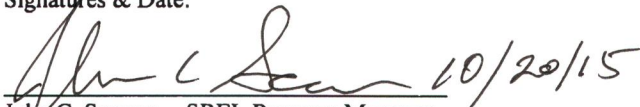


## SREL FY16 Test Plan: Chemical and Physical Properties of <sup>99</sup>Tc-Spiked Saltstone

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**Objective:** The current Test Plan reflects an extension of a previous SREL Test Plan, SREL Doc. R-15-001, supported by G-SOW-Z-00015. The project objectives include:

- (1) Evaluating the contaminant leaching properties of a set of simulant saltstone monoliths, produced utilizing Savannah River Remediation LLC (SRR) prescribed grout formulations, spiked with  $^{99}\text{Tc}$  and subjected to a defined curing regime under controlled temperature and humidity conditions chosen to mimic curing conditions within the Saltstone Disposal Unit (SDU) environment,
- (2) Applying the protocols developed in the first objective to analyze the contaminant leaching properties of a set of saltstone monolithic samples that were cored from Saltstone Disposal Unit (SDU) Cell 2A in April and May of 2015 following emplacement of fresh grout in August 2013 (see SRNL-L3100-2015-00108 Rev. 0 for sample details), and
- (3) Determining the distribution (partitioning) coefficient ( $K_d$ ) of radioiodine in the presence of solids and solution treatments relevant to the Saltstone Disposal Facility (SDF).

**Summary of Approach:** A detailed Task Schedule for FY16 is provided in Table 1. Simulant saltstone samples for characterization per Objective (1) will be prepared in a 1 to 2 kg batch that will be spiked with  $^{99}\text{Tc}$  at a concentration consistent with levels found in the Tank 50 feed waste ( $\approx 1 \text{ mg L}^{-1}$ ) at the SDF. An additional 1-2 kg batch of Re spiked grout will be created for use in optimizing any test methodologies before sacrificing the  $^{99}\text{Tc}$  spiked monoliths. After curing for 90 days in an oxic, high humidity atmosphere, monolithic samples will be analyzed per EPA Method 1315 and a novel dynamic leaching method (DLM), the details of which are provided in the subsequent text. EPA method testing will initially be conducted under an oxic (ambient air) atmosphere and subsequent determinations made to establish if testing under anoxic (Ultra-High Purity  $\text{N}_2$ ) and/or reducing ( $\text{H}_2$  (2%) and  $\text{N}_2$  (98%)) atmospheres are warranted. Contaminant leaching behavior will subsequently be evaluated with respect to  $^{99}\text{Tc}$ , Re (if applicable), and nitrate ( $\text{NO}_3^-$ ); nitrate is monitored for comparison as a non-sorbing saltstone constituent. The same protocols will then be used to evaluate  $^{99}\text{Tc}$  (and possibly other saltwaste contaminants) leaching from a limited set of saltstone cores extracted from SDU Cell 2A (i.e., Objective (2)). All unused saltstone samples will be retained for subsequent analysis as required. Samples will be stored in a high humidity, inert gas (i.e.,  $\text{N}_2$ ) environment at ambient room temperature. Objective (3) is a continuation of work conducted to establish  $K_d$  for iodine in the presence of SDF-relevant solids and solution treatments. Previous work utilized a non-radioactive source whereas the proposed work will determine  $K_d$  utilizing radioactive  $^{129}\text{I}$ .

**Table 1. TASK SCHEDULE**

Task	Duration	Notes
Finalize FY16 test plan*	9/1/15 – 10/23/15	Define oxidizing treatments and durations
Identify SDU 2A saltstone cores that are suitable for EPA 1315 Method tests	10/01/15 – 10/30/15	Note dimensions and identify samples that require sectioning prior to testing
Accept transfer of SDU 2A saltstone cores from SRNL	11/1/15 – 11/30/15	Store under inert atmosphere; evaluate $^{137}\text{Cs}$ activity on intact cores
Measure reductive capacity of new BFS and other dry feed materials	10/12/15 – 10/16/15	Revised Ce(IV) method
Create 8-10, 2" dia. x 4" $^{99}\text{Tc}$ -spiked saltstone monoliths	10/19/15 – 10/23/15	≈ 1-2 kg saltstone batch using new BFS supply; all supplies in stock
Cure $^{99}\text{Tc}$ -spiked monoliths for three months (≈ 90 days)	10/21/15 – 1/19/16	Follow SDU Cell 2B curing temperature profile
$^{129}\text{I}$ Batch $K_d$ study	1/04/16-2/29/16	Batch $^{129}\text{I}$ sorption equilibration and sample analysis
EPA1315 test on $^{99}\text{Tc}$ spiked saltstone cured for 3 months and then exposed to one of three test atmospheres	2/15/16 – 4/19/16	3-D test geometry of 2" x 4" cores, 9 sampling events, $^{99}\text{Tc}$ and $\text{NO}_3^-$ analysis
Dynamic leaching test on $^{99}\text{Tc}$ spiked saltstone	2/15/16 – TBD	Three sections leached simultaneously
EPA1315 test SDU saltstone monoliths	4/4/16 – 7/23/16	Remove SDU cores from inert atm., 3-D test geometry of 2" dia. cores, 3 cores, 9 sampling events, $^{99}\text{Tc}$ , $^{137}\text{Cs}$ , Nitrate, $^{129}\text{I}$ analysis
DLM test for SDU saltstone	4/04/16 – TBD	Limited test conditions: with and without $\text{O}_2$
Write draft task report*	7/25/16 – 8/19/16	Submit draft task report to SRR for review
SRR report review	8/22/16 – 8/31/16	
Revise project reports*	8/31/16 – 9/23/16	Submit final report

\*Deliverables

Details of the current task plan are divided into a series of specific tasks: (A) Acceptance and Storage of SDU Cell 2A Saltstone Cores; (B) Saltstone Simulant Preparation and Curing; (C) Semi-Dynamic Contaminant Leaching; (D) Saturated Dynamic Leaching Method (DLM); and (E) Radioiodine Partitioning.

### **A. Acceptance and Storage of SDU Cell 2A Saltstone Cores**

A set of saltstone core samples will be transferred to SREL for subsequent testing described in Sections C and D. Prior to transfer, the inventory of available cores will be evaluated to determine which samples are appropriate for testing, and to note any sectioning that may be required for core samples to conform to test specifications. Upon receipt at SREL, the saltstone cores from SDU Cell 2A will be stored under an inert environment (UHP N<sub>2</sub>, 99.999% purity) at high humidity until testing. SREL will conduct a gamma scan on the intact core samples to determine the total <sup>137</sup>Cs activity. In addition, the total <sup>99</sup>Tc and <sup>129</sup>I concentrations in the SDU Cell 2A samples will be determined as needed using an appropriate digestion protocol. The total <sup>99</sup>Tc concentration in the saltstone cores will be determined by liquid scintillation counting (LSC) following acid digestion according to EPA Method 3050B (USEPA 1992). To avoid iodine volatilization under acidic conditions, the total <sup>129</sup>I concentration in the saltstone core using an alkaline based extraction method recommended by Perkin Elmer (Perkin Elmer). This procedure has been demonstrated to be effective in extracting stable iodine from saltstone grouts and the dry feed materials (Seaman, 2015). The concentration of <sup>129</sup>I will be determined by ASTM D4785 (2013).

### **B. Saltstone Simulant Preparation and Curing**

A 1 to 2 kg batch of saltstone simulant spiked with <sup>99</sup>Tc will be created as part of this task. An additional batch of material spiked with Re will also be produced.

#### **Materials and Equipment**

1. Secure laboratory notebook dedicated to documenting all laboratory efforts associated with the preparation and curing of saltstone monoliths.
2. Deionized water, 18.2 MΩ cm at 25 °C (Milli-Q Element, Millipore, Inc., Billerica, MA 01821)
3. Laboratory balance, max. 5100 g, ± 0.01 g, calibration verified (PG5002 Delta Range)
4. Graduated cylinders
5. Dry powdered materials delivered from SRR
  - a. Class F fly ash (The SEFA Group, Inc. Lexington, SC 29073)
  - b. Grade 100/120 blast furnace slag (Lehigh Cement Company, Cape Canaveral, Florida 32920)
  - c. Type II Portland cement (Holcim US, Inc. Birmingham, AL 35221)
6. Concrete molds: standard 2" ID x 4" plastic concrete molds (Test Mark Industries, Inc.).
7. Humidity-controlled curing oven (Model 6105, Caron Products & Services, Inc.; 40 to 100 °C; RH 40 to 80%). Based on instructions from the manufacturer, set points were adjusted to expand the oven's factory set range, i.e., temperatures below 40 °C and RH values >95%.
8. Stir-Pak Laboratory Mixer, Model # 4554-10
9. ARP/MCU Salt Waste Simulant Solution (detailed instructions provided below).
10. 1 L and 0.5 L polycarbonate volumetric flasks.

**ARP/MCU Salt Waste Simulant Solution for making Saltstone (Standard Method for 1 kg dry feed batch; Table B1). Initial solutions will be prepared outside the Rad Laboratory one day in advance of grout processing.**

1. Record all pertinent details per preparation log (Table B2).
2. Weigh an empty 1 and 0.5 L polycarbonate volumetric flasks, plus caps.
3. Weigh all chemicals in Table B1 other than the NaOH soln. and combine in 1 L polycarbonate flask with about half of the total volume of DI water. Weigh out a second 0.5 L batch of saltwaste simulant. Stir.
4. Weigh and add the required NaOH as a 50% soln. to each flask.
5. Fill both flasks with DI water up to about 50 mL less than full volume.
6. Add magnetic stirring bar and cap the flask. Stir the solution overnight. Proceed with caution; the dissolution of simulant salt waste solution components is exothermic.

**Transfer solutions to the Rad Laboratory.**

7. Add contaminant spike solution (Tc and Re) as necessary just before making to final volume (Final  $^{99}\text{Tc}$  concentration in saltwaste simulant  $\approx 1.5 \times 10^4$  pCi mL $^{-1}$ ). Spike concentrations are consistent with the average levels found in Tank 50 saltwaste.
8. Remove the magnetic bar from the flask, and add DI water to make full volume. Put the magnetic bar back in and stir the solution. Remove the bar, and verify the final volume as 1 L. Repeat the process if necessary.
9. Weigh both flasks containing the solution plus the cap. The solution density should be  $\approx 1.2$ -1.3 g mL $^{-1}$ .
10. Calculate the solution density and the mass of water per unit mass of salt solution.

**Methods for Preparation of Simulant Saltstone (per 1 kg dry feed batch)**

**The dry materials shall be weighed and mixed outside the Rad Laboratory**

1. Record all pertinent details per cementitious paste preparation log (Table B3)
2. Weigh each of three dry powdered materials into 5QT disposable pails using plastic scoops.
  - a. Class F fly ash - 450 g (Mixing Pail 1)
  - b. Grade 100/120 blast furnace slag - 450 g (Mixing Pail 2)
  - c. Type II Portland cement - 450 g (Mixing Pail 3)
    - Caution: These materials are very fine powders. Wear proper PPE and a dust mask while handling these materials!
3. Slowly pour the weighed materials in Pails 2 and 3 into Pail 1 while in the hood. Mix them with a mechanical mixer at low rpm (30-50 rpm). While mixing, move the pail around the mixing arm to make sure the materials are thoroughly homogenized. Occasionally, stop the mixer, and scrape the bottoms and sides of the pail to homogenize any unmixed materials.

**Transfer dry materials to the hood inside the rad laboratory.**

4. The water to dry feeds ratio should be 0.6. Calculate the necessary salt solution mass for the dry feed materials.
5. Move Pail 1 and the mixer from the hood to a bench top. While slowly mixing the powders, add the salt solution in small increments.
6. Increase mixer speed to approximately 250 rpm. Stop the mixing occasionally, and check the mixture for powder agglomeration. Finish the mixing process within 20 min.
7. Pour the grout into the standing molds in one increment, and then cap immediately.

8. Survey the outside of each grout mold before transfer to the curing oven.
9. Transfer the capped saltstone molds into the humidity controlled curing oven and cure at a high degree of humidity (> 95 %) following the curing temperature profile provided in Table B4 (Figure B1). The temperature will be adjusted as necessary to conform to the curing profile.
10. Remove core monoliths from the curing oven as required for testing.
11. All cured samples (i.e., cores, core sections, etc.) will be stored under an inert atmosphere (i.e., N<sub>2</sub>) at ambient temperature and high humidity.

**Table B1. Base composition of ARP/MCU Saltwaste Simulant**

Material	ARP/MCU Salt Simulant	
	Molarity (moles/L)	Mass (g/L)
Sodium Hydroxide, NaOH (50 wt.% by weight)	1.594	127.50
Sodium Nitrate, NaNO <sub>3</sub>	3.159	268.48
Sodium Nitrite, NaNO <sub>2</sub>	0.368	25.39
Sodium Carbonate, Na <sub>2</sub> CO <sub>3</sub>	0.176	18.65
Sodium Sulfate, Na <sub>2</sub> SO <sub>4</sub>	0.059	8.37
Aluminum Nitrate, Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.054	20.33
Sodium Phosphate, Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	0.012	4.67

Table B2. Saltstone Waste Simulant and Permeant Preparation Log

<b>Logbook:</b>		<b>Requested by:</b>					
<b>Recipe ID:</b>		<b>Date:</b>					
<b>Sample # :</b>		<b>Task #:</b>					
<b>Order of Addition</b>	<b>Chemical</b>	<b>Assay</b>	<b>SREL #</b>	<b>Target Mass (g)</b>	<b>Actual Mass (g)</b>	<b>Balance ID</b>	<b>Date and Initials</b>
<b>Total Batch (g):</b>							
<b>Final Solution Density (g/mL):</b>							
<b>Reviewed by:</b>				<b>Date:</b>			

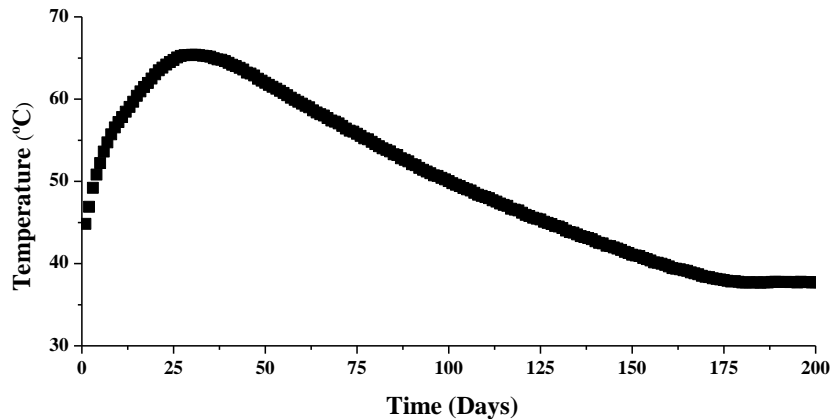
**Table B3. Saltstone Cementitious Paste Preparation Log**

<b>Recipe ID:</b>			<b>Date:</b>				
<b>Sample # :</b>			<b>Task #:</b>				
<b>Order of Addition</b>	<b>Chemical</b>	<b>Assay</b>	<b>SREL #</b>	<b>Target Mass (g)</b>	<b>Actual Mass (g)</b>	<b>Balance ID</b>	<b>Date and Initials</b>
<b>Total Mass (g)</b>							
<b>Reviewed by:</b>					<b>Date:</b>		
<b>Mixing Parameters</b>		<b>Comments</b>					
<b>Container:</b>							
<b>Mixing method:</b>							
<b>Start mixing time:</b>							
<b>End mixing time:</b>							
<b>Total mixing time:</b>							
<b>*Measured density:</b>							
<b>Reviewed by:</b>					<b>Date:</b>		
*Fresh grout density							



**Table B4. Grout curing temperature profile and data record for curing the <sup>99</sup>Tc-spiked saltstone simulant.**

Day	Avg. Temp.	Date	Humidity	Signature	Day	Avg. Temp.	Date	Humidity	Signature	Day	Avg. Temp.	Date	Humidity	Signature
1	44.8				31	65.4				61	59.2			
2	46.9				32	65.3				62	59.0			
3	49.2				33	65.3				63	58.6			
4	50.8				34	65.2				64	58.4			
5	52.2				35	65.2				65	58.2			
6	53.6				36	65.0				66	58.0			
7	54.7				37	64.8				67	57.7			
8	55.7				38	64.8				68	57.4			
9	56.5				39	64.6				69	57.2			
10	57.2				40	64.4				70	57.0			
11	57.8				41	64.2				71	56.7			
12	58.5				42	64.0				72	56.4			
13	59.0				43	63.8				73	56.2			
14	59.7				44	63.6				74	56.0			
15	60.4				45	63.2				75	55.8			
16	60.9				46	63.1				76	55.5			
17	61.5				47	62.9				77	55.2			
18	61.9				48	62.5				78	55.1			
19	62.5				49	62.2				79	54.8			
20	63.0				50	62.0				80	54.5			
21	63.5				51	61.7				81	54.3			
22	63.8				52	61.5				82	54.0			
23	64.2				53	61.3				83	53.8			
24	64.5				54	61.0				84	53.6			
25	64.7				55	60.8				85	53.3			
26	65.1				56	60.5				86	53.2			
27	65.2				57	60.2				87	52.8			
28	65.3				58	59.9				88	52.6			
29	65.3				59	59.7				89	52.4			
30	65.4				60	59.4				90	52.1			

**Figure B1. Curing profile for Saltstone Disposal Unit (SDU) Cell 2B (10.5 ft height).**

### C. Semi-Dynamic Contaminant Leaching

#### EPA Method 1315: Mass Transfer Rates for Monolithic Samples (USEPA, 2013)

A brief summary of the procedure as it applies to the testing of saltstone samples is provided. In the current application,  $^{99}\text{Tc}$ -spiked saltstone simulants and saltstone sample cores from SDU Cell 2A will be tested according to the three-dimensional geometry for estimating contaminant release under diffusion controlled release conditions; tests will initially be conducted under an oxic (ambient air) environment and a determination made regarding the need to test under anoxic, and/or reducing atmospheres. An artificial groundwater (AGW; see Tables C2 and C3 below for composition) surrogate based on routine sampling of non-impacted water table wells on the Savannah River Site (SRS) will be used as the test solution (Strom and Kaback, 1992). The volume of eluent used in each leaching interval will conform to a specific liquid-to-surface area ratio (L/A) of  $9 \pm 1 \text{ mL cm}^{-2}$ .

#### Materials and Equipment

1. Secure laboratory notebook in which the leaching core data will be documented using the standard data table provided in Table B1.
2. Atmosphere controlled equilibration chamber.
3. Deionized water, 18.2 MΩ cm at 25 °C (Milli-Q Element, Millipore, Inc., Billerica, MA 01821)
4. Four-place analytical balance, calibration verified,  $\pm 0.1 \text{ mg}$  (AT261 Delta Range, Mettler Toledo, Inc., Columbus, OH 43240)
5. Oxidation reduction potential (ORP)/pH meter and the required electrode, calibrated per manufacturer's instructions.
6. Electrical conductivity meter and electrode, calibrated per manufacturer's instructions (Radiometer, Inc.)
7. Laboratory pipettes, calibration verified (Gilson, Inc., Middleton, WI 53562)
8. Leaching Vessels
9. Scintillation vessels and cocktail.

**Method**

1. The semi-dynamic leaching test will be conducted at room temperature (i.e.,  $20 \pm 2$  °C). Record leaching data in the appropriate data sheet, see Table C1.
2. After curing the spiked specimen will be removed from the curing molds and tested intact.
3. Carefully suspend the specimen in the leaching vessel, and then fill the container with the correct amount of eluent equilibrated with the test atmosphere.

**Table C4 provides the equilibration time intervals after which the eluents will be removed for chemical analysis.**

4. At the end of a given leaching interval, carefully remove the specimen and allow any excess liquid to drain back into the leaching container. Record the weight of the core specimen and the total volume of eluent collected.
5. Determine the pH, conductivity, and ORP of the eluent within 15 min of exchange, and record the values in the appropriate data table.
6. Analyze  $^{99}\text{Tc}$  (and Re) present in the eluent by liquid scintillation counting (LSC) according to ASTM Method D7168. The TEVA DISC METHOD (Eichrom Technologies, LLC) for separating  $^{99}\text{Tc}$  from the eluent solution will be evaluated as a means of increasing the LSC detection limit and removing analytical interferences that may arise from other radionuclides present in the SDU saltstone cores.
7. Nitrate leaching for the gouts will be monitored using the chromotropic acid test method, *APHA Method-4500-Nitrogen, Standard Methods for the Examination of Water and Wastewater* (APHA, 1997).

**Data Analysis outlined in EPA Method 1315**

The monolith leaching data for the  $^{99}\text{Tc}$  (and Re) spiked saltstone simulant and the SDU Cell 2A saltstone cores will be analyzed as dictated in EPA Method 1315 to determine the cumulative mass release as a function of leaching time and observed diffusivity for  $^{99}\text{Tc}$  as impacted by the test atmosphere following curing or sample collection for the SDU cores.

**Table C1. Data sheet for recording monolith leaching data.**

		<b>EPA METHOD 1315</b>			
		<b>Report of Analysis</b>			
<b>SREL</b>					<b>Client: SRR</b>
	Material Code:			Particle Size:	
	Material Type:			Mass used in Column:	
	Date Recieved:			Moisture Content:	
	Test Start Date:			Sample Geometry:	
	Report Date:			Sample Diameter:	
				Sample Depth:	
	Test Type:			Mass of Sample & Holder:	
	Eluent:			Lab Temperature:	
<b>Test Interval</b>	<b>Replicate</b>	<b>Value</b>	<b>Units</b>		<b>Notes</b>
<b>T01</b>	<b>A</b>				
	Eluate Sample ID				
	Exchange Date				
	Target Exchange Time				
	Actual Exchange Time				
	Mass of Sample & Holder		g		
	Eluate Mass		g		
	Eluate pH				
	Eluate Conductivity		mS/cm		
	Eluate ORP		mV		
<b>Test Interval</b>	<b>Replicate</b>	<b>Value</b>	<b>Units</b>		<b>Notes</b>
<b>T02</b>	<b>A</b>				
	Eluate Sample ID				
	Exchange Date				
	Target Exchange Time				
	Actual Exchange Time				
	Mass of Sample & Holder		g		
	Eluate Mass		g		
	Eluate pH				
	Eluate Conductivity		mS/cm		
	Eluate ORP		mV		

**Table C2. Artificial Groundwater Simulant (AGW).**

Constituent/Parameter	AGW <sup>a</sup>
pH	5.0
	(mg L <sup>-1</sup> )
Na	1.39
K	0.21
Ca	1.00
Mg	0.66
Cl	5.51
SO <sub>4</sub>	0.73

<sup>a</sup>Artificial Groundwater: non-impacted groundwater derived from natural infiltration (Strom and Kaback, 1992)

**Table C3. Artificial Groundwater stock solution.**

Salt	g/L
CaCl <sub>2</sub> *2H <sub>2</sub> O (148 g/mol)	3.68
Na <sub>2</sub> SO <sub>4</sub> (142 g/mol)	1.07
KCl	0.40
NaCl (58.4 g/mol)	2.65
MgCl <sub>2</sub> *6H <sub>2</sub> O (203 g/mol)	5.51

Combine salts in 1L volumetric and bring to volume.

**Table C4. Schedule for fresh leachate renewals.**

Interval Label	Interval Duration (h)	Interval Duration (d)	Cumulative Leaching Time (d)
T01	2.0 ± 0.25		0.08
T02	23.0 ± 0.5		1
T03	23.0 ± 0.5		2
T04		5.0 ± 0.1	7
T05		7.0 ± 0.1	14
T06		14.0 ± 0.1	28
T07		14.0 ± 0.1	42
T08		7.0 ± 0.1	49
T09		14.0 ± 0.1	63

The schedule may be extended for additional 14 day intervals based on the continued trends in contaminant release.

## D. Saturated Dynamic Leaching Method (DLM)

Evaluate  $^{99}\text{Tc}$  (and Re) release and the inherent reductive capacity of  $^{99}\text{Tc}$  (and Re ) spiked saltstone grout simulants and SDU core samples using dynamic leaching techniques to mimic the eventual ingress of water into saltstone and subsequent pore volume exchange. The dynamic leaching system will be modified to accommodate the simultaneous leaching of multiple saltstone samples.

**Approach:** Evaluate  $^{99}\text{Tc}$  (and Re) release and the inherent reductive capacity of saltstone grout using dynamic leaching techniques to mimic the eventual ingress of water into saltstone and subsequent pore volume exchange. For the cores extracted from SDU Cell 2A other radionuclides in the effluents, such as  $^{129}\text{I}$ , may also be evaluated. Two-in length cylindrical sections of saltstone monoliths cured for 90 days will be subjected to continuous leaching with an artificial groundwater (AGW; Tables C2 and C3) simulant. Test variables will include the oxygen content (with and without 8 ppm  $\text{O}_2$ ) of the AGW leachate, and possibly the addition of  $^{99}\text{Tc}$  to evaluate the ability to immobilize additional  $^{99}\text{Tc}$ .

The leaching duration will be adjusted based on the effluent chemistry trends (i.e., pH, contaminant release, etc.) and changes in the materials hydraulic conductivity. Inlet pressures will be restricted to those deemed appropriate for measuring the materials hydraulic conductivity using the flexible-wall permeameter method, ASTM D5084. Changes in the relative hydraulic conductivity of the saltstone test material during the course of leaching will be estimated using Darcy's equation based on the hydrostatic pressure at the column inlet and effluent flow rate.

### Materials and Equipment

1. Cured 2" diameter saltstone monoliths produced in section B.
2. Flexible-Wall Permeameter; Tri Flex 2 Permeability Test System: Tri-Flex 2 Master Control (ELE International, Inc. Loveland, CO 80539)
3. Flex-wall test cells for 2" and 3" diameter cores
4. Vacuum pump
5. Compressed lab-grade air
6. Bladder Accumulator
7. Ultra-High Purity (UHP)  $\text{N}_2$  (<1 ppmv  $\text{O}_2$ )
8. AGW leaching solution (recipe provided in Tables C2 and C3)
9. Plastic syringes and 0.45- $\mu\text{m}$  pore-size syringe filters
10. Trace metal grade  $\text{HNO}_3$  (15.7 M) for acid stabilizing leachate samples until analysis

### Methods

1. Saltstone core sections will be soaked overnight in the appropriate AGW solution (i.e., equilibrated with lab-grade air or  $\text{N}_2$ ) to facilitate initial saturation.
2. Samples will be transferred to a flexible-wall cell and further saturated as specified in ASTM D5084 with the appropriate AGW solution.
3. To establish leaching, hydraulic conductivity estimates from previous saltstone testing will be used to predict initial flow rates associated with a given hydraulic gradient. Once flow is established at a constant gradient, changes in effluent volume can be used as a means of determining any changes in hydraulic conductivity throughout leaching.

4. Effluent pH, oxidation reduction potential (ORP), dissolved oxygen (DO), and electrical conductivity will be monitored and compared to the values recorded for the influent.
5. Technetium-99 present in the effluent will be analyzed by liquid scintillation counting according to ASTM Method D7168. As noted above, the TEVA DISC METHOD (Eichrom Technologies, LLC) for separating  $^{99}\text{Tc}$  from the eluent solution will be evaluated as a means of increasing the LSC detection limit and removing analytical interferences that may arise from other radionuclides present in the SDU saltstone cores.
6. Cesium-137 in the effluent will be determined EPA Method 901.1 Gamma Emitting Radionuclides in Drinking Water (USEPA, 1980).
7. Effluent nitrate will be monitored using chromatographic acid test method, APHA Method-4500-Nitrogen, Standard Methods for the Examination of Water and Wastewater (APHA, 1997).
8. Iodine-129 will be determined by ASTM D4785 - 08(2013), Standard Test Method for Low-Level Analysis of Iodine Radioisotopes in Water.

### E. Radioiodine Partitioning

Radioiodine partitioning ( $^{129}\text{I}$ ) to an SDF soil will be evaluated in four cement leachates representing a range of pore-water chemistries relevant to saltstone disposal, from potential leachate resulting from a fresh batch of saltstone waste (i.e., initial, near field conditions) through weathering/aging to non-impacted SRS groundwater (i.e., far-field conditions). Additionally, the impact of these saltstone solutions on contaminant partitioning will be evaluated under oxidizing and reducing conditions, and in the presence of SDF soil and Saltstone Disposal Unit (SDU) concrete (base mat and wall) sorbents. Each solution, oxidation environment, and sorbent treatment combination, including no-sorbent controls, will be evaluated in triplicate.

### Materials and Equipment

1. Secure laboratory notebook dedicated to the current statement of work (SOW).
2. Deionized water, 18.2 M $\Omega$  cm at 25 °C (Milli-Q Element, Millipore, Inc., Billerica, MA 01821)
3. Four-place analytical balance, calibration verified,  $\pm 0.1$  mg (AT261 Delta Range, Mettler Toledo, Inc., Columbus, OH 43240)
4. Oxidation reduction potential (ORP)/pH meter, calibrated per manufacturer's instructions (PHM 95 Ion/pH meter; Radiometer, Inc.)
5. Laboratory pipettes, calibration verified (Gilson, Inc., Middleton, WI 53562).
6. Subsurface soil and SDU concrete materials collected from the SDF, air-dried, homogenized and passed through a 1.70 mm sieve.
7. SRS Artificial-Groundwater Leachate (AGW): Final composition and recipe provided in Tables C2 and C3, respectively.
8. Three Cement Leachate Solutions: Lime [ $\text{Ca}(\text{OH})_2$ ] Saturated Leachate; Calcite ( $\text{CaCO}_3$ ) Saturated Leachate; and Weathered Saltstone Solution
9. Forty-eight 10-mL Polycarbonate Oak Ridge Centrifuge Tubes
10. NIST Traceable  $^{129}\text{I}$  stock solution (Eckert & Ziegler, Eckert & Ziegler Analytics, Inc.). The spike concentration (14 pCi/mL) is consistent with the average levels of  $^{129}\text{I}$  found in Tank 50 saltwaste (Bannochie, 2012).
11. 0.1- $\mu\text{m}$  syringe filters (compatible with high pH solutions)
12. Anaerobic chamber (95%  $\text{N}_2$ ; 5%  $\text{H}_2$  atm) (Coy Laboratory Products, Grass Lake, MI 49240)
13. Laboratory centrifuge (Sorvall RC5R plus, Thermo Scientific Inc.)

**a) Ca(OH)<sub>2</sub>-Saturated Leaching Solution (Ca(OH)<sub>2</sub>):**

Background: Because CO<sub>2</sub> in air is very soluble in water at high pH and the resulting dissolved carbonate will precipitate as calcite in the Ca(OH)<sub>2</sub>-saturated solution, care will be taken to minimize contact of the solution with atmospheric air. Excess solid Ca(OH)<sub>2</sub> is undesirable because it will buffer the pH at a higher than expected value.

Procedure:

1. Deoxygenate ~1-L of DI water by boiling and then purge with N<sub>2</sub> gas for 30 min. After purging with N<sub>2</sub>, place water in a Teflon bottle (because this material has a low air diffusion coefficient).
2. Add a sufficient quantity of fresh Ca(OH)<sub>2</sub> (~1.26 g L<sup>-1</sup> @ 25°C) to the deoxygenated water to saturate the solution.
3. To minimize exposure to air, purge head space with N<sub>2</sub> and if necessary periodically skim off any precipitates that may form. The pH of the final solution will then be determined while purging with N<sub>2</sub>.

**b) Calcite-Saturated Leaching Solution (Calcite):**

Explanation: By preparing the solution at a slightly elevated temperature the possibility of calcite precipitation during the test at room temperature will be minimized. (Calcite undergoes retrograde solubility, i.e., it is *more* soluble at low temperatures.) There will be no need to minimize contact of this solution with the atmosphere. After the solution is prepared, the pH value and calcium and carbonate concentrations will be measured and compared to expected equilibrium values and concentrations [pH = 8.3, Ca<sup>2+</sup> = 20 mg/L, Total Inorganic Carbon (TIC) = 58 mg/L, PCO<sub>2</sub> = 0.0003 atm (fixed)].

Procedure:

- Put 1 L of DI water on a stir/heating plate and raise the temperature of the solution by 3 to 10 °C from ambient room temperature. As solution is being stirred with a stir bar, add 0.01 g of CaCO<sub>3</sub> to the heated DI water. Leave mixture on stir/heating plate for 24 hr. The calcite-saturated solution will be prepared by adding excess powdered calcite to deionized water and stirring or shaking the mixture for 24 hours. Pass through a 0.45-μm membrane.

**c) Weathered-Saltstone Solution (WSS):** Ground saltstone provided by SRNL

The weathered saltstone solution will be created by equilibrating ground saltstone with DI water for 24 hrs at a 1/10 (g/g) saltstone to water ratio. After equilibration, the solution will be vacuum filtered (0.45 μm) and the pH will be recorded.

**Methods for Measuring Contaminant Sorption under Oxidizing Conditions**

12. Record the empty “tube weight” to within 0.001 g of labeled 15-mL Centrifuge Tubes with cap (including no-sorbent controls) as identified in example data sheet, Table E1.
13. Add 3 ± 0.1-g of SDF soil (or concrete sample) to each tube. Weigh and record “tube + sorbent” weight to within ± 0.001 g.
14. Equilibrating solids to the aqueous phase (pre-equilibration): Add the appropriate non-spiked treatment solution to each Oak Ridge tube prior to the addition of the contaminant spike



solution. This pre-equilibration step will facilitate approximating steady state conditions for a given solution treatment.

- a. Add  $10 \pm 0.1$ -mL of appropriate treatment solution to each tube as defined in Table E1. Place tubes on the shaker overnight ( $\approx 16$  hrs). The next day, allow the suspensions to settle for 1 hr. Decant liquid,  $\approx 7$  to 9 mL. If solids do not readily separate from the liquid, centrifuge for 15 min at 6000 rpm. Pipette or siphon off the clear supernatant and discard the clear liquid. Error on the side of leaving liquid in tube rather than accidentally losing reactive fines during pre-equilibration. Record the remaining tube weight in Table E1, i.e., “tube + residual” solution. Determine the residual solution weight (i.e., [tube + residual solution wt] – [tube + sorbent wt] = residual solution wt).
  - b. Add sufficient treatment solution to each tube to bring the solution volume back up to 9 mL, including the no-sorbent controls.
15. Add contaminant spike solution to suspensions: Add 1 mL of the  $^{129}\text{I}$  spike solution ( $\approx 140$  pCi/mL) to each tube for a total volume of 10 mL. Also add this to the no-sorbent controls. Initial contaminant spike is  $\approx 14$  pCi/mL in tube.
  16. Equilibration: Leave samples on the orbital shaker to equilibrate for a minimum of 5 days.
  17. pH and Redox Conditions: Determine pH and redox potential (Eh) of the residual suspensions and record the data in Table E1.
  18. Phase Separation: At end of equilibrium period, centrifuge the samples for 15 minutes at 10,000 rpm. Pipette 6 to 8 mL of clear supernatant and pass liquid through a 0.1- $\mu\text{m}$  filter into a labeled storage container.
  19. Contaminant Analysis: Determine the residual  $^{129}\text{I}$  concentration by gamma spectroscopy according to ASTM D4785-08 (ASTM, 2013).
  20. Data Management. Enter data into an EXCEL spreadsheet. Calculated  $K_d$  values as suggested in ASTM D-4646, using the following equation:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m_{\text{sorbent}}}$$

where  $C_i$  and  $C_f$  are the initial and final aqueous concentrations of each contaminant after equilibration;  $V$  = volume of liquid in the final equilibrated suspension (mL); and  $m_{\text{sorbent}}$  is the soil or concrete mass (g).

### Methods for Measuring Contaminant Sorption under Reducing Conditions

1. Record empty “tube weight” to within 0.001g of labeled 15-mL Centrifuge Tubes with cap (including no-sorbent controls) as identified in example data Table E1.
2. Add  $3 \pm 0.10$ -g of soil (or concrete sample) to each tube. Weigh and record “tube + sorbent” weight to within  $\pm 0.001$  g.
3. Equilibrating solids with the aqueous phase (pre-equilibration): *Solid Phase Chemical Conditioning*: The soil material will be equilibrated with the appropriate treatment solutions prior to spiking with the “Contaminant” solution. In contrast to the oxidizing treatment, the pre-equilibration will be conducted in two steps, the first pre-equilibration (steps a – b) is designed to promote the macro-chemistry stabilization, while the second pre-equilibration (step c) is designed to bring the redox into steady state.

- a. Add  $10 \pm 0.1$ -mL of the appropriate  $N_{2(g)}$ -sparged treatment solution to each Oak Ridge Centrifuge Tube as identified in Table E1, including the no-sorbent controls. Equilibrate suspensions overnight.
  - b. The next day, allow the suspensions to settle for 1 hr. Decant liquid,  $\approx 7$  to 9 mL. If solids do not readily separate from the liquid, centrifuge for 15 min at 6000 rpm. Pipette or siphon off the clear supernatant and discard the clear liquid. Error on the side of leaving liquid in tube rather than accidentally losing reactive fines during pre-equilibration. Record the remaining tube weight in Table E1, i.e., “tube + residual” solution. Determine the residual solution weight (i.e., [tube + residual solution wt] – [tube + sorbent wt] = residual solution wt).
  - c. Add sufficient  $N_{2(g)}$ -sparged treatment solution to each centrifuge tube to make the volume back up to 9 mL and then transfer the samples to the anaerobic chamber, including the no-sorbent, reducing controls. Open the centrifuge tubes inside the anaerobic chamber (95%  $N_2$ ; 5%  $H_2$ ) and allow suspensions to equilibrate for 16 hrs before spiking.
4. Add contaminant spike solution to suspensions: Add 1 mL of the  $^{129}I$  spike solution ( $\approx 140$  pCi/mL) to each tube for a total volume of 10 mL. Also add this to the no-sorbent controls. Initial contaminant spike is  $\approx 14$  pCi/mL in tube.
  5. Equilibration: Seal the tubes and agitate the samples on an orbital shaker in the anaerobic chamber for a minimum of 5 days.
  6. pH and Redox Conditions: Determine pH and redox potential (Eh) of the residual suspension while inside the anaerobic chamber and record in Table E1.
  7. Phase Separation: At end of equilibrium period, centrifuge the samples for 15 minutes at 10,000 rpm. Pipette 6 to 8 mL of clear supernatant and pass liquid through a 0.1- $\mu$ m filter into a labeled storage container.
  8. Contaminant Analysis: Determine the residual  $^{129}I$  concentration by gamma spectroscopy according to ASTM D4785-08 (ASTM, 2013).
  9. Contaminant Analysis: Determine the residual concentration of the contaminants of interest by ICP-MS according to standard protocols outlined in EPA Method 6020A.
  10. Data Management: Enter data into an EXCEL spreadsheet. Calculated  $K_d$  values as suggested in ASTM D-4646, using the following equation:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m_{sorbent}}$$

where  $C_i$  and  $C_f$  are the initial and final aqueous concentrations of each contaminant after equilibration);  $V$  = volume of liquid in the final equilibrated suspension (mL); and  $m_{sorbent}$  is the soil or concrete mass (g).

Table E1. Example data sheet for Task 1 Kd measurements in four different leachate solutions under oxidizing and reducing conditions.												
Oxidizing Treatment Matrix												
1	2	3	4	5	6	7	8	9	10	11	12	13
Tube No.	Treatment Solution	Rep. No.	Tube Weight (g)	Tube Weight + Soil (g)	Soil Weight (g)	Tube + Res. Sol. (g)	Res. Sol. (g)	Vol. Sol. Added (mL)	Vol. Spike Added (mL)	Vol. Base Added (mL)	Final pH	Final Eh
101	AGW	1										
102	AGW	2										
103	AGW	3										
No-Soil Control												
104	AGW	1		NA								
105	AGW	2		NA								
106	AGW	3		NA								
111	Ca(OH)2	1										
112	Ca(OH)2	2										
113	Ca(OH)2	3										
No-Soil Control												
114	Ca(OH)2	1		NA								
115	Ca(OH)2	2		NA								
116	Ca(OH)2	3		NA								
121	Calcite	1										
122	Calcite	2										
123	Calcite	3										
No-Soil Control												
124	Calcite	1		NA								
125	Calcite	2		NA								
126	Calcite	3		NA								
131	WSS	1										
132	WSS	2										
133	WSS	3										
No-Soil Control												
134	WSS	1		NA								
135	WSS	2		NA								
136	WSS	3		NA								
NA = Not Applicable												

**Safety, Hazards Assessment Package (HAP):**

The SREL Project Safety Appraisal for the current project is available in Lab 210.

**Hazards:**

1. Strong acid
2. Strong base

**Hazards Mitigation:**

1. Strong Acid: wear appropriate gloves and protective eye-ware
2. Strong Base: wear appropriate gloves and protective eye-ware

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