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Hydraulic Conductivity of Saltstone Formulated Using 1Q11, 2Q11 and 3Q11 Tank 50 Slurry Samples

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EXECUTIVE SUMMARY

As part of the Saltstone formulation work requested by Waste Solidification Engineering (WSE), Savannah River National Laboratory (SRNL) was tasked with preparing Saltstone samples for fresh property analysis and hydraulic conductivity measurements using actual Tank 50 salt solution rather than simulated salt solution. Samples of low level waste salt solution collected from Tank 50H during the first, second, and third quarters of 2011 were used to formulate the Saltstone samples. The salt solution was mixed with premix (45 wt % slag, 45 wt % fly ash, and 10 wt % cement), in a ratio consistent with facility operating conditions during the quarter of interest. The fresh properties (gel, set, bleed) of each mix were evaluated and compared to the recommended acceptance criteria for the Saltstone Production Facility. ASTM D5084-03, Method C was used to measure the hydraulic conductivity of the Saltstone samples. The hydraulic conductivity of Saltstone samples prepared from 1Q11 and 2Q11 samples of Tank 50H is 4.2E-9 cm/sec and 2.6E-9 cm/sec, respectively. Two additional 2Q11 and one 3Q11 sample were not successfully tested due to the inability to achieve stable readings during saturation and testing. The hydraulic conductivity of the samples made from Tank 50H salt solution compare well to samples prepared with simulated salt solution and cured under similar conditions (1.4E-9 – 4.9E-8 cm/sec).

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LIST OF ABBREVIATIONS

SDF	Saltstone Disposal Facility
SPF	Saltstone Processing Facility
SRNL	Savannah River National Laboratory
SS	Stainless steel
TCLP	Toxicity Characteristic Leaching Procedure
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAC	Waste Acceptance Criteria
WSE	Waste Solidification Engineering
wt %	Weight Percent

1.0 Introduction

Savannah River National Laboratory (SRNL) receives samples of Tank 50H every quarter to support regulatory compliance analyses. After material is utilized for Waste Acceptance Criteria (WAC) and Toxicity Characteristic Leaching Procedure (TCLP) analyses, the remaining sample from each quarter is available for formulation testing. As part of the Saltstone formulation work requested by Waste Solidification Engineering (WSE), SRNL was tasked with performing hydraulic conductivity measurements on Saltstone samples made in the laboratory with actual Tank 50H salt solution[1] as described in the task technical and quality assurance plan (TTQAP).[2] The results were compared to samples made from simulated salt solution cured under similar conditions[3]

Material collected from Tank 50H during the first, second, and third quarters of 2011 was used to make Saltstone samples for evaluating fresh properties and for hydraulic conductivity testing. Samples were formulated based on the operating conditions of the Saltstone Processing Facility (SPF) during the quarter of interest. When enough material remained after making the first set of samples, the formulation was varied, by adding or removing admixes, to determine the effect of changing the starting mix on the fresh properties and hydraulic conductivity of laboratory prepared Saltstone samples.

2.0 Experimental Procedure

Saltstone samples were prepared by mixing the premix materials and Tank 50H slurry followed by curing for at least 28 days at room temperature. After mixing, the fresh properties of the slurry (gel, set, and bleed) were tested. Once cured, the samples were cut to size, saturated, and tested for hydraulic conductivity. Figure 1 shows the flowchart for sample formulation and testing.

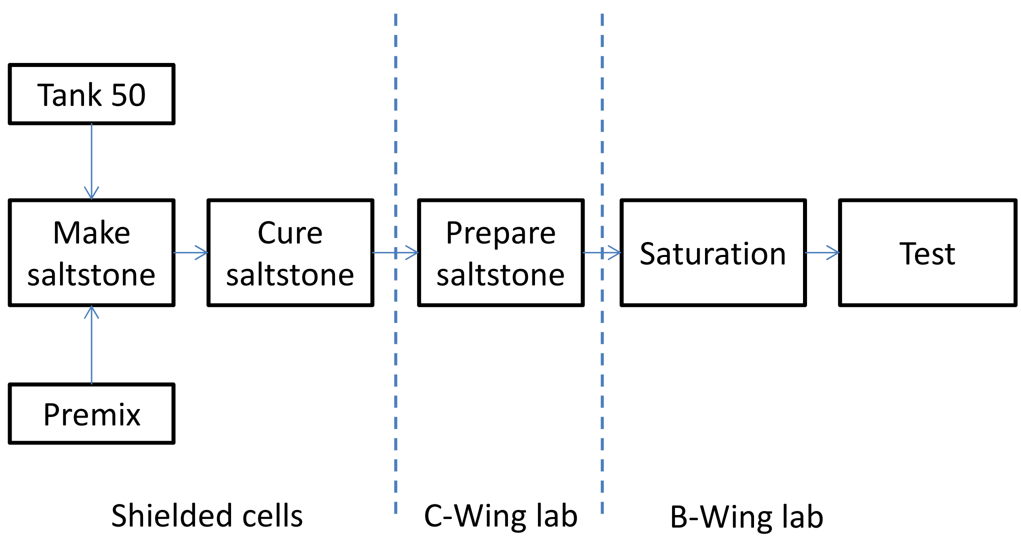

Figure 1. Flowchart of Saltstone preparation and testing

2.1 Making Saltstone

Saltstone samples were prepared from samples of Tank 50H salt solution collected during the first (1Q11)[4] second (2Q11)[5] and third (3Q11)[6] quarters of 2011. Premix (cement, slag, and fly ash), obtained from the SPF, was mixed with the Tank 50H salt solution in a specific water to premix ratio according to the facility operating conditions for the quarter of interest as provided by SPF engineering personnel (Table 1).[7]

Table 1. SPF processing conditions for the first, second, and third quarters of 2011

Processing Parameter	Units	1Q11	2Q11	3Q11
Dry Feed Rate	Tons/hr	33	33	33
Specific gravity set point	g/mL	1.19	not provided	1.2
Water to Premix ratio	Unitless	0.60	0.60	0.59
Daratard-17 rate	gpm	0	0	0.23 +/- 1
Q2-1383A rate	gpm	0.1 – 0.25	0.1 – 0.25	0.1 – 0.25

When enough Tank 50H salt solution remained after making the first set of samples, the formulation was varied, by adding or removing admixes, to determine the effect on the fresh properties and hydraulic conductivity of laboratory prepared Saltstone samples. Table 2 shows the specific sample formulations for the laboratory prepared Saltstone samples.

Table 2. Formulations for Saltstone prepared with 2011 Tank 50H salt solutions based on SPF processing conditions for the specific quarter

Parameter	Units	1Q11	2Q11 A & B	2Q11 C	3Q11 A & B
Density	g/mL	1.1995	1.2048		1.2152
Total Solids	wt %	24.43	24.80		25.20
Water Content	wt %	75.57	75.20		74.80
Water to Premix ratio	Unitless	0.60	0.60	0.60	0.59
Q2-1383A	wt % of premix	0.03	0.03	0.03	0.03
Daratard 17	wt % of premix	0	0	0.21	0.21
Cement	wt % in premix	10	10	10	10
Slag	wt % in premix	45	45	45	45
Fly Ash	wt % in premix	45	45	45	45

The 1Q11 and 2Q11 Saltstone samples were prepared in the shielded cells using the same preparation method as TCLP samples.[8] The salt solution, admixtures (Q2-1383A and Daratard 17) and premix materials were combined in a blender and mixed at low speed for one minute, inspected for incorporation of the premix, and then mixed at high speed for an additional two minutes. The grout poured smoothly and without clumps into 2 x 4 inch cylinders. After the fresh properties were measured, the cylinders were capped and allowed to sit undisturbed in the shielded cells for at least 28 days at room temperature. After curing, the samples were removed from the shielded cells to a radioactive laboratory hood for subsequent processing for hydraulic conductivity testing.

Since the dose was lower than the 1Q11 and 2Q11 salt solution, the 3Q11 Tank 50H samples were made in a radioactive laboratory hood, following the same procedure for mixing simulated Saltstone samples.[3] The admixtures, if used, were added to the salt solution. The paddle blade mixer was turned on and the premix materials were added to the liquid. Once all the dry feeds were incorporated, the grout slurry was mixed for approximately three minutes. The mixing was paused for approximately five seconds after the first 30 seconds of mixing to allow entrained air to escape from the grout. The grout poured smoothly and without clumps into 2 x 4 inch cylinders. After the fresh properties were measured, the cylinders were capped and allowed to sit undisturbed in the hood for at least 28 days at room temperature. After curing, the samples were prepared for testing.

2.2 Fresh Property Analysis

The fresh properties measured on the Saltstone mixes are gel time, set, and volume of bleed produced. The gel time is measured by pouring the fluid grout from one cup to the other every 5 minutes until the Saltstone did not flow under its own weight. The standing water is checked one day after mixing and three days after mixing. If liquid is present on top of the sample, it is poured off, weighed, and returned to the top of the sample. The volume percent of standing water is calculated based on the dimensions of the sample and the volume of standing liquid. Set is measured using the Vicat needle apparatus approximately every 12 hours after the sample was poured. The set time is recorded in days.

2.3 Preparing Samples for Testing

Extremity, whole body, and skin doses were measured during sample preparation for hydraulic conductivity. The results of these measurements are in Table 3. Samples were removed from the plastic mold, cut to length using a fine toothed saw (Figure 2), and placed in a desiccator for vacuum saturation using a simulated Tank 50H salt solution prior to hydraulic conductivity testing. The simulant was used both as the saturating liquid and permeant for hydraulic conductivity testing (Table 4).

Table 3. Dose readings taken during sample preparation

Sample	Extremity (mrem)	Whole Body (mrem)	Skin (mrem)	Comment
1Q11	NM	NM	NM	--
2Q11-A	61	3	27	60000 dpm βγ, 1000 dpm α
2Q11-B	204	4	28	--
2Q11-C	35	3	15	ND dpm βγ, 500 dpm α
3Q11-A	70	4	17	<1000 dpm βγ, <200 dpm α
3Q11-B	90	4	19	

NM – not measured

(a) (b)

Figure 2. Preparation of molded saltstone samples for hydraulic conductivity testing, (a) removal from 2 inch diameter plastic mold, (b) cutting to length

Table 4. Simulated Tank 50H salt solution used as the saturating liquid and permeant for hydraulic conductivity testing

Compound	Molarity	g/mol
50% by Weight NaOH	1.551	40.00
$NaNO_3$	2.116	85.00
$NaNO_2$	0.336	69.00
Na_2CO_3	0.148	105.99
Na_2SO_4	0.059	142.04
Aluminum Nitrate (9 H_2O)	0.110	375.13
Weight Percent Solids	25.85 wt %	
Total Sodium Molarity	4.42 M	
Density	1.2078 g/mL	

2.4 Hydraulic Conductivity Testing

Following vacuum saturation, the samples were tested in a flexible wall permeameter using ASTM D5084-03 Method C for determining hydraulic conductivity of saturated materials.[9,10] The samples were loaded into a tri-axial cell with a glass fiber filter, porous stainless steel (SS) disk, and a SS cap on both ends with a surrounding rubber membrane held in place with O-rings.[10] Back-pressure saturation was used to complete the saturation of the samples and remove any residual gas bubbles in the sample.[10] The permeation was started by increasing the influent pressure while keeping the effluent pressure constant to maintain the back-pressure. Testing was considered complete when at least four values of steady hydraulic conductivity were obtained.[9,10]

3.0 Results and Discussion

3.1 Fresh Properties

The fresh properties of the Saltstone mixes help ensure the product can be processed through the facility and transferred to the Saltstone Disposal Facility (SDF) disposal units. The recommended criteria for an acceptable formulation are listed in Table 5.

Table 5. Recommended fresh property criteria for an acceptable formulation

Property	Criterion	Duration
Gel Time	Pourable	$20 < T_{gel} < 60$ minutes
Standing Water	1% by volume [a]	3 days
Set Time	< 2.5 mm penetration by ASTM C 191[b]	6 days

[a]704-Z-4400, Saltstone Grout Lab Analysis
[b] ASTM C 191-04, Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle

The results of the fresh property testing are listed in Table 6. All the samples met the criteria for standing water and set time. However, only the 2Q11 C sample met the criteria for gel time. The results of the 2Q11 formulation study are documented in a memo to WSE.[11] Although the gel time for the 1Q11 sample is lower than the recommended criteria, further formulation work was not performed since the formulation work was performed after the quarter of interest had passed and there was not enough Tank 50H material to perform additional testing. The cure time is the total amount of time from when the sample was poured and when it was tested for hydraulic conductivity.

Table 6. Results of fresh property testing on 1Q11, 2Q11, and 3Q11 Saltstone samples

Fresh Property	Units	1Q11	2Q11 A & B	2Q11 C	3Q11 A & B
Gel time	minutes	10	< 10	30	NM
1-day standing water	vol %	0	0	0	0
Set	Days	1	1	2	2
Cure time	Days	77	112	112	50

3.2 Hydraulic Conductivity

The 1Q11 and 2Q11-A Saltstone samples were successfully saturated and tested (
Table 7).

Table 7. Results of flexible wall permeameter testing of 1Q11 and 2Q11-A Saltstone samples

Sample	Hydraulic Conductivity (cm/sec)	Test Pressure (psig)		Gradient
		Confining	Pore[1]	
1Q11	4.2E-9	90.7	86.5	33
2Q11-A	2.6E-9	--	49.0	29

The results from the 1Q11 and 2Q11-A samples are comparable to hydraulic conductivity measurements on Saltstone samples formulated with salt solution simulants at comparable water to premix ratios. Previous studies show that simulated Saltstone samples cured at room temperature (approximately 20 – 25 °C) have hydraulic conductivities on the order of 1.4E-9 – 4.9E-8 cm/sec.[3,12] Therefore, for laboratory prepared Saltstone samples cured at room temperature, the hydraulic conductivity values are on the same order of magnitude using either actual Tank 50H or simulated salt solution.

The 2Q11-B, 2Q11-C and 3Q11 Saltstone samples were not successfully tested. Several attempts were made to achieve stable back-pressure saturation and test conditions on these Saltstone samples. Stable readings could not be achieved during back-pressure saturation and therefore testing could not be performed. The additional 2Q11 and 3Q11-B samples were too short (due to minimal material available for formulation work) to allow both ends to be cut flush. The irregular end and the presence of small cavities on the surface of the samples from entrained air in the grout may have contributed to the unsuccessful back-pressure saturation and testing. Figure 3 shows the top surface and exterior of the 3Q11-B Saltstone sample. In addition, the salt solution permeant caused valves to malfunction and as a result, testing the 3Q11-A sample was not attempted.

(a) **(b)**

Figure 3. Irregular surface of the 3Q11-B sample due to entrained air

4.0 Conclusions

Two Saltstone samples made from Tank 50H slurry were successfully analyzed for hydraulic conductivity using ASTM D5084-03, Method C. The hydraulic conductivity of the 1Q11 and 2Q11-A samples of Tank 50H are 4.2E-9 cm/sec and 2.6E-9 cm/sec, respectively. These results which are consistent with results from simulated Saltstone samples, indicate that for laboratory prepared Saltstone, the hydraulic conductivity measurements are on the same order of magnitude as actual Tank 50H or simulated salt solution.

5.0 Recommendations, Path Forward or Future Work

Formulation work with the actual Tank 50H salt solution provides valuable data for processing Saltstone slurry through the SPF. In addition, performing work on the cured properties of Saltstone formulated with actual Tank 50H salt solution will provide more insight into the performance properties of Saltstone and bridge the gap between simulant and radioactive samples. However, in order to execute this work, additional material will be needed from Tank 50H. Future work for this task would be to work with the Tank Farm to obtain additional material for formulation testing.

Another path forward will be to research the effect of the permeant used in hydraulic conductivity measurements of Saltstone. If water can be substituted for salt solution for these measurements, the required maintenance on the permeameter can be reduced and the system will be more robust.

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