

Contaminant Leaching From Intact Saltstone Monoliths – 17517

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ABSTRACT

At the Department of Energy's (DOE's) Savannah River Site (SRS) chemically reducing materials, such as blast furnace slag (BFS), are added to grout formulations mixed with low-level radioactive salt solution in order to enhance the attenuation of redox sensitive contaminants (e.g., technetium-99 (Tc-99)). The resulting cementitious material, known as *saltstone*, is deposited in a series of concrete vaults for permanent disposal at the Saltstone Disposal Facility (SDF). Under oxidizing conditions, Tc persists as an anion in the +7 oxidation state, i.e., pertechnetate (TcO_4^-), with very limited retention generally associated with amphoteric soil oxides. However, Tc(VII) is subject to chemical reduction to the +4 oxidation state, which is less soluble and mobile in the environment. Thus, chemically reducing grouts provide both a physical (i.e., low saturated hydraulic conductivities (K_{sat}) that limit H_2O turnover and O_2 exposure) and chemical barrier (i.e., residual reductive capacity) to contaminant release. However, many of the previous experiments evaluating the ability of saltstone to chemically reduce and immobilize Tc have been conducted using ground saltstone materials as sorbents, a practice that is likely to reduce the moisture level in the material, enhance exposure to O_2 and alter sorbent properties in an unpredictable manner. Therefore, the objective of the current study was to evaluate contaminant leaching from intact monoliths that better represent the initial physical and chemical state of saltstone within the SDF disposal units.

For the current study, saltstone simulants were produced utilizing SRR prescribed formulations: initial batches were spiked with rhenium (Re) to serve as non-radioactive analog for Tc-99, and subsequent batches were spiked with Tc-99 for comparison. The relative concentrations of I, Re and Tc-99 in the saltwaste simulants were consistent with the average concentrations of I-129 and Tc-99 in the low-level feed waste. In addition, SRR retrieved intact monoliths from Saltstone Disposal Unit (SDU) Cell 2A in 2015 for testing.

Contaminant mass transfer rates for Tc-99 and other contaminants from spiked saltstone simulants and actual SDF saltstone samples were assessed using EPA Method 1315, *Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure*. This method was recently adopted for evaluating contaminant leaching from intact monolithic materials. Given the importance of redox speciation in controlling the mobility of Tc-99, the EPA mass transfer tests for the spiked simulants were initially conducted using leachates in equilibrium with three different test atmospheres: (1) oxic, (2) anoxic, and (3) anoxic reducing. Nitrate (NO_3^-) leaching was evaluated as a poorly retained waste constituent. The leaching behavior of cesium-137 (Cs-137), representing about 98% of the initial radioactivity of the saltstone, was also evaluated for the SDU-extracted samples.

Results from Method 1315 were also compared to a novel Dynamic Leaching Method (DLM) in which a flexible-wall permeameter was used to achieve saturated leaching under an elevated hydraulic gradient in an effort to evaluate the persistence of reductive capacity and subsequent changes in contaminant partitioning within intact saltstone monoliths. The composition of the chemical leachates from both tests was thoroughly analyzed in an effort to identify potential solid phases controlling contaminant partitioning through geochemical modeling.

For the EPA 1315 tests using spiked simulants, Re leaching rates (and other poorly sorbing contaminants like NO_3^- and iodine), as indicated by high effective diffusivities (D_e) and low leachability indices (*i.e.*, $LI = -\log[D_e]$), were much higher than Tc-99, which was attributed to poor initial reduction and/or rapid oxidation of Re, indicating that Re is a poor chemical analog for evaluating Tc partitioning under reducing conditions. Technetium-99 leaching rates for the spiked saltstone samples also appeared to be sensitive to the estimated reduction capacity of the dry feed materials used in making grout, a characteristic that can vary between different BFS sources. Technetium-99 leaching rates for the intact saltstone samples in the EPA 1315 test were quite similar, with less variability between the three test samples. This may be indicative of the longer curing time before the SDF samples were tested (≈ 3 years). Somewhat surprisingly, the leaching rates for Cs-137 from the SDF samples were generally lower than the poorly sorbing contaminants, NO_3^- and iodine. For the DLM tests, Re leaching from spiked saltstone was much higher than observed for Tc-99, with rates similar to that of non-reactive grout constituents, consistent with EPA 1315 leaching rates.

INTRODUCTION

Reactivity and saturated hydraulic conductivity (K_{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 solution materials in order to enhance the attenuation of redox sensitive contaminants, *e.g.*, Tc-99. The persistence of chemically reducing conditions within the grout is an important factor driving long-term risk potential in the Performance Assessment (PA) 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 O_2 (DO) is restricted, which is dependent on the material's K_{sat} .

Several studies have demonstrated both the difficulty in reducing pertechnetate (TcO_4^- ; *i.e.*, Tc(VII)) and the rapid oxidation of reduced Tc (*i.e.*, Tc(IV)) when exposed to even moderate levels of O_2 [1-3]. Concretes incorporating BFS are generally considered to be resistant to chemical degradation because of their low permeability [4], a factor that can limit O_2 exposure and inhibit oxidation. Dissolved sulfides are generally thought to control the redox environment of pore water in slag rich cements [3, 5].

Many of the previous experiments evaluating the ability of saltstone to reduce and immobilize Tc have been conducted using ground saltstone materials as sorbents, a practice that is likely to expose new surfaces to oxidation and alter sorbent properties in an unpredictable manner. In addition, controlled H₂ atmospheres have been used as a means of restricting O₂ exposure for studies evaluating contaminant partitioning despite the fact H₂ may serve as a general chemical reductant and may alter the redox speciation of the target contaminants (i.e., Tc, Cr, Pu, etc.) and other important chemical elements (i.e., Fe, Mn, etc.) in the presence and even absence of the test sorbent, i.e., soil, saltstone, etc.

To address such issues, the EPA Method 1315, *Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure* [6], was developed for evaluating the leaching potential of contaminants found in cementitious materials [7-9]. EPA Method 1315 is similar to American National Standards Institute, Inc. / American Nuclear Society Method 16.1, *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure* [10], 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 leaching potential of contaminants from solid waste, including “size-reduced” cementitious materials, has previously been evaluated using the batch extraction method defined in EPA Method 1311, *Toxicity Characteristic Leaching Procedure (TCLP)* [11]. The TCLP method was designed to represent the leaching conditions present in a municipal waste landfill scenario. However, contaminant mass transport in monolithic materials is controlled by diffusion through the tortuous pore network combined with the aqueous phase partitioning reactions at the solid/solution interface (i.e., adsorption/desorption, precipitation/dissolution, complexation reactions, etc.).

As noted above, the physical structure of the saltstone material combined with maintaining a high degree of saturation serves as a barrier against exposure to O₂. 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 objective of the current study was to evaluate the leaching behavior of Tc-99 and other contaminants from spiked saltstone simulant monoliths in comparison with actual intact saltstone samples collected from Saltstone Disposal Unit (SDU) Cell 2A.

DESCRIPTION

Spiked Saltstone Simulant

Technetium-99-spiked saltstone was produced utilizing SRR-prescribed grout formulations and then subjected to a temperature/humidity curing profile that mimicked the environmental conditions in an SDU. The relative concentrations of Tc-99 in the saltwaste simulants ($\approx 740 \text{ Bq mL}^{-1}$) were consistent with the average concentrations of Tc-99 in the Tank 50 feed waste at the SDF (12-13). The dry feed materials consisted of (1) Class F fly ash, (2) Grade 100/120 blast furnace slag,

and (3) Type II Portland cement. The dry feed material ratio was 45% fly ash, 45% BFS and 10% Portland cement.

All of the chemicals in Table I, except for the NaOH solution, were combined with \approx 0.5 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% solution. The contaminant spike solution was added to the saltwaste flasks just before making up the solution to its final volume. The required masses of the three powdered grout materials were weighed in three separate containers. The three dry powdered materials were then mixed together in a single bucket. After thorough homogenization of the combined dry powders, the saltwaste simulant solution was slowly added to the dry materials while mixing at 250 rpm for 20 minutes.

Table I. Composition of saltwaste simulant.

Material	Molarity (moles/L)	Mass for 1L (g/L)
Sodium Hydroxide, 50 wt% NaOH	1.594	127.52
Sodium Nitrate, NaNO ₃	3.159	268.52
Sodium Nitrite, NaNO ₂	0.368	25.39
Sodium Carbonate, Na ₂ CO ₃	0.176	18.66
Sodium Sulfate, Na ₂ SO ₄	0.059	8.38
Aluminum Nitrate, Al(NO ₃) ₃ .9H ₂ O	0.054	20.25
Sodium Phosphate, Na ₃ PO ₄ .12H ₂ O	0.012	4.56

The saltwaste solution was added at a water to dry materials ratio of 0.6. After mixing, the Tc-99 spiked slurries were poured into plastic concrete molds and sealed with plastic lids for curing. The plastic concrete molds were then placed in a humidity-controlled curing oven and heated according to a curing profile derived from SDU interior temperature measurements.

SDU Cell 2A Core Extraction

Samples of field-emplaced saltstone from the SDF were collected in April-May 2015 to support ongoing SDF PA activities. As summarized in Simner [14], a set of emplaced saltstone core samples were collected from SDU Cell 2A (SDU-2A) approximately 20 months after the materials had been poured. The core samples were collected using a wet core drilling method. The goal of the sampling effort was to collect saltstone materials that retained the chemical and physical properties of emplaced saltstone for comparison with laboratory-prepared samples that are often used as surrogates for predicting saltstone behavior. The retrieved samples were immediately placed in an inert N₂ environment to prevent oxidation prior to testing. Three of the SDU core samples were included in the current study for comparison, designated SDU-A, SDU-B and SDU-C.

EPA 1315 Leaching Test

As discussed previously, EPA Method 1315 and ANSI/ANS16.1 are believed to be more relevant than batch extraction methods for testing monolithic materials as both procedures more-realistically mimic the physical nature of the intact cementitious material. After set curing intervals, Tc-99 spiked saltstone monoliths were removed from the curing oven and sectioned for testing. Given the importance of redox speciation in controlling the mobility of Tc-99, the initial mass transfer tests were conducted using leachates in equilibrium with three different test atmospheres: (1) ambient laboratory atmosphere (oxic), (2) Ultra High Purity (UHP) N₂ (99.99% N₂) purged atmosphere (anoxic), and (3) 98% N₂/2% H₂ atmosphere (anoxic reducing). In subsequent tests, the spiked monoliths were sectioned approximately 7.6 cm (\approx 3 inches) above the base and removed from the curing mold immediately before the start of the leaching test. The SDU samples were also sectioned to be of similar size to the Tc-99 spiked samples and provide subsections of a given SDU sample for additional testing, e.g., Dynamic Leaching Method (DLM) testing, chemical analysis, etc.

Technetium-99 present in EPA leachates was analyzed by liquid scintillation counting [15]. Cesium-137 present in the EPA Method 1315 test leachates from the SDU-2A samples was determined by gamma spectrometry. Nitrate leaching for the SDU and Tc-99 spiked grout samples was monitored using a chromotropic acid test method [16].

The effective diffusivity, D_e (cm/s²), for Tc-99, Cs-137 and NO₃⁻ was calculated using the simplified approach outlined in ANSI/ANS-16.1 (10):

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

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, Δt_n is the duration of the n^{th} interval, V is the volume of the sample (cm³), S is the surface area of the sample (cm²), and T is the generalized mean square root of the leaching time:

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

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. Additionally, a more-specific solution that accounts for the geometry of the specimen is required when more than 20% of the contaminant has leached from the sample [10].

For comparison, the leachability index (LI), a unit-less parameter derived from the effective diffusion coefficient, i.e., D_e (cm^2/s), was calculated using the equation:

$$LI_n = -\log[D_e] \quad (\text{Eq. 3})$$

where LI_n is the leachability index for sampling interval n . The reported LI values in the current study reflect the average for all sampling intervals where less than 20% of the initial inventory has been leached. A summary of the EPA 1315 results is provided in Table II. It is important to note that the “diffusional” release of retained contaminants from cementitious waste reflects 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. A LI value of 6 or greater is generally considered the threshold for a given matrix as adequate for immobilization of radioactive wastes [10].

DLM Testing

The DLM is based on ASTM D5084-10 [17] for determining the K_{sat} of cementitious materials using a flexible-wall permeameter to develop the necessary hydraulic gradient and ensure internal flow. Darcy’s Law was used to establish the initial leaching conditions:

$$q = \frac{Q}{A} = \frac{K_{sat}\Delta H}{L} \quad (\text{Eq. 4})$$

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 (cm^2), K_{sat} (cm sec^{-1}) is the hydraulic conductivity, ΔH 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) [18]. A diagram of the DLM system is provided in Figure 1.

Changes in the relative K_{sat} 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. The porosity of the Tc-spiked sample was determined by the mass loss of water upon heating samples to 105 °C in a laboratory oven, with the heated sample measured repeatedly until the mass change on consecutive days was < 0.5%. For the current saltstone materials, the average % moisture content \approx 58%, consistent with other estimates for similar materials [19]. This was used as an estimate of sample pore volume (PV) for comparing sample monoliths of differing dimensions.

The confining pressure was set at 20-25 psi and the initial driving pressure was set at 12 psi. After flow began, the driving pressure was adjusted as necessary to provide continuous flow. Samples for chemical analysis were generally collected on a weekly basis. As described above for EPA Method 1315, Tc-99 present in effluents was analyzed by LSC, Cs-137 was determined by gamma spectrometry, and NO_3^- was monitored using the chromotropic acid test method.

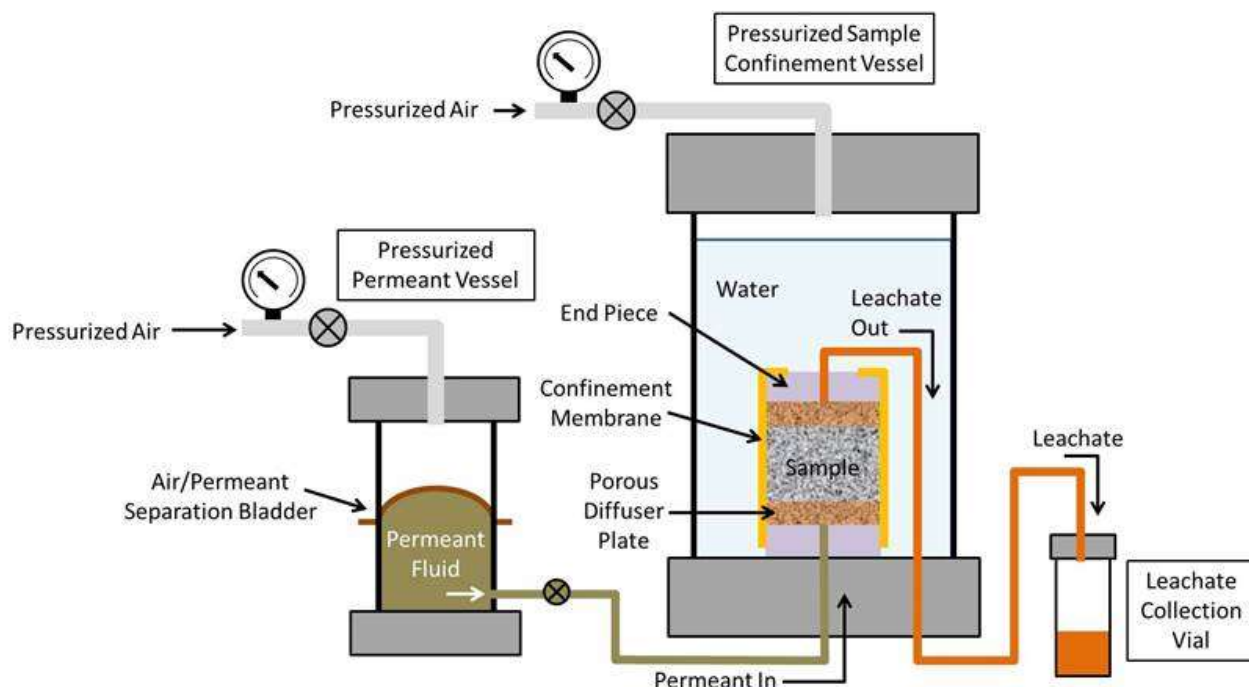


Fig. 1. Diagram of the DLM testing apparatus showing the flex-wall permeameter cell, inlet permeant source within a bladder attenuator, and sample collection outlet.

DISCUSSION

EPA Method 1315

An example of the Tc-99 leaching data (derived from EPA Method 1315) for spiked samples tested under oxic and anoxic-reducing test conditions is presented in Figure 2A, with cumulative recovered Tc-99 presented in Figure 2B. Technetium-99 leaching was generally insensitive to the atmosphere under which the test was conducted, with a similar trend observed for saltstone spiked with Re. However, Re was leached from the spiked monoliths at a much greater rate than observed for Tc-99 (Figure 3), indicated that Re is a poor chemical analog for predicting Tc-99 behavior under reducing conditions.

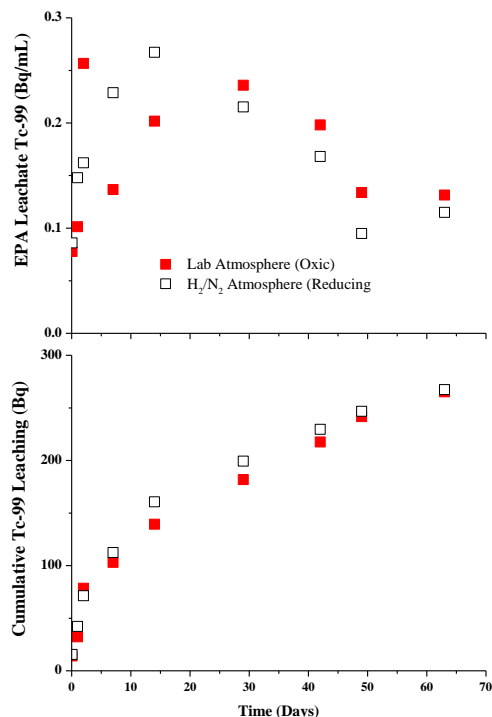


Fig. 2. EPA Method 1315 leaching results for Tc-99 spiked saltstone simulants cured for six months: leachate concentration (A), cumulative Tc-99 leaching over the course of testing (B).

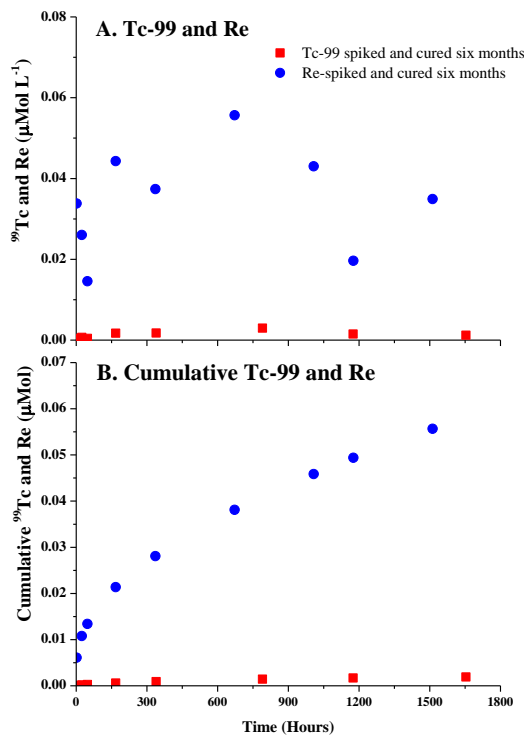


Fig. 3. EPA Method 1315 leaching results for Re and Tc-99 spiked saltstone simulants: (A) leachate concentration, (B) cumulative Re and Tc-99 leaching.

The relative Tc-99 leaching profiles for the three SDU samples are quite similar (Figure 4A), yielding almost identical cumulative Tc-99 leaching profiles (Figure 4C). In contrast the Tc-99 leaching data for Tc-99 spiked samples made from the two different BFS source materials are quite different, with higher leaching rates observed for saltstone made from the older Holcim BFS source. In addition the Tc-99 leaching data for the Lehigh BFS indicates that extended curing may further enhance Tc-99 immobilization.

The difference in Tc-99 leaching behavior for the SDU and spiked samples may reflect the greater chemical reduction capacity of the new Lehigh BFS compared to the Holcim BFS used at the time the SDU saltstone was poured, despite the much longer curing time for the SDU materials. The Lehigh BFS apparently has about twice the reductive capacity as the Holcim BFS, which can be attributed to Lehigh's higher Fe and S contents.

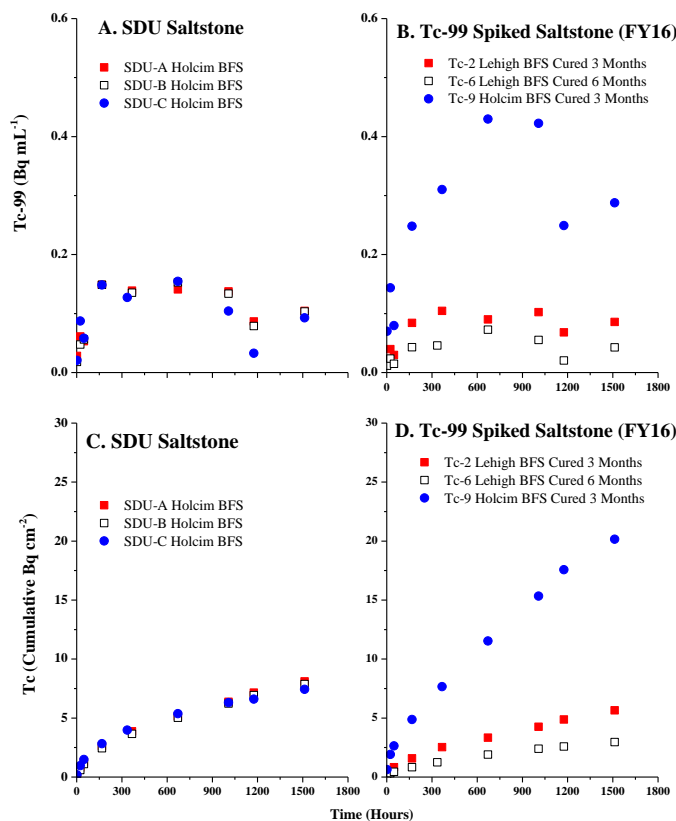


Fig. 4. EPA Method 1315 leaching results for SDU Cell 2A (A and C) materials and Tc-99 spiked saltstone simulants (B and D): leachate concentration (A and B), cumulative Tc-99 leaching as a function of exposed surface area (C and D).

The measured concentrations of Cs-137 in the leachate from the three SDU samples are presented in Figure 5. Two of the three samples yielded very similar leachate concentrations, samples SDU-B and SDU-C. Sample SDU-A yielded Cs-137 leachate levels that were somewhat higher than the other two, but the results are consistent with the initial Cs-137 levels present in the three SDU samples, with SDU-A having a greater Cs-137 content ($2.9 \times 10^4 \text{ Bq gm}^{-1}$) than SDU-B ($1.8 \times 10^4 \text{ Bq gm}^{-1}$) and SDU-C ($1.8 \times 10^4 \text{ Bq gm}^{-1}$). The reported Cs-137 concentration in Tank 50 at the time these materials were poured, third quarter of 2013, was $4.5 \times 10^4 \text{ Bq mL}^{-1}$ (13). The concentration in the resulting saltstone can be generally estimated by dividing the tank waste concentration by three, i.e., $4.5 \times 10^4 \text{ Bq mL}^{-1}$ yields $\approx 1.5 \times 10^4 \text{ Bq gm}^{-1}$, generally consistent the levels of Cs-137 present in samples SDU-B and SDU-C.

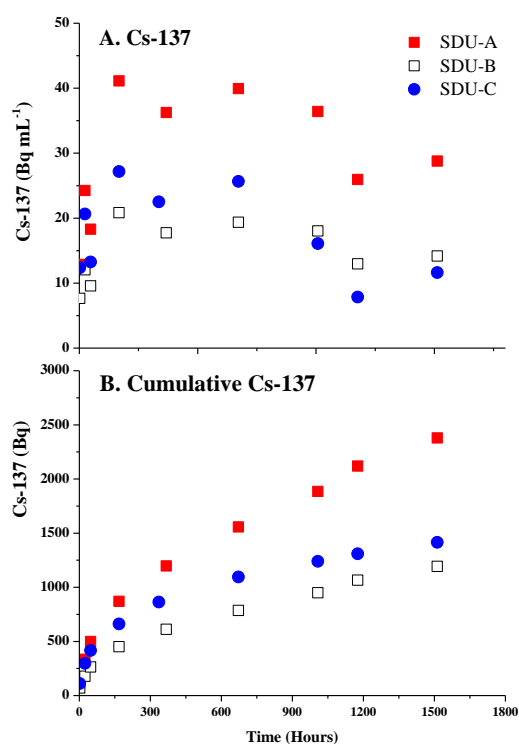


Fig. 5. Leaching results for Cs-137 from EPA Method 1315 for three SDU Cell 2A monoliths: (A) leachate concentration, (B) cumulative Cs-137 leaching as a function of exposed surface area.

The Cs-137 effective diffusivity values, D_e , ranged from 1.1×10^{-10} to $4.9 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$ with LI values of 9.4, 9.9, and 9.3 for SDU-A, SDU-B, and SDU-C, respectively (see Table 2). The Cs-137 D_e and LI values for three SDU samples illustrates the importance of knowing the initial concentration of contaminant present in the test material in order to properly analyze the leaching results. The LI values observed for Cs-137 in the current study are generally higher than those reported previously for ordinary Portland cement ($LI \approx 6$ to 8.5) [20-22]. Other materials, such as fly ash, zeolites, and slag, are often added to cement materials to enhance Cs-137 retention (20-22). For instance, previously reported LI values

for Cs-137 ranged from 8.1 to 12 for ordinary Portland cement blended with various ratios of sand materials. The higher *LI* values observed with the addition of sand results from a reduction in porosity when compared to ordinary Portland cement (OPC) [22].

Cesium generally forms simple aqueous ions and interacts with mineral surfaces through electrostatic ion exchange, with sorption controlled by the presence of similar competing ions, Na, K, Ca. Additional Si tends to increase the number of cation exchange sites that develop with cement hydration [3].

Table II. Summary of effective diffusivities (D_e) and leachability indices (*LI*) derived from EPA Method 1315. Higher *LI* values indicate slower leaching rates.

Sample	Curing Duration	Materials	⁹⁹ Tc		Re		¹³⁷ Cs	
			D_e (cm ² /sec)	<i>LI</i>	D_e (cm ² /sec)	<i>LI</i>	D_e (cm ² /sec)	<i>LI</i>
Spike Batch 1 ^a								
	3 Months	Old BFS (Holcim)	2.4E-10	9.9	3.0E-08	7.6	NA	NA
	6 Months	Old BFS (Holcim)	2.8E-10	9.7	3.3E-08	7.6	NA	NA
Spike Batch 2								
Tc1	3 Months	New BFS (Lehigh)	2.6E-11	10.6	NA	NA	NA	NA
Tc2	6 Months	New BFS (Lehigh)	5.7E-12	11.3	NA	NA	NA	NA
Tc3 (1D)	6 Months	New BFS (Lehigh)	3.8E-11	10.4	NA	NA	NA	NA
Tc4	3 Months	Old BFS (Holcim)	3.0E-10	9.6	NA	NA	NA	NA
Sample A (SDU A)	20 Months ^b	Old BFS (Holcim)	6.4E-11	10.2	NA	NA	4.2E-10	9.4
Sample B (SDU B)	20 Months ^b	Old BFS (Holcim)	5.8E-11	10.3	NA	NA	1.1E-10	9.9
Sample C (SDU C)	20 Months ^b	Old BFS (Holcim)	5.2E-11	10.3	NA	NA	4.9E-10	9.3

^aReflects the average of three tests (1D configuration) in three different atmospheres

^b20 months curing in SDU Cell 2A before sampling

NA Not Applicable

Sample A = SDU2A-0931-C-1-U-2

Sample B = SDU2A-0931-C-1-U-5

Sample C = SDU2A-0931-C-2-U-2

Dynamic Leaching Method

A Tc-99 spiked sample has been continuously leaching with degassed artificial groundwater (AGW) for ≈ 1 year. Two 5 cm diameter, ≈ 2.5 cm long SDU core sections representing samples SDU-A (SDU2A-0931-C-1-U-2) and SDU-B (SDU2A-0931-C-1-U-5) were added to the test manifold with SDU-A leached with AGW equilibrated with laboratory air and SDU-B leached with degassed AGW. The pore volume for the saltstone monoliths was based on porosity estimates derived from moisture loss at 105 °C for the Tc-99 spiked sample, accounting for $\approx 58\%$ of the monolith volume. While this makes it possible to directly compare data from monolith samples of differing sizes, including the two SDU samples, it is unclear if this measure of porosity is actually indicative of the conductive volume within each of the saltstone samples.

Attempts were made to directly measure the pH, ORP, and DO levels in the DLM effluents after sample collection, factors which control the mobilization of contaminants within saltstone, i.e., Cs-137, I-129, Tc-99, etc. However, it soon became apparent that the three parameters were subject to significant change while the effluent samples were being collected due to the low flow rates. The pH of the samples decreased, likely the result of CO₂ absorption by the alkaline solutions,

while the ORP and DO levels increased with storage prior to measurement. In addition, DO electrodes proved unreliable when measuring the highly concentrated, alkaline leachates. To resolve this limitation, the small sample remaining in the effluent tubing was drained into a fresh sample vial and the pH was measured immediately upon collection. Using this method, effluent tubing pH values were typically a full 0.5 to 1.0 unit higher than the pH of the bulk effluent solution in the effluent collection vial. In future DLM tests described below, a flow through system will be used to capture these results before the sample is exposed to the atmosphere.

The cumulative fractions of Tc-99 and Cs-137 that have been leached from the three samples are provided in Figure 6. Less of the initial Tc-99 when compared to Cs-137 has been leached from the two SDU columns, with an even smaller fraction of the total Tc-99 ($\approx 2\%$) extracted from the Tc-99 spiked saltstone.

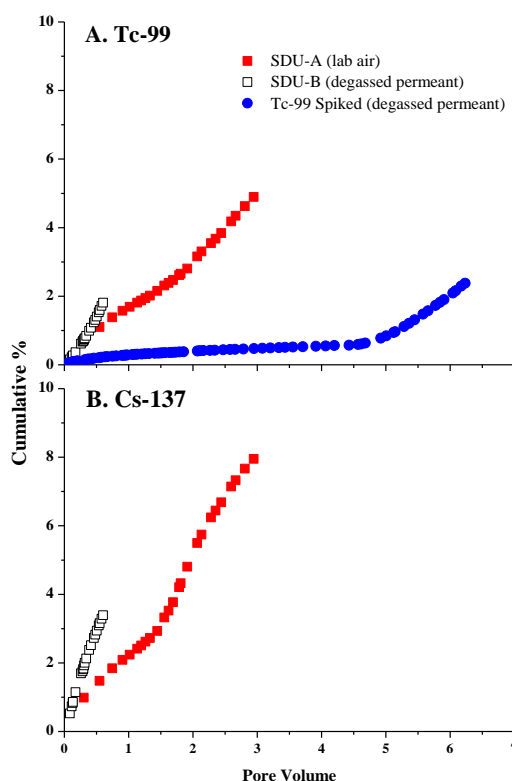


Fig. 6. Cumulative % of Tc-99 (A) and Cs-137 (B) leached from each sample.

These results for Tc-99 and Cs-137 are in stark contrast to the leaching pattern observed for NO_3^- (Figure 7), which is generally considered to be poorly retained within cementitious materials. For SDU-A, the NO_3^- leaching pattern is quite similar to that of Cs-137, despite much higher cumulative levels of NO_3^- leached over the course of the test (Figure 7B). The NO_3^- leaching for SDU-A is also similar to the leaching behavior of Tc-99 (at much lower cumulative levels than Tc-99), but the secondary increase is transient for NO_3^- (same as Cs-137), while the Tc-99 level has remained elevated. For SDU-B, the NO_3^- leaching pattern is similar to that of Cs-137

as well, i.e., generally decreasing since the onset of leaching, while the Tc-99 concentration has remained high. For the Tc-99 spiked column, the recent increase in NO_3^- leaching is generally similar that observed for Tc-99.

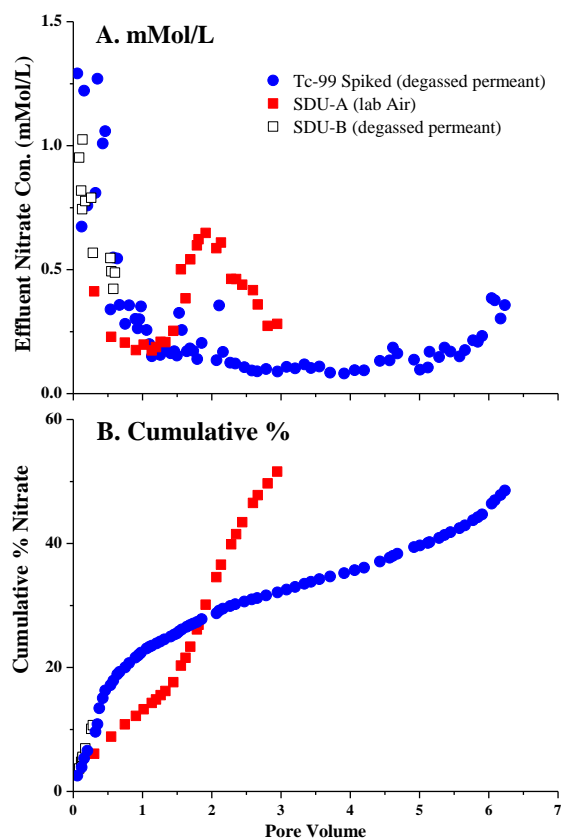


Fig. 7. Nitrate (NO_3^-) leaching from the two SDU samples and the Tc-99 spiked saltstone samples: (A) effluent NO_3^- concentration, and (B) cumulative % of NO_3^- leached from each sample.

CONCLUSIONS

EPA Method 1315 results were generally consistent for Tc-99 spiked saltstone simulants and saltstone samples collected from SDU Cell 2A. Differences in leaching rates for SDU and simulant samples generally suggest that the chemical reductive capacity of the BFS and the curing duration are important factors controlling Tc-99 immobilization. Furthermore, results for the SDU samples displayed significant Cs-137 ($LI \approx 9.3-9.9$) immobilization capacity when compared to the mobile contaminant, NO_3^- , which can be attributed to the greater binding affinity for alkaline earth metals of grout materials made from Portland cement combined with BFS and fly ash.

DLM tests demonstrated the ability to maintain continuous saturated flow through SDU samples as a means of evaluating the reactions occurring within the intact materials. However, flow rates and residence times were quite different for the three test samples and varied to some degree for a given sample, with generally

lower K_{sat} values observed for the SDU samples when compared to saltstone simulants, which complicates the interpretation of contaminant leaching behavior. Furthermore, the low flow rates made it difficult to monitor the geochemical properties of the effluents that are critical to evaluating the mechanisms controlling contaminant partitioning (i.e., pH, DO, ORP, etc.), especially for Tc-99 because of its tendency to oxidize when exposed to even limited DO levels. Although efforts were made to control the level of DO present in the permeant solutions, it is difficult to draw definitive conclusions regarding the possible impact of DO based on the limited effluent data set.

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