Contract No:

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Reactive Amendment Saltstone (RAS): A Novel Approach for Improved Sorption/Retention of Radionuclides such as Technetium and Iodine

This project focused on the application of reactive amendments to saltstone for improving the retention of radionuclides. Chemically reactive amendments have been used to improve contaminant retention in aquatic capping systems and have potential to improve the retention properties of saltstone either by incorporation into the bulk saltstone matrix or as a reactive barrier between saltstone and the environment. Improved retention of radionuclides in saltstone may lead to a reduction in environmental compliance risk by reducing projected dose associated with the long term release of these radionuclides. Amendments evaluated included activated carbon, hydroxyapatite, and two types of organoclays. Amendments were incorporated into the baseline saltstone formulation (45% slag, 45% fly ash, and 10% cement) on a percentage basis by reducing the amount of fly ash contained in the baseline formulation by a proportional amount. Grout samples were batched using salt simulant spiked with non-radioactive surrogates for technetium (rhenium) and iodine (stable iodine). After a minimum 28 day curing period, leachability experiments were conducted to evaluate whether the active amendments improved retention relative to the baseline saltstone formulation. The results of this project suggest that the addition of the two types of organoclays (up to 10%) improved retention of rhenium and to a lesser extent iodine in saltstone. Hydraulic and physical property testing showed the incorporation of organoclays (up to 10%) into the saltstone dry blend did not substantially alter hydraulic performance properties. Batch sorption experiments were conducted to determine rhenium partition coefficients (K_d) for the organoclays. These values were used in the current saltstone performance assessment model to investigate the benefits of incorporating active amendments into the saltstone dry blend and to investigate the benefits of using active amendments as a reactive barrier between saltstone and the environment.

Reactive Amendment Saltstone: A Novel Approach for Improved Sorption/Retention of Radionuclides such as Technetium and Iodine

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Thrust Area: (e.g., ST1, ST2, ST3)
ST1

Project Type: Standard

Project Start Date: October 1, 2014
Project End Date: September 30, 2015

Low-level radioactive waste at the Savannah River Site (SRS) is blended with a mixture of cementitious materials and pumped into storage vaults where it hardens into a monolith known as saltstone. The release of radionuclides, particularly technetium (^{99}Tc) and iodine (^{129}I), into the environment from saltstone is a concern because these radionuclides are the primary contributors to dose. This study examined the use of reactive amendments (hydroxyapatite, activated carbon, and two types of organoclays) that prior research suggests may improve retention of ^{99}Tc and ^{129}I. Tests were conducted using surrogates for ^{99}Tc ($NaReO_4$) and ^{129}I (NaI). Results showed that adding up to 10% of organoclay improved the retention of Re without adversely impacting hydraulic properties. To a lesser extent, iodine retention was also improved by adding up to 10% organoclay. Numerical modeling showed that using organoclay as a reactive barrier may significantly retard ^{99}Tc release from saltstone disposal units.

FY2015 Objectives

The main objective of this project was development of reactive amendment saltstone (RAS) formulations using novel sequestering agents that will improve retention of Tc and I in saltstone. More specific objectives of this project were the following:

- identification of active amendments based on previous research for incorporation into the existing saltstone dry blend,
- development of multiple formulations of reactive amendment saltstone (RAS),
- experimental identification of RAS formulations that strongly sorb and retain ^{99}Tc and ^{129}I ,
- evaluation of basic physical and hydraulic properties of RAS, and lastly to
- conduct numerical modeling to demonstrate the selected RAS benefit of improving ^{99}Tc and ^{129}I retention over model time scales

Introduction

The U.S. Department of Energy (DOE) has made a substantial investment in the treatment and disposal of radioactive liquid wastes stored in tanks at the Savannah River Site (SRS). Multiple treatment processes are employed that result in both high and low-level liquid radioactive waste streams. The low-level waste stream is blended with a mixture of cementitious materials at the Saltstone Processing Facility (SPF) and pumped into storage vaults where it hardens into a cement monolith. The release of radionuclides, particularly iodine (^{129}I) and technetium (^{99}Tc), into the environment from saltstone is a primary concern (SRR, 2014). The most recent Special Analysis (SA) conducted for the Saltstone Disposal Facility (SDF) identifies ^{129}I and ^{99}Tc as the primary contributors to dose (SRR, 2014).

Dose from ^{129}I and ^{99}Tc is strongly influenced by the partition coefficient (K_d) value over the model time scale (10000 years). Early in the life cycle of saltstone, reducing conditions prevail due to the slag, fly ash, and cement contained in the saltstone dry blend. Under reducing conditions, the speciation of Tc is dominated by Tc(IV) forming relatively low solubility compounds. For example, at cementitious conditions, the solubility of $TcO_2 \cdot 1.6H2O$ (a commonly assumed phase) is approximately 1E-8 moles/liter. Under reducing conditions Tc can also form low solubility sulfide compounds, if sufficient reduced sulfur is available. Under reduced conditions, Tc is precipitated and not very mobile. In oxidizing conditions, Tc(VII) exists as pertechnetate (TcO_4^-) which is soluble and only weakly sorbs to soils. Thus, under oxidizing conditions, Tc is typically highly mobile due to its low partition coefficient (<1.0 ml/g). Improving the partition coefficient of Tc may significantly reduce dose over the model timescales.

Chemically reactive amendments have been used to improve contaminant retention in active capping systems (Knox et al. 2014) and have potential to improve the retention properties of saltstone. Additionally, Li et al. (2014) demonstrated the effectiveness of several active amendments (i.e. sorbents) at removing ^{99}Tc and ^{129}I from groundwater. The objectives of this project were to examine the use of active amendments as additives to the existing saltstone dry blend and to examine the use of active amendments as a reactive barrier to reduce the flux of ^{99}Tc and ^{129}I from saltstone disposal units.

Approach

Four active amendments were selected for incorporation into the existing saltstone dry blend – hydroxyapatite, activated carbon, organoclay-OCB (ClayFloc™ 750), and organoclay-MRM™ (Figure 1).

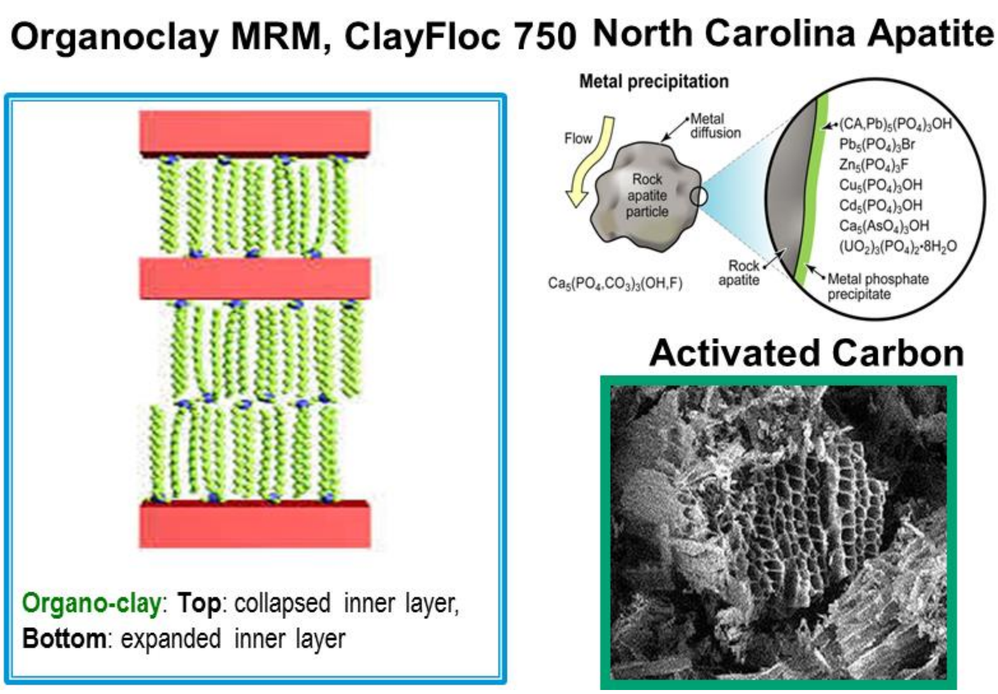

Figure 1 - Amendments tested for development of RAS.

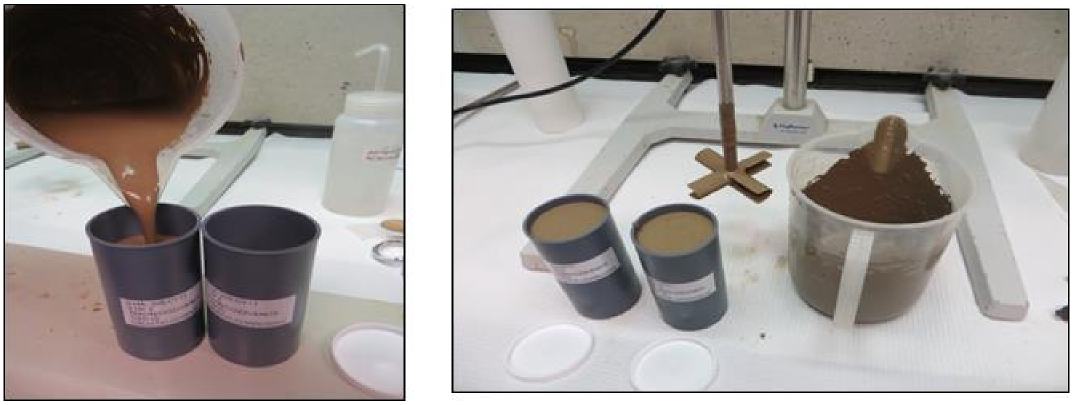

Figure 2 - Preparation of RAS formulations.

Saltstone dry blend is comprised of 45% blast furnace slag, 45% fly ash, and 10% Portland cement. Active amendments were incorporated into the saltstone dry blend on a weight percentage basis by replacing an equivalent amount of fly ash. Eleven formulations, with up to 10% active amendment, were batched with salt simulant spiked with non-radioactive surrogates for ^{99}Tc ($NaReO_4$) and ^{129}I (NaI). Samples were poured in 2x4 inch plastic molds and allowed to cure for at least 28 days at ambient temperature under laboratory conditions (Figure 2). Following the minimum 28 day curing period, samples from each formulation were crushed to yield a sand fraction and subjected to EPA 1311 toxicity characteristic leaching protocol (TCLP) testing using extraction fluid 1, extraction fluid 2, and a 10% nitric acid fluid (Figure 3). Aliquots from the leaching tests were submitted for both rhenium and iodine analysis. For rhenium analysis, samples were analyzed by Inductively Coupled Plasma–Atomic Emission Spectrometry (SRNL, 2014). For iodine analysis, samples were analyzed by Gas Chromatography–Mass Spectrometry (Zhang, 2010). The results from the TCLP testing were used as a screening tool to identify the most promising amendments. Based on the TCLP results, batch sorption experiments were conducted similar to those described by Li et al. (2014) except that spiked salt simulant was used as the test fluid rather than simulated groundwater. Sorption to the selected amendments was calculated as described by Li et al. (2014). Sorption coefficients determined from these experiments were used in the existing saltstone performance assessment (PA) model to demonstrate potential benefit (i.e. dose reduction) from the incorporation of the active amendments in the saltstone dry blend.

Figure 3 - Two TCLP extractions for screening successful RAS formulations. Sample preparation (gravel and sand fractions) and extraction process (120 samples).

Samples containing the selected active amendments were tested for compressive strength following ASTM C39/C39M and hydraulic conductivity following ASTM D-5084 (Figure 4). The results of these tests were compared to the properties of the baseline saltstone formulation to identify impacts to performance properties associated with incorporation of the active amendments into the saltstone dry blend.

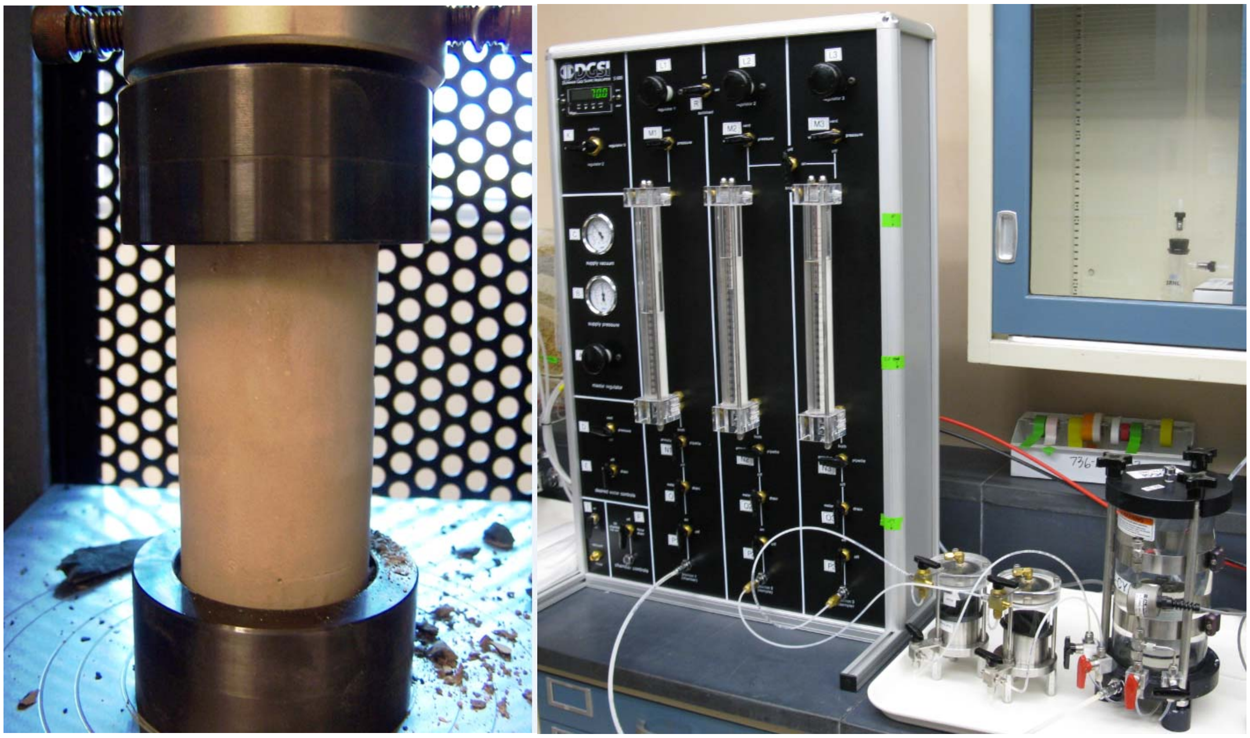

Figure 4 - Uniaxial compressive strength and hydraulic conductivity of RAS was measured following ASTM methods.

Results/Discussion

Identification of RAS formulations that strongly sorb and retain ^{99}Tc and ^{129}I

Multiple extractions were performed on the 11 RAS formulations loosely following the EPA 1311 TCLP procedure. Extractions were initially performed using the standard TCLP extraction fluids and subsequently using a 10% nitric acid fluid for selected amendments. These extracts were selected to assure performance of RAS formulations under changing conditions (pH and redox); these conditions determine Tc and I speciation and their retention in saltstone as indicated by Kaplan (2009) and Li and Kaplan (2012). Analytical results from these leaching experiments indicate that organoclay-OCB and organoclay-MRM™ have the most potential for improving sorption and retention of Tc and to a lesser extent I (Figures 5-7) even under drastically changing pH values from 12 to 2.

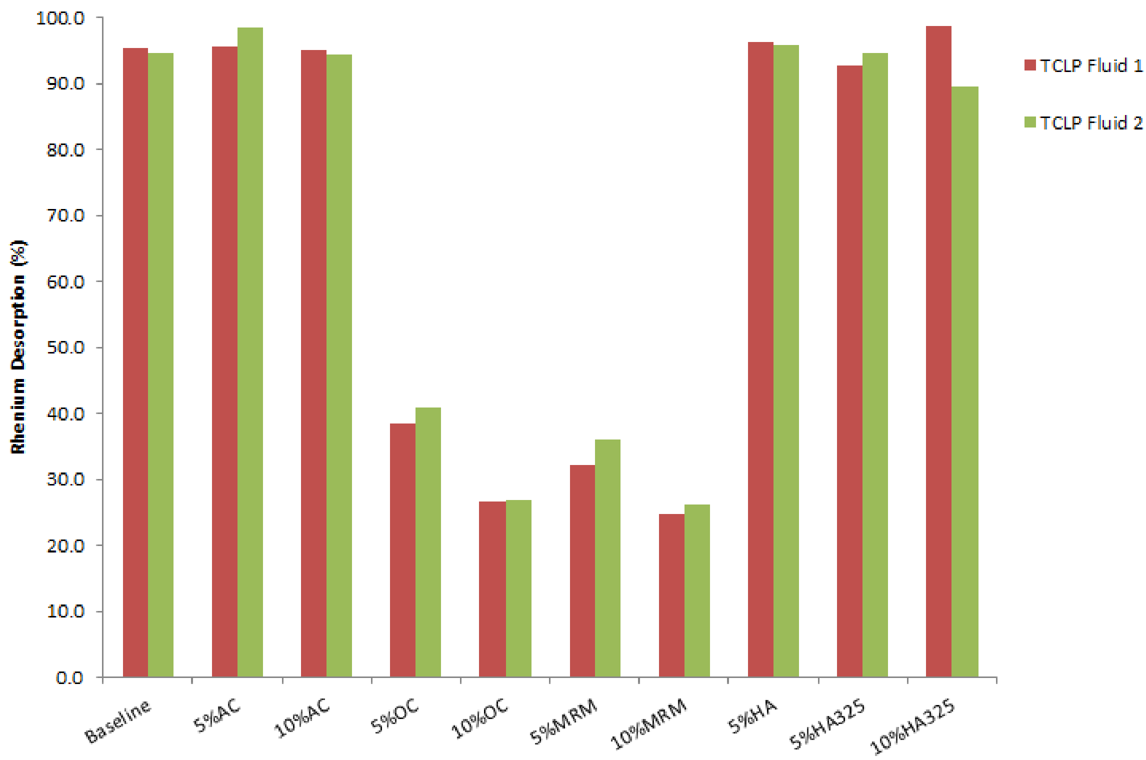

Figure 5 - Desorption percentage of rhenium from baseline and RAS formulations with active amendments based on two TCLP Extraction Fluids, fluid 1 and 2 with the final pH 12 and 10 after contact with saltstone or RAS, respectively.

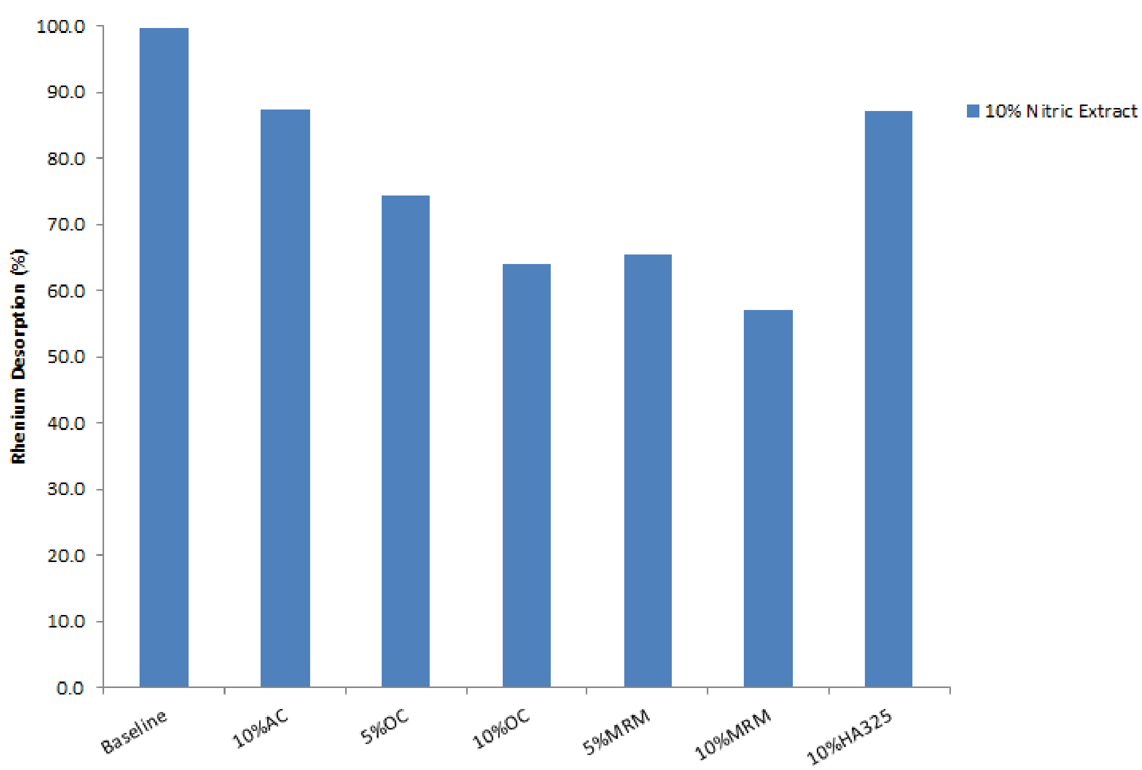

Figure 6 - Desorption percentage of rhenium from active amendments using 10% nitric extract.

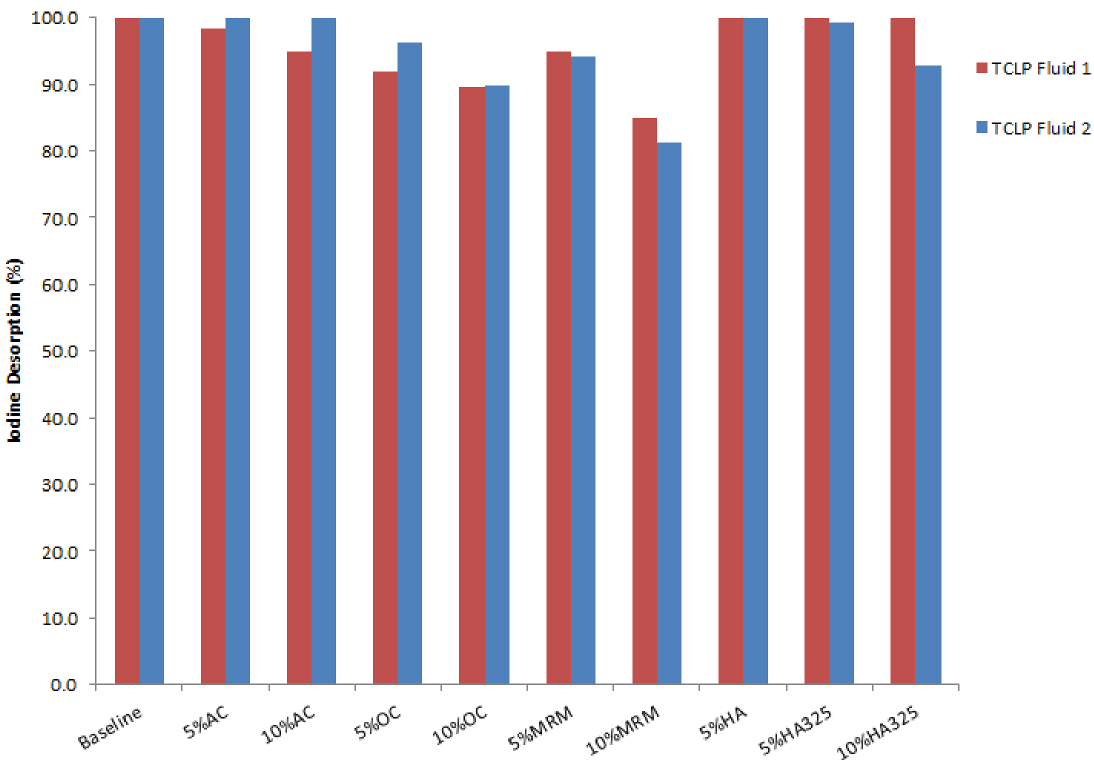

Figure 7 - Desorption percentage of iodine from baseline and RAS formulations with active amendments based on two TCLP Extraction Fluids, fluid 1 and 2 with the final pH 12 and 10 after contact with saltstone or RAS, respectively.

Based on the results of the desorption experiments, organoclay-OCB and organoclay-MRM^{TM} were selected as the most promising amendments. Batch sorption experiments were conducted with these amendments using spiked salt simulant. Iodine analysis proved problematic and as a result no useful iodine data were obtained from the sorption experiments. Sorption coefficients were calculated for rhenium using 10 replicates for each amendment. The calculated rhenium sorption coefficients for organoclay-OCB and organoclay-MRM^{TM} were 29.1 (pH~13) and 48.5 ml/g (pH~13), respectively (Figure 8).

Hydraulic and Physical Properties

Samples containing 10% organoclay-OCB, organoclay-MRM^{TM}, and the baseline saltstone formulation were tested for compressive strength and hydraulic conductivity. The compressive strength data are shown in Table 1. The compressive strength of typical SRS saltstone (28 day cure) has been reported by Reigel et al. (2012) as approximately 1850 psi and the minimum requirement for saltstone is 500 psi. Compared to typical saltstone, all three formulations substantially exceeded the strength of typical saltstone including the baseline mix. This may be partially explained by the longer curing period for the samples tested for this project (>90 days compared to >28 days). Although the addition of 10% organoclay (OCB and MRM^{TM}) resulted in a reduction in compressive strength compared to the baseline formulation, both mixes substantially exceeded the minimum required 500 psi.

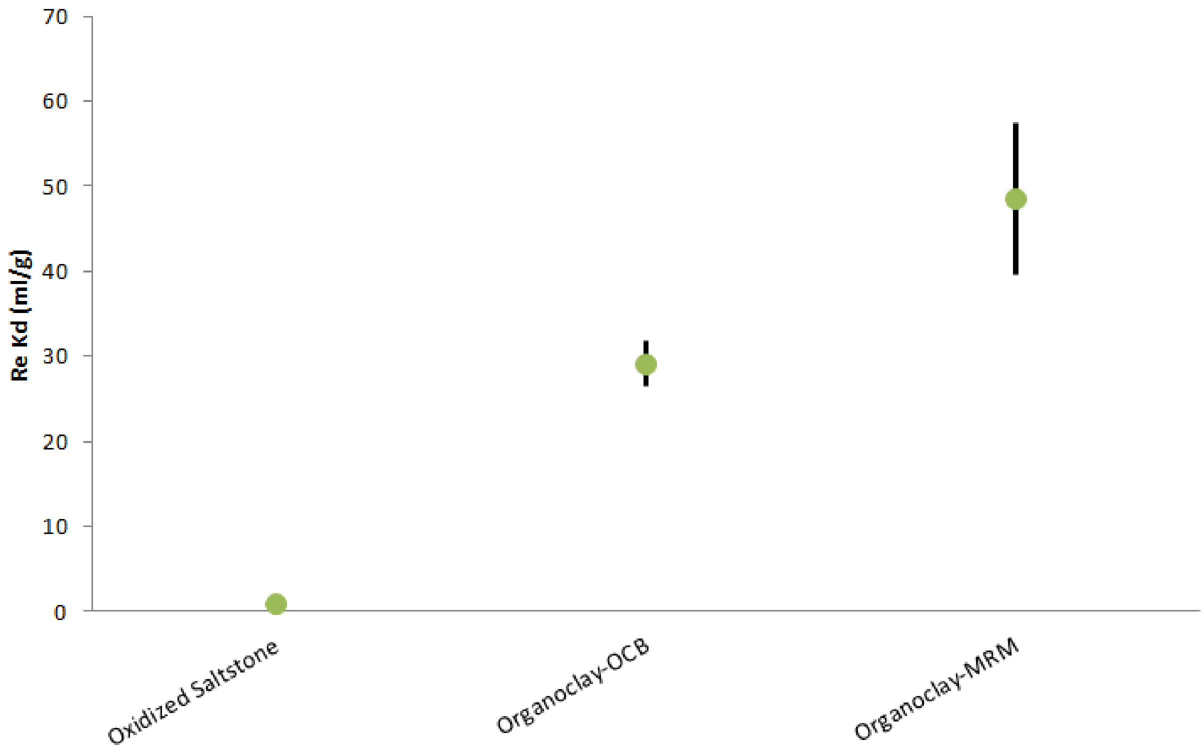

Figure 8 - Rhenium partition coefficients for organoclay-OCB and organoclay-MRM in salt simulant compared to oxidized saltstone.

Table 1. Compressive Strength and Hydraulic Conductivity Data for Test Mixes

Mix ID	> 90-day Compressive Strength (psi)	Hydraulic Conductivity (cm/sec)
Baseline	4599	3.4E-08
10% Organoclay-OCB	2797	1.0E-09
10% Organoclay-MRM	2947	1.5E-08

Hydraulic conductivity tests were conducted on the two formulations containing 10% organoclay (OCB and MRM^{TM}) and the baseline formulation (Table 1). The hydraulic conductivity of typical SRS saltstone is reported as 2.0E-09 cm/sec (Reigel et al. 2012). However, the hydraulic conductivity of saltstone varies considerably as a function of compositional and operational factors and can span more than two orders of magnitude depending on factors such as curing temperature, length of curing, water to premix ratio, and simulant content (Reigel et al. 2011). The hydraulic conductivity of the baseline formulation tested for this project was somewhat higher than typical SRS saltstone. The addition of 10% organoclay (OCB and MRM) did not appear to adversely impact hydraulic conductivity.

Performance Assessment Implications

Figure 9 depicts PORFLOW simulation results at 15,000 years for Tc-99 transport, dissolved oxygen transport, and reduction capacity consumption for a representative Saltstone Performance Assessment (PA) modeling case (SRNL-STI-2014-00505 Rev. 0). Also, shown is the Tc-99 molar transport rate to the water table from 1000 to 100,000 years. The PA analysis assumes a solubility limit of 1.e-8 mol/L and negligible sorption (Kd = 0.01 mL/g) in cementitious materials under reducing conditions, and minimal sorption under oxidizing conditions (Kd = 0.5 mL/g). Through 30,000+ years,Tc-99 is released from the bottom of the Saltstone at solubility. In the upper portion of the grout, dissolved oxygen infiltration consumes reduction capacity. Tc-99 released from the upper grout zone migrates downward into the reduced grout region and is recaptured via the solubility limit. The increasing Tc-99 release to the water table is due to increasing advective flow through grout; the concentration is essentially fixed at the solubility limit. When the oxidation front breaks through the bottom of the disposal unit, Tc-99 concentrations increase significantly as indicated by the peak release observed after 30,000 years in the lower-right image of Figure 9.

Figure 10 shows the same Tc-99 data from Figure 9 but plotted on linear rather than logarithmic scales and the period 0-10,000 years. Also plotted are the release curves for grout amended with organoclay-OCB and organoclay-MRM™, which are assumed to increase the sorption coefficient under both reducing and oxidizing conditions to Kd = 29.1 and 48.5 mL/g respectively. The organoclay amendments are observed to have no appreciable impact. The reason is the solubility limit under reducing conditions is controlling the concentration of Tc-99 in the lower portion of grout, rather than sorption. This fact can be seen more clearly from Figure 11, which shows the relationships between liquid and solid phase Tc-99 concentration in the PORFLOW simulations. The baseline and organoclay sorption coefficients impart varying slopes to the liquid versus solid concentration curves, but all three curves flat-line at 1.e-8 mol/L = 1.e-11 mol/mL due to the solubility constraint. The approximate PA initial condition is shown in Figure 11 and corresponds to an effective Kd of 650 mL/g. Because of the high initial inventory of Tc-99, the solid concentration is high and the liquid concentration is controlled by solubility.

Figure 12 illustrates simulated Tc-99 release when organoclay amendments are present in the concrete barrier surrounding grout. Here the amendments are observed to significantly retard Tc-99 release through several thousand years. The reason is that Tc-99 concentration is controlled by sorption rather than solubility within the initially clean concrete.

Inclusion of organoclay as an amendment to the disposal unit concrete, or as a new permeable reactive barrier, would significantly reduce Tc-99 doses in the 0-1000 year compliance period and beyond.

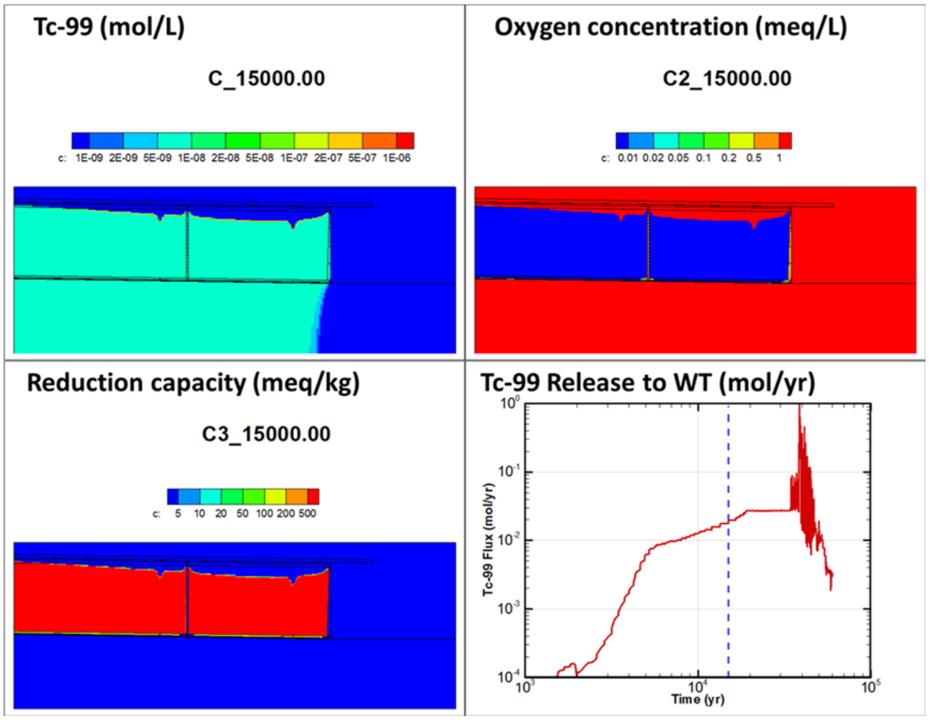

Figure 9 - PORFLOW results at 15,000 years (SRNL-STI-2014-00505 Figure 11-11) for a representative Saltstone Performance Assessment base case simulation.

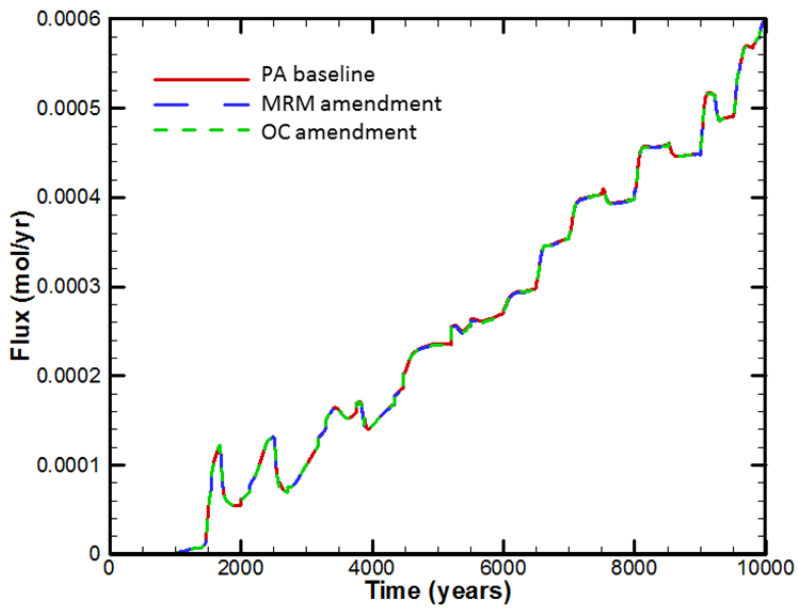

Figure 10 - Tc-99 flux to the water table for the FY14 Saltstone Disposal Unit Column Degradation Sensitivity Analysis modeling case (SRNL-STI-2014-00505), without and with organoclays (MRM and OC) added to grout.

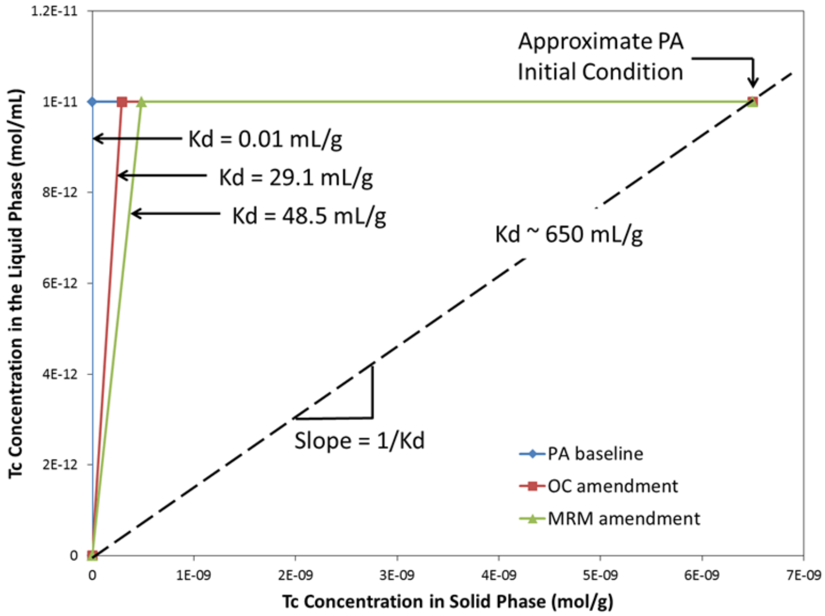

Figure 11 - Relationship between liquid and solid phase Tc-99 concentrations in grout in PORFLOW simulations.

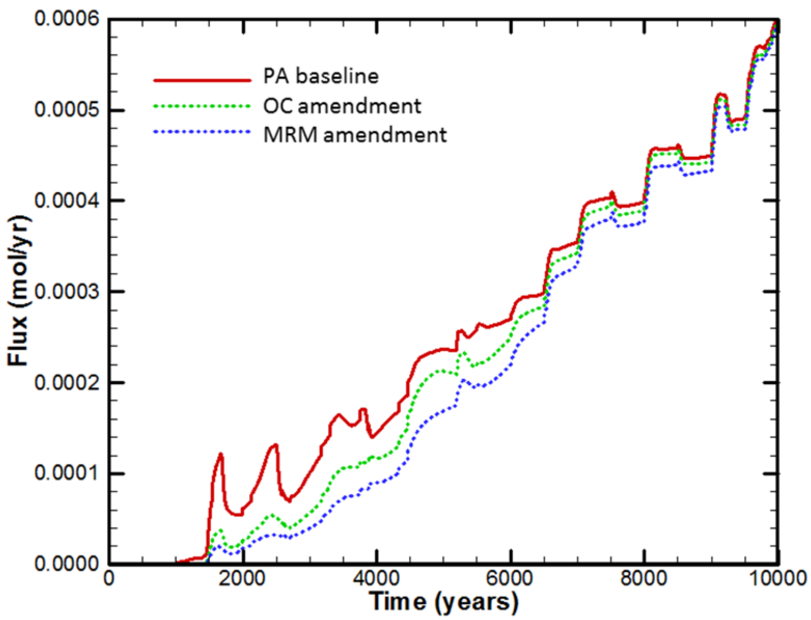

Figure 12 - Tc-99 flux to the water table for the FY14 Saltstone Disposal Unit Column Degradation Sensitivity Analysis modeling case (SRNL-STI-2014-00505), without and with organoclays (MRM and OC) added to concrete.

FY2015 Accomplishments

The primary benefit of this research is a potential reduction in radionuclide mobility achieved through the use of active amendments as a reactive barrier between saltstone and the environment.

The specific accomplishments of the project are the following:

- Identified four active amendments for testing in RAS based on prior research including hydroxyapatite, activated carbon, organoclay-OCB (ClayFloc™ 750), and organoclay-MRM™.
- Developed and batched eleven formulations of RAS with up to 10% (weight percent basis) active amendments.
- Conducted leaching experiments using three different extraction fluids to identify successful formulations of RAS. Organoclay-OCB and organoclay-MRM™ were identified as the most promising for improved retention of technetium and iodine on saltstone.
- Conducted batch sorption experiments using organoclay-OCB and organoclay-MRM™ and spiked salt simulant to determine partition coefficients.
- Measured compressive strength of RAS containing 10% organoclay (OCB and MRM™). Compressive strength of RAS was somewhat lower than baseline but substantially exceeded design criteria of 500 psi.
- Conducted numerical modeling using existing saltstone PA model to investigate potential benefits from incorporating organoclays into the saltstone dry blend.
- Conducted numerical modeling using existing saltstone PA model to investigate potential benefits from incorporating organoclays into reactive barriers.

Future Directions

- Verification of long term sorption/desorption of radionuclides (or surrogates) from RAS and concrete formulations containing organoclays
- Verify partition coefficients used in numerical modeling
- Evaluate the cost of incorporating organoclay into the concrete surrounding saltstone or as a new permeable barrier

FY 2015 Publications/Presentations

1. Presented poster (SRNL-MS-2015-00xxx) at SRNL Annual LDRD Year End Review
2. Dixon, K. L., Knox, A. S., Cozzi, A. D., Flach, G. P., Hill, K. A.. *Reactive Amendments Saltstone: A Novel Approach for Improved Sorption/Retention of Radionuclides such as Technetium and Iodine. Summary Report for LDRD-2015-00001*, SRNL-STI-2015-00476 (in draft).

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Acronyms

AC	Activated Carbon
GC-MS	Gas Chromatography-Mass Spectrometry
HA	Hydroxyapatite
I	iodine
ICP-AES	Inductively Coupled Plasma-Optical Emission Spectrometry
K_d	partition coefficient
M	molar
MRM	Organoclay-MRM
OC	Organoclay-OCB
PRB	permeable reactive barriers
RAS	reactive amendment saltstone
Re	rhenium
SRS	Savannah River Site
Tc	technetium
TCLP	Toxicity Characteristic Leaching Protocol
wt%	weight percent

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None