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Results and Analysis of Saltstone Cores Taken from Saltstone Disposal Unit Cell 2A

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EXECUTIVE SUMMARY

As part of an ongoing Performance Assessment (PA) Maintenance Plan, Savannah River Remediation (SRR) has developed a sampling and analyses strategy to facilitate the comparison of field-emplaced samples (i.e., saltstone placed and cured in a Saltstone Disposal Unit (SDU)) with samples prepared and cured in the laboratory. The primary objectives of the Sampling and Analyses Plan (SAP) 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) PA modeling. The analysis and property data for Sample Set 9 (i.e. six core samples extracted from SDU Cell 2A (SDU2A)) are documented in this report, and where applicable, the results are compared to the results for Sample Set 3. Relevant properties to demonstrate the aforementioned objectives include bulk density, porosity, saturated hydraulic conductivity (SHC), and radionuclide leaching behavior.

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. Both the higher porosities, and the range of the porosities, for the SDU cores is perhaps indicative of the variability in processing saltstone in the field (including the mixing technique, line transfer, and free-fall placement all of which can affect the air content) in comparison to the use of consistent laboratory preparation techniques in a controlled environment. 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.

Desorption leaching experiments were performed on two groups of ground saltstone samples. One group was leached in a nitrogen atmosphere (anoxic condition), and one in ambient (oxic) conditions. The leaching time was seven days in all tests. 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) because equilibrium may not have been reached during the seven days of the extraction test. For Sample Set 9, leachate concentrations of Tc-99 and the average R_d of Sr-90 and I-129 (in both oxic and anoxic environments) are provided in the table overleaf. 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.

Calculated distribution ratios for I-129 ranged between -5 and +4 mL/g; negative values are related to the analytical uncertainties associated with the leachate analysis and subsequent R_d 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 mL/g for anoxic and 15 mL/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 to >176) than the anoxic values (36 to 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). Both sets of R_ds are significantly higher than the value employed by the SDF PA, which is 15 mL/g for both oxic and anoxic conditions[1].

The SDF model analyzes solubility or sorption of Tc-99 depending on whether it is assumed to be oxidized or reduced, respectively. The conceptual model is that aqueous Tc-99 concentrations are controlled by sorption when oxidized and by solubility when reduced. In addition, the conceptual model is that Tc-99 leachate concentrations should be higher in oxidized solutions compared to reduced solutions. However, this study found that measured Tc-99 leachate concentrations were approximately the same under both anoxic and oxic environments, which is an unexpected finding. It is possible that during the oxic experiments, the exposure to air was not sufficient to fully oxidize the samples. Alternatively, inadvertent exposure to air at some point in the field or laboratory, could have partially oxidized the samples intended to be anoxic. Since it is not certain that equilibrium was attained during the 7-day leach experiments, desorption distribution ratios presented in this study should be regarded as upper bounds, and solubilities interpreted from leachate concentrations should be regarded as lower bounds.

Sample ID (Sample Set 9)	**Tc-99 Leachate Concentration* (mol/L)**		**Tc-99 R_d (mL/g)**	**Sr-90 R_d (mL/g)**		**I-129 R_d (mL/g)**	
	Anoxic	Oxic	Oxic	Anoxic	Oxic	Anoxic	Oxic
SDU2A-0931-A-1-L-3	<1.16E-08	2.62E-08	32	70	>79	4	2
SDU2A-0931-A-2-L-2	3.95E-08	2.52E-08	27	36	73	0	0
SDU2A-0931-C-1-L-2	3.32E-08	2.27E-08	24	46	108	0	0
SDU2A-0931-B-1-L-2	1.87E-08	2.03E-08	31	65	119	4	0
SDU2A-0931-C-2-L-5	7.02E-09	2.42E-08	25	41	>119	1	0
SDU2A-0931-C-2-L-2	2.41E-08	2.16E-08	27	70	>176	0	0

*If no oxidation of cores occurred in the field or laboratory, and if anoxic conditions were successfully met during the experiments, then leachate concentrations for the anoxic experiments can be interpreted as solubility.

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LIST OF ABBREVIATIONS

AD	Analytical Development
K_d	Distribution Coefficient
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
PA	Performance Assessment
QA	Quality Assurance
R_d	Distribution ratio
SAP	Sampling and Analysis Plan
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SDU2A	Saltstone Disposal Unit Cell 2A
SHC	Saturated Hydraulic Conductivity
SHE	Standard Hydrogen Electrode
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation LLC
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

At the Savannah River Site (SRS), low-level waste (LLW) from Tank 50H is immobilized as a cementitious waste form known as saltstone. The Saltstone Disposal Facility (SDF) Performance Assessment (PA) and Special Analyses model the performance of the waste form and other aspects of the SDF over thousands of years after closure to determine the transport of radionuclides and other hazardous constituents in LLW.[1] Performance properties of the waste form, such as saturated hydraulic conductivity (SHC), and contaminant sorption and solubility, are used to inform the PA modeling; however, to date, the performance property inputs into the PA have been derived from saltstone simulants produced in the laboratory. As part of an ongoing PA Maintenance Plan, Savannah River Remediation (SRR) has developed a sampling and analyses strategy to facilitate the comparison of field-emplaced samples (i.e. saltstone placed and cured in a Saltstone Disposal Unit (SDU)) with samples prepared and cured in the laboratory.

The primary objectives of the Sampling and Analysis Plan (SAP)[2] are to 1) 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) validate property values assumed in the SDF modeling from the field emplaced samples. It is also of note that a third sample group (Sample Set 8) was analyzed as part of this endeavor. Sample Set 8 represents actual saltstone grout that was retrieved (in cylindrical molds) from the process room in the Saltstone Production Facility (SPF), and subsequently transferred to the laboratory for curing. Comparison of properties for Sample Sets 8 and 9 would potentially highlight the influence of grout pumping to the SDU and free-fall into the SDU as well as the effect of curing in the laboratory versus the field. However, for the purpose of this study, Sample Set 8 was utilized as a means of validating the methodologies to be employed for radiochemical separation and analysis prior to analyzing Sample Set 9.

SRR tasked Savannah River National Laboratory (SRNL) with receiving and storing saltstone cores, developing analysis protocols for the analyses listed in the technical task request[3], and performing mock-up testing of non-radioactive (simulant) and radioactive samples prior to analyzing the core samples.[4] The results of mock-up testing and radiological samples from the SPF Process Room (Sample Set 8) are reported in SRNL-L3100-2015-00073, Revision 2.[5] Through the analysis of Sample Set 8, it was determined that the Se-79 and Ra-226 concentration in the saltstone is too low to be experimentally measured in the R_d leachates. In addition, it was determined that there would not be sufficient leachate to measure the radionuclides of interest and measure the nitrate/nitrite concentrations. Therefore, Se-79, Ra-226, and the nitrate/nitrite concentrations were not included in the analysis of Sample Set 9 even though they are called out in the work control documents.[3-5] This report includes the results of the analysis of the saltstone core samples from Saltstone Disposal Unit (SDU) Cell 2A (SDU2A) as well as a comparison to the simulant, laboratory-prepared saltstone (i.e. Sample Sets 9 and 3, respectively).

1.1 Background

The objective of the SAP is to provide "a basis for the quantity (and configuration) of Saltstone grout samples required for conducting a study directed towards correlation of the SDF PA related properties of field-emplaced samples (core drilled from SDU2A), field-processed samples (grout slurries retrieved from the Saltstone Production Facility (SPF) and subsequently cured in the laboratory), and samples both processed and cured in the laboratory."[2] As outlined in the SAP, there are nine Sample Sets that could be analyzed; however, as previously stated, the overriding objective of the SAP is property comparison of field- and laboratory-derived samples and to validate PA modeling assumptions. Other Sample Sets would only be subjected to analysis if the properties measured for Sample Sets 3 and 9 were sufficiently disparate. However, Sample Set 8 (radioactive grout retrieved from the SPF and cured in the laboratory) was analyzed in order to validate test methodologies prior to analyzing Sample Set 9 (Table 1-1). This report focuses on measured property data for Sample Sets 3 and 9.

Table 1-1. Saltstone Sample Sets Analyzed as Part of SAP.

Sample Set	Dry Feeds & Salt Solution	Grout Preparation Location	Curing Conditions	Curing Time
3	Simulated field composition; Non-radioactive simulant based on Tank 50*	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

* Tank 50 simulant based on composition of actual Tank 50 sample retrieved in July 2013.[6]

The execution of the SAP began in 2013 with SRNL performing a statistical analysis to determine the number of samples needing to be taken from SDU2A,[7] as well as a study to determine the effects of transporting fresh saltstone across the SRS before it has set.[8] On August 12, 2013, saltstone samples were taken from the processing room in the SPF (Sample Set 8). The samples were allowed to sit overnight and then were transported to SRNL to cure in a humidity oven under simulated field conditions. The humidity of the oven was kept constant at 95 % per SRR's direction and the temperature was changed as required to correspond with the grout temperature in SDU2A at the same elevation as the rest of the saltstone processed during the middle of August.[9] Also delivered with the samples were individual dry feeds, cement, slag, and fly ash, used during field processing of Sample Sets 8 and 9.

In order to prepare Sample Set 3, a simulant salt solution was batched based on the same composition of Tank 50 used to make Sample Sets 8 and 9.[6] On September 12, 2013, the salt solution simulant was mixed with the dry feeds received in August 2013 to make Sample Set 3 in the laboratory. The samples were placed in a humidity oven and cured under simulated field conditions.[9]

Wet core drilling of SDU2A was conducted between April 18 and May 6, 2015 in order to retrieve the field-emplaced samples of varying quality (Sample Set 9).[10] After extraction, the cores were placed in inert tubes (flushed with 99.99 % N_2) and transported to SRNL for storage and analysis.[11]

1.2 Sample Set 9 Receipt and Storage

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.[5,11] 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 and prevent oxidation during storage. The samples were photographed upon removal from the inert transport tubes and each section was placed in a sealable, plastic bag labeled with sample and depth identifications.[11] The plastic bags containing the samples were placed in air tight containers (Lock & Lock®) with a moist towel.[11]

The inerted chamber is a standard 4 port working chamber by Cleatech LLC with a custom transfer chamber (Figure 1-1). The 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 between 0.01- 1.0 % and recorded twice daily.

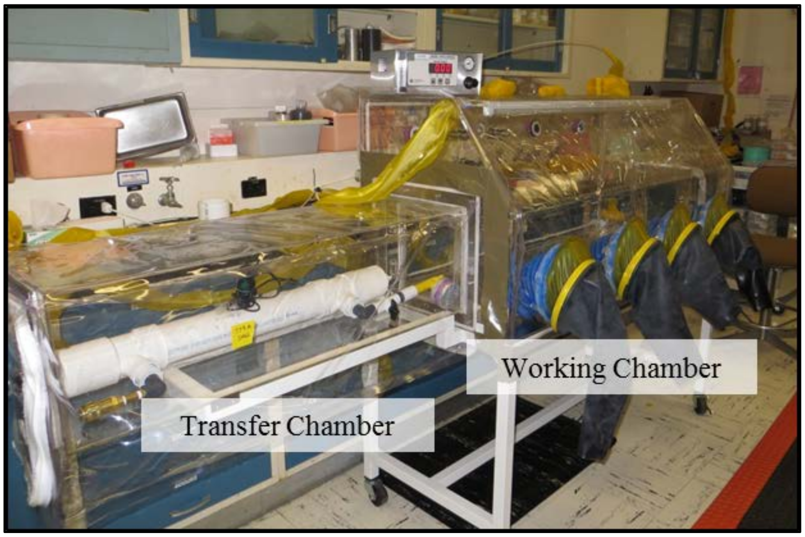

Figure 1-1. Photo illustrating the inert chamber for core sample receipt, storage and preparation. An example of the inert transfer tube is shown in the transfer chamber.

2.0 Saltstone Core Characterization

Prior to analyzing Sample Set 9, Sample Sets 3 and 8 were used for mock-up tests to ensure all the measurement analysis techniques were executable and provided the necessary data.[4] The mock-up tests were performed sequentially, starting with the non-radioactive samples (Sample Set 3). The testing on Sample Set 3 was conducted with respect to the physical properties outlined in the experimental plan developed for the SAP.[5] These included saturated hydraulic conductivity (SHC), density, porosity, and other physical properties. After the results of Sample Set 3 were accepted[4], Sample Set 8 was analyzed with respect to the physical, chemical, and radiochemical analyses described in the experimental plan.[5] Sample Set 9 was subsequently analyzed according to the methods described below.

2.1 Saltstone Core Subsampling and Analyses

In addition to visual observation of the samples, several physical and chemical properties of the material are summarized in Table 2-1 and described in more detail in the subsequent text. An example of the sampling location within the core is depicted in Figure 2-1. Sample interiors were utilized for measuring those properties that are considered sensitive to oxygen exposure. The samples were sectioned using a miter box and saw as well as a reciprocating hand saw (Rockwell model RK5102K). Table 2-2 provides information on the major equipment utilized for the analyses. The percent oxygen in the chamber remained within the required specifications (0.01 – 1.0%)[12] while preparing and working with the samples. In fact, the oxygen level never exceeded 0.25% when working with the samples. Samples were not removed from their sealed containers until the oxygen content had reached a minimum and stable level within the working chamber. A hand-held oxygen meter, Industrial Scientific Pro Gas Badge, capable of measuring levels of oxygen inside the chamber, was used to record oxygen levels during sample processing in addition to the oxygen analyzer/purge controller (Neutronics Model 1100) connected to the chamber. Relative humidity sensor (Fisher Scientific Traceable® Hygrometer) was placed in the chamber and monitored during sample processing. Temperature and humidity values were recorded during preparation of the samples and are noted where applicable.

Table 2-1. List of properties to be tested for Sample Set 9 including sample configuration and sample amount needed for testing.

Property	Sample Configuration	Sample Requirements
Density, Porosity, Moisture Content	Fractured samples – exposure to O_2 will not affect data.	Approx. 15 grams
SHC	Cylindrical sample with little or no observable surface damage.	2 in. x 2 in. (D x H)
Total Activity (Tc-99, Sr-90, I-129)	Fractured samples – exposure to O_2 will not affect data.	Approx. 45 grams for all isotopes
(Tc-99, Sr-90, I-129) Leachate concentrations or R_d with pH/E_h measurements	Sub-sample removed from interior of intact sample to ensure minimal O_2 exposure and ground for measurement. pH/E_h measurements taken on slurry.	Approx. 10 mL for all isotopes – leachate separated for individual isotope measurements

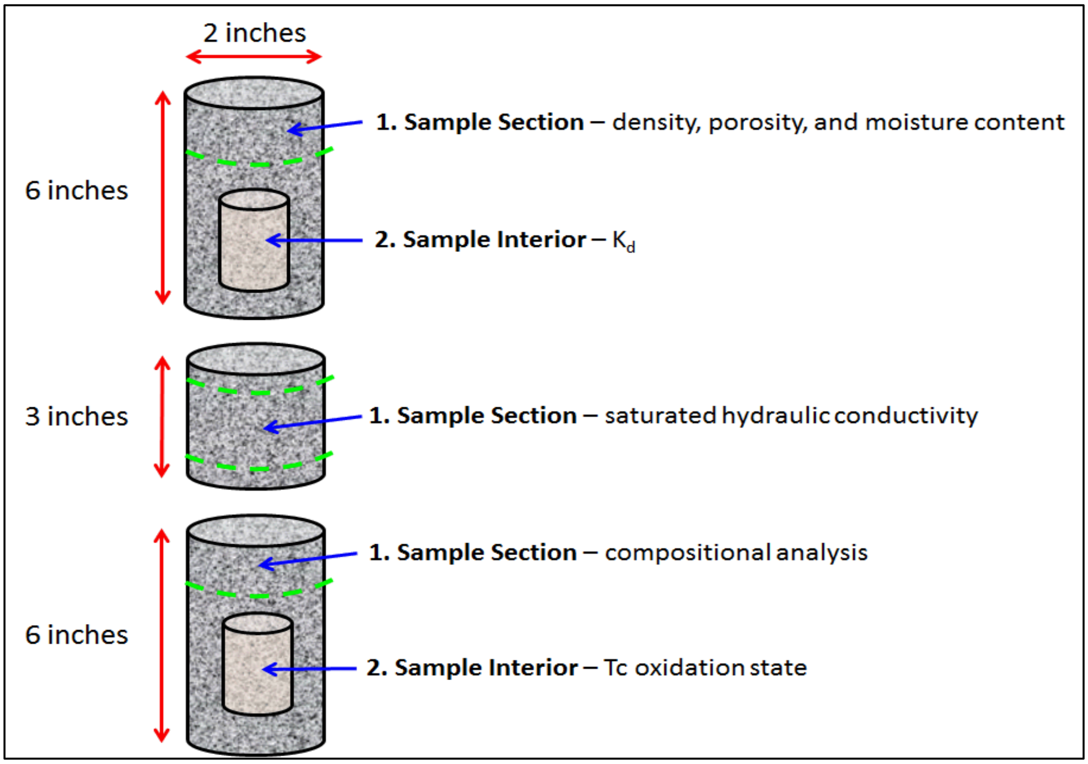

Figure 2-1. Graphic depiction of how cores will be sampled. Note: Section lengths are approximated and based on estimated depths of daily pours to SDU Cell 2A between August 11-16, 2013.

Table 2-2. List of properties tested and equipment used for the analysis of Sample Set 3, 8 and 9.

Property	Equipment	Quality Assurance (QA)
SHC	ELE TriFlex permeameter (Models 25-0696/02 and 25-0696)	MT&E burettes
pH	Oakton pHTestr™ (anoxic samples) and HI98121 combo by Hanna (oxic samples)	Calibration checks and sample controls
E_h	Oakton ORPTestr™ and HI98121 combo by Hanna	Sample controls and checks against a standard solution
Tc-99 Concentration	Liquid Scintillation Counting (LSC) (quantitation) Gamma spectrometer (extraction yield)	Covered under Analytical Development (AD) Measurement Control Program
Sr-90 Concentration	LSC (quantitation), Neutron Activation Analysis (extraction yield)	Covered under AD Measurement Control Program
I-129 Concentration	Gamma spectrometer (quantitation) Neutron Activation Analysis (extraction yield)	Covered under AD Measurement Control Program

2.1.1 Saturated Hydraulic Conductivity (SHC)

The SHC of samples was measured per ASTM D 5084, *Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter*.[13] Samples were prepared in the inert working chamber then removed for measurement in a radioactive fume hood. For hydraulic conductivity testing, the selected cores were of sufficient length to facilitate trimming to approximately two inches long. Ideal samples were without surface defects to mitigate breakthrough of the permeant. Each sample was cut to slightly over two inches long in the inert chamber. Once it was removed from the chamber, the core was trimmed and sanded to its final length in a radiological hood. The permeant used was a simplified version of the salt solution simulant used to make the simulant saltstone. Table 2-3 shows the recipe for the hydraulic conductivity permeant used in this study.

Table 2-3. Permeant Recipe for Saturated Hydraulic Conductivity Measurements.

Compound	Formula	Mass (g)
Water	H_2O	200.0
Potassium Nitrate	KNO_3	1.80
Sodium Sulfate	Na_2SO_4	14.92
Sodium Hydroxide	NaOH, 50 wt %	399.61

Each sample was vacuum saturated in the simulant for at least four days prior to being loaded into the measurement chamber (Figure 2-2). Once loaded, the samples were allowed to equilibrate for approximately two days before the test was initiated. The samples were tested according to Method C, falling head – rising tail, of the ASTM procedure.[13] The permeant was under a hydraulic gradient of approximately 30:1 which is the maximum gradient suggested by the method.

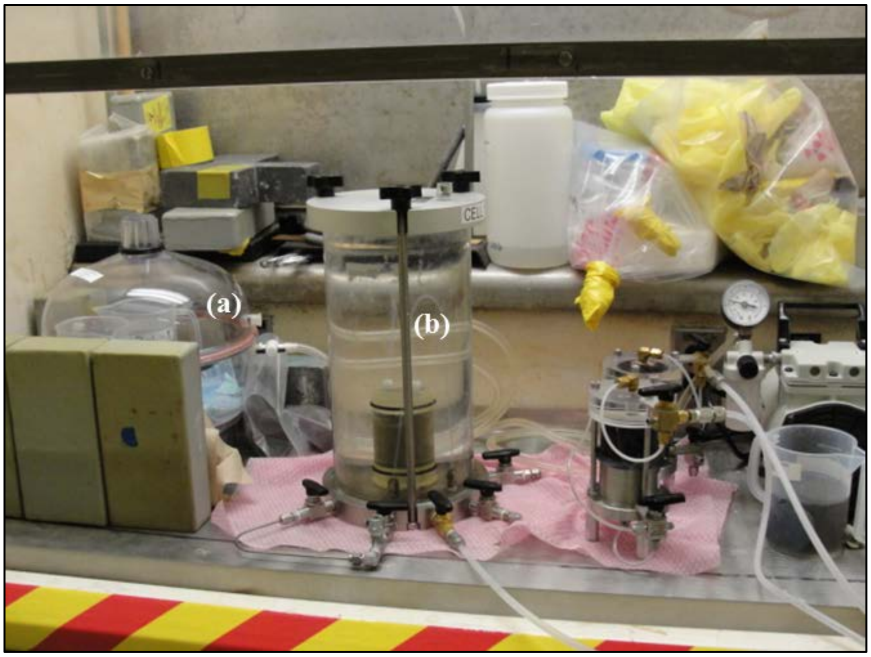

Figure 2-2. SHC test setup in a radiological hood, showing (a) the vacuum saturation chamber and (b) the measurement chamber.

2.1.2 Density, Porosity, Water Content

Modified 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 of Sample Set 9.[14] The ASTM method was followed with the exception of sample size and immersion and boiling medium. Section 4.1 of the ASTM procedure specifies a sample size of approximately 800 grams. Since the core samples cannot be analyzed whole due to equipment limitations, a reduced sample size was used. A simulated salt solution (used to make Sample Set 3 (3QCY13),[15] 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 (Figure 2-3), which were then immersed, boiled, and dried. After all the measurements were taken, the density was calculated by following the equations in the ASTM method. For the purposes of this study, the "bulk density after immersion and boiling"[14] was used as the reported density of the saltstone samples. The results from the triplicate samples were averaged and reported as the density for the respective sample.

The water content of the samples was calculated by drying the samples according to the ASTM method and taking the difference of the original sample mass and the dried sample mass. The porosity of the sample was determined from the simulant volume, the ratio of water to simulant and the density of the sample.

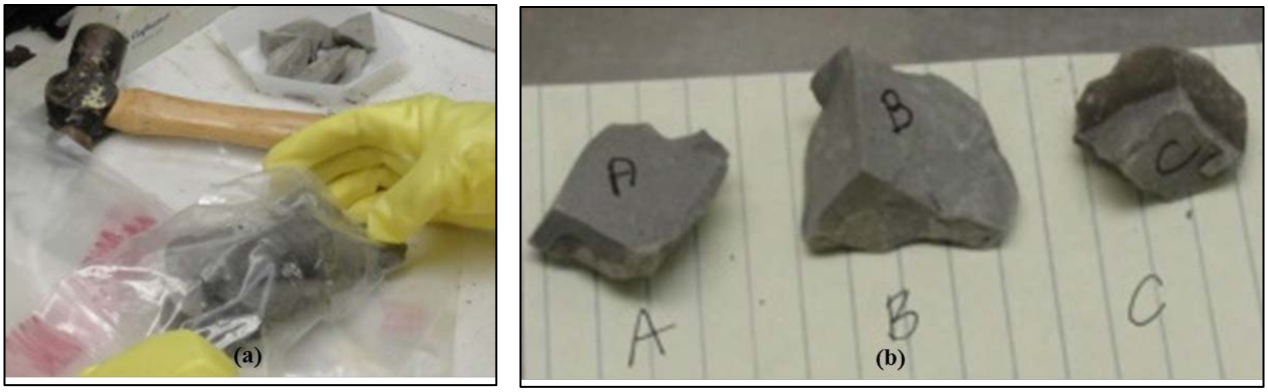

Figure 2-3. Sample preparation for density, porosity and water content measurements.

2.1.3 Total Activity in Saltstone Core Subsamples

For total activity analysis, a section of core was cleaved from the bulk sample then crushed and ground to a powder. Approximately 45 grams of crushed powder for each sample were submitted to the SRNL Analytical Development (AD) Laboratory for digestion and analysis using the methods described by isotope below. The solid samples are analyzed for total activity of Tc-99, Sr-90, and I-129 in triplicate.

Technetium (Tc-99): Samples of solids were spiked with Tc-99m and digested with concentrated acids. Aliquots of aqueous samples were spiked directly with Tc-99m. The technetium species were extracted from the matrix using an Aliquat-336® based solid phase extractant. Tc-99 concentrations were measured by liquid scintillation analysis. Tc-99m yields were measured with a well-type NaI gamma spectrometer, and were used to correct the Tc-99 analyses for any technetium losses from the radiochemical separations.

Strontium (Sr-90): Aliquots of solid samples were spiked with an elemental strontium carrier and were digested with concentrated acids. Aliquots of aqueous samples were spiked directly with an elemental strontium carrier. The strontium species were extracted from the matrix using a crown-ether-based solid phase extractant. Sr-90 concentrations were measured by liquid scintillation analysis. Elemental strontium carrier yields were measured by neutron activation analysis, and were used to correct the Sr-90 analyses for any strontium losses from the radiochemical separations.

Iodine (I-129): Samples of solids were dissolved in concentrated acid with an added potassium iodide (KI) carrier. Aliquots of aqueous samples were spiked directly with a KI carrier. Actinide and AMP (ammonium molybdophosphate) resins were then added to the mixture to facilitate removal of interfering isotopes. Sodium sulfite was added to reduce the iodine. Silver nitrate was added to the solution to precipitate the iodine as AgI, which is separated via filtration. The filtrate was analyzed for I-129 content using low energy photon/x-ray, thin-windowed, semi-planar, high purity germanium spectrometers. Elemental iodine yields were measured by neutron activation analysis, and were used to correct the I-129 analyses for any iodine losses from the radiochemical separation.

2.1.4 Distribution ratio (R_d) and Technetium Solubility

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*.[16] For Sample Set 9, each interior sample was broken with a hammer and ground to a fine powder using a grinder (Figure 2-4); however for Sample Set 8, samples were crushed to a powder using a mortar and pestle. The different preparation methods were due to the number of samples being analyzed and the need to have all the analyses started on the same day for consistency. Triplicate, approximately 1 g samples of powder were added to 10mL of solution (Table 2-4, Figure 2-5a). After the slurries were prepared, the samples were continuously tumbled end over end at 15 rpm for seven days (Figure 2-5b). At the end of the seven days, the solids were separated from liquids through a 0.45 micron filter. The aqueous phase was submitted to AD for analysis as described in Section 2.1.3. No attempt was made to determine if equilibrium was reached. It should be noted that the work control documents state the K_d for each radionuclide be determined from the extraction tests; however, due to the short duration of the test (seven days) and no verification that equilibrium was reached, it was determined that R_d is the more appropriate method to present the data.[3,4,16]

Figure 2-4. Example of a saltstone core sub-sample ground to a fine powder in the inert chamber.

The leaching experiments were conducted under both oxic and anoxic conditions. For oxic conditions, a portion of the powder was removed from the chamber, solution added, and samples tumbled in a radiological hood. For the anoxic conditions, deoxygenated (boiled) solution was added to the solids and tumbled inside the inert chamber. For Sample Set 9, the pH and E_h of the slurry was measured before and after tumbling. The pH probe was calibration checked using standard buffer solutions before and after use. The E_h probe was conditioned in tap water prior to use and the functionality was confirmed using a standard ORP solution of 220 mV.

Table 2-4. Solution used for leaching experiments.

Salt	g/L
$CaCl_2.2H_20$	3.68
Na_2SO_4	1.07
KCl	0.40
NaCl	2.65
$MgCl_2.6H_2O$	5.51

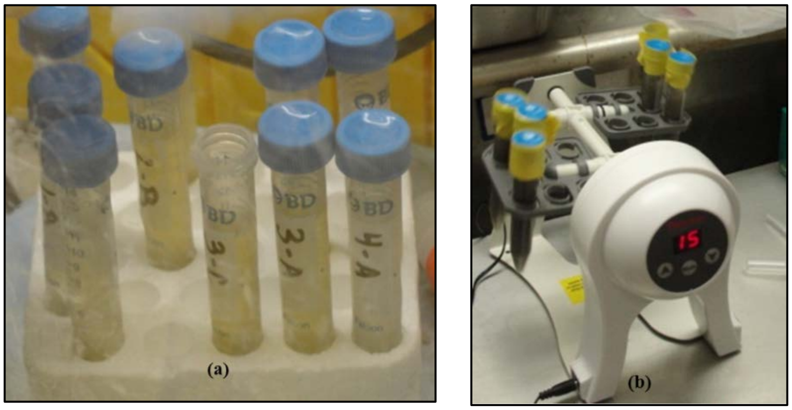

Figure 2-5. Preparation for R_d analysis, where (a) shows the slurry and (b) is the slurry tumbling.

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

The results and analysis of six Sample Set 9 samples are discussed in this section, and where applicable, the results are compared to the results of Sample Set 3. The samples are labeled according to the port they were taken from and the location (height) within the core.[10,11] Two core lengths (denoted upper (U) and lower (L)) were retrieved from Ports A and C, Holes 1 and 2. Only a single core length was retrieved from Port B. Each core length was named with sampling event (SDU2A-0931), Port (A, B, or C), Hole (1 or 2), Upper or Lower (U or L), and core section number starting with 1 at the top.[10,11] Therefore the second section from the lower core from hole 1 at Port A would be labeled SDU2A-0931-A-1-L-2.[11] Details of the field coring process are described in SRR-CWDA-2015-00066.[10] Each core length is divided into multiple core section samples due to the existence of through-diameter fractures that occurred during the core-drilling and extraction processes; fractures were observed to have occurred both at and between cold joints.[10,11] The lower cores are of primary interest and are associated with the August 2013 time-frame during which the SDU2A was filled to around a 16-foot elevation and comparative saltstone material was retrieved from the grout hopper outlet in the Saltstone Production Facility (Sample Set 8).[10]

3.1 Visual Observation

When the samples arrived at SRNL they were unloaded in the inert chamber, visually inspected and photographed.[11] In addition, during preparation of the cores for analysis, the cores were inspected. The condition of example cores prior to analysis are shown and discussed in Table 3-1. It is important to note that Table 3-1 is not an exhaustive list of each core sample analyzed for all the properties discussed in this report. Due to various core sizes and conditions, multiple core sections from the entire core were used to complete the analyses. Details of all the as-received core sections can be found in reference 11.

Table 3-1. Example of Analyzed Sample Set 9 Cores.

Sample ID	Selected Core Section(s) Prior to Analysis	Comments
SDU2A-0931-A-1-L-3		Sample is light grey on external surface. The surface shows defects from drilling. Internal surfaces are very dark and appear moist. Sample fractured and chipped during sectioning, but was relatively easy to cut.
SDU2A-0931-A-2-L-2		Sample is light grey with some darker spots on the external surface. Inspection of the internal grout after cutting shows some darker areas that appear moist. Sample is easy to section with minimal fracturing.

Sample ID	Selected Core Section(s) Prior to Analysis	Comments
SDU2A-0931-C-1-L-2		Sample is light grey on the external surface and darker just below the surface. Internal surface is mostly dark grey and appears moist. Sample is easy to section with minimal fracturing or chipping.
SDU2A-0931-B-1-L-2		Sample is light grey on external and internal surfaces of the sample. Internal surface has some slightly darker areas that appear moist. Sample was very difficult to section and fractured easily.

Sample ID	Selected Core Section(s) Prior to Analysis	Comments
SDU2A-0931-C-2-L-5	 	Sample is light grey on external and internal surfaces. Various parts of the sample are darker on the outside surface (above or below cold joint). Sample was difficult to section.
SDU2A-0931-C-2-L-2	 	Sample was dark and appeared moist on both the external and internal surfaces. Sample sectioned easily with minimal fracturing.

3.2 Saturated Hydraulic Conductivity

Six core samples were measured to determine their SHC and the results are shown in Table 3-2. Four of the samples had a SHC below the detection limit for the 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. As noted in Table 3-1, Sample SDU2A-0931-B-1-L-2 was difficult to cut and fractured easily, resulting in surface defects. The sample took a long time to equilibrate and reach four sequential steady state readings which is required by the ASTM.[13] Sample SDU2A-0931-A-1-L-3 also had some surface defects from the core drilling (Table 3-1) that couldn't be excluded from the SHC sample due to the size of the original core and requirements of the method. All six cores showed very low SHC values similar to the values measured from the Sample Set 3 samples (Table 3-3).[8] It is also noteworthy that all samples indicated SHCs less than the 6.4E-09 cm/sec assumed in the current PA modeling.[1]

Table 3-2. Saturated Hydraulic Conductivity Data and Results for Sample Set 9 Samples.

Sample ID	Length (cm)	Diam (cm)	Lat. Press (psig)	Head Press (psig)	Tail Press (psig)	K Final (cm/sec)
SDU2A-0931-A-1-L-3	5.33	5.03	59.9	51.9	49.9	1.20E-09
SDU2A-0931-A-2-L-2	4.84	5.02	59.7	51.8	49.6	<1.00E-9
SDU2A-0931-C-1-L-2	5.26	5.00	59.9	51.8	49.7	<1.00E-9
SDU2A-0931-B-1-L-2	5.35	5.03	59.9	51.9	50.0	4.40E-09
SDU2A-0931-C-2-L-5	5.42	5.03	59.9	49.8	51.9	<1.00E-9
SDU2A-0931-C-2-L-1	5.10	5.03	59.8	49.8	51.9	<1.00E-9

Table 3-3. Saturated Hydraulic Conductivity Data and Results for Sample Set 3 Samples.[8]

Sample Id	Length (cm)	Diam (cm)	Lat Press (psig)	Head Press (psig)	Tail Press (psig)	K Final (cm/sec)
3-05-2	5.19	5.11	60.0	52.0	50.0	<1.00E-9
3-01-2	5.75	5.08	60.0	52.0	50.0	<1.00E-9

3.3 Density and Porosity

As discussed in Section 2.1.2, the density and porosity and water content of each core sample was measured in triplicate. Table 3-4 shows the average density, water content, total porosity, and apparent (or permeable) porosity for each Sample Set 9 core sample. Additional density calculations and raw data are provided in Appendix A. It should be noted that the ASTM method does not involve a determination of absolute density. 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, especially that for the volume of permeable pore spaces.[14] The porosity was calculated from the volume of simulant divided by the sample volume and accounts the impermeable and permeable pores.

Table 3-4. Average Density, Water Content, and Porosity for Sample Set 9 Samples.

Sample ID	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 density shown in Table 3-4 is the "bulk density after immersion and boiling" in the ASTM method. The volume of permeable pore spaces is also calculated according to the ASTM method. The equations used to calculate these values are provided in Appendix A. These values are similar to the values measured for Sample Set 3 (Table 3-5). The porosity values for Sample Set 3 are lower than Sample Set 9 and this is most likely due to the differences in processing the samples (i.e., variable field-processing compared to controlled and consistent laboratory-preparation).

Table 3-5. Average Density, Water Content, and Porosity for Sample Set 3 Samples.[8]

Sample ID	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

3.4 Total Activity

Total activity was used to provide information on the total proportions of the selected isotopes (Tc-99, Sr-90, and I-129) in the saltstone core and were utilized for the calculation of the distribution ratio (R_d). The averaged results of the triplicate analyses of each Sample Set 9 sample are shown in Table 3-6. The entire data set is provided in Appendix B. Reported concentrations of Tc-99 in saltstone cores were approximately 25% of that predicted by the third quarter 2013 Tank 50 waste acceptance criteria analysis (1.93E+04 pCi/mL).[6] Although this result is consistent with that obtained for Sample Set 8[5], the basis for the lower than predicted Tc-99 recovery has not been determined.

Table 3-6. Average Total activity ($pCi/g_{saltstone}$) for Sample Set 9.

Sample Id	Tc-99	Sr-90	I-129
SDU2A-0931-A-1-L-3	1.85E+03	5.59E+02	4.71E+00
SDU2A-0931-A-2-L-3	1.57E+03	5.69E+02	3.48E+00
SDU2A-0931-C-1-L-2	1.32E+03	8.00E+02	4.17E+00
SDU2A-0931-B-1-L-2	1.41E+03	8.71E+02	5.58E+00
SDU2A-0931-C-2-L-4	1.41E+03	7.55E+02	3.52E+00
SDU2A-0931-C-2-L-2	1.33E+03	1.09E+03	3.31E+00

3.5 Leachate Results for I-129, Sr-90 and Tc-99

The leachate concentrations of radionuclides of interest can be used to estimate distribution ratios as well as solubility. 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. Since equilibrium was not demonstrated for these tests, the R_d values are considered upper bounds and solubilities lower bounds for the mobility of the radionuclides of interest. As discussed in Section 2.1.4, interior subsamples of Sample Set 9 cores were ground to a powder, triplicate slurries were prepared for the extraction test and filtered leachates were analyzed in order to calculate the R_d for I-129 and Sr-90 as well as Tc-99 solubility.

As part of analyzing the R_d samples, pH and E_h of the leachates were measured before and after tumbling to confirm the anoxic and oxic environments. The results are shown in Table 3-7. The pH probe functionality was verified by standard buffer solutions and the E_h probe functionality was verified using a standard solution. For the E_h probes, the readout on the probe must be adjusted for the electrolyte used in the probe and convert the results to a standard hydrogen electrode (SHE). Therefore, for the anoxic E_h results obtained from the Oakton Testr10 probe with a 3 molar KCl electrolyte, 209 mV must be added to the probe readout. For the oxic E_h results obtained from the Hanna HI98121 combo probe with a 3.5 molar KCl electrolyte, 204 mV must be added to the probe results. Table 3-7 shows the results after the correction factor has been applied and shows that the leaching solution became more reducing in the anoxic environment after the seven day tumble while the oxic leaching solution showed no change after seven days of the extraction test.

Table 3-7. E_h (mV, SHE) and pH Results for R_d Leachates Pre- and Post-Tumbling.

	Anoxic (Oakton Instrument)				Oxic (Hanna Instrument)			
Sample ID	**Pre-leaching**		**Post leaching**		**Pre-leaching**		**Post leaching**	
	pH	**Eh**	**pH**	**Eh**	**pH**	**Eh**	**pH**	**Eh**
SDU2A-0931-A-1-L-3	9.4	105	10.4	-186	9.6	164	10.6	178
SDU2A-0931-A-2-L-2	--	--	10.4	-220	9.6	162	10.8	148
SDU2A-0931-C-1-L-2	9.4	93	10.6	-240	9.7	150	10.7	144
SDU2A-0931-B-1-L-2	--	--	10.4	-222	9.8	154	10.6	146
SDU2A-0931-C-2-L-5	9.3	99	10.5	-220	9.8	149	10.7	170
SDU2A-0931-C-2-L-2	9.4	102	10.6	-211	9.7	173	10.8	144

-- No measurement was performed.

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/L) to be consistent with the data presented in the SDF modeling.[1] The solubility is calculated by dividing the activity per volume (pCi/mL) by the specific activity (Ci/g) 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 can be expressed as a distribution coefficient (K_d) or distribution ratio (R_d). K_d or R_d (mL/g) is calculated by:

$$K_d\ (or\ R_d) = \frac{A_s}{A_d}$$

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 the following sections 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. The test conducted in this study is a desorption R_d rather than the standard R_d per the ASTM. 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 mL) 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. Also, the SDF transport model uses K_d (distribution coefficient) values which is calculated by the same equation but K_d implies equilibrium has been reached. This report uses R_d rather than K_d since it was not confirmed that equilibrium was reached.

3.5.1 Distribution ratio for I-129

The calculated R_d results for the anoxic and oxic environments are provided in Table 3-8 and Table 3-9, respectively. For both analysis environments, the I-129 results produced some negative R_d values, which are most likely artifacts 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). 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 mL/g for anoxic and 15 mL/g for oxic conditions.[1]

3.5.2 Distribution ratio for Sr-90

The calculated R_d results for the anoxic and oxic environments are provided in Table 3-10 and Table 3-11, respectively. 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 to >176) than the anoxic values (36 to 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). Both R_ds are higher than those 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 (Table 3-10 and Table 3-11). 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 values currently assumed in the SDF modeling for strontium is 15 mL/g for both oxic and anoxic conditions.[1]

3.5.3 Leachate Results for Tc-99

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 3-12 and Table 3-13, 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 Eh data in Table 3-7 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 (Table 3-1). 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.

Table 3-8. I-129 Leachate and Solids Activity and R_d Results in Anoxic Conditions.

Sample Id	Replicate	Leachate				Average Bulk Solid (pCi/g)	Average Solid Mass Leached (g)	Corrected Solids Activity Post Leaching (pCi/g) (A_s)	R_d (mL/g)	Adjusted R_d (mL/g)
		dpm/mL	one sigma % uncert.	average (dpm/mL)	**average (pCi/mL) (A_d)**					
SDU2A-0931-A-1-L-3	A	7.07E-01	12.40	7.23E-01	3.26E-01	4.71E+00	1.00	1.46E+00	4	4
	B	8.88E-01	15.00							
	C	5.73E-01	19.90							
SDU2A-0931-A-2-L-2	A	9.14E-01	13.30	8.36E-01	3.76E-01	3.48E+00	1.01	-2.63E-01	-1	0
	B	8.28E-01	21.80							
	C	7.65E-01	15.30							
SDU2A-0931-C-1-L-2	A	1.26E+00	17.50	1.05E+00	4.71E-01	4.17E+00	1.03	-4.71E-01	-1	0
	B	9.01E-01	12.30							
	C	9.77E-01	14.70							
SDU2A-0931-B-1-L-2	A	9.75E-01	12.50	9.21E-01	4.15E-01	5.58E+00	1.01	1.47E+00	4	4
	B	9.67E-01	20.90							
	C	8.22E-01	12.70							
SDU2A-0931-C-2-L-5	A	6.01E-01	20.50	7.09E-01	3.20E-01	3.52E+00	1.00	3.33E-01	1	1
	B	9.00E-01	22.90							
	C	6.27E-01	15.70							
SDU2A-0931-C-2-L-2	A	1.07E+00	14.20	1.38E+00	6.22E-01	3.31E+00	1.00	-2.88E+00	-5	0
	B	1.79E+00	17.20							
	C	1.28E+00	12.50							

Table 3-9. I-129 Leachate and Solids Activity and R_d Results in Oxic Conditions.

Sample Id	**Replicate**	**Leachate**				**Average Bulk Solid (pCi/g)**	**Average Solid Mass Leached (g)**	**Corrected Solids Activity Post Leaching (pCi/g) (A_s)**	**R_d (mL/g)**	**Adjusted R_d (mL/g)**
		dpm/mL	one sigma % uncert.	average (dpm/mL)	**average (pCi/mL) (A_d)**					
SDU2A-0931-A-1-L-3	A	8.97E-01	13.70	9.05E-01	4.08E-01	4.71E+00	1.01	6.59E-01	2	2
	B	9.28E-01	20.70							
	C	8.90E-01	12.10							
SDU2A-0931-A-2-L-2	A	1.15E+00	8.10	1.49E+00	6.70E-01	3.48E+00	1.01	-3.15E+00	-5	0
	B	1.71E+00	11.40							
	C	1.60E+00	18.80							
SDU2A-0931-C-1-L-2	A	8.57E-01	12.80	1.02E+00	4.58E-01	4.17E+00	1.00	-3.87E-01	-1	0
	B	1.15E+00	12.50							
	C	1.04E+00	22.80							
SDU2A-0931-B-1-L-2	A	8.96E-01	12.10	1.83E+00	8.25E-01	5.58E+00	1.01	-2.60E+00	-3	0
	B	2.65E+00	9.70							
	C	1.95E+00	23.60							
SDU2A-0931-C-2-L-5	A	7.63E-01	18.60	8.30E-01	3.74E-01	3.52E+00	1.00	-2.03E-01	-1	0
	B	9.27E-01	18.80							
	C	7.99E-01	18.20							
SDU2A-0931-C-2-L-2	A	1.66E+00	8.70	1.50E+00	6.74E-01	3.31E+00	1.00	-3.40E+00	-5	0
	B	1.48E+00	17.60							
	C	1.35E+00	10.30							

Table 3-10. Sr-90 Leachate and Solids Activity and R_d Results in Anoxic Conditions.

Sample Id	**Replicate**	**Leachate**				**Average Bulk Solid (pCi/g)**	**Average Solid Mass Leached (g)**	**Corrected Solids Activity Post Leaching (pCi/g) (A_s)**	**R_d (mL/g)**
		dpm/mL	one sigma % uncert.	average (dpm/mL)	**average (pCi/mL) (A_d)**				
SDU2A-0931-A-1-L-3	A	1.64E+01	51.20	1.54E+01	6.95E+00	5.59E+02	1.00	4.89E+02	70
	B	1.51E+01	51.50						
	C	1.48E+01	44.10						
SDU2A-0931-A-2-L-2	A	1.70E+01	41.80	2.75E+01	1.24E+01	5.69E+02	1.01	4.46E+02	36
	B	2.31E+01	40.30						
	C	4.24E+01	35.30						
SDU2A-0931-C-1-L-2	A	3.54E+01	34.10	3.18E+01	1.43E+01	8.00E+02	1.03	6.61E+02	46
	B	2.49E+01	42.00						
	C	3.50E+01	36.80						
SDU2A-0931-B-1-L-2	A	2.22E+01	39.20	2.57E+01	1.16E+01	8.71E+02	1.01	7.56E+02	65
	B	3.92E+01	31.00						
	C	1.56E+01	36.20						
SDU2A-0931-C-2-L-5	A	3.05E+01	64.30	3.27E+01	1.47E+01	7.55E+02	1.00	6.08E+02	41
	B	3.10E+01	50.50						
	C	3.66E+01	43.00						
SDU2A-0931-C-2-L-2	A	<2.03E+01	mda	3.00E+01	1.35E+01	1.09E+03	1.00	9.51E+02	70
	B	2.87E+01	49.30						
	C	3.13E+01	54.10						

\# Result is the average of two data points since one replicate had a less than detect.

Table 3-11. Sr-90 Leachate and Solids Activity and R_d Results in Oxic Conditions.

Sample Id	**Replicate**	**Leachate**				**Average Bulk Solid (pCi/g)**	**Average Solid Mass Leached (g)**	**Corrected Solids Activity Post Leaching (pCi/g) (A_s)**	**R_d (mL/g)**
		dpm/mL	one sigma % uncert.	average (dpm/mL)	**average (pCi/mL) (A_d)**				
SDU2A-0931-A-1-L-3	A	<1.40E+01	mda	<1.39E+01	<6.26E+00	5.59E+02	1.01	4.96E+02	>79
	B	<1.50E+01	mda						
	C	<1.27E+01	mda						
SDU2A-0931-A-2-L-2	A	1.74E+01	59.90	1.52E+01	6.85E+00	5.69E+02	1.01	5.01E+02	73
	B	<1.27E+01	mda						
	C	1.30E+01	53.50						
SDU2A-0931-C-1-L-2	A	<1.08E+01	mda	1.51E+01	6.80E+00	8.00E+02	1.00	7.33E+02	108
	B	1.14E+01	54.70						
	C	1.88E+01	53.10						
SDU2A-0931-B-1-L-2	A	<1.58E+01	mda	1.51E+01	6.78E+00	8.71E+02	1.01	8.04E+02	119
	B	1.76E+01	63.30						
	C	1.25E+01	66.00						
SDU2A-0931-C-2-L-5	A	<1.22E+01	mda	<1.30E+01	<5.86E+00	7.55E+02	1.00	6.97E+02	>119
	B	<1.12E+01	mda						
	C	<1.56E+01	mda						
SDU2A-0931-C-2-L-2	A	<1.53E+01	mda	<1.30E+01	<5.84E+00	1.09E+03	1.00	1.03E+03	>176
	B	<1.30E+01	mda						
	C	<1.06E+01	mda						

***** All less than values are the reported detection limit (MDA)
# Result is the average of two data points since one replicate had a less than detect.

Table 3-12. Tc-99 Leachate and Solids Activity and Solubility Results in Anoxic Conditions.

Sample Id	**Replicate**	**Leachate**				**Average Bulk Solid (pCi/g)**	**Average Solid Mass Leached (g)**	**Corrected Solids Post Leaching (pCi/g) (A_s)**	**Leachate Concentration (mol/L)****
		dpm/mL	one sigma % uncert.	average (dpm/mL)	**average (pCi/mL) (A_d)**				
SDU2A-0931-A-1-L-3	A	<4.39E+01#	mda	<4.33E+01	<1.95E+01	1.85E+03	1.00	1.66E+03	<1.16E-08
	B	--*	--*						
	C	<4.26E+01	mda						
SDU2A-0931-A-2-L-2	A	1.79E+02	11.26	1.48E+02	6.65E+01	1.57E+03	1.01	9.05E+02	3.95E-08
	B	1.52E+02	12.61						
	C	1.12E+02	16.75						
SDU2A-0931-C-1-L-2	A	1.08E+02	15.30	1.24E+02	5.58E+01	1.32E+03	1.03	7.72E+02	3.32E-08
	B	9.76E+01	15.48						
	C	1.66E+02	12.33						
SDU2A-0931-B-1-L-2	A	7.71E+01	18.80	6.98E+01	3.14E+01	1.41E+03	1.01	1.10E+03	1.87E-08
	B	8.35E+01	17.83						
	C	4.87E+01	29.74						
SDU2A-0931-C-2-L-5	A	2.30E+01	21.50	2.62E+01	1.18E+01	1.41E+03	1.00	1.29E+03	7.02E-09
	B	2.68E+01	20.50						
	C	2.89E+01	16.60						
SDU2A-0931-C-2-L-2	A	8.53E+01	8.82	9.00E+01	4.05E+01	1.33E+03	1.00	9.22E+02	2.41E-08
	B	9.22E+01	8.17						
	C	9.25E+01	8.51						

* data not reportable due to insufficient yield

\# All less than values are the reported detection limit (MDA)

** interpretable as solubility if no oxidation of sample occurred in field or laboratory, and if anoxic conditions were successfully maintained during experiment.

Table 3-13. Tc-99 Leachate and Solids Activity and Solubility Results in Oxic Conditions.

Sample Id	**Replicate**	**Leachate**				**Average Bulk Solid (pCi/g)**	**Average Solid Mass Leached (g)**	**Corrected Solids Post Leaching (pCi/g) (A_s)**	**R_d (mL/g)**	**Leachate Concentration (mol/L)**
		dpm/mL	one sigma % uncert.	average (dpm/mL)	**average (pCi/mL) (A_d)**					
SDU2A-0931-A-1-L-3	A	9.25E+01	8.09	9.79E+01	4.41E+01	1.85E+03	1.01	1.41E+03	32	2.62E-08
	B	1.08E+02	7.63							
	C	9.33E+01	7.62							
SDU2A-0931-A-2-L-2	A	9.00E+01	9.02	9.43E+01	4.25E+01	1.57E+03	1.01	1.15E+03	27	2.52E-08
	B	9.50E+01	9.04							
	C	9.78E+01	9.52							
SDU2A-0931-C-1-L-2	A	8.88E+01	8.97	8.48E+01	3.82E+01	1.32E+03	1.00	9.35E+02	24	2.27E-08
	B	7.53E+01	9.37							
	C	9.04E+01	9.02							
SDU2A-0931-B-1-L-2	A	7.27E+01	10.30	7.59E+01	3.42E+01	1.41E+03	1.01	1.07E+03	31	2.03E-08
	B	7.68E+01	10.00							
	C	7.83E+01	11.10							
SDU2A-0931-C-2-L-5	A	1.00E+02	7.98	9.05E+01	4.08E+01	1.41E+03	1.00	1.00E+03	25	2.42E-08
	B	8.17E+01	8.47							
	C	8.97E+01	8.80							
SDU2A-0931-C-2-L-2	A	7.96E+01	8.89	8.06E+01	3.63E+01	1.33E+03	1.00	9.64E+02	27	2.16E-08
	B	9.07E+01	8.00							
	C	7.16E+01	9.95							

4.0 Conclusions

As part of an ongoing PA Maintenance Plan, SRR 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. Both the higher porosities, and the range of the porosities, for the SDU cores is perhaps indicative of the variability in processing saltstone in the field (including the mixing technique, line transfer, and free-fall placement all of which can affect the air content) in comparison to the use of consistent laboratory preparation techniques in a controlled environment. 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 PA modeling.

For Sample Set 9, 7-day leaching tests were performed for Tc-99, Sr-90 and I-129 (in both oxic and anoxic environments), and are interpreted in terms of solubility and distribution ratio (R_d). Analyzing the R_d or the solubility, 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. The I-129 results generated R_ds between -5 and +4 mL/g, with no significant difference between oxic and anoxic conditions. For data use, negative R_ds should be taken as zero. The data in this report indicates that the mobility of I-129 is unaffected by the environment in which the measurements were conducted. The current SDF modeling assumes an iodine R_d of 9 mL/g for anoxic and 15 mL/g for oxic conditions.[1]

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). Both sets of R_ds are significantly higher than the K_d employed by the SDF PA, which is 15 mL/g for both oxic and anoxic conditions.[1]

The SDF model analyzes solubility or sorption of Tc-99 depending on whether it is assumed to be oxidized or reduced, respectively. The conceptual model is that aqueous Tc-99 concentrations are controlled by sorption when oxidized and by solubility when reduced. In addition, the conceptual model is that Tc-99 leachate concentrations should be higher in oxidized solutions compared to reduced solutions. However, this study found that measured Tc-99 leachate concentrations were approximately the same under both anoxic and oxic environments, which is an unexpected finding. It is possible that during the oxic experiments, the exposure to air was not sufficient to fully oxidize the samples. Alternatively, inadvertent exposure to air at some point in the field or laboratory could have partially oxidized the samples intended to be anoxic. For all leaching experiments, since it is not certain that equilibrium was attained during the 7-day leaching tests, distribution ratios should be regarded as upper bounds, and solubilities interpreted from leachate concentrations should be regarded as lower bounds.

5.0 References

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Appendix A. Density, Porosity, and Water Content Data

The equations outlined in the ASTM standard with the masses designated as A through D, are:

A = mass of oven-dried sample in air between 100 to 110 °C, g
B = mass of surface-dry sample in air after immersion, g
C = mass of surface-dry sample in air after immersion and boiling, g
D = apparent mass of sample in water after immersion and boiling, g

The equations are shown in the tables above the data. The Sample Set 9 samples were analyzed in two separate groups. As a result, two different batches of salt solution were utilized, resulting in different densities. The density utilized for the calculations is noted below the table.

Formulas used for porosity determination:

$$Water\ Mass = Crucible\ and\ Sample - Dry\ Mass$$

$$Simulant\ Volume = (Water\ Mass)/(ratio\ of\ water\ to\ simulant) * 1/\rho\_ss$$

$$Sample\ Volume = (\ Sample\ Mass)/(Apparent\ Density)$$

$$Porosity = (Simulant\ Volume)/(Sample\ Volume) * 100$$

Table A-1. Density calculations for Sample Set 9 group 1 samples.

Sample ID	Replicate	Absorption after immersion and Boiling (%)	Bulk Density, dry	Bulk Density after immersion and boiling	Apparent Density	Volume of permeable pore spaces (%)	Water Content (%)
		[(C-A)/A)]*100	[A/(C-D)]*ρ	[C/(C-D)]*ρ	[A/(A-D)]*ρ	[(C-A)/(C-D)]*100	--
SDU2A-0931-A-1-L-5	A	47.201	1.167	1.717	2.127	45.145	29.63
	B	47.261	1.166	1.718	2.128	45.197	29.99
	C	45.487	1.194	1.737	2.152	44.522	29.84
SDU2A-0931-B-1-L-1	A	44.387	1.192	1.721	2.104	43.367	30.06
	B	43.739	1.204	1.731	2.119	43.180	32.52
	C	43.824	1.197	1.722	2.100	43.010	31.06
SDU2A-0931-C-2-L-6	A	41.112	1.257	1.774	2.181	42.365	30.32
	B	47.304	1.158	1.706	2.102	44.912	31.49
	C	42.047	1.237	1.757	2.156	42.633	29.73

[*] Density of salt solution (ρ) is 1.2197 g/mL

Table A-2. Porosity data for Sample Set 9 group 1 samples.

Sample ID	Replicate	Simulant Volume (cm3)	Sample Volume (cm3)	Porosity (%)
SDU2A-0931-A-1-L-5	A	4.69	7.367	63.64
	B	5.31	8.245	64.42
	C	4.45	6.867	64.82
SDU2A-0931-B-1-1	A	3.52	5.435	64.68
	B	5.50	7.806	70.39
	C	4.79	7.166	66.87
SDU2A-0931-C-2-L-6	A	3.92	5.832	67.24
	B	7.37	10.968	67.18
	C	7.03	10.770	65.30

Table A-3. Density calculations for Sample Set 9 group 2 samples.

Sample ID	Replicate	Absorption after immersion and Boiling (%)	Bulk Density, dry	Bulk Density after immersion and boiling	Apparent Density	Volume of permeable pore spaces (%)	Water Content (%)
		[(C-A)/A)]*100	[A/(C-D)]*ρ	[C/(C-D)]*ρ	[A/(A-D)]*ρ	[(C-A)/(C-D)]*100	--
SDU2A-0931-A-2-L-5	A	41.920	1.228	1.742	2.117	42.015	29.33
	B	41.833	1.228	1.742	2.116	41.950	28.90
	C	41.471	1.233	1.745	2.118	41.758	28.90
SDU2A-0931-C-2-L-8	A	47.384	1.200	1.769	2.241	46.430	32.26
	B	48.495	1.127	1.673	2.034	44.606	31.97
	C	55.588	1.076	1.674	2.102	48.817	32.07
SDU2A-0931-C-1-L-5	A	41.789	1.242	1.761	2.154	42.360	28.40
	B	41.589	1.232	1.744	2.117	41.821	29.46
	C	40.272	1.271	1.782	2.182	41.774	29.55

[*] Density of salt solution (ρ) is 1.2249 g/mL

Table A-4. Porosity data for Sample Set 9 group 2 samples.

Sample ID	Replicate	Simulant Volume (cm3)	Sample Volume (cm3)	Porosity (%)
SDU2A-0931-A-2-L-5	A	3.66	5.707	64.19
	B	6.49	10.261	63.25
	C	4.56	7.193	63.35
SDU2A-0931-C-2-L-8	A	4.80	6.700	71.70
	B	7.27	10.815	67.19
	C	4.25	6.303	67.43
SDU2A-0931-C-1-L-5	A	5.98	9.514	62.82
	B	6.80	10.537	64.55
	C	7.28	11.006	66.17

Appendix B. Raw data for solids activity.

Table B-1 . Total Activity Data for Sample Set 9.

Sample Id	Replicate	Tc-99			Sr-90			I-129		
		dpm/g	average (dpm/g)	average (pCi/g)	dpm/g	average (dpm/g)	average (pCi/g)	dpm/g	average (dpm/g)	average (pCi/g)
SDU2A-0931-A-1-L-3	A	5.28E+03	4.11E+03	1.85E+03	1.22E+03	1.24E+03	5.59E+02	1.13E+01	1.05E+01	4.71E+00
	B	4.26E+03			1.07E+03			1.12E+01		
	C	2.78E+03			1.43E+03			8.86E+00		
SDU2A-0931-A-2-L-3	A	2.91E+03	3.48E+03	1.57E+03	1.52E+03	1.26E+03	5.69E+02	7.93E+00	7.72E+00	3.48E+00
	B	3.91E+03			1.11E+03			8.44E+00		
	C	3.61E+03			1.16E+03			6.78E+00		
SDU2A-0931-C-1-L-2	A	2.74E+03	2.92E+03	1.32E+03	1.20E+03	1.78E+03	8.00E+02	1.04E+01	9.26E+00	4.17E+00
	B	3.37E+03			1.83E+03			7.94E+00		
	C	2.65E+03			2.30E+03			9.45E+00		
SDU2A-0931-B-1-L-2	A	2.93E+03	3.13E+03	1.41E+03	1.71E+03	1.93E+03	8.71E+02	1.11E+01	1.24E+01	5.58E+00
	B	3.09E+03			1.68E+03			8.23E+00		
	C	3.36E+03			2.41E+03			1.78E+01		
SDU2A-0931-C-2-L-4	A	3.38E+03	3.12E+03	1.41E+03	1.71E+03	1.68E+03	7.55E+02	6.21E+00	7.81E+00	3.52E+00
	B	3.33E+03			2.08E+03			7.58E+00		
	C	2.66E+03			1.24E+03			9.64E+00		
SDU2A-0931-C-2-L-2	A	2.76E+03	2.94E+03	1.33E+03	2.10E+03	2.41E+03	1.09E+03	3.87E+00	7.35E+00	3.31E+00
	B	3.34E+03			2.11E+03			5.88E+00		
	C	2.73E+03			3.02E+03			1.23E+01		

Distribution:

T. B. Brown, 773-A
M. E. Cercy, 773-42A
D. A. Crowley, 773-43A
D. E. Dooley, 773-A
A. P. Fellinger. 773-42A
S. D. Fink, 773-A
C. C. Herman, 773-A
D. T. Hobbs, 773-A
E. N. Hoffman, 999-W
J. E. Hyatt, 773-A
K. M. Kostelnik, 773-42A
B. B. Looney, 773-42A
D. A. McGuire, 773-42A
T. O. Oliver, 773-42A
F. M. Pennebaker, 773-42A
G. N. Smoland, 773-42A
B. J. Wiedenman, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)
J. S. Contardi, 704-56H
V. Jain, 766-H
M. A. Rios-Armstrong, 766-H
S. P. Simner, 705-1C
K.H. Rosenberger, 705-1C
P. R. Jackson, DOE-SR, 703-46A
J. A. Crenshaw, 703-46A
D. I. Kaplan, 773-42A
T. W. Coffield, 705-1C
R. L. Nichols, 773-41A