

## **Contaminant Leaching from Saltstone Simulants: Summary of EPA 1315 and Dynamic Leaching Method Results for FY2019**

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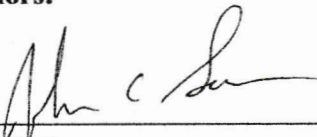
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## 1.0 Executive Summary

At the Department of Energy's Savannah River Site (SRS) chemically reducing materials, such as blast furnace slag (BFS), are added to grout formulations containing ordinary portland cement (OPC) and fly ash (FA) and combined with low-level radioactive salt waste solutions in order to enhance the attenuation of redox sensitive contaminants (e.g., technetium-99 ( $^{99}\text{Tc}$ )). The resulting cementitious material, known as *saltstone*, is deposited in a series of concrete vaults for long-term disposal at the Saltstone Disposal Facility (SDF). Once in place, saltstone provides both a physical (i.e., low saturated hydraulic conductivities ( $K_{\text{sat}}$ ) that limit  $\text{H}_2\text{O}$  turnover and  $\text{O}_2$  exposure) and a chemical barrier (i.e., residual reductive capacity) to contaminant release. The current objective was to evaluate contaminant partitioning and retention using intact saltstone materials that better mimic conditions within the disposal vaults, including testing the efficacy of cement-free grout formulations as an alternative to the current saltstone recipe. For the purposes of this report, L45:45:10 will represent the current premix containing 45 weight percent (wt%) Grade 120 BFS, 45 wt% Class F FA, and 10 wt% OPC, while L60:40 represents the recommended cement-free formulation consisting of 60 wt% BFS and 40 wt% FA (SRR-CWDA-2019-00003). In both cases L stands for the Lehigh BFS that is in current use at the SDF.

The current report focuses on a series of ongoing leaching studies evaluating the immobilization of both  $^{99}\text{Tc}$  and  $^{129}\text{I}$ , the major risk drivers controlling long-term saltstone disposition, in various saltstone formulations. Spiked saltstone simulants were produced utilizing SRR prescribed formulations, including the newly proposed 60:40 cement-free saltstone formulation. For the current tests the surrogate saltwaste composition was modified somewhat to account for recent changes in Tank 50 waste. The spiked simulants were subjected to curing for a minimum of six months under controlled humidity and elevated temperatures that mimic the curing environment within an SDU vault. Non-spiked saltstone samples were also created using the same formulations.

After curing for approximately nine months, several L60:40 and L45:45:10 monoliths were removed from the curing oven for testing. Contaminant mass transfer rates for the spiked saltstone simulants were assessed using EPA Method 1315, *Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure*. Results from Method 1315 were also compared to a novel test method developed at the Savannah River Ecology Laboratory (SREL) known as the Dynamic Leaching Method (DLM). In the DLM method a flexible-wall permeameter cell is used to achieve saturated leaching through intact grout monoliths under an elevated hydraulic gradient in an effort to evaluate the persistence of reductive capacity and subsequent changes in contaminant partitioning that occur within intact saltstone monoliths.

For the EPA 1315 tests  $^{129}\text{I}$  and  $^{99}\text{Tc}$  leaching rates for the spiked saltstone monoliths, including the cement-free materials, were generally consistent with previous tests involving both SDF-SDU Cell 2A samples and previous spiked simulants. The LI values were 10.5 and 8.5 for  $^{99}\text{Tc}$  and  $^{129}\text{I}$ , respectively, for the cement free saltstone (i.e., L60:40), generally on the higher end of values reported for these radionuclides in saltstone. Iodine-129 was retained slightly more than  $\text{NO}_3^-$  in both the conventional saltstone (L45:45:10) and the cement-free formulation (i.e., L60:40), as indicated by high effective diffusivities ( $D_e$ ) and low leachability indices (i.e.,  $LI = -\log[D_e]$ ). However,  $^{129}\text{I}$  was

retained to a much lesser degree than observed for  $^{137}\text{Cs}$  and  $^{99}\text{Tc}$  in both spiked simulants and the SDF-SDU Cell 2A samples. Iodine-129 and  $^{99}\text{Tc}$  leaching behavior was also consistent with previous reported values for Cast Stone grout, a very similar cementitious material being investigated for the disposal of salt waste materials at the Hanford facility.

For DLM testing, the current data set reflects leaching experiments using just the spiked L45:45:10 and L60:40 formulations. Two samples of each formulation were dedicated to DLM testing, with initial leaching starting in May/June 2019. The discussion of DLM results is limited to initial trends observed within the first pore volume of leaching. As observed in previous DLM tests,  $^{129}\text{I}$  leaching from both saltstone formulations was quite similar, with high effluent recoveries that are similar to that observed for  $\text{NO}_3^-$ , with a significant fraction ( $>50\%$ ) of  $^{129}\text{I}$  being leached within the first pore volume. In contrast, very limited  $^{99}\text{Tc}$  leaching ( $\approx 1$  to  $2\%$ ) was observed in the first pore volume. Effluent pH values for all saltstone DLM tests were initially quite high and remained above pH 12.5. The oxidation reduction potential (ORP) values were generally between  $-60$  and  $-100$  mV and appear to be increasing slowly with continued leaching. However, the ORP values were higher than expected given that effluent  $^{99}\text{Tc}$  levels are generally consistent with the solubility for possible Tc(IV) solid phases, i.e.,  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ .

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### ***List of Acronyms and Abbreviations***

AGW	Artificial Groundwater
ANS	American Nuclear Society
ANSI	American National Standards Institute, Inc.
APHA	American Public Health Association
ARP/MCU	Actinide Removal Process/Modular Caustic Side Solvent Extraction Unit
ASTM	American Society for Testing and Materials
BFS	Blast Furnace Slag
DIW	Deionized Water
DLM	Dynamic Leaching Method
DOE	Department of Energy
EPA	Environmental Protection Agency
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
K <sub>sat</sub>	Saturated Hydraulic Conductivity
LI	Leachability Index
OPC	Ordinary Portland Cement
ORP	Oxidation Reduction Potential
PA	Performance Assessment
psi	per square inch
QA	Quality Assurance
QC	Quality Control
SD	Standard Deviation
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SHC	Saturated Hydraulic Conductivity
SREL	Savannah River Ecology Laboratory
SRR	Savannah River Remediation LLC
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
UHP	Ultra-High Purity
USEPA	United States Environmental Protection Agency
w/cm	Water-to-Cementitious Material Ratio

## 2.0 Introduction

Reactivity and saturated hydraulic conductivity (SHC;  $K_{\text{sat}}$ ) are important factors controlling the rate of weathering and stability of cementitious materials used for the long-term disposal of low-level radioactive wastes. At the Savannah River Site (SRS) chemically reducing materials, such as blast furnace slag (BFS), are added to saltstone grout formulations mixed with low-level radioactive salt waste materials in order to enhance the attenuation of redox sensitive contaminants, e.g., technetium ( $^{99}\text{Tc}$ ). However, several studies have demonstrated both the difficulty in reducing pertechnetate ( $\text{TcO}_4^-$ ; i.e.,  $\text{Tc(VII)}$ ), the oxidized form of Tc, and the rapid oxidation of reduced Tc (i.e.,  $\text{Tc(IV)}$ ) when exposed to even moderate levels of  $\text{O}_2$  (Cantrell and Williams, 2013; Kaplan et al., 2011; Kaplan et al., 2008; Almond et al., 2012; Lukens et al., 2005; Ochs et al., 2016). Therefore, the persistence of chemically reducing conditions within the grout is an important factor driving long-term contaminant partitioning for the Saltstone Disposal Facility (SDF). The residual reductive capacity of saltstone materials is a function of the grout formulation (i.e., the type and amount of reductive components like BFS), curing conditions, and the degree to which subsequent exposure to dissolved  $\text{O}_2$  is restricted, an obvious function of the material's SHC.

The United States Environmental Protection Agency (USEPA; EPA for short) Method 1315, *Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure* (USEPA 2013), was developed for evaluating the leaching potential of contaminants found in cementitious materials (Garraabrants et al., 2014; Kosson et al., 2014; Serne et al., 2015). EPA Method 1315 is similar to American National Standards Institute, Inc./American Nuclear Society Method 16.1 (ANSI/ANS16.1), *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure* (ANS 2003), with the leaching intervals modified to accommodate a more complex interpretation of contaminant release mechanisms. However, both methods are seen as vast improvements over previous tests using size-reduced materials that focus on equilibrium partitioning rather than the rate of contaminant release under physically realistic conditions.

The physical structure of the saltstone material combined with maintaining a high degree of saturation serves as a barrier against exposure to  $\text{O}_2$ . Grinding saltstone for sorption/desorption tests, and even removal from high humidity environments, may facilitate contaminant oxidation and the consumption of saltstone's inherent reductive capacity. The current report focuses on documenting saltstone simulant samples that were created for current and future testing, as well as results from ongoing tests concerning both  $^{99}\text{Tc}$  and  $^{129}\text{I}$ , the major risk drivers controlling long-term saltstone disposition. Current tests focused on evaluating the impact of changes in source materials (i.e., Holcim vs Lehigh BFS), dry feed formulations (conventional and cement free grouts), and even salt waste composition on contaminant retention properties of saltstone.



### 3.0 Materials and Methods

#### 3.1 $^{99}\text{Tc}/^{129}\text{I}$ Spiked Saltstone Formulations for EPA 1315 and DLM Testing

A series of spiked and non-spiked saltstone simulants were created in FY2018 for testing in FY2019 (Table 1). The relative concentrations of  $^{99}\text{Tc}$  and/or  $^{129}\text{I}$  in the salt waste simulants (i.e.,  $\approx 2 \times 10^4$  pCi mL $^{-1}$   $^{99}\text{Tc}$ ; 15 pCi mL $^{-1}$   $^{129}\text{I}$ ) were consistent with the average concentrations of  $^{99}\text{Tc}$  and  $^{129}\text{I}$  in the Tank 50 feed waste at the SDF (Bannochie, 2012, 2014). The test grout samples were created using the following dry-feed materials: (1) Type I/II Ordinary Portland Cement (Holcim US, Inc. Birmingham, AL 35221), (2) Class F fly ash (The SEFA Group, Inc. Lexington, SC 29073), and (3) Grade 120 blast furnace slag (Lehigh). Two dry feed formulations were tested, L45:45:10 which represents the current premix containing 45 weight percent (wt%) Grade 120 BFS, 45 wt% Class F FA, and 10 wt% Type I/II OPC, while L60:40 represents the recommended cement-free formulation consisting of 60 wt% BFS and 40 wt% FA (SRR-CWDA-2019-00003). In both cases L stands for the Lehigh BFS that is in current use at the SDF.

**Table 1. Inventory of spiked and non-spiked saltstone samples available for testing.**

Labels	BFS Type	Material %			Spike Level	Salt Waste
Synthesized 6-14-18						
L45:45:10	Lehigh	45	45	10	Control	New SWPF
L60:40	Lehigh	60	40		Control	New SWPF
L45:45:10TcI	Lehigh	45	45	10	<sup>99</sup> Tc 19,000 pCi mL <sup>-1</sup> ; <sup>129</sup> I 15 pCi mL <sup>-1</sup>	New SWPF
L60:40TcI	Lehigh	60	40		<sup>99</sup> Tc 19,000 pCi mL <sup>-1</sup> ; <sup>129</sup> I 15 pCi mL <sup>-1</sup>	New SWPF

BFS: Blast Furnace Slag

FA: Fly Ash

OPC: Ordinary Portland Cement

**Figure 1. Photograph of the three dry feed materials used to make the FY18 saltstone formulations (L to R: Type I/II ordinary portland cement, Lehigh Grade 100/120 blast furnace slag, and SEFA Class F fly ash).**



Previously the Actinide Removal Process/Modular Caustic Side Solvent Extraction Unit (ARP/MCU) salt waste has been routinely used as a surrogate for the major element composition of Tank 50 waste (Table 2). For the most recent testing, a modified solution was developed (New SWPF) to reflect more recent changes in the general composition of Tank 50 waste. To create a given salt waste surrogate, all of the chemicals in Table 2, except for the NaOH solution, were combined with  $\approx 0.6$  L of deionized water (DIW) in multiple 1-L volumetric polycarbonate flasks depending on the total mass of saltstone being created. The NaOH was then added as a 50 wt% solution. When required, the contaminant spike solution was added to the salt waste flasks just before bringing the solution to its final volume.

**Table 2. Composition of various salt waste simulant solutions.**

<b>Material</b>	<b>ARP-MCU<sup>a</sup> (moles/L)</b>	<b>New SWPF<sup>b</sup> (moles/L)</b>
<b>Sodium Hydroxide, 50 wt% NaOH</b>	1.594 (1.378)*	2.391 (1.823)*
<b>Sodium Nitrate, NaNO<sub>3</sub></b>	3.159	1.475
<b>Sodium Nitrite, NaNO<sub>2</sub></b>	0.368	0.583
<b>Sodium Carbonate, Na<sub>2</sub>CO<sub>3</sub></b>	0.176	0.262
<b>Sodium Sulfate, Na<sub>2</sub>SO<sub>4</sub></b>	0.059	0.055
<b>Aluminum Nitrate, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O</b>	0.054	0.142
<b>Sodium Phosphate, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O</b>	0.012	0.004

\*Free OH molarity based on Aluminum content of salt waste mixture. The simulant salt solutions were chemically designed to represent the average salt solution present in Tank 50:

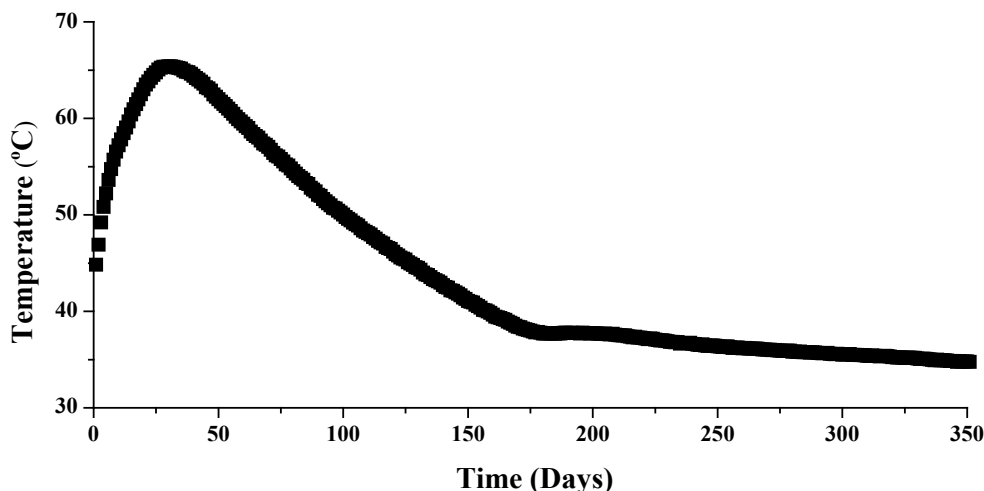
a) After being treated via the Actinide Removal Process (ARP) and Modular Caustic side solvent extraction Unit (MCU)

b) After undergoing treatment at the Salt Waste Processing Facility (SWPF)

The required masses of the dry feed materials were weighed and mixed together in a single bucket. After thorough homogenization of the combined dry powders, the salt waste simulant solution was slowly added to the dry materials while mixing at 250 rpm for 20 minutes. The final water to cementitious material ratio (w/cm) used for the current formulations was 0.6. After mixing, the saltstone slurries were poured into several 2" ID x 4" L plastic concrete molds and sealed with plastic lids for

curing (Test Mark Industries, Inc.). The plastic concrete molds were then placed in a humidity-controlled curing oven (Model 6105, Caron Products & Services, Inc.) and heated according to the curing profile from SDU Cell 2B (Figure 2) (Simner, 2016). The FY2018 samples were cured for approximately 9 months prior to testing.

**Figure 2. Curing profile for Saltstone Disposal Unit (SDU) Cell 2B (10.5 ft height) (Simner, 2016).**



### ***3.2 Saltstone Reductive Capacity***

The reductive capacity of the dry feed materials and the cured saltstone was estimated using the Ce(IV) method by Angus and Glasser (1985), as modified by Roberts and Kaplan (2009). This method requires sample dissolution, so reaction time is an important factor. Approximately 0.5 gm of ground saltstone (or saltstone constituent materials) was weighed into a series of labeled centrifuge tubes and then extracted for four hours using 25 mL of 0.0608 M Ce(IV) solution (10% sulfuric acid) solution. After extraction, the 0.100 mL of phenanthroline indicator solution, also known as the Ferrion indicator, was added to the supernatants to develop a greenish color. The solutions were then titrated with 0.050 M  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$  (ammonium iron sulfate hexahydrate) until the equivalence point was reached based on oxidation reduction potential (ORP) values. The titration was calibrated using aliquots of the Ce(IV) solution that had not been exposed to the saltstone materials. The reducing equivalents per mass of solid sample (eq/gm) were determined from the difference between the total oxidizing equivalents in the Ce(IV) solution and the number of reducing equivalents needed to neutralize the Ce(IV) solution after it reacted with a given sample, divided by the mass of the solid sample. The dry feed materials (i.e., OPC, BFS and FA) were analyzed as delivered. The cured grout materials (L45:45:10 and L60:40) were crushed and ground to fine powder using a mortar and pestle under an inert atmosphere, and then stored inside of the COY chamber to avoid oxidation prior to reductive capacity analysis.

### 3.3 Contaminant Mass Transfer: EPA Method 1315: Mass Transfer Rates for Monolithic Samples

EPA Method 1315 was used to evaluate the leaching of  $^{129}\text{I}$  and  $^{99}\text{Tc}$  from spiked saltstone samples. Sodium (Na) and nitrate ( $\text{NO}_3^-$ ) were also monitored for comparison in both the spiked and non-spiked samples. Prior to testing, the cured samples were removed from the curing oven and sectioned to conform to the EPA 1315 Method recommendations. An artificial groundwater (AGW; see Table 3) surrogate based on routine sampling of non-impacted water table wells on the SRS was used as the leaching solution (Strom and Kaback, 1992). The mass transfer tests were conducted at room temperature (i.e.,  $22 \pm 2$  °C) under ambient laboratory atmosphere. Previous studies detailed in Seaman (2015) demonstrated that  $^{99}\text{Tc}$  leaching from monolithic saltstone simulants was generally insensitive to the test atmosphere. The volume of eluent used in each leaching interval conformed to the liquid-to-surface area ratio (L/A) of  $9 \pm 1$  mL cm $^{-2}$ .

The pH and ORP of the leachant was recorded just prior to being replaced with fresh AGW solution according to the modified schedule provided in Table 4. Iodine-129 in the leachants was analyzed using low energy gamma analysis, while  $^{99}\text{Tc}$  was analyzed by liquid scintillation counting (LSC), with counting results verified by inductively coupled plasma-mass spectrometry (ICP-MS; NexION 300, Perkin Elmer Inc.) according to Lehto and Hou (2001). At the same time, the EPA 1315 test was also performed using control saltstone samples without  $^{129}\text{I}$  and  $^{99}\text{Tc}$  to provide non-radioactive samples for additional characterization. The leachant of both spiked and unspiked samples was analyzed for  $\text{NO}_3^-$  by the chromotropic acid test method, *APHA Method-4500-Nitrogen, Standard Methods for the Examination of Water and Wastewater* (APHA, 1997), and major cations (i.e., Na, K, Mg, and Ca) by ICP-MS according to EPA Method 6020B Rev. 2 (USEPA 2014).

**Table 3. Composition of the artificial groundwater (AGW) simulant.**

Constituent/Parameter	AGW <sup>a</sup>
pH	5.0
	(mg L $^{-1}$ )
Na	1.39
K	0.21
Ca	1.00
Mg	0.66
Cl	5.51
SO $_4$	0.73

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

**Table 4. Recommended schedule for fresh leachate renewals for EPA 1315, and actual sampling schedule used in testing the  $^{99}\text{Tc}/^{129}\text{I}$  spiked saltstone simulants, L45:45:10 and L60:40.**

Interval	Duration (h)	Duration (d)	Cumulative	Actual (d)**
			Leaching Time (d)*	
T01	$2.0 \pm 0.25$		0.08	0.11
T02	$23.0 \pm 0.5$		1	0.98
T03	$23.0 \pm 0.5$		2	1.91
T04		$5.0 \pm 0.1$	7	6.98
T05		$7.0 \pm 0.1$	14	14.0
T06		$14.0 \pm 0.1$	28	28.0
T07		$14.0 \pm 0.1$	42	42.0
T08		$7.0 \pm 0.1$	49	49.2
T09		$14.0 \pm 0.1$	63	63.0

\*Recommended versus \*\*actual cumulative leaching durations differ due to logistical limitations associated with collecting radioactive samples

### 3.3 EPA 1315 Leachate Data Analysis

The effective diffusivities,  $D_e$  ( $\text{cm}^2 \text{ s}^{-1}$ ), for  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ ,  $\text{Na}^+$  and  $\text{NO}_3^-$  were calculated using the simplified approach outlined in ANSI/ANS-16.1 (ANSI/ANS, 2003):

$$D_e = \pi \left[ \frac{a_n/A_0}{\Delta t_n} \right]^2 \left[ \frac{V}{S} \right]^2 T \quad [1]$$

where  $a_n$  is the quantity of contaminant released during interval  $n$ ,  $A_0$  is the total quantity of contaminant initially present in the sample being tested,  $\Delta t_n$  is the duration of the  $n^{\text{th}}$  interval,  $V$  is the volume of the sample ( $\text{cm}^3$ ),  $S$  is the surface area of the sample ( $\text{cm}^2$ ), and  $T$  is the generalized mean square root of the leaching time:

$$T = \left[ \frac{\sqrt{t_n} + \sqrt{t_{n-1}}}{2} \right]^2 \quad [2]$$

where  $t_n$  is the elapsed time at the end of the current sampling interval and  $t_{n-1}$  is the elapsed time at the end of the previous sampling interval. The approach outlined above using the incremental fraction of the contaminant leached during each interval provides an estimate of diffusivity for each sampling interval that is independent of the other sampling intervals, and not subject to any bias that may occur during early sampling times when surficial materials may be released. When greater than 20% of the initial contaminant inventory has been leached from the sample, as is often seen for  $\text{NO}_3^-$ , the release data

become non-linear with the square root of time due to depletion within the sample, and are not included in reported estimates of diffusivity (ANSI/ANS, 2003).

For comparison, the leachability index (LI), a unit-less parameter derived from the effective diffusion coefficient, i.e.,  $D_e$  ( $\text{cm}^2 \text{s}^{-1}$ ), was calculated as follows:

$$LI_n = -\log[D_e] \quad [3]$$

where  $LI_n$  is the leachability index for sampling interval  $n$  (Serne et al., 2015). The  $LI$  is then reported as the average for the set of  $LI_n$  values for a given test sample (ANSI/ANS, 2003). It is important to note that the “diffusional” release of retained contaminants from cementitious waste may reflect a combination of both chemical and physical transport processes, such as dissolution or desorption in response to changes in pore solution composition combined with diffusional transport. This complicates the mechanistic interpretation of leaching results.

### 3.4 Dynamic Leaching Method

The Dynamic Leaching Method (DLM) is based on ASTM D5084 for determining the SHC of cementitious materials using a flexible-wall permeameter to develop the necessary hydraulic gradient and ensure continuous internal flow. Darcy’s Law was used to characterize the initial leaching conditions:

$$q = \frac{Q}{A} = \frac{K\Delta H}{L} \quad [4]$$

where  $q$  is the flux density (i.e., volume flowing through a specific cross-sectional area),  $Q$  ( $\text{cm}^3 \text{sec}^{-1}$ ) is the discharge volume per unit time (i.e.,  $V/t$ ),  $A$  is the cross sectional area ( $\text{cm}^2$ ),  $K$  ( $\text{cm sec}^{-1}$ ) is the hydraulic conductivity,  $\Delta H$  is the hydraulic head difference between the column inlet and outlet (i.e.,  $\Delta H = H_i - H_o$ ; cm), and  $L$  is the length of the column (cm) (Hillel, 1980).

Given a two-inch diameter saltstone monolith (i.e., cross-sectional area of  $20.27 \text{ cm}^2$ ) with a core length of one inch ( $2.54 \text{ cm}$ ), and an assumed SHC of  $5 \times 10^{-9} \text{ cm sec}^{-1}$ , the pressure required to achieve a leaching rate of approximately 5 mL per day (i.e.,  $5.79 \times 10^{-5} \text{ cm}^3 \text{sec}^{-1}$ ) can be calculated as:

$$q = \frac{Q}{A} = \frac{5.79 \times 10^{-5} \text{ cm}^3 \text{s}^{-1}}{20.27 \text{ cm}^2} = 2.86 \times 10^{-6} \text{ cm s}^{-1} = \frac{K\Delta H}{L} \quad [5]$$

The equation is then solved for  $\Delta H$ , the required hydraulic gradient in cm.

$$\Delta H = \frac{qL}{K} = \frac{2.86 \times 10^{-6} \text{ cm s}^{-1} L}{K} = \frac{2.86 \times 10^{-6} \text{ cm s}^{-1} \times 2.54 \text{ cm}}{5 \times 10^{-9} \text{ cm s}^{-1}} = 1453 \text{ cm} \quad [6]$$

The hydraulic gradient is then converted to psi.

$$psi = \frac{1453cm}{70.38 cm psi^{-1}} = 20.61 psi \quad [7]$$

Changes in the relative SHC during the course of leaching can be estimated using Darcy's equation based on the set hydrostatic pressure at the column inlet and the observed effluent flow rate, regardless of sample porosity. However, the porosity of each sample was determined by the mass loss of water upon heating samples to 105 °C in a laboratory oven, with samples measured repeatedly until the mass change on consecutive days was < 5% (Westsik et al., 2013). This was used as an estimate of sample Pore Volume (PV) for comparing sample monoliths of differing dimensions.

Technetium-99 and  $^{129}I$  present in the DLM leachates from spiked saltstone simulants was analyzed by liquid scintillation counting (LSC) according to ASTM D7283-13, *Standard Test Method for Alpha and Beta Activity in Water by Liquid Scintillation* (ASTM, 2013), using a Beckman/Coulter LS6500.

## 4.0 Results

### 4.1 Reduction Capacity

The results of the reductive capacity measurements are summarized in Table 5. The results reflect the repeated analysis of at least three subsamples. As expected, the Lehigh BFS had the highest reductive capacity of the dry feed materials, i.e., 870 µeq/g, followed by the OPC and then the FA, consistent with previous reports (Seaman et al., 2014; Kmiec, 2015). The two saltstone samples that had cured over 14 months also displayed considerable residual reductive capacity, with the L45:45:10 sample having a marginally higher reductive capacity than the cement free L60:40 formulation, although the differences are not necessarily significant.

**Table 5. Reductive capacity titration for the three dry feed materials and cured saltstone grout formulations**

				µeq/gm	
				Average	SD
FY18 Lehigh BFS				870	71
FY18 OPC				173	10
FY18 SEFA Fly Ash				38.0	6.1
L45:45:10	Non-Spiked Sample Cured 14+ Months			640	14
L60:40	Non-Spiked Sample Cured 14+ Months			625	23

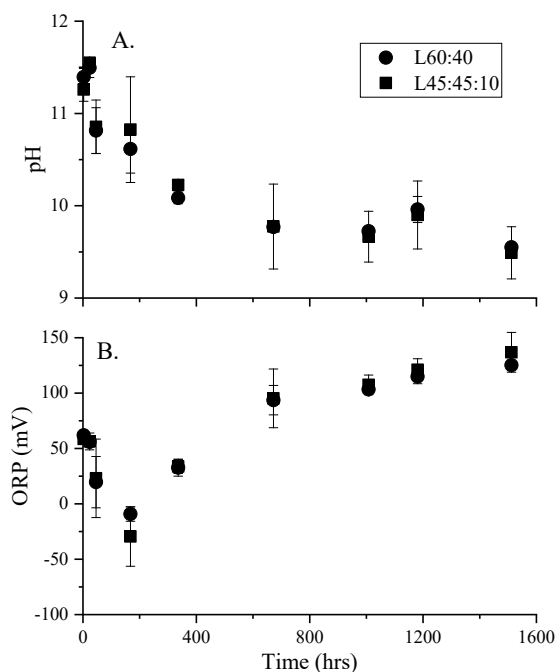
Angus and Glasser Method (1985)

The method of Angus and Glasser (1985) relies on sample dissolution for reductive components to be liberated and quantified. As is the usual case in testing this type of materials, full sample dissolution was not achieved, with residual solid materials present after the initial reaction.

## 4.2 EPA 1315 Results

A summary of the data for the EPA 1315 tests is included in Appendix A. The effluent pH and ORP values for EPA 1315 leachate from both tested dry feed formulations are presented in Figure 3. The initial pH for both formulations was about 11.5 and decreased throughout the course of leaching. ORP values initially decreased with the initial increase in leachate residence time, and then increased as testing progressed.

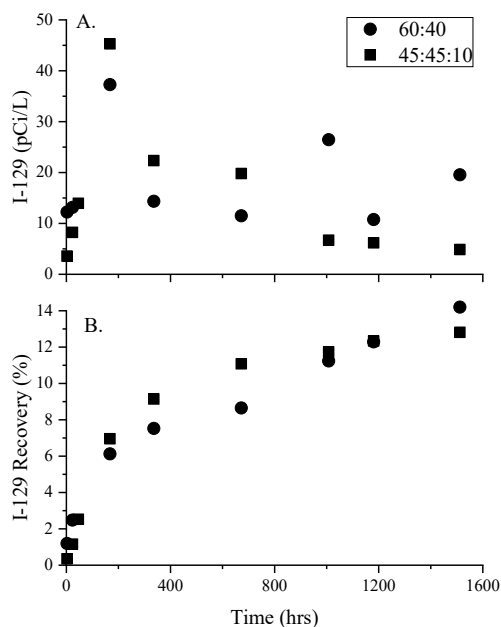
**Figure 3. Average EPA 1315 leachate pH (A) and ORP (B) results for spiked and non-spiked saltstone simulants (i.e., L60:40 and L45:45:10) made with the “New SWPF” salt waste simulant.**



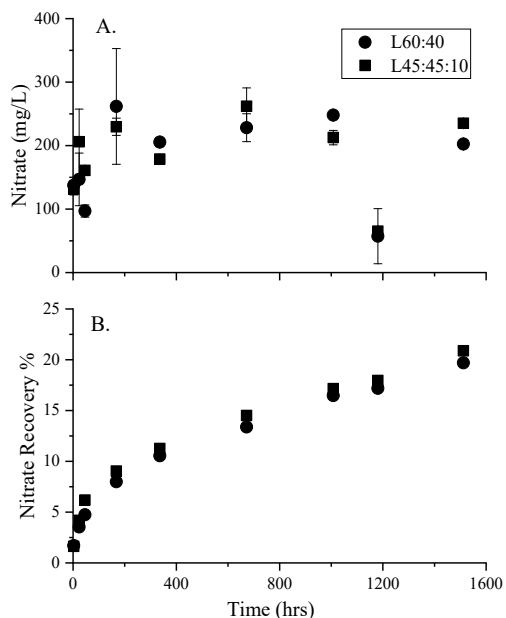
The relative levels of  $^{129}\text{I}$  and the cumulative  $^{129}\text{I}$  leaching fraction for both formulations are presented in Figure 4, with approximately 12.8% (L60:40) to 14.2% (L45:45:10) of the  $^{129}\text{I}$  leached from each monolith over the course of the test. The EPA 1315 results are generally consistent with the leaching patterns observed in prior tests using spiked materials and samples from SDU Cell 2A (Seaman et al., 2018; SREL R-18-0006). It is important to note that the  $^{129}\text{I}$  levels in the leachate are still quite low compared to the salt waste solution, i.e.,  $5 \times 10^{-3}$  to  $5 \times 10^{-2}$  pCi mL $^{-1}$ , compared to 14.3 pCi mL $^{-1}$  for Tank 50 waste from the third quarter of 2013 (Bannochie, 2014). Note that a  $^{129}\text{I}$  concentration of 15 pCi mL $^{-1}$  was used in spiked saltstone synthesis (Table 1).



**Figure 4. Leaching results for  $^{129}\text{I}$  from EPA Method 1315 spiked saltstone simulants (i.e., L60:40 and L45:45:10) made with the “New SWPF” salt waste simulant: (A) eluate concentration, (B) cumulative  $^{129}\text{I}$  leaching.**



**Figure 5. Leaching results for  $\text{NO}_3^-$  from EPA Method 1315 for both spiked and non-spiked saltstone simulants (i.e., L60:40 and L45:45:10) made with the “New SWPF” salt waste simulant: (A) eluate concentration, (B) cumulative  $\text{NO}_3^-$  leaching. Error bars reflect the standard deviation of the average for the spiked and non-spiked saltstone simulants.**

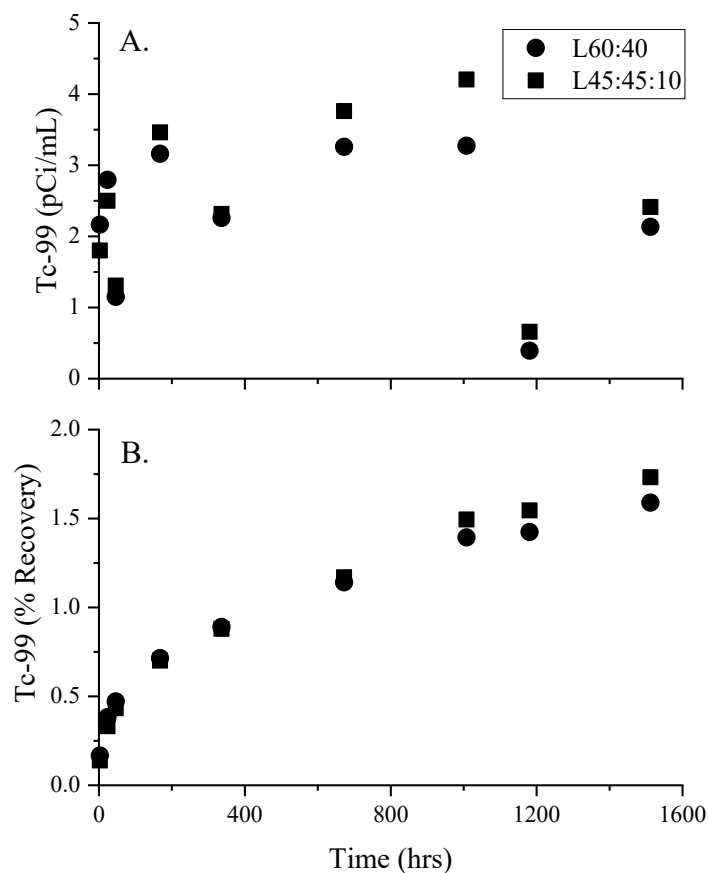


The average concentrations of  $\text{NO}_3^-$  in the EPA 1315 leachate from the spiked and non-spiked samples are presented in Figure 5A, with the cumulative leaching fraction for  $\text{NO}_3^-$  presented in Figure

5B. The relative  $\text{NO}_3^-$  levels and the cumulative fraction of  $\text{NO}_3^-$  leached are quite similar to the results for  $^{129}\text{I}$  for both formulations, with somewhat more  $\text{NO}_3^-$  leached for both materials.

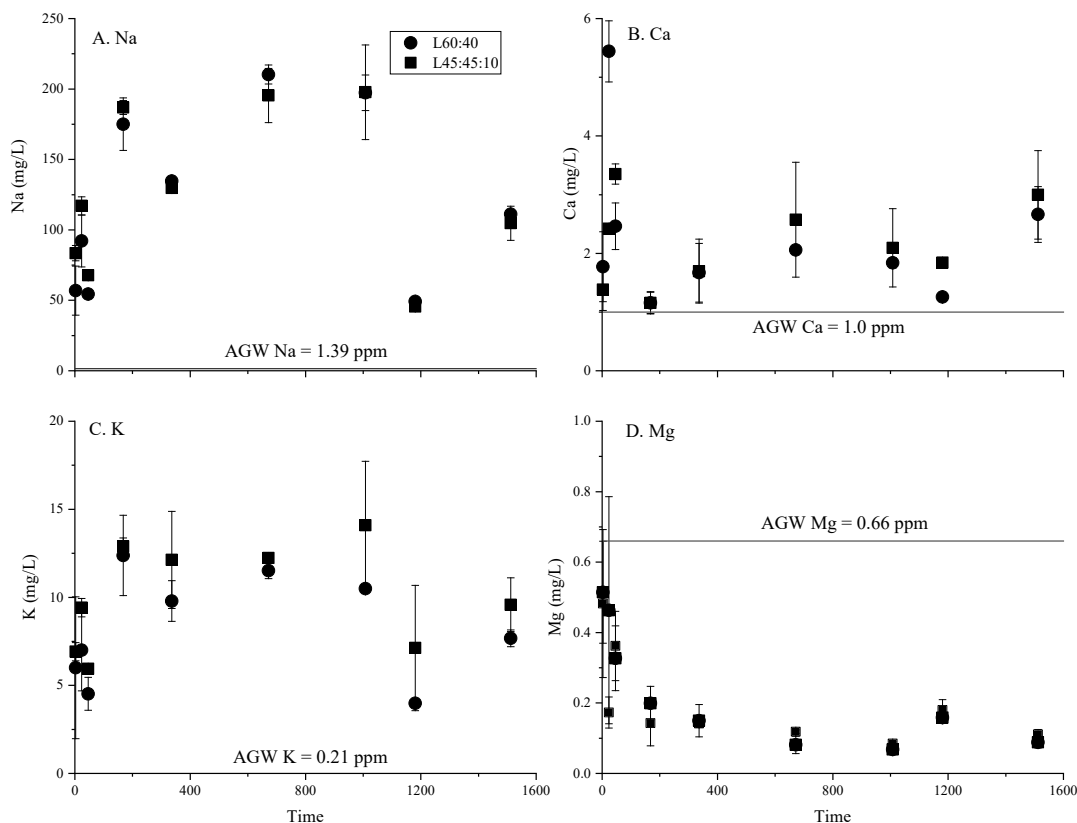
The concentrations of  $^{99}\text{Tc}$  in the EPA 1315 leachate from the spiked samples are presented in Figure 6A, with the cumulative leaching fraction for  $^{99}\text{Tc}$  presented in Figure 6B. In contrast to the results for  $^{129}\text{I}$  and  $\text{NO}_3^-$ , a very limited amount of  $^{99}\text{Tc}$  ( $< 2\%$ ) was leached over the course of the EPA 1315 test.

**Figure 6. Leaching results for  $^{99}\text{Tc}$  from EPA Method 1315 for spiked saltstone simulants (i.e., L60:40 and L45:45:10) made with the “New SWPF” salt waste simulant: (A) eluate concentration, (B) cumulative  $^{99}\text{Tc}$  leaching.**



The concentration of major cations in the EPA 1315 test solutions at the end of each equilibration period is provided in Figure 7. For comparison, the starting concentration in the AGW test solution is also noted in the Figure. The Na concentration (Figure 7A) in each leachate is much higher than the starting AGW solution due to the highly sodic nature of the saltwaste. This makes it possible to evaluate  $\text{Na}^+$  leaching in the same manner used for the radionuclides, i.e.,  $^{129}\text{I}$  and  $^{99}\text{Tc}$ . Significant amounts of  $\text{Ca}^{2+}$  (Fig. 7B) and  $\text{K}^+$  (Fig. 7C) were leached from the saltstone as well, while magnesium ( $\text{Mg}^{2+}$ ) (Fig. 7D) is the only major cation that appears to be taken up by the saltstone monoliths.

**Figure 7. Leaching results for Na (A), Ca (B), K (C), and Mg (D) from EPA Method 1315 for spiked and non-spiked saltstone simulants (i.e., L60:40 and L45:45:10) made with the “New SWPF” salt waste simulant. The concentration of each cation in the starting AGW background solution is provided for comparison.**



An updated summary of the data for all EPA 1315 leaching tests conducted by SREL is provided in Table 6 for comparison, with the current data set given in Appendix A. When greater than 20% of the initial inventory of a specific contaminant has been leached from the sample, the release generally no longer conforms to the diffusional model, and such data are not included in estimates of diffusivity or the leachability index, *LI*. This was only true for the last sampling interval for  $\text{NO}_3^-$  in the L45:45:10 formulation. At these later sampling intervals when the contaminant source within the monolith is depleted, the apparent diffusivity ( $D_e$ ) decreases, which results in anomalously high *LI* values. It is important to note that the diffusivities reported in Table 6 reflect the average of all incremental sampling intervals, and not the antilog of the *LI*.

In general, the EPA 1315 results for the cement-free saltstone formulation (i.e., L60:40) are consistent with previous tests, with *LI* values of 10.5 and 8.5 for  $^{99}\text{Tc}$  and  $^{129}\text{I}$ , respectively. In fact, the values are generally on the higher end for those reported by SREL for saltstone.

Westsik et al. (2013) reported effective diffusivities for sodium ( $\text{Na}^+$ ), and  $\text{NO}_3^-$  that are similar to the current data set, and indicative of poorly sorbed constituents. Mattigod et al. (2011) also reported very limited retention of iodine in Cast Stone, with initial diffusivities that ranged from  $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  to  $\sim 3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  after 90 days of curing ( $\text{LI} \approx 6.5$  to  $7.0$ ), generally lower than the values observed for iodine in SRS saltstone of various formulations. One might expect an increase in the LI value for  $^{99}\text{Tc}$  given the higher BFS content of the L60:40 formulation compared to L45:45:10. However, in the present case there was little difference in the two formulations and the difference was not evident in reduction capacity titrations for L60:40 and L45:45:10 (Table 5).

**Table 6. Summary of effective diffusivities ( $D_e$ ) and leachability indices (LI) derived from EPA 1315 (new data set highlighted in gray).**

						<sup>99</sup> Tc													

### 4.3 Dynamic Leaching Method

The current report seeks to provide a summary of DLM tests using the L60:40 and L45:45:10 materials that were spiked with both  $^{99}\text{Tc}$  and  $^{129}\text{I}$  (Table 1). The effluent pH and ORP values for the DLM samples are presented in Figure 8. In general, all pH values started off above 13 and dropped to  $\approx 12.5$  with continued leaching.

**Figure 8. Effluent pH (A) and ORP (B) for two L45:45:10 samples and two L60:40 samples.**

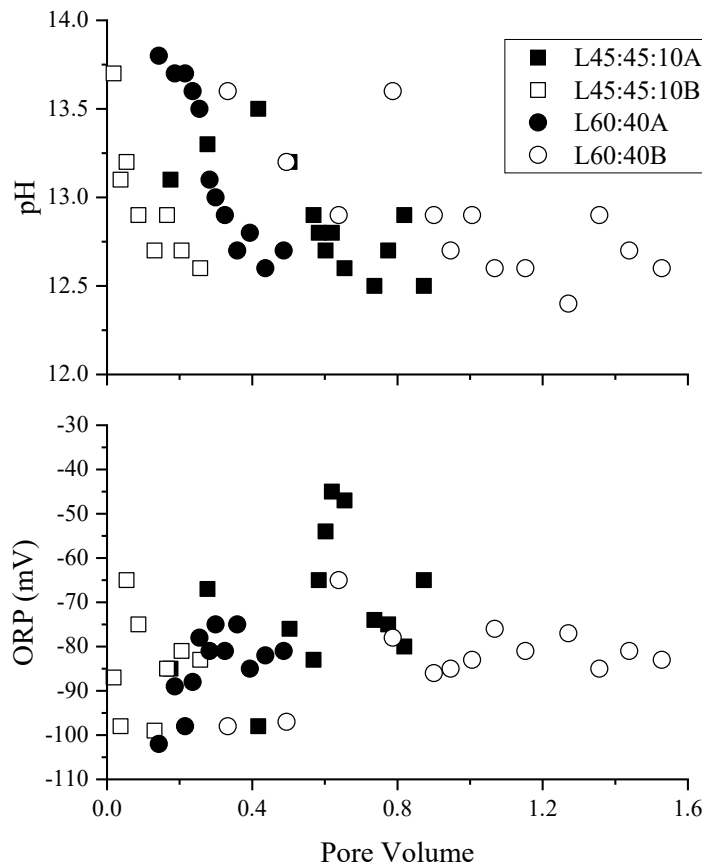


Figure 9 displays the effluent  $^{99}\text{Tc}$  concentration and the cumulative effluent  $^{99}\text{Tc}$  recovery (1 = 100%) for the spiked samples (L45:45:10 and L60:40). Given the limited leaching durations, it is difficult to draw definitive conclusions, especially when comparing the efficacy of the two formulations. However,  $^{99}\text{Tc}$  retention for the L60:40 formulation does appear to be similar to that observed for the previous DLM tests, with less than 3% having been leached to date. In addition, the relative levels  $^{99}\text{Tc}$  in the effluent are much lower than those observed for  $^{129}\text{I}$  (see Figure 11). Using a similar leaching system at much higher pressures, Dinwiddie and Pickett reported similar effluent  $^{99}\text{Tc}$  levels from an intact, spiked saltstone sample (Dinwiddie and Pickett, 2017).

**Figure 9. Effluent  $^{99}\text{Tc}$  (A) and cumulative  $^{99}\text{Tc}$  recovery (B) for two L45:45:10 samples and two L60:40 samples.**

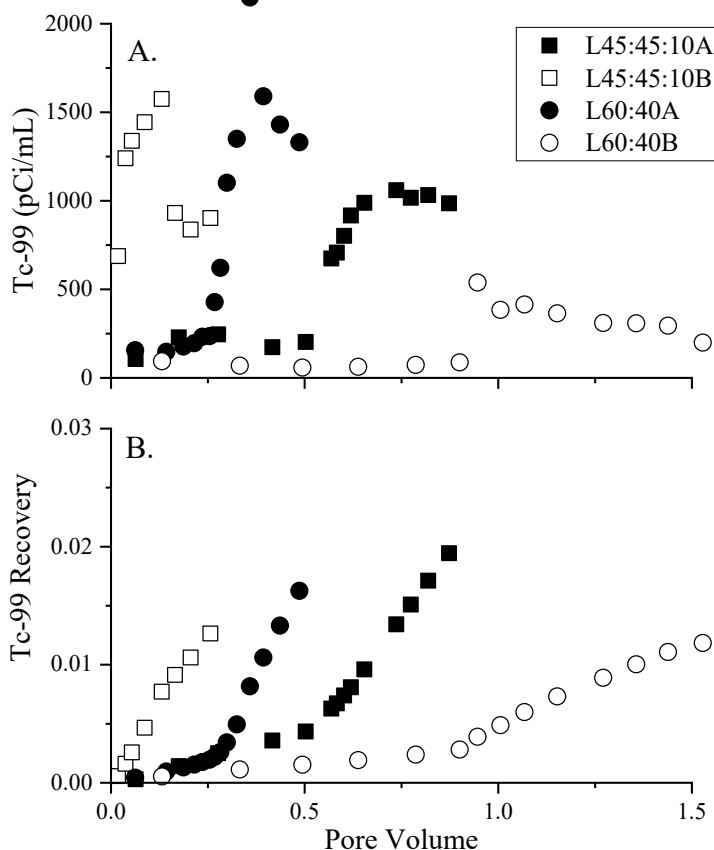


Figure 10 provides a graph of the solubility of two possible Tc(IV) solid phases that are thought to control the partitioning and release of  $^{99}\text{Tc}$  in reducing grouts (i.e.,  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ ) as a function of pH at two different Eh values, -0.20 and -0.4 V. A more-thorough explanation of the modeling results is provided Seaman and Coutelot (2018; SREL R-18-0004) and Seaman et al. (2018; SREL R-18-0006). All of the DLM data points for  $^{99}\text{Tc}$  from this and previous DLM tests are added to the graph as a function of pH. Soluble  $^{99}\text{Tc}$  (i.e.,  $10^{-6}$  to  $10^{-7}$  mol  $\text{L}^{-1}$ ) for the current data set are consistent with previous DLM tests; however, the initial pH is somewhat higher than previous tests. This data suggests that the measured ORP values (Figure 8) are higher than actual pore solutions within the intact monoliths.

**Figure 10. Solubility diagram for possible  $^{99}\text{Tc}$  solid phases (i.e.,  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ ) as a function of pH at two different Eh values, -0.2 and -0.4 V. Effluent data for  $^{99}\text{Tc}$  DLM tests graphed as a function of sample pH. Redrawn from Seaman et al. (2018; R-18-0006) to include the data from current report, i.e., FY18-L45:45:10 and FY18-L60:40.**

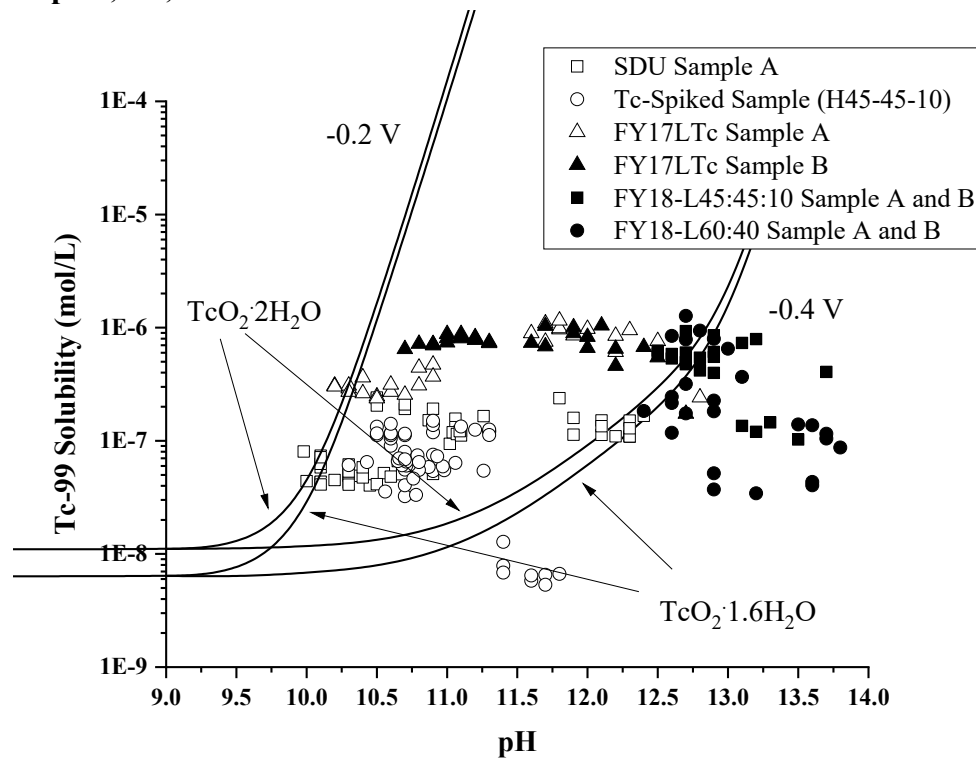
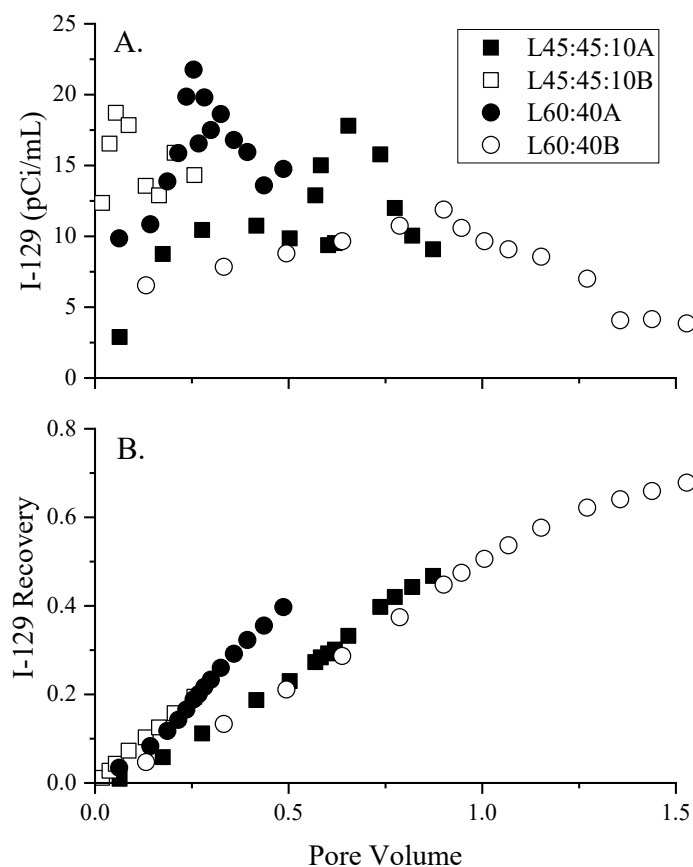


Figure 11 displays the effluent  $^{129}\text{I}$  concentration and the cumulative effluent  $^{129}\text{I}$  recovery (1 = 100%) for the spiked samples (L45:45:10 and L60:40). To date, there is a great deal of scatter in the  $^{129}\text{I}$  leaching data, with values ranging from about 5 to 15 pCi/L, quite similar to the levels found in the Tank 50 waste (Bannochie, 2012, 2014). Even so, greater than 50% of the total  $^{129}\text{I}$  appears to be leached within the first pore volume for both formulations, which is consistent with previous DLM tests using  $^{129}\text{I}$  spiked saltstone simulants.

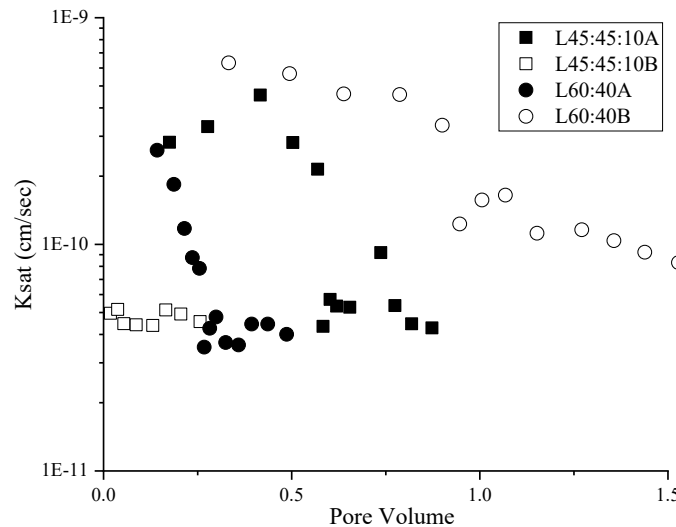


**Figure 11. Effluent  $^{129}\text{I}$  (A) and cumulative  $^{129}\text{I}$  recovery (B) for two L45:45:10 samples and two L60:40 samples.**



Estimates of the saturated hydraulic conductivity (SHC;  $K_{\text{sat}}$ ) of the four DLM test are presented in Figure 12. The initial  $K_{\text{sat}}$  for all DLM samples was  $< 1 \times 10^{-9} \text{ cm sec}^{-1}$ , with most decreasing to  $< 1 \times 10^{-10} \text{ cm sec}^{-1}$  with continued leaching. Such low  $K_{\text{sat}}$  values preclude rapid DLM testing.

**Figure 12. Saturated hydraulic conductivity values for all DLM samples, i.e., L45:45:10 and L60:40.**



## 5.0 Discussion

EPA 1315 and DLM leaching tests were conducted using spiked (i.e.,  $^{129}\text{I}$  and  $^{99}\text{Tc}$ ) saltstone, including both the standard (L45:45:10) and cement-free (L60:40) formulations. Leaching data for  $^{99}\text{Tc}$  and  $^{129}\text{I}$  (measured via EPA Method 1315) indicated almost identical performance of the standard and cement-free formulations. DLM tests using the two formulations are still in progress and limited leaching data is available to date. However, the initial trends with respect to  $^{129}\text{I}$  and  $^{99}\text{Tc}$  retention are consistent (for both the standard and cement-free formulations) with previously reported DLM data. Iodine-129 appears quite mobile in the cured saltstone samples, with DLM effluent concentrations that are similar to the Tank 50 waste. In contrast,  $^{99}\text{Tc}$  is retained to a greater degree, yielding effluent concentrations that are at least an order of magnitude lower than the Tank 50 waste stream. Additionally, the estimated  $K_{sat}$  values (based on DLM tests) are consistent with previous tests, including the new data for the cement-free formulation. The data presented in this report confirms that the leaching behavior of cement-free (L60:40) saltstone is equivalent to that of the currently utilized standard (L45:45:10) saltstone material.

## 6.0 Acknowledgements

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## 8.0 Appendix A: Data Summary for EPA Method 1315

<b>Formulation:</b>		<b>L60:40</b>					
<b>Curing Duration:</b>		<b>9 Months</b>					
<b>Sample No.</b>	<b>Days</b>	<b>pH</b>	<b>ORP (mV)</b>	<b><sup>99</sup>Tc (pCi mL<sup>-1</sup>)</b>	<b><sup>129</sup>I (pCi L<sup>-1</sup>)</b>	<b>Na<sup>+</sup> (mg L<sup>-1</sup>)</b>	<b>NO<sub>3</sub><sup>-</sup> (mg L<sup>-1</sup>)</b>
1	0.11	11.4	62.0	2.17	12.2	56.8	137.5
2	0.98	11.5	56.0	2.79	13.2	92.2	146.8
3	1.91	10.8	19.6	1.15	NA	54.3	96.9
4	6.98	10.6	-9.2	3.16	37.3	175.0	261.7
5	14.00	10.1	32.8	2.26	14.4	134.6	205.5
6	28.00	9.8	93.6	3.26	11.5	210.3	228.1
7	42.00	9.7	103.4	3.27	26.4	197.3	248.0
8	49.19	10.0	115.0	0.39	10.8	49.2	57.3
9	63.01	9.6	125.2	2.13	19.5	111.1	202.5
<b>Formulation:</b>		<b>L45:45:10</b>					
<b>Curing Duration:</b>		<b>9 Months</b>					
<b>Sample No.</b>	<b>Days</b>	<b>pH</b>	<b>ORP (mV)</b>	<b><sup>99</sup>Tc (pCi mL<sup>-1</sup>)</b>	<b><sup>129</sup>I (pCi L<sup>-1</sup>)</b>	<b>Na<sup>+</sup> (mg L<sup>-1</sup>)</b>	<b>NO<sub>3</sub><sup>-</sup> (mg L<sup>-1</sup>)</b>
1	0.11	11.3	58.6	1.80	3.6	83.5	131.4
2	0.98	11.6	56.4	2.50	8.2	117.0	206.1
3	1.91	10.9	23.1	1.31	14.0	67.8	160.9
4	6.98	10.8	-29.5	3.46	45.3	186.9	229.7
5	14.00	10.2	33.7	2.31	22.3	129.6	178.7
6	28.00	9.8	95.3	3.76	19.8	195.4	262.0
7	42.00	9.7	107.5	4.20	6.7	197.7	212.6
8	49.19	9.9	121.1	0.66	6.2	45.6	65.2
9	63.01	9.5	136.8	2.41	4.9	104.7	235.2