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Technetium Leaching from Cementitious Materials

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ABSTRACT

At the Savannah River Site (SRS) low activity salt solution is stabilized via encapsulation within a grout termed saltstone. Saltstone is emplaced into large (multi-million gallon) concrete storage facilities referred to as Saltstone Disposal Units (SDUs). Technetium-99 (^{99}Tc) is a long-lived radionuclide contained in the low activity salt waste and subsequently incorporated into the grout waste form: it is considered a significant contributor to risk with respect to the long-term radiation exposure of the environment surrounding the SDUs. In the reducing, high pH environment within the grout, ^{99}Tc is expected to be relatively immobile since it exists in a reduced Tc(IV) oxidation state in the form of sparingly soluble sulfides (TcS$_x$) or hydrated oxides (TcO$_2$.xH$_2$O). However, in the presence of O$_2$ (associated with the future infiltration of air or oxygenated ground waters into the saltstone monolith) it is possible for redox-sensitive Tc(IV) to transition into highly soluble (and mobile) Tc(VII) species, pertechnetate (TcO$_4^-$), which is more readily transported to the surrounding environment. Traditional approaches to quantifying the leaching behavior of ^{99}Tc from cementitious matrices have involved partitioning experiments using size-reduced (crushed/ground) saltstone samples, and determination of the ^{99}Tc fraction immobilized by the cementitious solids. Such experiments create artificially high solid-solution contact areas that likely result in higher ^{99}Tc leachate concentrations than would be expected for intact, monolithic samples. In the current study a new technique, termed the Dynamic Leaching Method (DLM), is being used to investigate the ^{99}Tc leaching behavior of monolithic saltstone samples. The data derived using this technique is intended to inform the SRS Saltstone Disposal Facility (SDF) Performance Assessment (PA) which models the long-term transport of radionuclides from the SDUs to the environment. The DLM utilizes a flexible-wall permeameter to achieve saturated leaching under an elevated hydraulic gradient in an effort to simulate the transport of groundwater through saltstone. Initial findings indicate that the ^{99}Tc concentrations in the leachate are on the order of 1E-08 mol/L which suggests that the saltstone leaching behavior is controlled by the solubility of TcO$_2$.xH$_2$O compounds.

INTRODUCTION

The treatment and dispositioning of high-level waste (HLW) at the Savannah River Site (SRS) will generate approximately 100 million gallons of low activity salt solution containing less than 0.1% of the total SRS radionuclide inventory. The salt solution is dispositioned at the Saltstone Disposal Facility (SDF) via combination with a mixture of mixture of blast furnace slag (BFS), fly ash (FA), and ordinary Portland cement (OPC) at the Saltstone Production Facility (SPF) to form a flowable grout referred to as saltstone. Once mixed the radioactive grout is transferred to concrete vaults, termed Saltstone Disposal Units (SDUs), where it subsequently cures and encapsulates the waste (Figure 1).

Figure 1: SRS SDF: low activity salt solution is mixed with cementitious materials in the SPF and transferred to the SDUs for permanent storage.

A Performance Assessment (PA) is conducted for the SDF to model the long-term (hundreds to thousands of years after SDF closure) fate and transport of the grout-encapsulated contaminants, and to determine the potential for future interactions with the public and the environment [1]. The predominant mechanism controlling the release of contaminants from the SDF is the adsorption characteristics of the saltstone which are element dependent and differ as the reduction potential (E_h) and pH of the saltstone environment changes over time. In some instances contaminant mobility may be controlled by solubility limits. This is indeed the case for ^{99}Tc, a redox sensitive contaminant that under reducing conditions exists in its reduced Tc(IV) oxidation state in the form of sparingly soluble sulfides (TcS_x) or hydrated oxides ($TcO_2.xH_2O$). It is believed that sulfide (S^{2-}) and ferrous iron (Fe^{2+}), both present in the BFS component of saltstone, serve as Tc reductants. However, in the presence of O_2 (associated with the future infiltration of air or oxygenated ground waters into the saltstone monolith) it is possible for redox-sensitive Tc(IV) to transition into highly soluble (and mobile) Tc(VII) species, such as pertechnetate (TcO_4^-), and adsorption to the saltstone solids is expected to subsequently control ^{99}Tc transport characteristics. The SDF PA generally utilizes empirically derived data (from simulant samples) as inputs for contaminant transport simulation. However, this data has traditionally been derived from exposing size-reduced (crushed/ground) saltstone materials to leachate liquid and determining solid-liquid partitioning coefficients (K_d) that describe the distribution of contaminant between a leachate and the saltstone material. Such experiments create artificially high solid-solution contact areas that likely result in higher ^{99}Tc leachate concentrations than would be expected for intact, monolithic samples. Alternate techniques evaluating intact, monolithic samples have been developed at Vanderbilt University as part of the Leaching Environment Assessment Framework (LEAF) (http://www.vanderbilt.edu/leaching/). In particular, United States Environmental Protection Agency (USEPA) Method 1315, *Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure* [2], has been previously utilized to evaluate ^{99}Tc leaching characteristics from saltstone, and is considered a vast improvement over previous tests using size-reduced materials that focus on equilibrium partitioning rather than the rate of contaminant release under physically realistic conditions. EPA Method 1315 is considered a semi-dynamic method in which a sample is submerged in a leachate solution and the leachate periodically removed and analyzed to determine the concentrations of relevant contaminants; this data is subsequently used to estimate the diffusivity of the contaminants. In the current study a new

technique, termed the Dynamic Leaching Method (DLM), is being used to investigate the ^{99}Tc leaching behavior of intact, monolithic saltstone samples. The DLM facilitates the continuous transport of leachate through an intact monolith via application of a hydraulic gradient across the sample. The method is described in more detail in the subsequent section. Preliminary development of the DLM utilized simulant saltstone samples spiked with rhenium (Re), a non-radioactive surrogate for [99]Tc. Subsequent samples have included simulant saltstone samples spiked with ^{99}Tc, and actual saltstone samples extracted from an SDU. This paper is focused on the DLM application to a ^{99}Tc-spiked, simulant saltstone sample which has now been subjected to continuous leaching characterization for over one year.

EXPERIMENTAL

The dynamic leaching method is based on American Society for Testing and Materials (ASTM) D5084, *Standard Test Method for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter* [3], which is typically used for determining saturated hydraulic conductivity (K_{sat}). A photo and line drawing of the DLM set-up are provided in Figures 2 (a) and (b).
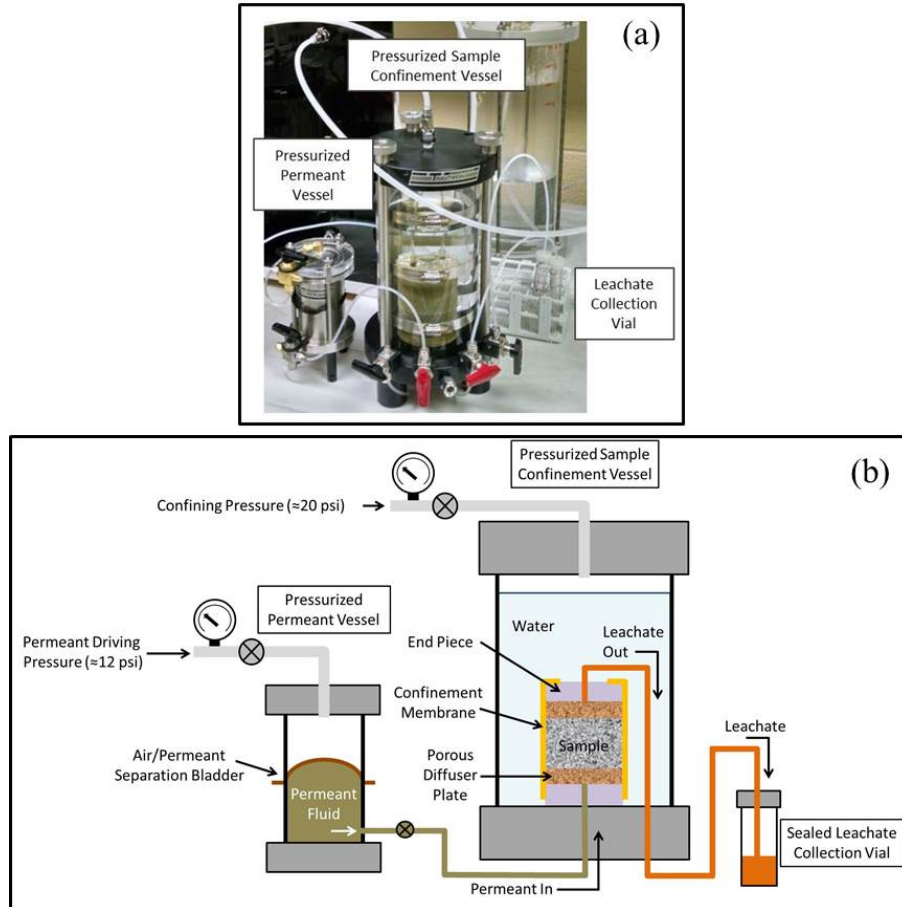

Figure 2: Photo (a) and line drawing (b) illustrating the DLM set-up.

Samples tested on the DLM are typically 2.5-cm (1-inch) in height by 5-cm (2-inch) diameter. Diffuser plates and end pieces (for permeant delivery and leachate removal) are placed at the top and bottom of the sample which is subsequently fitted with a rubber,

confinement membrane. The entire sample configuration is immersed in water inside the confinement vessel. A confining pressure of approximately 140 kPa (20 psi) is applied to the sample to compress the rubber membrane against the exterior sample surface in order to prevent leachate flowing around rather than through the saltstone monolith. The permeant used was an SRS-simulated groundwater solution which is contained in a vessel pressurized to approximately 80 kPa (12 psi). The permeant requires isolation from the pressurizing gas by a separation bladder that prevents above atmospheric gas dissolution; this was necessary since the gas would re-evolve in the equipment tubing at the sample outlet, and result in discrepancies with respect to measuring the permeant flow. The leachate from the sample was collected in a vial and subsequently measured with respect to pH and relevant constituent concentration. For experiments conducted to date constituent analysis primarily included ^{99}Tc and nitrate (NO$_3^-$). Nitrate is expected to be poorly retained within the saltstone pores as the permeant passes through the sample and can be used as an indicator with respect to the test validity. The permeant (or leachate) flow rate is dependent on the sample K$_{sat}$. For a constant hydraulic gradient across a sample, a lower K$_{sat}$ will result in a lower permeant flow-through. The average K$_{sat}$ for the ^{99}Tc-spiked sample was 1E-09 cm/sec and the average permeant/leachate flow rate was 0.6 mL/day.

Simulant saltstone samples were produced using a dry feeds ratio of 45/45/10 wt.% BFS/FA/cement, and a water-to-dry feeds ratio of 0.6. The salt solution used to prepare the saltstone is defined in Table 1.

Table 1: Salt solution used in preparation of simulant saltstone.

Material	Molarity (M)
Sodium Hydroxide, NaOH	1.594
Sodium Nitrate, NaNO$_3$	3.159
Sodium Nitrite, NaNO$_2$	0.368
Sodium Carbonate, Na$_2$CO$_3$	0.176
Sodium Sulfate, Na$_2$SO$_4$	0.059
Aluminum Nitrate, Al(NO$_3$)$_4$.9H$_2$O	0.054
Sodium Phosphate, Na$_3$PO$_4$.12H$_2$O	0.012

Prior to mixing the dry feeds and the salt solution approximately 2E+04 pCi/mL of ^{99}Tc was added to the solution. This spike concentration is equivalent to approximately 1 mg/L ^{99}Tc (or 1E-05 mol/L) and is consistent with ^{99}Tc concentration in the salt solution feed at SRS [4]. Once mixed the saltstone was poured into a cylindrical mold and cured for 6 months iN a temperature/humidity controlled environment.

RESULTS

The data subsequently presented indicates the variation of ^{99}Tc and NO$_3^-$ concentrations, pH, and K$_{sat}$ with respect to pore volume exchange. The PA modeling simulations estimate chemical changes within the saltstone as a function of the number of pore volumes of infiltrate water that reacts with grout minerals. Saltstone contains approximately 50-60% total porosity which is equivalent to about 35 mL for the samples associated with this study: hence 1 pore volume exchange indicates that 35 mL of leachate has been collected from the sample. Through FY2016, 6.5 pore volumes have been exchanged within the sample. Figure 3(a) indicates the ^{99}Tc concentration in the leachate as a function of pore volume. The first leachate to be analyzed

indicated ^{99}Tc concentrations on the order of 1E-07 mol/L but this dropped to 1E-08 mol/L after one pore volume had been exchanged. Figure 4 presents the solubility of various Tc species against pH. It is the $TcO_2.xH_2O$ compounds that are indicative of the measured 1E-08 mol/L ^{99}Tc concentrations. The 1E-08 mol/L ^{99}Tc leachate concentration was maintained until 4.5 pore volumes had been exchanged at which point the concentration rapidly returned to 1E-07 mol/L. The increase in ^{99}Tc leachate concentration appears to occur concurrently with decreases in both pH (12.0 to 10.5), Figure 3(b), and K_{sat} (2E-09 to 4E-10 cm/sec), Figure 3(c). Figure 4 indicates that the solubility of $TcO_2.xH_2O$ compounds is expected to decrease as pH drops but this is converse to the data, and it is conceivable that Figure 4 may provide an oversimplified interpretation of an extremely complex mineralogical system. With respect to decreasing K_{sat} it is possible that a drop in pH within the saltstone pores resulted in mineral precipitation; ettringite has been observed to form in pores during prolonged EPA Method 1315 testing of materials similar to saltstone [5]. Figure 3(d) indicates the NO_3^- concentrations in the leachate and the cumulative % of the initial NO_3^- (contained in the saltstone simulant) that has been leached from the sample. As previously stated NO_3^- is expected to poorly adsorb to solids in high pH environments and this is evidenced by the fact that 50% of the total NO_3^- was leached after the exchange of 6.5 pore volumes; in contrast only 2.5% of the ^{99}Tc had been leached; Figure 3(a).
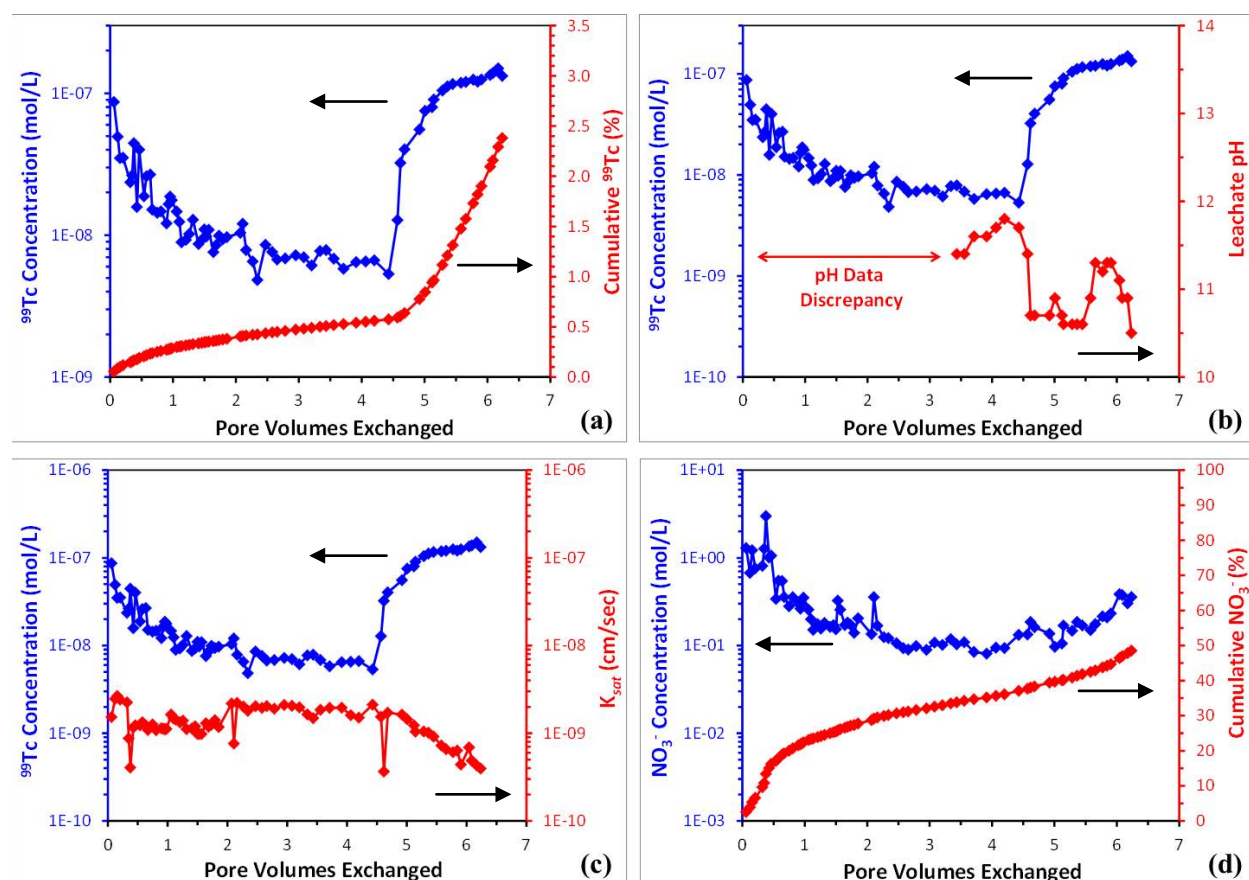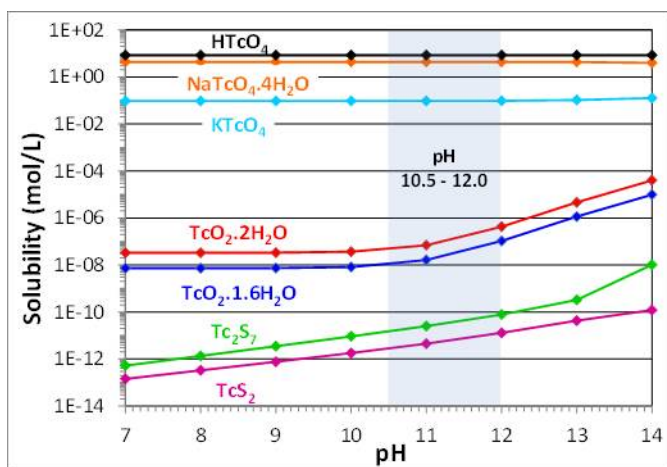

Figure 3: Relationships between (a) ^{99}Tc concentration, (b) pH, (c) K_{sat}, (d) NO_3^- concentration and pore volumes exchanged.

Note: This figure was generated by Dr. John Seaman's group at the Savannah River Ecology Laboratory (SREL) using the geochemical computer code PHREEQC-2 (USGS-99-4259) and the Lawrence Livermore National Laboratory (LLNL) thermodynamic data base (thermo.com.V8.R6.230). This LLNL database was prepared by Jim Johnson (LLNL) in Geochemist's Workbench format, and subsequently converted to the Phreeqc format by Greg Anderson (LLNL) with the assistance of David Parkhurst (US Geological Survey [USGS]).

Figure 4: pH-dependent solubility of reduced Tc species (see note below)

CONCLUSION

A dynamic leaching method (DLM) has been used to evaluate the leaching characteristics of ^{99}Tc from a cured cementitious monolith. The method enables continuous flow of permeant through the monolith and subsequent (periodic) analysis of the leachate to determine potential changes in ^{99}Tc leaching characteristics with pore volumes exchanged within the monolith. To date approximately six pore volumes have been passed through the monolith; up to 4.5 pore volumes the ^{99}Tc concentration in the leachate was measured at approximately 1E-08 mol/L. However, an order of magnitude increase (1E-07 mol/L) in ^{99}Tc concentration was observed for subsequent pore volumes exchanged. Mechanisms responsible for the observed changes in ^{99}Tc concentration have not been determined though more extensive studies are planned (beginning in FY2017) in which leachate samples will be analyzed for other components (including Al, Ca, Fe, S, and Si), and the saltstone samples will be analyzed with X-ray diffraction and fluorescence (XRD and XRF) techniques prior to and after DLM testing. The intent is to be able to potentially associate changes in ^{99}Tc concentrations with variations in pore solution chemistry and saltstone mineralogy.

REFERENCES

1. SRR-CWDA-2009-00017, *Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site*, Rev. 0, Savannah River Site, Aiken, SC, October 2009.

2. USEPA (2013) Method 1315, Mass transfer rates of constituents in monolithic or compacted granular materials using a semi-dynamic tank leaching procedure. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Office of Solid Waste, Washington, DC.

3. SRNL-STI-2013-00651, *Results for the Third Quarter 2013 Tank 50 WAC Slurry Sample: Chemical and Radionuclide Contaminants*, Rev. 1, Savannah River Site, Aiken, SC, September 2013.

4. ASTM D5084-16a, Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter, ASTM International, West Conshohocken, PA, 2016.

5. Asmussen, R. M., et al., *Solid State Characterizations of Long-Term Leached Cast Stone Monoliths*, PNNL-25578, Rev. 0, September 2016.