes from the start of addition of the dry blend. At the completion of mixing, samples were taken for measuring fresh paste properties and the remaining Cast Stone material was poured into 2-in. × 4-in. cylindrical forms and capped. The capped monoliths were placed in humidified containers and allowed to cure at room temperature for 28 days before testing.

# **Fresh Properties Testing**

The following tests were conducted for the 26 original and 12 additional parameter combinations. Flow consistency via modified ASTM D6103, *Standard Test Method for Flow Consistency of Controlled Low Strength Material (CLSM)* [11] gives an indication of rheological properties under field conditions. Slurry rheology was measured via cup and bob viscometer to obtain plastic viscosity and with a vane rheometer to estimate yield stress. Gel time is a method developed by SRNL to determine the time required for a mix to gel sufficiently to resist flow. Set time is

measured by ASTM C191 Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle [12]. A modified version of the final set described in the ASTM procedure was used to allow for up to 2 mm of penetration. The measurement time unit for the Cast Stone mixes was days rather than minutes as in the ASTM procedure due to the retardation of the hydration reactions caused by the high concentrations of salts in the solutions being solidified. Set time corresponds to the development of structure from hydration reactions and may be used as a process control point for allowing the movement of Cast Stone waste packages from the production facility to interim storage or the disposal facility. Slurry samples of each of the mixes were also monitored for change in ultrasonic pulse velocity (UPV) as the mix cured. Isothermal heat of hydration for the Cast Stone mixes was measured in accordance with ASTM C1679, Standard Method for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry [13]. Salt solution components can affect either the total energy produced during hydration, or to a greater extent, the time frame over which the energy is released. The composition of dry blend components and composition and amount of additives can also affect the magnitude and timing of hydration heat generation. Heat generation directly affects cure temperature and can alter the mineralogy and microstructure development and influence cured waste form properties. Finally, each of the mixes was tested for the presence of free liquids at 24 hrs and after 3 days of cure time.

### **Cured Waste Form Properties**

After curing for 28 days, the Cast Stone waste form monoliths were characterized with respect to chemical composition, density, porosity, compressive strength, TCLP, and contaminant leachability via EPA Method 1315. The characterization work was conducted at both PNNL and SRNL. Chemical composition was measured via standard analytical laboratory methods for sample digestion and analysis. Compressive strength was measured via ASTM C39 *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens* [14]. Cured density and porosity were measured via helium pycnometry.

# **RESULTS AND DISCUSSION**

Highlights of the test results and data evaluation are presented in this section. Detailed statistical analyses were performed but due to the level of detail and complexity were outside the scope of this paper. Interested readers may consult the comprehensive report that was prepared to describe this work for details of those analyses [3].

#### **Fresh Mix Rheological Properties**

Average flow diameter in the modified ASTM D6103 flow test ranged from 94 mm to just under 300 mm. Gel times ranged from 1 minute to 121 minutes. Plastic viscosity results for the 38 Cast Stone mixes appear in Figure 3. As expected, the mixes with the 0.4 mix ratio were more viscous than the mixes with the higher water content at a mix ratio of 0.6. Plastic viscosities were in the range of 220 to 580 centipoise (cP) for the 0.4 mixes and 54 to 165 for the 0.6 mixes. There appears to be a smaller trend with the mixes prepared with the SE fly ash being more viscous than those prepared with the NW fly ash. No data were obtained for Mix 1 because it had set before the test could be completed. Such a formulation would not be considered for actual production without evaluating set retarding or rheology modifying additives.

# **Isothermal Heat Generation**

Heat-of-hydration results include the total energy generated over 300 hours of testing, the maximum (peak) heat generation rate, and the elapsed time to reach the maximum heat flow. Figure 4 shows the cumulative heat generated over the 300 hours for the 38 Cast Stone mixes. Total heat generated was in the range of 150 to 434 joules/gram (J/g) of dry blend material. There appears to be a trend of higher heat generation for the 0.6 mix ratio mixes compared with the 0.4 mix ratio mixes. The peak heat generation rate ranged from 890 to 4260 mW/g and the time to peak heat generation ranged from 16 to 164 hours.

# Set Time and Free Liquid

The set time for the 38 Cast Stone mixes ranged from 21 hours to 223 hours. The results are shown in Figure 5. In general, formulations with higher water to dry mix ratio have longer set times and formulations at higher sodium concentrations tend to have longer set times. Formulations with set times greater than 72 hours would require increased space in a production facility for curing. Such formulations would be evaluated for additives to accelerate set and cure time.



Figure 3. Results of Plastic Viscosity Measurements for the 38 Cast Stone Slurries



Figure 4. Heat generation at 300 hours for the 38 Cast Stone mixes



Figure 5. Vicat Set Time Measurements for the 38 Cast Stone mixes

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Five of the test mixes resulted in samples with free liquids after 24 hours. Three of the mixes (Mixes 17, 23, and 32) all produced free liquid that persisted to 3 days. Free liquids generated by the other mixes were reabsorbed between the 1-day and 3-day measurements. Table III shows the free liquid results for the five mixes generated from duplicate samples cast from the same mix after 1 and 3 days of setting.

Mix Number	Random Run Order	Free Liquid (Vol%)				
		Da	y 1	Day 3		
		Duplicate 1	Duplicate 2	<b>Duplicate 1</b>	<b>Duplicate 2</b>	
12	29	1.09	1.11	0.00	0.00	
9	31	0.45	0.40	0.00	0.00	
23	20	2.33	2.39	2.43	2.20	
16	36	0.84	0.68	0.00	0.00	
17	25	0.52	0.45	0.28	0.21	
32(12a)	8	5.84	5.91	4.47	4.46	

TABLE III. Cast Stone Mixes Generating Free Liquids

### **Compressive Strength**

Compressive strength for the 38 Cast Stone mixes was measured at 28 days cure time +/- 20 hours as specified in ASTM C39. The results appear in Figure 6. Compressive strengths of the different mixes ranged from 6.6 to 55.4 MPa (960 to 8040 psi). All of the mixes exceeded the target minimum compressive strength of 3.4 MPa (500 psi). The lower compressive strengths tended to be from mixes with the 7.8M Na simulants and the 0.6 water-to-dry-blend mix ratio. The higher compressive strengths tended to be from mixes with the 7.8M Na simulants and the 5 M Na simulants and/or those with the 0.4 water-to-dry-blend ratio.



Figure 6. Compressive Strength Results for 38 Cast Stone Mixes

# **Toxicity Characteristic Leaching Procedure**

The TCLP, EPA Method 1311 [15], was conducted to demonstrate that the Cast Stone screening test formulations will meet RCRA land disposal restrictions for hazardous wastes. The LAW is projected to include RCRA metals including As, Ba, Cd, Cr, Pb, Hg, Se, and Ag; and underlying hazardous constituents (UHCs) including Sb, Be, Ni, and Tl. In addition, some of the dry materials may include these same and other hazardous materials. The TCLP testing was conducted at the Southwest Research Institute (SwRI) in San Antonio, Texas.

The results of the TCLP testing are shown in TABLE IV (note that the table is populated with only values above the detection limit). As described previously, the simulants used in the Cast Stone specimens were spiked with only Cr, Pb, Ni, and Cd. Neither Pb nor Cd was detected in any of the TCLP extracts. Chromium and Ni were measured in most but not all of the extracts. The As, Ba, and Se were not included in the simulants. They are present in the dry materials used to make the Cast Stone. Even with a 100% contribution from the dry materials, the TCLP results for As and Se would be below the UTS limits. For the values in Table IV, all of the 26 Cast Stone mixes easily met the UTS limits.

Element	UTS limit, µg/L	Reporting Limit, µg/L	Minimum	Maximum
Ag	140	<5	<5	<5
As	5000	<10	<5	45.1
Ba	21000	<5	101	1120
Be	1220	<5	<5	<5
Cd (Spike)	110	<5	<5	<5
Cr (Spike)	600	<5	<5	106
Pb (Spike)	750	<10	<10	<10
Hg	25	<0.2	< 0.2	< 0.2
Ni (Spike)	11000	<5	<5	119
Sb	1150	<20	<20	<20
Se	5700	<10	15.7	68.1
Tl	200	<25	<25	<25

TABLE IV. Toxicity Characteristic Leaching Procedure Results

#### EPA Method 1315 Leach Testing

The EPA Draft Method 1315 [16] leach tests were conducted for a total of 91 days with additional leachant changes at 77 and 91 cumulative days, which were 14 and 28 days beyond the standard 63 days of the EPA Draft Method 1315 but similar in duration to the ANSI/ANS 16.1 method. Figure 7 shows the resulting effective diffusivities for Na, nitrate, nitrite, I (added as iodide), Tc (added as pertechnetate), Cr (added as chromate), and U (added as uranyl) for Cast Stone Mix 5 (Average 7.8 M Na simulant mixed with NW/NW dry blend and a free-water-to-dry-blend ratio of 0.4). The figure shows the relative leaching performance of the different constituents with Na, nitrate, nitrite, and I having comparable effective diffusivities and with Tc, Cr, and U having increasingly lower effective diffusivities.

Figure 8 shows the range of Tc effective diffusivities observed among the 26 Cast Stone mixes in the screening test matrix. Mix 23 had the highest Tc diffusivities of the 26 mixes. Because of processing properties (e.g., set time), this mix would not be considered for actual production. Mix 18 had the lowest Tc diffusivities from 28 through 63 days. At 63 days, the range of Tc effective diffusivities among the 25 mixes is between  $6.8 \times 10^{-12}$  and  $2.3 \times 10^{-10}$  cm<sup>2</sup>/s (Mixes 18 and 8, respectively).

Figure 9 compares the effective diffusivities for mixes with NW dry blend components and mixes with the SE dry blend components for the High  $SO_4$ , High Al, and SST Blend simulants at the same Na molarities and water-to-dry-blend solids ratios. The source of the dry blend components appears to have an impact, but the trend is not consistent across the three simulants. Technetium diffusivities are lower for the SE dry blend components with the High  $SO_4$  and SST Blend simulants. However, for the High Al simulant, the Tc diffusivities are lower Cast Stone prepared with the NW dry blend ingredients.



Figure 7. Relative Diffusivities



Figure 8. Range of Technetium Diffusivities





Figure 9. Effect of Dry Blend on Technetium Diffusivity

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Figure 10 shows the Tc effective diffusivities for the NW dry blend components and the four simulants used in the screening test matrix. All three Tc diffusivity figures show in general that the Tc effective





Figure 10. Variation of Technetium Diffusivity with Simulant Type

diffusion coefficients for the duplicate samples (a and b) for each mix yield very similar values. The Tc effective diffusion coefficient values for a few of the mixes at particular leach times show some variation between the two duplicates, but the differences are small and show no time or mix consistency and thus are not considered practically important.

### CONCLUSIONS

The screening tests demonstrated that for the range of parameters studied, the formulations could be processed and would provide acceptable waste forms. With the exception of two mixes, the formulations have shown good processing and waste form properties and have not touched any unacceptable waste form boundaries. Mix 1 at the mix ratio of 0.4 set quickly and would not be considered an acceptable formulation. The other mix (Mix 23) at the 0.6 mix ratio had generally poorer waste form properties than the other formulations and would not be considered for use. The screening test results suggest that there are opportunities to increase waste loading by increasing the mix ratio and increasing the waste concentration.

All of the Cast Stone mixes had acceptable properties with respect to anticipated waste acceptance criteria for the IDF. Compressive strengths well exceeded the 500 psi (3.45 MPa) target. The leachates from the TCLP test easily met treatment standards to address Land Disposal Restrictions for hazardous metals in 40 CFR 268.

Leach tests on cured Cast Stone cylinders were conducted for 91 days using EPA Method 1315 to measure the effective diffusivity of key constituents of concern including Tc, I, U, Cr, Na, and nitrates and nitrites. Effective diffusivities are used in performance assessments and risk assessments to describe the release of contaminants from the waste form. Effective diffusivities for Na, I, nitrate, and nitrite averaged over the 28- to 91-day cumulative leach intervals were all in the same range of  $1 \times 10^{-8}$  to  $2 \times 10^{-9}$  cm<sup>2</sup>/s for all but one of the 26 Cast Stone mixes. The corresponding leachability indices (LIs) were in the range of 8 to 8.7. Technetium effective diffusivities were in the range of  $2 \times 10^{-10}$  to  $6 \times 10^{-12}$  cm<sup>2</sup>/s (LI = 9.7 to 11.2) for the same 25 mixes and total leach interval. Chromium effective diffusivities were in the range of  $9 \times 10^{-13}$  to  $8 \times 10^{-15}$  cm<sup>2</sup>/s (LI = 12.0 to 14.1). Uranium was not detected in most of leachates from the 25 mixes, indicating that the U is retained in the Cast Stone and is being minimally released under the conditions of the EPA 1315 leach test.

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