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Analysis of Saltstone Cores Taken from Saltstone Disposal Unit Cell 2A – 17350

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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 better understand the transport history of radionuclides and other hazardous constituents in low-level waste. As part of ongoing Performance Assessment Maintenance, Savannah River Remediation (SRR), with Savannah River National Laboratory (SRNL), designed a sampling and analyses plan to correlate the properties of field-emplaced samples and samples processed and cured in the laboratory. The primary objectives of the Sampling and Analyses Plan are; (1) to demonstrate a correlation between the measured properties of laboratory-prepared, simulant samples (termed Sample Set 3), and the field-emplaced saltstone samples (termed Sample Set 9), and (2) to validate property values assumed for the Saltstone Disposal Facility (SDF) Performance Assessment modeling. The analysis and property data for Sample Set 9 (i.e. core samples extracted from Saltstone Disposal Unit Cell 2A (SDU2A)) are documented, and where applicable, the results are compared to the results for Sample Set 3. SRNL received, stored and analyzed the samples cored from SDU2A. This paper discusses the results of the SRNL analysis of the SDU2A samples as well as the simulant saltstone 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 better understand 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 ongoing PA Maintenance, Savannah River Remediation (SRR), with Savannah River National Laboratory (SRNL), has designed a sampling and analyses plan to correlate the properties of field-emplaced samples to 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 – May 2015
8	Processed in field	Processed in field	Simulated field temp and humidity profile in laboratory humidity oven	August 2013 – May 2015
9	Processed in field	Processed in field	Cured in field	August 2013 – May 2015

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

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 eventually develop a method to connect the laboratory prepared and field-emplaced saltstone.

EXPERIMENTAL APPROACH

Phase I testing includes collecting samples from the process room in the Saltstone Production Facility (SPF) and curing them at SRNL. These samples are known as sample set 8. Phase I also includes making and curing simulant saltstone samples known as 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 analyzing field emplaced samples, referred to as sample set 9.

Sample Preparation and Curing (sample sets 3 and 8)

At SRNL, sample sets 3 and 8 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 SDU2A [2]. Per SRR, the relative humidity in SDU2A is 95% based on a month of constant readings; therefore, the samples were cured under 95% relative humidity at SRNL. Figure 1 shows the curing profile for sample set 8.

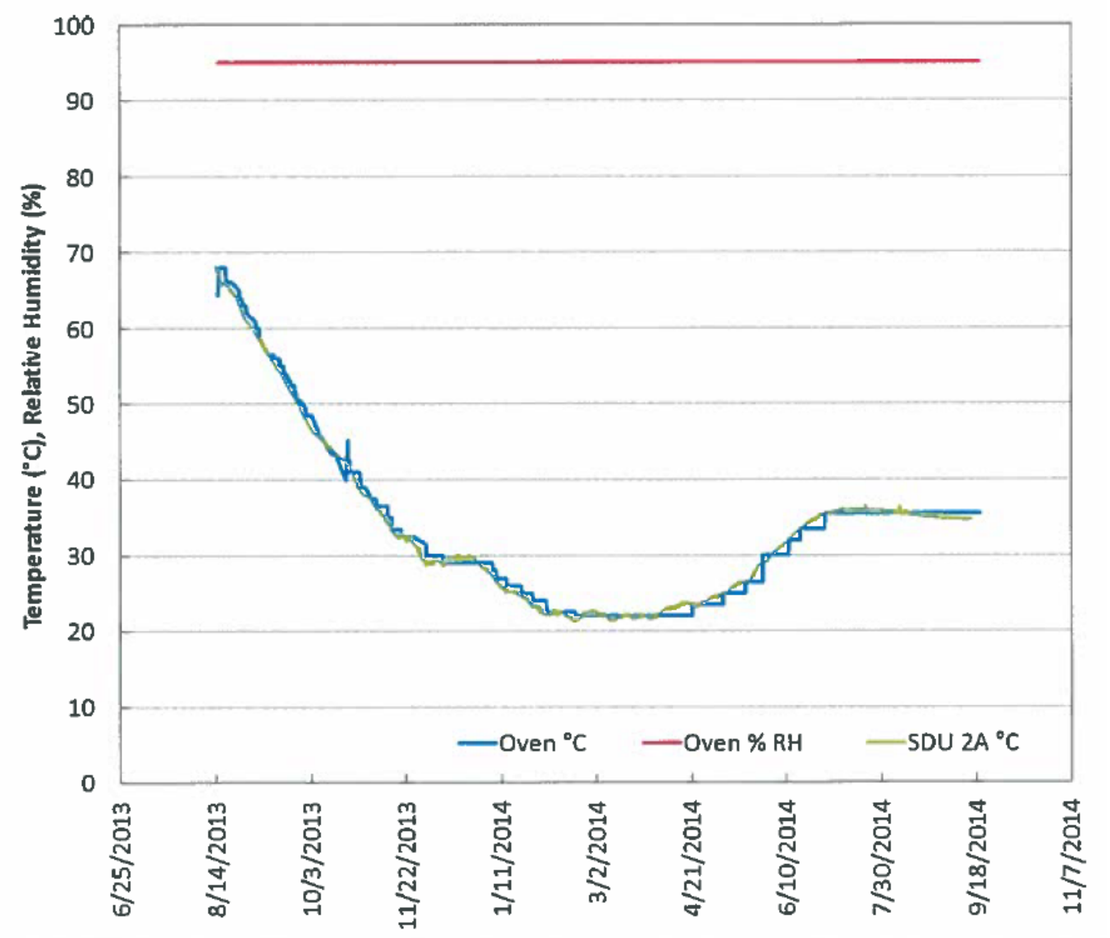

Fig. 1. Laboratory curing profile for sample set 8 [2].

Sample Storage (Sample set 9)
Following extraction from SDU2A, 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 was performed in an inert atmosphere designed to maintain the as-retrieved physical and chemical characteristics of the samples. The samples were photographed, labeled and stored in in air tight containers [3].

The inert chamber (Figure 2) was purged with nitrogen (99.99% purity). The oxygen was measured, and the nitrogen gas flow regulated, by an O_2 analyzer. Oxygen levels were maintained to between 0.01- 1.0 % and recorded twice daily.

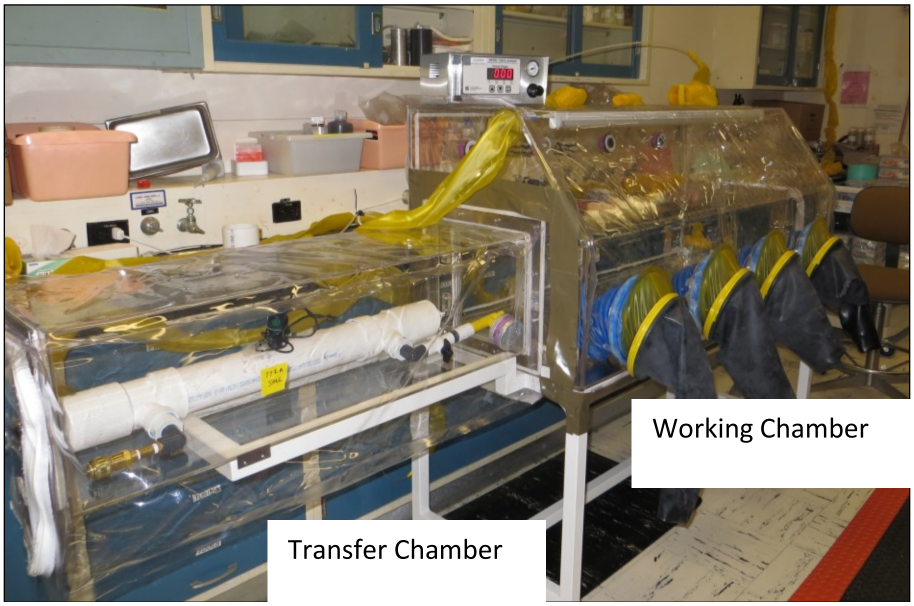

Fig. 2. Photo illustrating transfer and working chambers for core sample receipt, storage, and preparation.

SAMPLE ANALYSES

Several physical and chemical properties of the material were measured as part of this study. An example of the core configuration is depicted in Figure 3. Sample interiors were utilized for measuring those properties that are sensitive to oxygen exposure such as the isotope distribution ratios (R_d). Interior samples were acquired by sectioning a core sample to remove the portions exposed to the atmosphere.

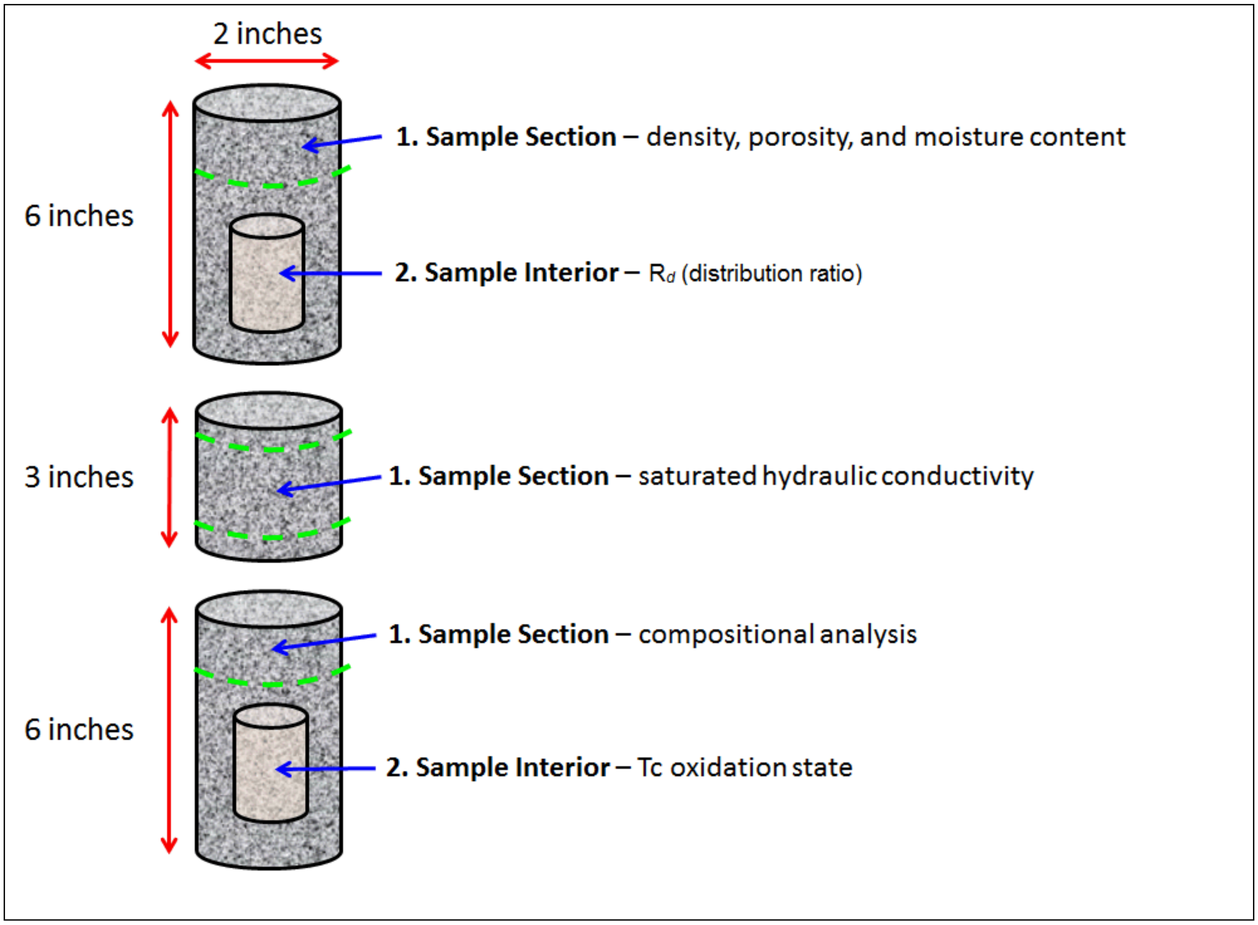

Fig. 3. Graphic depiction of sampling of saltstone cores.

Bulk Density, Porosity, and Water Content

ASTM C 642, *Standard Test Method for Density, Absorption, and Voids in Hardened Concrete*, was used to measure the bulk density (after boiling), porosity, and water content [4]. The ASTM method was followed with the exception of sample size and medium for immersion and boiling. A simulated salt solution (used to make Sample Set 3), was used instead of water as the medium to immerse and boil the samples. This was performed to mitigate washing out of salts during immersion and boiling. To maintain the salt concentration and density, the condensate from boiling was replaced with water as required. For these analyses, whole core samples were removed from the inert chamber in a plastic bag and the measurements conducted in a radiological hood. Each core was broken up with a hammer to obtain three pieces, weighing between 5-25 grams which were then immersed, boiled, and dried.

Saturated Hydraulic Conductivity

The saturated hydraulic conductivity (SHC) of samples were measured per ASTM D 5084, *Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter* [5]. Samples were sectioned and prepared in the working chamber and removed from the chamber in plastic bags for measurement in a radioactive fume hood. For hydraulic conductivity testing each core was sectioned to approximately 5 cm in length. Samples utilized for this measurement had minimal or no surface defects to mitigate breakthrough of the permeant. The permeant used was a simple 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 not only provides information on the total proportions of the selected isotopes in the waste form but also the distribution ratio (R_d), described below. Sectioned and crushed samples of the cores were dissolved and analyzed for the individual isotopes.

Distribution Ratio (Sr-90, I-129) and Technetium Solubility

The R_d is a measurement technique for determining the degree of partitioning between liquid and solid, under a certain set of laboratory conditions, for the species of interest. Analyzing the R_d of radioactive species within saltstone is designed to provide insight into how contaminants immobilized in saltstone may leach from the saltstone matrix in oxic or anoxic conditions. A distribution ratio was used in this study rather than a distribution coefficient (K_d) since it is unlikely equilibrium was reached during the seven days of the extraction test. It is important to note that although R_d values are discussed in this paper, the saltstone PA and SDF modeling utilize K_d values; therefore, the calculated R_d values from this study are compared to previously reported K_d results modeled in the saltstone PA. In the transport simulation modeling, the release of redox-sensitive Tc-99 is solubility-controlled under reducing conditions. In contrast, the release of Sr-90 and I-129 are controlled by sorption and expressed as a K_d.

An interior sample of each core was used to measure the R_d following the modified ASTM D 4319, *Standard Test Method for Distribution Ratios by the Short-Term Batch Method* [6]. For the R_d determination, 1 g of crushed sample was added to 10 cm^3 of Artificial Groundwater (AGW). Samples were continuously tumbled end over end for seven days. After tumbling, the solution was filtered and an aliquot of the aqueous phase was analyzed. This experiment was conducted under both oxic and anoxic conditions. For oxic conditions, the crushed solids were removed from the inert chamber, and all further sample manipulations were performed in a radiological hood. For the anoxic conditions, all sample preparations and manipulations were performed inside the inert chamber. In addition, pH and E_h of the leachates were measured before and after tumbling to confirm the anoxic and oxic environments.

RESULTS AND DISCUSSION

Six core samples from sample set 9 were measured to determine their SHC and the results are shown in Table II. These results of the sample set 3 cores are also shown in Table II. Four of the samples had a SHC below the detection limit for the specific instrument, measurement technique, and sample size (1E-9 cm/sec). These samples performed well during testing with no issues noted. Samples SDU2A-0931-A-1-L-3 and SDU2A-0931-B-1-L-2 had a SHC above the detection limit, but within the same order of magnitude. Both samples had surface defects either from core drilling or sample preparation that couldn't be avoided in the SHC sample due to the size of the original core and requirements of the method. All six sample set 9 cores showed very low SHC values similar to the values measured from the Sample Set 3 samples (Table II) [1]. It is also noteworthy that all samples indicated SHCs less than the 6.4E-09 cm/sec assumed in the current PA modeling [7].

TABLE II. Saturated Hydraulic Conductivity (K) Sample Sets 9 and 3.

Sample ID (Sample Set 9)	K Final (cm/sec)	Sample ID (Sample Set 3)	K Final (cm/sec)
SDU2A-0931-A-1-L-3	1.20E-09	3-05-2	<1.00E-9
SDU2A-0931-A-2-L-2	<1.00E-9	3-01-2	<1.00E-9
SDU2A-0931-C-1-L-2	<1.00E-9		
SDU2A-0931-B-1-L-2	4.40E-09		
SDU2A-0931-C-2-L-5	<1.00E-9		
SDU2A-0931-C-2-L-1	<1.00E-9		

The density, porosity and water content of each core sample was measured in triplicate. Table III shows the average density, water content, total porosity, and apparent (or permeable) porosity for each Sample Set 9 core sample. It should be noted that the ASTM method does not involve a determination of absolute density [4]. Hence, such pore space as may be present in the specimen that is not emptied during the specified drying or is not filled with water during the specified immersion and boiling or both is considered "impermeable" and is not differentiated from the solid portion of the specimen for the calculations [4]. The porosity was calculated from the volume of simulant divided by the sample volume and accounts the impermeable and permeable pores.

Table III. Average Density, Water Content, and Porosity for Sample Set 9 Samples.

Sample ID (Sample Set 9)	**Density (g/cm^3)**	**Water Content (%)**	**Porosity (%)**	**Vol. Permeable Pore Spaces (%)**
SDU2A-0931-A-1-L-5	1.72	29.82	64.29	44.95
SDU2A-0931-B-1-L-1	1.72	31.21	67.31	43.19
SDU2A-0931-C-2-L-6	1.74	30.51	66.57	43.30
SDU2A-0931-A-2-L-5	1.74	29.04	63.60	41.91
SDU2A-0931-C-2-L-8	1.71	32.10	68.77	46.62
SDU2A-0931-C-1-L-5	1.76	29.14	64.51	41.99

The values in Table III are similar to the values measured for Sample Set 3 (Table IV). The porosity values for Sample Set 3 are lower than Sample Set 9 which is most likely due to the differences in processing the samples (i.e., variable field-processing compared to controlled and consistent laboratory-preparation).

Table IV. Average Density, Water Content, and Porosity for Sample Set 3 Samples.

Sample ID (Sample Set 3)	**Density (g/cm^3)**	**Water Content (%)**	**Porosity (%)**	**Vol. Permeable Pore Spaces (%)**
3-03-2	1.76	30.51	59.92	41.62
3-07-2	1.76	30.40	59.64	40.60
3-10-2	1.76	30.42	59.86	40.19

Analyzing the R_d or solubility of species within saltstone is designed to provide insight into how readily species immobilized in saltstone will leach from the saltstone under oxic or anoxic conditions. The calculations derived from the extraction test leachate analyses differ for Tc-99, and Sr-90 and I-129. In the SDF transport simulation model, the release of redox-sensitive Tc-99 is treated as solubility-controlled under reducing conditions. Thus for Tc-99, the results are expressed as concentration (solubility) in the leachate (mol/m^3) to be consistent with the data presented in the SDF modeling [7]. The solubility is calculated by dividing the activity per volume by the specific activity of the isotope of interest and the atomic mass of the isotope of interest. In contrast, the release of Sr-90 and I-129 are controlled by sorption and expressed as distribution coefficient (K_d). K_d or R_d (cm^3/g) is calculated as shown in equation 1.

$$K_d (or\ R_d) = \frac{A_s}{A_d} \qquad \text{(Eq. 1)}$$

where A_s is the direct concentration or radionuclide activity measured in the solids corrected for mass of the element desorbed during leaching and A_d is the direct concentration or radionuclide activity in the aqueous phase at the end of the experiment. The results reported in this paper are reported as R_d which is calculated the same way as K_d, but equilibrium is not assumed.

It is important to note the difference between a standard R_d measurement and the measurement conducted for analyzing SDU2A cores. In a standard measurement soil (or a cementitious material) is mixed with a liquid containing a known concentration of the radionuclide of interest. After tumbling of the solid and liquid over a seven day period the liquid is analyzed with respect to its radionuclide concentration which in turn reveals the proportion of radionuclide associated with the solid phase. The test is evaluating the ability of the solid to remove the radionuclide from solution via sorption or precipitation. In contrast the tests conducted for SDU2A cores involve the addition of the ground cores (1 gram) (containing the radionuclide(s) of interest) to a liquid phase (10 cm^3) that initially contains no radionuclides. This is often termed a reverse R_d measurement and evaluates the proportion of radionuclide transferred from the solid phase to the liquid phase due to desorption or dissolution.

For both analysis environments, the I-129 results produced negative R_d values, which is not feasible and implies the generation of iodine. The negative value is most likely an artifact of the uncertainty associated with the I-129 leachate analysis. For these samples, the negative values were set to 0 (i.e., all I-129 released from sample into leachate solution) (Table V). This data indicates that the mobility of I-129 is unaffected by the environment in which the measurements were conducted since there is low variability between oxic R_d values (0 – 2) as well as the anoxic values (0 – 4). The current SDF modeling assumes an iodine R_d of 9 cm^3/g for anoxic and 15 cm^3/g for oxic conditions.

The R_d values for Sr-90 (Table V) vary from sample to sample in both environments but the oxic R_d values have a larger range (73 – >176) than the anoxic values (36 – 70). The data shows that the average Sr-90 oxic R_d values are statistically different and higher (112±37) than the average anoxic results (55±16). This is contrary to the conceptual model currently being utilized in the SDF modeling. SRNL recognizes the low levels of Sr-90 in the leachate led to high analytical uncertainty, but method development wasn't in the scope of the project. In addition, due to the relatively small sample size analyzed and low Sr-90 activity in the leachate, there is high analytical uncertainty in many of the leachate measurements. If the analytical uncertainty, is considered in the analysis of the results, the anoxic and oxic strontium R_d values could become closer together. The R_d value currently assumed in the SDF modeling for strontium is 15 cm^3/g for both oxic and anoxic conditions.

Table V. Distribution Ratio (Sr-90, I-129) and Technetium Solubility Results

Sample ID (Sample Set 9)	**Tc-99 Solubility (mol/m^3)**		**Sr-90 R_d (cm^3/g)**		**I-129 R_d (cm^3/g)**	
	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic
SDU2A-0931-A-1-L-3	<1.16E-05	2.62E-05	70	>79	4	2
SDU2A-0931-A-2-L-2	3.95E-05	2.52E-05	36	73	0	0
SDU2A-0931-C-1-L-2	3.32E-05	2.27E-05	46	108	0	0
SDU2A-0931-B-1-L-2	1.87E-05	2.03E-05	65	119	4	0
SDU2A-0931-C-2-L-5	7.02E-06	2.42E-05	41	>119	1	0
SDU2A-0931-C-2-L-2	2.41E-05	2.16E-05	70	>176	0	0

The SDF model considers solubility or sorption of Tc-99 depending on whether it is assumed to be reduced or oxidized, respectively. The conceptual model is that aqueous Tc-99 concentrations are controlled by sorption when oxidized and by solubility when reduced. If no oxidation of saltstone cores occurred in the field or laboratory, and if anoxic conditions were successfully met, then the leachate concentrations for the anoxic experiments can be interpreted as solubility. In addition, the conceptual model is that Tc-99 leachate concentrations should be higher in oxidized solutions compared to reduced solutions. As shown in Table V, the Tc-99 leachate concentrations were approximately the same under both anoxic and oxic environments, respectively, which could suggest a resistance of Tc-99 to mobilization following short term exposure under oxidizing conditions. Another explanation of these unexpected results is that the oxic conditions tested in this study were not fully oxidizing or the anoxic conditions were not fully reducing. However, the E_h data demonstrates that the conditions tested, at least during the actual experiment, were as expected. Another factor that could impact the results is the starting condition of the saltstone cores. Further studies could be performed to help understand the effects of a partially reduced or oxidized solution as well as the impact of the starting condition of the matrix being analyzed.

CONCLUSIONS

As part of ongoing PA Maintenance, SRR, with SRNL, has developed a sampling and analyses strategy to facilitate the comparison of field-emplaced samples (i.e., saltstone placed and cured in a SDU) with samples prepared and cured in the laboratory. The primary objectives of the SAP are; (1) to demonstrate a correlation between the measured properties of laboratory-prepared, simulant samples (Sample Set 3), and the field-emplaced saltstone samples (Sample Set 9), and (2) to validate property values assumed for the SDF PA modeling. Overall, the physical properties agreed well between sample sets 3 and 9.

The bulk densities of SDU-emplaced and laboratory-prepared saltstone were in the range of 1.71 – 1.76 g/cm^3 and comparable to historically produced saltstone samples. The porosities were, however, different with Sample Set 3 consistently measured at 60% compared to a range of 60-69% for Sample Set 9. Whilst the total porosities in the SDU cores were higher than the laboratory-prepared samples, this factor did not impact SHC. For both Sample Sets, the SHCs were on the order of E-09 cm/s or less. It is also noteworthy that all samples indicated SHCs less than the 6.4E-09 cm/sec assumed in the current PA modeling.

The distribution ratio (R_d) is a measurement technique for determining the degree of partitioning between liquid and solid, under a certain set of laboratory conditions, for the species of interest. Analyzing the R_d, of radioactive species within saltstone is designed to provide insight into how contaminants immobilized in saltstone may leach from the saltstone matrix in oxic or anoxic conditions. A distribution ratio was used in this study rather than a distribution coefficient (K_d) since it is unlikely equilibrium was reached during the seven days of the extraction test. It is important to note that although R_d values are reported in this report, the saltstone PA and SDF modeling utilize K_d values; therefore, the calculated R_d values from this study are compared to previously reported K_d results modeled in the saltstone PA. In the transport simulation modeling, the release of redox-sensitive Tc-99 is solubility-controlled under reducing conditions. In contrast, the release of Sr-90 and I-129 are controlled by sorption and expressed as a K_d.

For both environments (oxic and anoxic), results from this study indicated negative I-129 R_d values, which is not viable since it implies that iodine was being generated during analysis; therefore, the negative values are related to the analytical uncertainties associated with the leachate analysis and subsequent Rd calculation. For these samples, the negative values were thus set to 0 which signifies that all of the iodine contained in the saltstone matrix leached into the surrounding solution. The current SDF modeling assumes an I-129 K_d of 9 cm^3/g for anoxic and 15 cm^3/g for oxic conditions.

The R_d values for strontium vary from sample to sample in both environments but the oxic R_d values have a larger range (73 – >176) than the anoxic values (36 – 70). The data shows that the average Sr-90 oxic R_d values are statistically different and higher (112±37) than the average anoxic results (55±16). This is contrary to the conceptual model currently being utilized in the SDF modeling which is that oxic environments result in higher leachate concentrations. The R_d value currently assumed in the SDF modeling for strontium is 15 cm^3/g for both oxic and anoxic conditions.

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