Update on SRNL Support of Saltstone Sampling and Analysis – 16325

Marissa Reigel *, Steven Simner **, Kimberly Roberts *, Katie Hill *
* Savannah River National Laboratory
** Savannah River Remediation

ABSTRACT

At the Savannah River Site, low-level waste is immobilized in cementitious waste form known as saltstone. The saltstone Performance Assessment models the performance of the waste form and other aspects of the Saltstone Disposal Facility over ten thousand years after closure to determine the transport history of radionuclides and other hazardous constituents in low-level waste. As part of an ongoing Performance Assessment Maintenance Plan, Savannah River Remediation with Savannah River National Laboratory, has designed a sampling and analyses plan to correlate the properties of field-emplaced samples and samples processed and cured in the laboratory. As part of the plan, SRR has retrieved field-emplaced samples from SDU 2A. Prior to analyzing the field emplaced samples, SRNL is developing the strategy, protocols and equipment necessary to retrieve, store in an inert environment, and analyze the three sample sets of interest outlined in the analysis plan. To date, the simulant saltstone samples have been analyzed for hydraulic conductivity, porosity, density, and other properties. This paper will give an update to the current protocols and equipment being utilized at Savannah River National Laboratory for storing and analyzing the field-emplaced and simulant samples, results from the simulant saltstone analyses, as well as analysis plans for the samples retrieved from the Saltstone Processing Facility and the field-emplaced samples.

INTRODUCTION

At the Savannah River Site, low-level waste (LLW) from Tank 50H is immobilized in cementitious waste form known as saltstone. The saltstone Performance Assessment (PA) models the performance of the waste form and other aspects of the Saltstone Disposal Facility (SDF) over ten thousand years after closure to determine the transport history of radionuclides and other hazardous constituents in LLW. Multiple performance properties of the waste form, such as hydraulic conductivity, porosity and density, are used as inputs in to the PA model; however, to date, the performance property inputs into the PA have been from saltstone simulants produced in the laboratory. As part of an ongoing PA Maintenance Plan, Savannah River Remediation (SRR) designed a sampling and analyses plan to correlate the properties of field-emplaced samples and samples processed and cured in the laboratory [1].

The testing outlined in the Saltstone Disposal Unit (SDU) Sampling and Analyses Plan (SAP) is being conducted in phases. The primary goal of phase I testing is to demonstrate a correlation between laboratory prepared simulant samples and the field-emplaced saltstone samples [1]. Table 1 outlines the samples that are included in phase I (sample sets 3, 8, and 9). Although the SAP includes sample sets 1 – 9, only the samples analyzed for this report are shown in Table 1.

TABLE I. Saltstone sample sets analyzed as part of the SAP Phase I.

Sample Set	Dry Feeds & Salt Solution	Grout Preparation Location	Curing Conditions	Curing Time
3	Simulated field composition; Non-radioactive simulant based on Tank 50[a]	Mixed in laboratory	Simulated field temp and humidity profile in laboratory humidity oven	September 2013 – October 2015
8	Processed in field	Processed in field	Simulated field temp and humidity profile in laboratory humidity oven	August 2013 – October 2015
9	Processed in field	Processed in field	Cured in field	August 2013 – December 2015

a Tank 50 simulant based on composition of actual Tank 50 sample utilized for Sample Sets 4-6.

Objective

The objective of this research is to correlate the properties of laboratory prepared “simulant” saltstone with field-emplaced saltstone such that the permanent waste form does not need to be sampled in the future. Alternatively, if there is not a correlation between the different saltstone formulations, this study will help identify the point of divergence from the properties of the emplaced waste form and develop a method to connect the laboratory prepared and field-emplaced saltstone.

EXPERIMENTAL APPROACH

The initial testing (Phase I) includes collecting samples from the process room in the Saltstone Production Facility (SPF) and curing them at Savannah River National Laboratory (SRNL), sample set 8. Phase I also includes making and curing simulant saltstone samples (sample set 3). The simulant samples are cured under the same conditions as those used to cure the samples from the process room (Table I). The final part of the initial testing is retrieving, storing and analyzing field emplaced samples (sample set 9).

Sample Preparation and Curing (sample sets 3 and 8)

At SRNL, sample sets 3 and 8 have cured in the laboratory under a simulated SDU environment. SRNL continuously monitored and adjusted the temperature of the simulated SDU environment to mimic the actual conditions in SDU 2A [2]. Per SRR, the relative humidity in SDU 2A is 95% based on a month of constant readings, therefore it was determined that the relative humidity for curing the samples at SRNL is held constant at 95%. Figure 1 shows the curing profile for sample set 8.

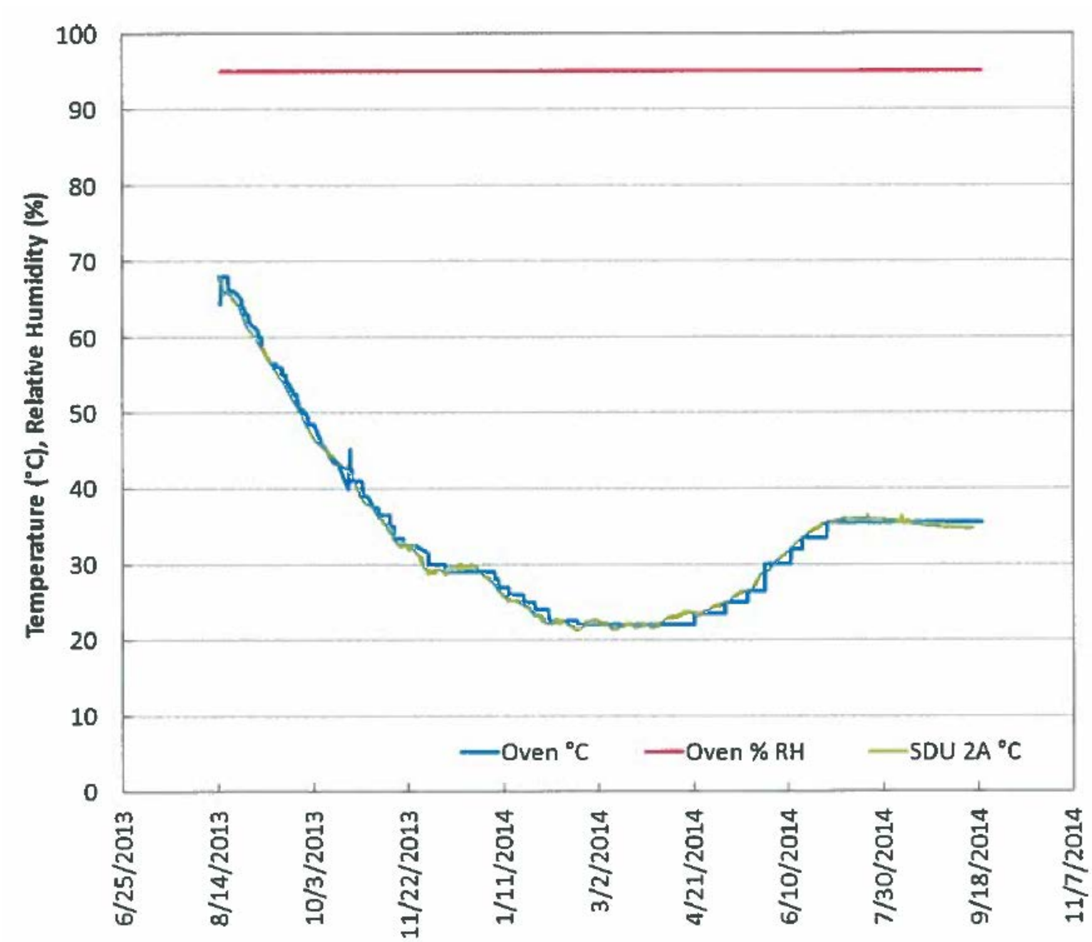

Fig. 1. Laboratory curing profile for sample set 8 [2].

Sample Storage (Sample set 9)

Following extraction from SDU Cell 2A, the radioactive core samples (sample set 9) were transferred to SRNL. Once in the laboratory, the samples were transferred into an inert chamber purged with nitrogen, removed from the transport tubes and visually inspected for fractures, uniformity and integrity [3]. Sample handling (receipt, storage and preparation to analyze) was carried out in an inert atmosphere designed to maintain the as-retrieved physical and chemical characteristics of the samples. The samples were photographed and each section was placed in a sealable, plastic bag labeled with sample and depth identifications. The plastic bags containing the samples were placed in air tight containers (Lock & Lock®) with a moist towel. The boxes were labeled with the sample and depth identifications located within [3].

The inerted chamber is a standard 4 port working chamber by Cleatech LLC with a custom transfer chamber (Figure 2). The inerted chamber is purged with building supplied nitrogen (99.99% purity). The oxygen is measured, and the nitrogen gas flow regulated, by a Cleatech LLC supplied Model 1100 O_2 analyzer. Oxygen levels are maintained to between 0.01- 1.0 % and recorded twice daily.

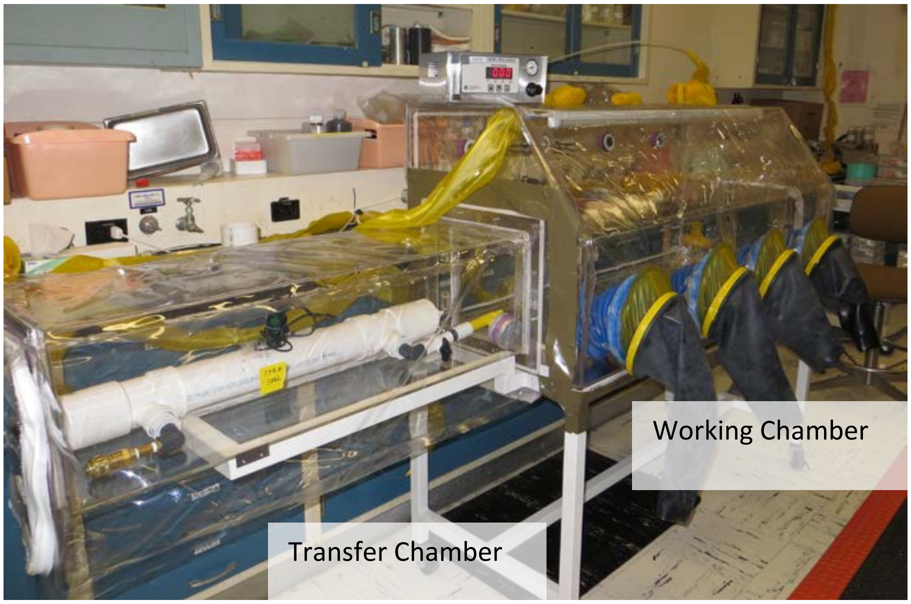

Fig. 2. Photo illustrating transfer and working chambers for core sample receipt, storage, and preparation.

SAMPLE ANALYSES

Several physical and chemical properties of the material will be measured as part of this study. An example of the anticipated core configuration is depicted in Figure 3. Sample interiors will be utilized for measuring those properties that are sensitive to oxygen exposure. Interior samples will be acquired by sectioning a core sample to remove the portions exposed to the atmosphere. Once the samples are properly sectioned, the individual analyses will begin.

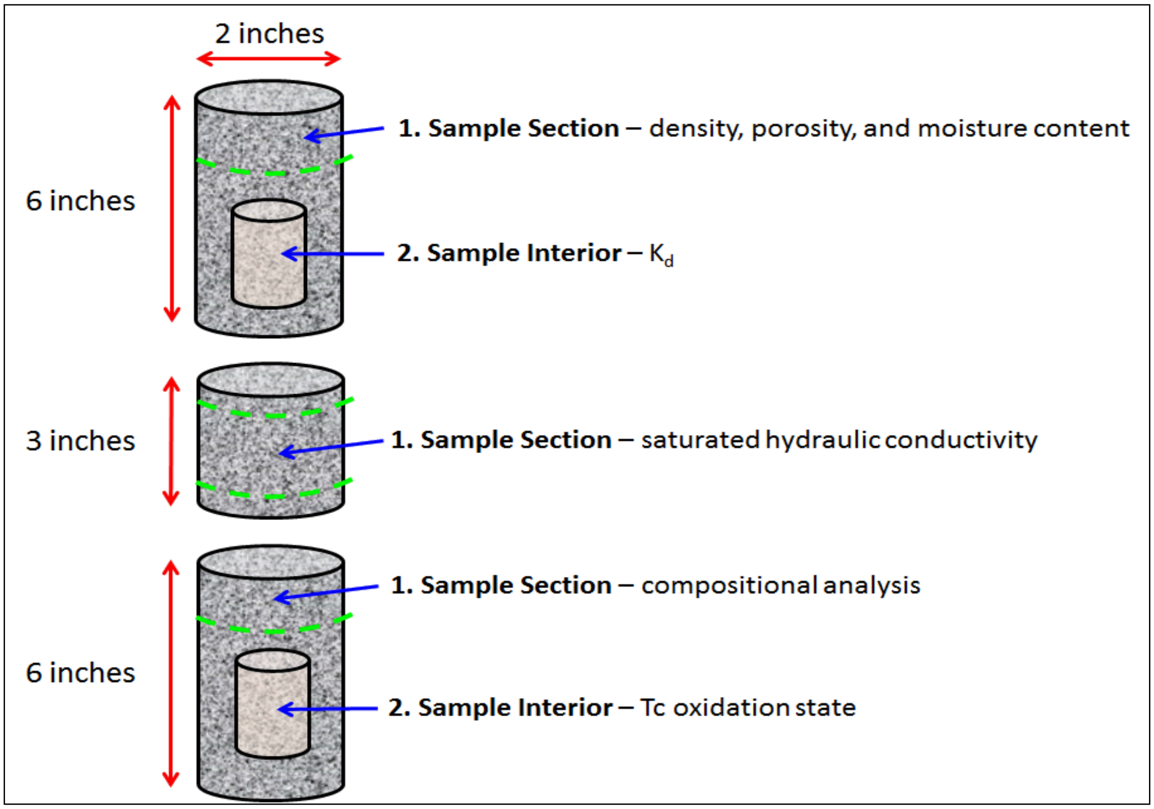

Fig. 4. Graphic depiction of how cores will be sampled.

Bulk Density, Porosity, and Water Content

ASTM C 642, *Standard Test Method for Density, Absorption, and Voids in Hardened Concrete*, will be used to measure the bulk density (after boiling), porosity, and water content. For each core, three pieces, ideally weighing between 5-25 grams will be immersed, boiled, and dried together. The average results from the three pieces will be the reported value. For these analyses, samples will be removed from the inerted chamber in a plastic bag and the methods described below will be conducted in a radiological hood.

Saturated Hydraulic Conductivity

The saturated hydraulic conductivity (SHC) of samples will be measured per ASTM D 5084, *Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter*. Samples will be prepared in the working chamber and then removed from the chamber in plastic bags for measurement in a radioactive fume hood. For hydraulic conductivity testing each core should be long enough to be trimmed to approximately 5 cm in length. Ideal samples are without surface defects to mitigate breakthrough of the permeant. The permeant will be a simplified version of the salt solution to avoid washing out the salts in the samples.

Total Activity (Tc-99, Sr-90, I-129)

Total activities of the specified isotopes will not only provide information on the total proportions of the selected isotopes in the waste form but will also be utilized for the determination of K_d (distribution coefficient) and Tc(VII)/Tc(total) ratio. Solid samples will be dissolved and analyzed for the individual isotopes.

Leachate Concentrations (Tc-99, Sr-90, I-129)

An interior sample will be sectioned as shown in Figure 4. The material will be ground until it is a fine homogenous powder. For the K_d determination 1 g of powder will be added to 10mL of Artificial Groundwater (AGW) and allowed to equilibrate on a tumbler for 1 week. At the end of one week, the solution will be filtered and an aliquot of the aqueous phase will be analyzed. This experiment will be conducted under both oxic and anoxic conditions. For oxic conditions, the solids will be removed from the inert chamber, AGW added, and samples equilibrated in a rad hood overnight. For the anoxic conditions, deoxygenated (boiled) artificial groundwater will be added to the solids and equilibrated inside the inerted chamber. The data derived from the analyses differs for Tc-99 and Sr-90 or I-129, respectively. In the PA transport simulation model, the release of redox-sensitive Tc-99 is solubility-controlled under reducing conditions. Thus for Tc-99, the results in Table 2 are expressed as solubility in the leachate (mol/L) to be consistent with the data presented in the Saltstone PA. In contrast, the release of Sr-90 and I-129 are controlled by sorption and expressed as distribution coefficients (K_d) (Table 2).

Determination of Tc(VII) / Tc(total) Ratio

This method assumes that all leachable Tc-99 is in a soluble +7 oxidation state and that the non-leachable Tc-99 is in a reduced, non-soluble form. The ratio of the leachable Tc-99 from the K_d analysis method will be compared with the total Tc-99 obtained from the analysis of a digested sample. The same leachate will also be analyzed for nitrogen as an independent verification of Tc(VII) data validity. The total nitrogen, determined by summing nitrate and nitrite, would be unaffected by sample oxidation and should thus be consistent from sample-to-sample.

RESULTS

Sample Set 3 and 8 Results

Non-radioactive sample set 3 was analyzed first and the results are discussed below. Radioactive sample set 8 has been analyzed for all of the physical and chemical properties identified in the previous section. These mock-up analyses will be used to validate the test methodologies presented in this report and to provide confidence that the indicated analysis will be performed correctly on the core drilled sample set 9. Upon satisfactory completion of both mock up tests, six SDU 2A cores (sample set 9) will be analyzed for physical and chemical properties.

The SHC of two simulated saltstone samples (sample set 3) was measured using ASTM D5084-10 Method C Falling head - rising tail method. The average SHC of the two simulated saltstone samples is $<1x10^{-9}$ cm/sec (Table 2). This value, $1x10^{-9}$ cm/sec, is the minimum detection limit reported for the method and sample size. The test was conducted using a simple salt solution for the permeant under a hydraulic gradient of approximately 30:1, which is the maximum gradient suggested by the standard method [4]. The SHC of saltstone sample set 8 is <2x10-9 cm/sec. 2x10-9 cm/sec is the minimum detection limit for the sample size and test method.

Of the twelve replicates made in the laboratory, three samples of sample set 3 were tested for bulk density and porosity. Three samples of sample set 8 were also measured. The data and results were determined by ASTM International Standard Test Method C 642-06 [5]. All of the samples had an average density of 1.7 g/cm^3 which is consistent with other saltstone samples [6]. All data from Sample Sets 3, 8 and 9 are shown in Table 2.

TABLE II. Analysis results for Sample Sets 3, 8 and 9.

Analaysis	**Sample Set 3**	**Sample Set 8**	**Sample Set 9**
Average Density (mg/cm^3)	1.76	1.76	TBD
Average Porosity (%)	59.81	63.26	TBD
Average SHC (cm/s)	$<1x10^{-9}$	$<2x10^{-9}$	TBD
Tc-99 Total Activity (pCi/g)	NM	1.42E+03	TBD
Sr-90 Total Activity (pCi/g)	NM	6.10E+02	TBD
I-129 Total Activity (pCi/g)	NM	3.39E+00	TBD
Tc-99 Oxic Solubility (mol/L)	NM	2.12E-08	TBD
Tc-99 Anoxic Solubility (mol/L)	NM	5.78E-09	TBD
Sr-90 Oxic K_d (mL/g)	NM	<4.1E+01	TBD
Sr-90 Anoxic K_d (mL/g)	NM	<5.1E+01	TBD
I-129 Oxic K_d (mL/g)	NM	2.00E+00	TBD
I-129 Anoxic K_d (mL/g)	NM	3.50E+00	TBD

NM = Not Measured
TBD = Analysis in progress, results to be determined (TBD)

CONCLUSIONS

At the Savannah River Site, LLW from Tank 50H is immobilized in cementitious waste form known as saltstone. The saltstone PA models the performance of the waste form and other aspects of the SDF over ten thousand years after closure to determine the transport history of radionuclides and other hazardous constituents in LLW. Multiple performance properties of the waste form, such as hydraulic conductivity, porosity and density, are used as inputs in to the PA model; however, to date, the performance property inputs into the PA have been from saltstone simulants produced in the laboratory. As part of an ongoing PA Maintenance Plan, SRR has designed a sampling and analyses plan to correlate the properties of field-emplaced samples and samples processed and cured in the laboratory [1].

The testing outlined in the SDU SAP is being conducted in phases. The initial testing (Phase I) includes collecting samples from the process room in the SPF and curing them at SRNL, sample set 8. Phase I also includes making and curing simulant saltstone samples (sample set 3). The simulant samples are cured under the same conditions as those used to cure the samples from the process room (Table I). The final part of the initial testing is retrieving, storing and analyzing field emplaced samples (sample set 9).

To date, the samples for phase I have completed curing under simulated and actual field conditions and have been placed in an inert chamber. Non-radioactive saltstone simulant samples, sample set 3, have been tested and the results are consistent with previous laboratory results. Sample set 8 testing is also complete and is a final verification of the test methodologies that will be used to analyze the field emplaced samples (sample set 9).

REFERENCES

1. Simner, S.P., Saltstone Sampling and Analyses Plan, Savannah River Remediation, SRR-SPT-2012-00049, Revision 1, (2013).

2. Miller, D.H., Controlled Environment Curing Data for Saltstone Samples Set 3 and 8 from August 15, 2013 to September 14, 2014, Savannah River National Laboratory, SRNL-L3100-2014-00234, (2014).

3. Roberts, K.A., Experimental Plan for SRNL Support for Saltstone Sampling and Analysis, Savannah River National Laboratory, SRNL-L3100-2015-00073, Revision 1, (2015).

4. Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter, ASTM International, ASTM D5084 - 10 (Method F), (2010).

5. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, ASTM International, ASTM C 642 - 06, (2006).

6. Dixon, K.L., J.R. Harbour, and M.A. Phifer, Hydraulic and Physical Properties of ARP/MCU Saltstone Grout, Savannah River National Laboratory, SRNL-STI-2009-00419, Revision 0, (2010).