Solidification Tests For LLW Sludges at ORNL – 9161

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ABSTRACT

The Oak Ridge Transuranic Waste Processing Center (TWPC), operated by EnergX TN, LLC, must process about 350,000 gallons of remote-handled (RH) sludge from ten liquid low-level waste (LLLW) tanks at Oak Ridge National Laboratory (ORNL). In order to solidify and stabilize the waste to meet the Waste Acceptance Criteria for the Nevada Test Site (NTS), the waste must be mixed with solidification/stabilization agents, remain flowable during mixing, be self-leveling in the waste disposal container, and produce a solid waste form that is not hazardous and has no free liquids, suitable for transportation and disposal at the NTS.

Lab-scale tests using a surrogate sludge were performed at MSE Technology Applications, Inc. (MSE-TA) to evaluate a range of grouting recipes, using Portland cement, fly ash and ground blast furnace slag, plus other additives. The viscosity of the wet grout and the amount of free water, if any, after various time intervals, was measured. EnergX personnel supplied the initial grout recipe, based on testing with a simplified sludge surrogate (calcium nitrate and diatomaceous earth). The tests at MSE-TA showed that ratios of dry blend ingredients to surrogate of from 0.75:1 to 1:1 would produce flowable grouts with viscosities of 1300 to 2200 cP that had no free water at any time during curing.

The recipe for a surrogate sludge slurry was developed at ORNL, which matches the primary constituents of the average tank waste sludge composition, including, in decreasing concentrations, calcium, aluminum, magnesium, uranium, iron, and thorium. The target total suspended solids (TSS) concentration in the surrogate is 5.0 wt%, which is the planned concentration for sluicing the sludge from the tanks for solidification. Soluble ions in the surrogate include nitrate, nitrite, carbonate, chloride, sulfate, sodium and potassium. The surrogate was prepared by adding soluble salts of the metals to water, and then precipitating the sludge by adding calcium hydroxide and sodium hydroxide.

New samples of the actual waste sludge have been collected from four tanks at ORNL, and small-scale grouting tests are being performed, using the most promising grout recipes tested at MSE-TA. The presence of free water during curing was evaluated, and the cured grouts will be analyzed using the Toxicity Characteristic Leaching Procedure (TCLP) to determine if any of the hazardous metals in the sludge (Hg, Pb, Cr, etc.) leach above the Resource Conservation and Recovery Act (RCRA) limits.

Larger scale surrogate tests (55-gal) will then be conducted at MSE-TA to examine any scale-up issues.

INTRODUCTION

Oak Ridge National Laboratory (ORNL) has ~350,000 gal of a low-level waste sludge stored in ten LLLW tanks, which has been collecting for over 20 years. EnergX is responsible for disposing of the sludge, and is evaluating using grouting to solidify this waste. The goal is to produce a non-transuranic waste that could be disposed of at the Nevada Test Site (NTS). The sludge would be retrieved from the tanks as a dilute slurry (~5 wt% suspended solids) and grouted by adding a mixture of Portland cement, fly ash, and ground blast furnace slag (GBFS), plus other additives. The sludge contains various heavy metals, including mercury, chromium, and lead, which could cause the grouted sludge to fail the Toxicity Characteristic Leaching Procedure (TCLP), thus being a hazardous waste under RCRA. To meet the waste acceptance criteria (WAC) for NTS, the grouted waste must be non-transuranic, non-hazardous, and have no free water.

MATERIALS AND METHODS

The surrogate recipe for the sludge waste was developed at ORNL to match the average chemical composition of the waste sludge. The chemical composition to make about 6 liters (L) of the surrogate is presented in Table I; however, the amount of water added is adjusted as needed to produce a slurry with 5.0 wt% suspended solids. The surrogate was prepared by adding soluble salts of the metals to water, and then precipitating the sludge by adding calcium hydroxide and sodium hydroxide. The standard surrogate has a pH of 10, which is the average of the tank sludges. Sodium hydroxide or nitric acid is used to adjust the pH to the desired value. The surrogate also contains a mixture of organics (see Table II) at a concentration of 7600 mg/L total organic carbon (TOC), which is the average organic concentration in the actual sludge samples. The organic mixture is the Savannah River Site (SRS) Legacy plutonium/uranium extraction (PUREX) process waste surrogate, which had been used previously by MSE-TA for other projects, and should be similar to the organics present in the waste sludge. Most of the organics present in the waste sludge have not been identified by chemical analysis, but show up in a total organic carbon (TOC) analysis.

Several different surrogate recipes were used during the testing sequence. A high and low pH version of the surrogate (pH = 8.7 and 12) was tested to mimic the minimum and maximum pH values for the sludge. The standard surrogate has a concentration of 7600 mg/L total organic carbon (TOC), which is the average organic concentration in the actual sludge samples. A higher organic concentration (13,400 mg/L TOC), which is the maximum found in any of the actual sludge samples, was also tested. Another recipe that simulates using a sodium nitrate/sodium nitrite waste solution to slurry the waste sludge was also tested.

The dry-blend solidification ingredients included Portland cement (Type I/II), fly ash (Type F), and GBFS (Grade 120). Later tests used small amounts of an inorganic and organic additive to control free water formation. The goal is to have no free water at anytime during the curing process, so that the actual waste containers can be closed and readied for shipping immediately after being mixed.

MSE-TA performed bench scale grouting tests using the surrogate sludge to determine optimum waste-loading ratios for solidification of the sludge. The solidified wasteforms must be compatible with handling equipment and should maintain stability under a variety of conditions that could occur during generation, storage, shipment, and disposal. The viscosity of the wet grout mixtures was measured. In an attempt to correlate viscosity to the stickiness of the wet grout, a dipstick test was performed on each of the samples by dipping a metal strip measuring 5-7/8 inches by 1 inch by 3/16 inch into the samples immediately after mixing and weighing the amount of grout mixture adhering to the strip.

Table I. Sludge Waste Surrogate Recipe

Chemical Name	Compound	Target Weight (g)
Sodium Sulfate	Na_2SO_4	3.4
Calcium Nitrate	$Ca(NO_3)_2\ 4H_2O$	29.5
Ferric Nitrate	$Fe(NO_3)_3\ 9H_2O$	26.2
Ferric Chloride	$FeCl_3$	3.2
Potassium Nitrate	KNO_3	29.6
Magnesium Nitrate	$Mg(NO_3)_2\ 6H_2O$	145.9
Thorium Nitrate	$Th(NO_3)_4\ 4H_2O$	28.7
Uranyl Nitrate	$UO_2(NO_3)_2\ 6H_2O$	103.6
Sodium Aluminate	$NaAlO_2$	33.8
Calcium Hydroxide	$Ca(OH)_2$	140.6
Sodium Carbonate	Na_2CO_3	12.7
Sodium Silicate	$Na_2SiO_3\ 5H_2O$	82.7
Sodium Nitrite	$NaNO_2$	7.1
Organic (PUREX surrogate)	Mixture	8.1
	Total	**655.1**

Table II. SRS Legacy PUREX Surrogate

Chemical Name	Compound	Target Weight (g)
Tri-n-butyl Phosphate	$[CH_3(CH_2)_3O]_3PO_4$	179.8
n-Undecane	$CH_3(CH_2)_9CH_3$	114.2
n-Dodecane	$CH_3(CH_2)_{10}CH_3$	112.9
n-Tridecane	$CH_3(CH_2)_{11}CH_3$	111.7
n-Tetradecane	$CH_3(CH_2)_{12}CH_3$	110.8
Diethylbenzene	$[CH_2CH_3]_2C_6H_4$	241.8
1,4, Di-isoproplybenzene	$[CH(CH_3)_2]_2C_6H_4$	245.0
Di-n-octylamine	$[CH_3(CH_2)_7]_2NH$	82.6
	Total	**1,198.8**

Core samples from four of the waste tanks (W-23, W-25, W-28, and W-35) were collected, with 2 or 3 sample tubes required per tank to collect a full depth sample. The tubes from each tank were combined and mixed to give four homogenous sludge samples. Multiple sub-samples were collected from each blended sample, one for physical, chemical, and radionuclide analysis and the rest for grout testing. The grouting tests were conducted inside a glove box, using an electric mixer to blend the samples. Figure 1 shows a photograph of the mixer and impeller. Each grout sample was diluted with water to produce a slurry with the desired total suspended solids (TSS) prior to adding the grouting ingredients. Figures 2 and 3 show a concentrated and diluted sludge sample. Ratios of dry blend solids to waste slurry of 0.75:1 to 1.2:1 were tested. Ferrous sulfide was added to one sample from each tank, to determine the impact on the leaching of mercury. It is possible that boric acid may need to be added to the sludge as a neutron poison, so it was added at a concentration of 0.1 wt% to one sample from each tank, to determine any impact on the grout properties. Table III shows a summary of the grouting mixtures that were prepared. The grouted samples were monitored for free water, and will be analyzed for TCLP metals after curing for at least 28 days.

Fig. 1. Mixer and impeller.

Fig. 2. Concentrated sludge (19.8 wt% TSS)

Fig. 3. Diluted sludge (5.0 wt% TSS)

Table III. Summary of grouting test conditions for actual waste tests

Tank	Slurry TSS (wt%)	Cement (wt%)	Fly ash (wt%)	GBFS (wt%)	Inorganic Additive (wt%)	Dry Blend to Slurry ratio (g/g)	Organic Additive (wt%)	Other Additives
W-25	2.6%	30%	30%	30%	10%	1.0	1.6%	
W-25	2.3%	23%	23%	23%	8%	0.75	1.2%	
W-25	5.0%	30%	30%	30%	10%	1.0	1.6%	
W-25	6.6%	30%	30%	30%	10%	1.0	1.6%	
W-25	5.0%	36%	36%	36%	12%	1.2	1.9%	
W-25	5.0%	30%	30%	30%	10%	1.0	1.6%	FeS
W-25	5.0%	30%	30%	30%	10%	1.0	1.6%	H_3BO_3
W-25	10.0%	30%	30%	30%	10%	1.0	1.6%	
W-25	5.0%	30%	30%	30%	10%	1.0	0.0%	
W-28	5.0%	30%	30%	30%	10%	1.0	1.6%	
W-28	5.0%	23%	23%	23%	8%	0.75	1.2%	
W-28	5.0%	36%	36%	36%	12%	1.2	1.9%	
W-28	5.0%	30%	30%	30%	10%	1.0	0.8%	
W-28	5.0%	30%	30%	30%	10%	1.0	1.6%	H_3BO_3
W-28	5.0%	30%	30%	30%	10%	1.0	1.6%	FeS
W-28	10.0%	30%	30%	30%	10%	1.0	1.6%	
W-28	5.0%	30%	30%	30%	10%	1.0	0.0%	
W-35	5.0%	30%	30%	30%	10%	1.0	1.6%	
W-35	5.0%	23%	23%	23%	8%	0.75	1.2%	
W-35	5.0%	36%	36%	36%	12%	1.2	1.9%	
W-35	5.0%	30%	30%	30%	10%	1.0	1.6%	FeS
W-35	5.0%	30%	30%	30%	10%	1.0	1.6%	H_3BO_3
W-35	10.0%	30%	30%	30%	10%	1.0	1.6%	
W-35	5.0%	30%	30%	30%	10%	1.0	0.0%	
W-35	5.0%	30%	30%	30%	10%	1.0	0.8%	
W-23	5.0%	30%	30%	30%	10%	1.0	1.6%	
W-23	5.0%	23%	23%	23%	7%	0.75	1.2%	
W-23	5.0%	36%	36%	36%	12%	1.2	1.9%	
W-23	5.0%	30%	30%	30%	10%	1.0	1.6%	H_3BO_3
W-23	5.0%	30%	30%	30%	10%	1.0	1.6%	FeS
W-23	10.0%	30%	30%	30%	10%	1.0	1.6%	

W-23	5.0%	30%	30%	30%	10%	1.0	0.0%	
W-23	5.0%	30%	30%	30%	10%	1.0	0.8%	

RESULTS AND DISCUSSION

Small-scale laboratory grouting tests were performed at MSE-TA using the surrogate sludge and various ratios of Portland cement, fly ash, and GBFS. These initial tests did not use any other additives. The grouted samples were checked daily for a curing period of 3 days to ensure no bleed water was present. The criteria for successful grout mixtures were a free-flowing grout before solidification and no free-standing liquid on the top of the samples. The small-scale samples were generated using 100 g of the surrogate and 200 g of the dry-blend mixture. Mixtures using 0 g, 5 g, 10 g, 15 g, and 20 g of Portland cement were tested, which correlate to weight percents of 0%, 2.5%, 5%, 7.5%, and 10%, respectively. For each of the different cement amounts, three different ratios of fly ash to GBFS amounts were also tested. The results for these tests, which all used the standard surrogate, are presented in Table IV.

Table IV. Results for Surrogate Grout Mixtures at a 2:1 Solid-to-Surrogate Ratio.

Surrogate pH	Dry Blend-to-Surrogate Ratio (g/g)	Dry Blend Mixture Information			Dipstick Weight (g)	Viscosity (centiPoise)
		Cement (Wt %)	Fly Ash (Wt %)	GBFS (Wt %)		
10	2:1	0	50	50	1.93	7820
10	2:1	0	55	45	1.90	7245
10	2:1	0	45	55	1.98	8652
10	2:1	2.5	48.75	48.75	1.76	6780
10	2:1	2.5	53.75	43.75	1.86	6490
10	2:1	2.5	43.75	53.75	1.89	8340
10	2:1	5.0	47.5	47.5	2.69	5130
10	2:1	5.0	52.5	42.5	2.35	4730
10	2:1	5.0	42.5	52.5	1.89	5560
10	2:1	7.5	46.25	46.25	2.11	4720
10	2:1	7.5	51.25	41.25	1.92	4350
10	2:1	7.5	41.25	51.25	1.79	5640
10	2:1	10	45	45	1.84	4490
10	2:1	10	50	40	1.80	4140
10	2:1	10	40	50	1.83	5100

All of the samples created at the 2:1 dry blend solids-to-surrogate ratio for the pH 10 surrogate had no bleed water and the wet mixtures had a consistency of a medium paste that was free-flowing. Increasing the ratio of fly ash to GBFS reduced the viscosity of the mixture for each of the cement concentrations.

Additional small-scale sample sets were generated using the three different pH surrogates, with 10% Portland cement, 45% fly ash and 45% GBFS but varying the solid-to-surrogate ratios from 0.5:1 up to 3:1. The results for these tests are shown in Table V. Once again, each of the samples used 100 g of the surrogate sludge.

As expected, the viscosity values increase as the solids in the samples increase. Increasing the pH of the surrogate generally causes a small increase in the viscosity, at a given solids concentration. The dipstick weight values also increase as the viscosity increases until a viscosity of 4400 − 8400 cP was reached, depending on the pH of the surrogate, and then the dipstick weight values decreased as the mixtures became thicker, and less grout adhered to the dipstick.

Table V. Results for Surrogate Grout Mixtures at Varying Solid-to-Surrogate Ratios

Surrogate pH	Dry Blend-to-Surrogate Ratio (g/g)	Dipstick Weight, (g)	Viscosity (centiPoise)	Sample Consistency During Mixing	Bleed Water (g)
10	0.5:1	0.24	1,180	Thin Slurry	0.5
10	0.75:1	0.23	1,315	Thin Slurry	0
10	1:1	0.52	1,500	Slurry	0
10	1.25:1	0.70	2,040	Slurry	0
10	1.5:1	1.50	2,360	Thick Slurry	0
10	1.75:1	2.01	2,770	Thin Paste	0
10	2:1	1.84	4,490	Paste	0
10	2.25:1	1.23	7,750	Thick Paste	0
10	2.5:1	0.37	8,040	Thick Paste	0
10	2.75:1	0.05	17,025	Thick Paste	0
10	3:1	0.02	116,850	Thick Paste	0
8.7	0.5:1	0.18	1,050	Thin Slurry	7.9
8.7	0.75:1	0.26	1,340	Thin Slurry	0
8.7	1:1	0.54	1,485	Slurry	0
8.7	1.25:1	1.05	2,160	Slurry	0
8.7	1.5:1	1.34	2,180	Thick Slurry	0
8.7	1.75:1	1.67	2,390	Thick Slurry	0
8.7	2:1	1.50	5,120	Thin Paste	0
8.7	2.25:1	1.36	7,820	Paste	0
8.7	2.5:1	0.49	8,690	Thick Paste	0
8.7	2.75:1	0.03	16,830	Thick Paste	0
8.7	3:1	0.02	105,320	Semi-Solid	0
12	0.5:1	0.23	1,241	Thin Slurry	17.6
12	0.75:1	0.33	1,520	Thin Slurry	5.1
12	1:1	0.58	1,735	Slurry	0
12	1.25:1	0.67	2,060	Slurry	0
12	1.5:1	0.74	2,690	Thick Slurry	0
12	1.75:1	2.06	2,690	Thick Slurry	0
12	2:1	2.56	5,380	Paste	0
12	2.25:1	2.36	8,430	Paste	0
12	2.5:1	0.12	8,920	Thick Paste	0
12	2.75:1	0.07	101,250	Semi-Solid	0
12	3:1	0.01	123,850	Semi-Solid	0

All of the samples at the 0.5:1 ratio failed the bleed water criteria, and the sample using the pH=12 surrogate at a 0.75:1 ratio also failed. The samples generated at solid-to-surrogate ratio greater than 2:1 were difficult to mix and were not free-flowing.

EnergX personnel developed a variation of the grout recipe that used small amounts of two additives, one inorganic and the other organic, and a higher concentration of Portland cement to produce a grout with no free water at anytime during curing. This recipe was developed using a simplified sludge surrogate that contained calcium nitrate and diatomaceous earth. MSE-TA conducted bench-scale tests (250 g of surrogate for each sample) using this new recipe on the full surrogate. The concentration of the inorganic additive was 10 wt% and that of the organic additive was 1.6 wt% for all of the tests. The results for these tests are shown in Table VI. All of the samples had a wet sheen on top of the grout after generation, but no free liquid was present at any time; consequently, the samples passed the bleed water criteria. The samples were exothermic during curing, reaching a maximum temperature of 33−34 °C.

Three solid-to-surrogate ratios (1:1, 0.75:1 and 0.5:1) were tested, with varying amounts of fly ash to GBFS in the solids mixture. The test matrix and sample data are presented in Table V. All of the 0.75:1 solid-to-surrogate ratio samples passed the bleed water criteria after mixing with only a sheen of moisture on top of the samples with no free liquid. However, all of the 0.5:1 ratio samples failed the bleed water criteria, with 3 to 5 milliliters of standing liquid after the mixing process was completed. The samples were slightly exothermic during curing with maximum temperatures reaching 22 °C to 25 °C. After comparing the data, it is apparent that the 0.75:1 ratio samples produced grout mixtures with lower viscosity and dipstick values than the 1:1 ratio samples. The 0.75:1 ratio samples, which contained a larger amount of fly ash compared to GBFS, produced samples that passed the bleed water criteria and had lower viscosities that result in easier mixing than the 1:1 solid-to-surrogate ratio samples.

Table VI. Results for Surrogate Grout Mixtures, Using the New Grout Recipe

Surrogate pH	Dry Blend-to-Surrogate Ratio (g/g)	Cement Mixture Information			Dipstick Weight (g)	Viscosity (Centipoise)
		Cement (Wt %)	Fly Ash (Wt %)	GBFS (Wt %)		
8.7	1:1	30	30	30	3.04	2235
10	1:1	30	30	30	2.97	2203
12	1:1	30	30	30	2.31	1949
10 – HO*	1:1	30	30	30	1.89	1571
10 – HN**	1:1	30	30	30	1.95	1563
8.7	0.75:1	20	40	30	1.79	1410
8.7	0.5:1	20	40	30	1.67	1340
10	0.75:1	20	40	30	1.77	1390
10	0.5:1	20	40	30	1.26	1245
12	0.75:1	20	40	30	1.53	1318
12	0.5:1	20	40	30	10	1179
* = High Organic Surrogate ** = High Nitrate/Nitrite Surrogate						

The lab-scale actual waste tests used the new grout recipe that was tested on the surrogate slurry samples. The observations for the tests are shown in Table VII. The only samples that showed free water at any time were those without the organic additive.

Table VII. Results for Lab-Scale Tests with Actual Waste Samples

Tank	Slurry TSS	Dry Blend to Slurry Ratio (g/g)	Organic Additive	Consistency at Completion of Mixing, and Free Water Observations
W-25	2.6%	1.0	1.6%	Thin slurry
W-25	2.3%	0.75	1.2%	Very thin slurry
W-25	5.0%	1.0	1.6%	Thin slurry
W-25	6.6%	1.0	1.6%	Thin slurry
W-25	5.0%	1.2	1.9%	Medium slurry
W-25	5.0%	1.0	1.6%	Thin slurry
W-25	5.0%	1.0	1.6%	Thin slurry
W-25	10.0%	1.0	1.6%	Medium slurry
W-25	5.0%	1.0	0.0%	Very thin slurry, ~1 mL free water for 30 min
W-28	5.0%	1.0	1.6%	Thin slurry
W-28	5.0%	0.75	1.2%	Very thin slurry
W-28	5.0%	1.2	1.9%	Medium slurry
W-28	5.0%	1.0	0.8%	Very thin slurry
W-28	5.0%	1.0	1.6%	Thin slurry
W-28	5.0%	1.0	1.6%	Thin slurry
W-28	10.0%	1.0	1.6%	Medium paste
W-28	5.0%	1.0	0.0%	Very thin slurry, ~1 mL free water for 30 min
W-35	5.0%	1.0	1.6%	Medium slurry
W-35	5.0%	0.75	1.2%	Very thin slurry
W-35	5.0%	1.2	1.9%	Medium slurry
W-35	5.0%	1.0	1.6%	Medium slurry
W-35	5.0%	1.0	1.6%	Medium slurry
W-35	10.0%	1.0	1.6%	Medium paste
W-35	5.0%	1.0	0.0%	Thin slurry, ~0.5 mL free water for 30 min
W-35	5.0%	1.0	0.8%	Thin slurry
W-23	5.0%	1.0	1.6%	Thin slurry
W-23	5.0%	0.75	1.2%	Very thin slurry
W-23	5.0%	1.2	1.9%	Thin slurry
W-23	5.0%	1.0	1.6%	Thin slurry
W-23	5.0%	1.0	1.6%	Thin slurry
W-23	10.0%	1.0	1.6%	Thick slurry

W-23	5.0%	1.0	0.0%	Very thin slurry, ~1 mL free water for 30 min
W-23	5.0%	1.0	0.8%	Very thin slurry