

April 14, 2011

MEMORANDUM TO: Christopher McKenney, Chief
Performance Assessment Branch
Environmental Protection
and Performance Assessment Directorate
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

FROM: George Alexander, Systems Performance Analyst /RA/
Performance Assessment Branch
Environmental Protection
and Performance Assessment Directorate
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
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SUBJECT: DESCRIPTION OF RESEARCH BEING PERFORMED BY THE
CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES
AND THE U.S. NUCLEAR REGULATORY COMMISSION:
COLUMN EXPERIMENT ON TECHNETIUM RELEASE FROM
REDUCING GROUT

The U.S. Nuclear Regulatory Commission (NRC) contractor, the Center for Nuclear Waste Regulatory Analyses, in coordination with NRC staff, has conducted experimental work pertaining to the release of technetium from reducing grout under Contract No. NRC-02-07-006.

A preliminary assessment of these results is summarized in the enclosure.

Docket. No.: PROJ0734

Enclosure: Technical Review Summary

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Column Experiment on Technetium Release from Reducing Grout

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Contract No. NRC-02-07-006

The release of technetium from saltstone grout is a key factor in determining compliance with the performance objectives for the Saltstone Disposal Facility at the Savannah River Site (NRC, 2005; NRC, 2007; NRC 2009). Accordingly, adequate support for the assumed reduction and retention of technetium in saltstone is essential to providing the technical basis for model results. The Center for Nuclear Waste Regulatory Analyses (CNWRA), in coordination with the U.S. Nuclear Regulatory Commission (NRC), has conducted experimental work and developed additional test plans to reduce the level of uncertainty in the fate of redox-sensitive radionuclides such as technetium and selenium under Contract No. NRC-02-07-006.

A column leaching experiment was conducted to (i) characterize the release behavior of Tc-99 initially sequestered in reducing grout as the system chemistry evolves due to the interaction with percolating water, and (ii) assess the potential of saltstone to reduce technetium and provide conditions for the long-term retention of technetium. The experiment used simulated saltstone prepared using a dry grout formulation of 10 wt% cement, 45 wt% fly ash, and 45% blast furnace slag mixed with a simulated Deliquification, Dissolution, and Adjustment simulant solution (Kaplan et al., 2008) that was spiked with 101.5 μCi of Tc-99. The simulated saltstone nominal blend composition then comprises 5 wt% cement, 25 wt% fly ash, 25 wt% blast furnace slag, and 45 wt% salt solution. The formulation was mixed in a Hobart mixer that was open to the atmosphere, poured into a cylindrical plastic mold, capped, and cured for 28 days at room temperature. After curing, the saltstone simulant was crushed and sieved to less than 0.50 mm and stored under a N_2 (g) atmosphere to minimize oxidation prior to beginning the experiment. Several analyses were conducted on the saltstone simulant prior to experimentation, including surface area (N_2 adsorption), surface imaging (scanning electron microscopy), phase determination (x-ray diffraction), and elemental surface composition (energy dispersive x-ray spectroscopy and x-ray fluorescence).

The experiment consisted of percolating a simulated Savannah River Site groundwater (Denham, 2008) at a flow rate of 0.066 mL/min through a column containing the crushed and sieved saltstone simulant. In-line Eh and pH measurements were taken periodically and Tedlar bags were used for effluent collection. Effluent samples were taken periodically and analyzed by liquid scintillation, inductively coupled plasma–optical emission spectrometry, and ion chromatography.

Care should be taken in drawing conclusions from this research at this time as (i) the following results and discussion are preliminary in nature and (ii) spatial and temporal scaling was required to conduct these experiments in a laboratory setting. The differences in technetium release between actual field conditions for emplaced saltstone and this column experiment with simulated saltstone may be significant. Additional experimentation is underway to reduce the uncertainty when extrapolating laboratory results to field conditions and to resolve the variability observed in this study. A description of the experimental limitations of this research is provided below in Table 1.

Table 1: Experimental Limitations

Limitation	Uncertainty	Implication
Formulation of Simulants	Composition of saltstone and groundwater are simulants of the emplaced grout and natural infiltrate	It is not clear what effect the variability between the simulants and emplaced grout and infiltrate will have on the reduction and retention of Tc-99.
Preparation of Grout	Variations exist between the mixing, curing, and sample preparation of the laboratory and emplaced grout.	
	The saltstone simulant was open to the atmosphere during mixing.	The degree of oxygen interaction during mixing in the laboratory may under- or over-represent the degree of oxygenation of emplaced saltstone.
	The poured grout sample was capped and cured for 28 days at room temperature. Humidity and temperature during curing was not controlled and may differ from field conditions.	Micro- and macro-porosity of the laboratory prepared grout may not be representative of the emplaced saltstone. Elevated field curing temperatures would likely lead to larger pores and increased Tc-99 release rates.
	Crushing of the saltstone simulant was required for experimental investigations.	Particle size reduction will lead to highly reactive sites and diffusive lengths that are likely to over-represent releases of Tc-99 relative to a monolithic sample.
Flow Rate of Infiltrate	A flow rate in excess of the anticipated matrix flow rates was required for characterizing the longer-term reduction capacity of saltstone. Accordingly, the experimental flow rate was not intended to be representative of flow rates for field conditions.	The high experimental flow rate may under-represent the ability of saltstone to condition water. Matrix flow rates through emplaced saltstone should be slower and may therefore condition the water to a greater extent. However, this experimental flow rate may be representative of fracture flow.

The evolution of the effluent Eh and pH versus the number of pore volumes is shown in Figure 1. The pH initially was 12.9 and decreased to almost 11 by 133 pore volumes. The Eh initially was -410 mV, but relatively quickly increased to higher redox potentials. The system increased more gradually after this initial period with the exception of a stepwise increase at 46 pore volumes. Note that gas bubbles, which were observed to form in the column during the first several pore volumes, sometimes lingered inside the pH and redox microflow cells and interfered with the pH and Eh measurements.

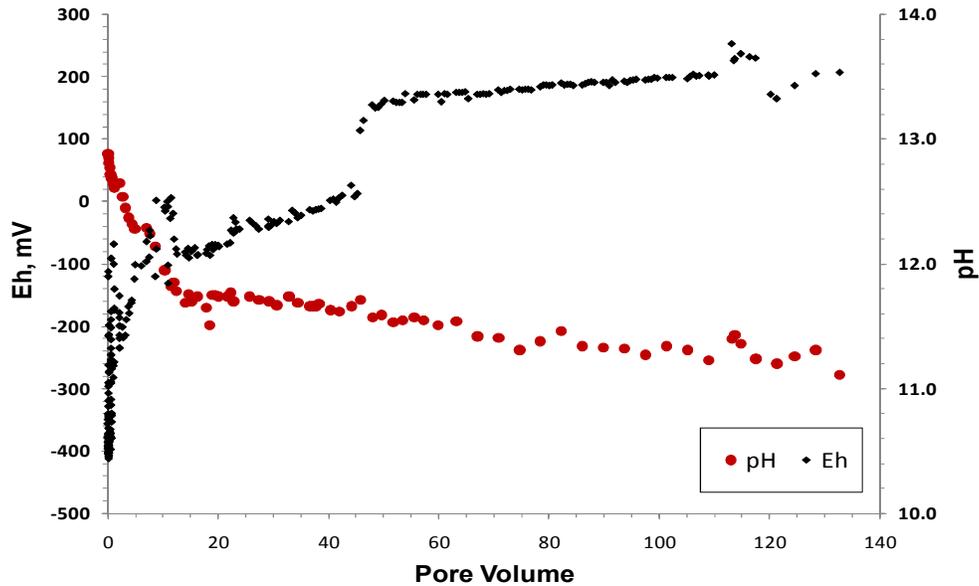


Figure 1: Eh-pH evolution of column effluent

The cumulative mass fraction of Tc-99 leached from the grout as a function of pore volumes is shown in Figure 2. The changes in Eh, pH, and Tc-99 release during the first 5 to 10 pore volumes, illustrated in Figures 1 and 2, are likely due to the dissolution of highly reactive, ultrafine particles and/or the release of grout pore solution. After the initial 10 pore volumes, Tc-99 was relatively retained by the saltstone simulant before its release at 52 pore volumes.

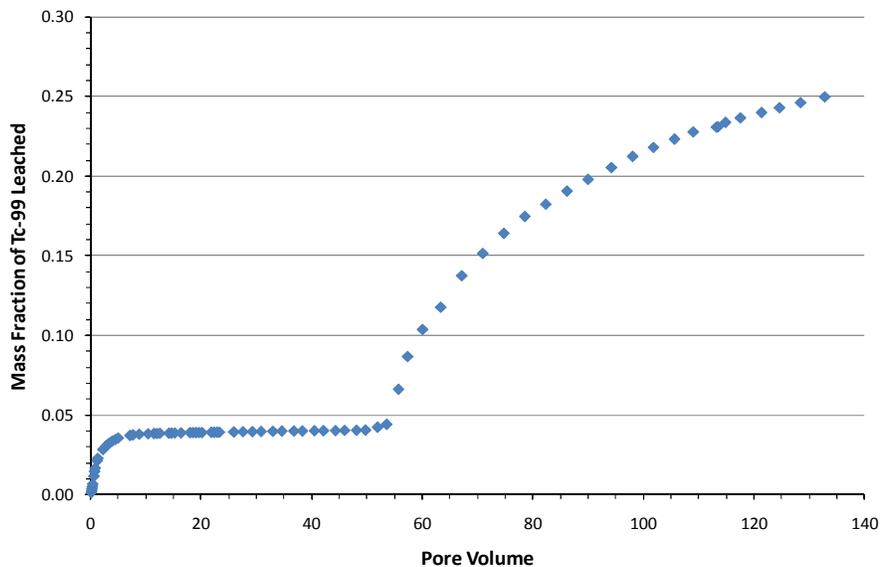


Figure 2: Cumulative mass fraction of Tc-99 leached from the saltstone simulant

Acknowledging that the spatial and temporal variation in chemical conditions along the column flow path is complex, it appears that the release of Tc-99 corresponded to the step increase in Eh that occurred at approximately 42 pore volumes. The speciation diagram with the experimental Eh and pH values graphed in Figure 3 indicates that Tc-99 may have been reduced earlier in the experiment but is expected to have transitioned from technetium IV to the more soluble technetium VII as the Eh increased. Although it is not clear why the release of Tc-99 lagged behind the step increase in Eh, additional research is being conducted to better understand the chemical changes and the corresponding Tc-99 release mechanisms.

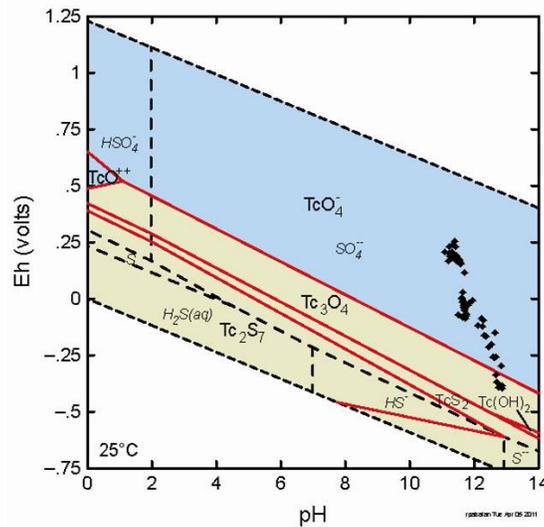


Figure 3: Eh–pH diagram of technetium speciation and experimental Eh and pH values

Although this study indicates that technetium was initially reduced and retained in the simulated saltstone prior to partial oxidation and release, NRC staff cautions against drawing conclusions from preliminary research. In addition, the differences between actual field conditions for emplaced saltstone and a simulated laboratory setting may be significant. Efforts were taken to minimize these experimental artifacts; however, it is recognized that certain differences are necessary. The CNWRA and NRC staffs are working to resolve some of these aspects to better understand current and future states of the actual saltstone system with respect to redox-sensitive radionuclides.

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