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Waste Disposal Authority




RESEARCH RESULTS/STATUS-

SAVANNAH RIVER SITE SALT WASTE DISPOSAL NRC ONSITE OBSERVATION VISIT

APRIL 21, 2016

SRR-CWDA-2016-00053, Revision 1

Overview

- **Property data for cores extracted from SDU Cell 2A (SDU2A) compared to laboratory-prepared simulant samples, and PA input values (SRNL).**
  - Density, porosity, water content.
  - Saturated hydraulic conductivity.
  - Radionuclide leaching behavior ⇨ solubility and/or liquid-solid partitioning (ground samples).
- **Leaching behavior of radionuclides from monolithic SDU2A cores and Tc-spiked saltstone simulant (SREL).**
  - *EPA Method 1315* – intact samples submerged in leachate for 63 days with intermittent leachate analysis for radionuclide concentrations.
  - *Dynamic Leaching* –permeant forced through a monolithic sample and radionuclide concentrations in effluent determined.

SDU2A Core Sampling and Analyses

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SDU 2A Core Sampling Objectives

We do the right thing.

- **TASK: Compare the key properties of the following field and laboratory-prepared saltstone:**
  - Actual saltstone mixed in SPF and emplaced/cured in SDU Cell 2A ⇨ Sample Set #9.
  - Simulant saltstone (*non-radioactive*) mixed and cured in the laboratory ⇨ Sample Set #3.

- **OBJECTIVES:**
  - Demonstrate that the properties of laboratory-prepared saltstone are representative of the properties of “actual” saltstone emplaced and cured in the SDU.
  - Validate the saltstone property values used for the PA contaminant transport modeling.

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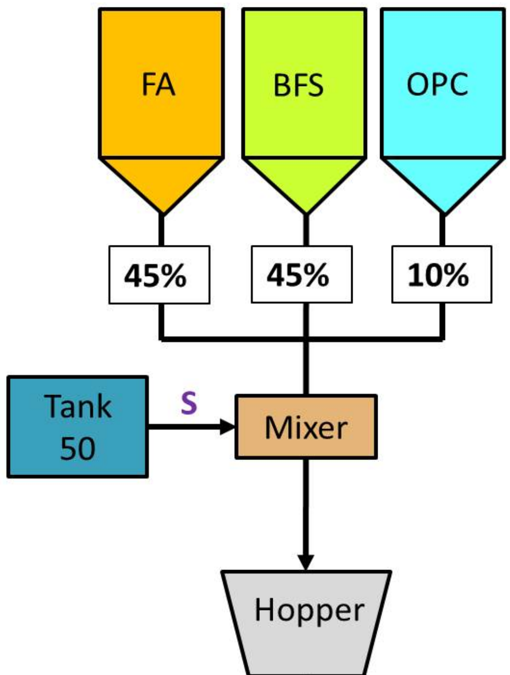
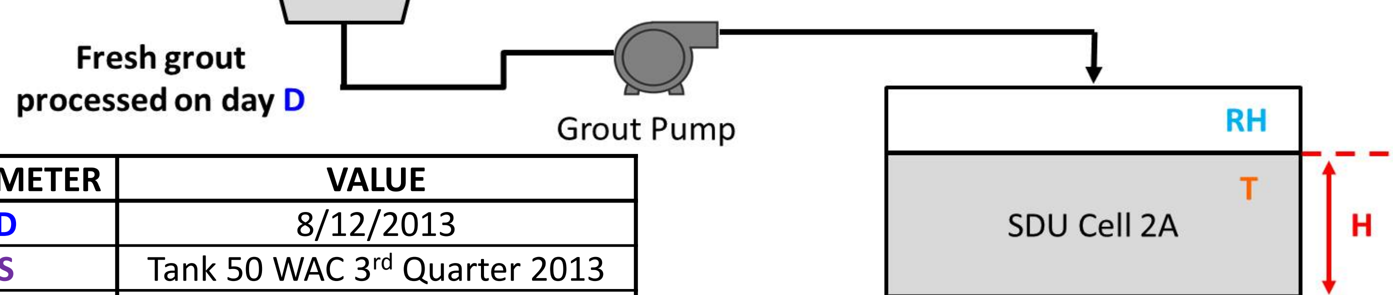
SDU Core Sampling Strategy



- Fresh grout processed in SPF on day **D** with actual Tank 50 salt composition **S** and FA, BFS, & OPC (45/45/10 wt%) dry feeds (**Sample Set #9).**
- Fresh grout from SPF emplaced/cured in SDU2A **(Sample Set #9)**; height **H** of grout in SDU on day **D** is the height from which the core samples were targeted for extraction.
- Fresh grout prepared in laboratory with non-radioactive salt simulant based on composition **S** **(Sample Set #3)** and cured in laboratory.
- Time-dependent temperature profile **T** recorded in SDU2A at height **H** used for laboratory curing.
- Humidity **RH** recorded in SDU2A vapor space used for laboratory curing.



PARAMETER	VALUE
D	8/12/2013
S	Tank 50 WAC 3rd Quarter 2013
H	16’ 0” – 16’ 3”
T	15’ 6” SDU2A Thermocouple
RH	>95%

Simulated Curing Profile

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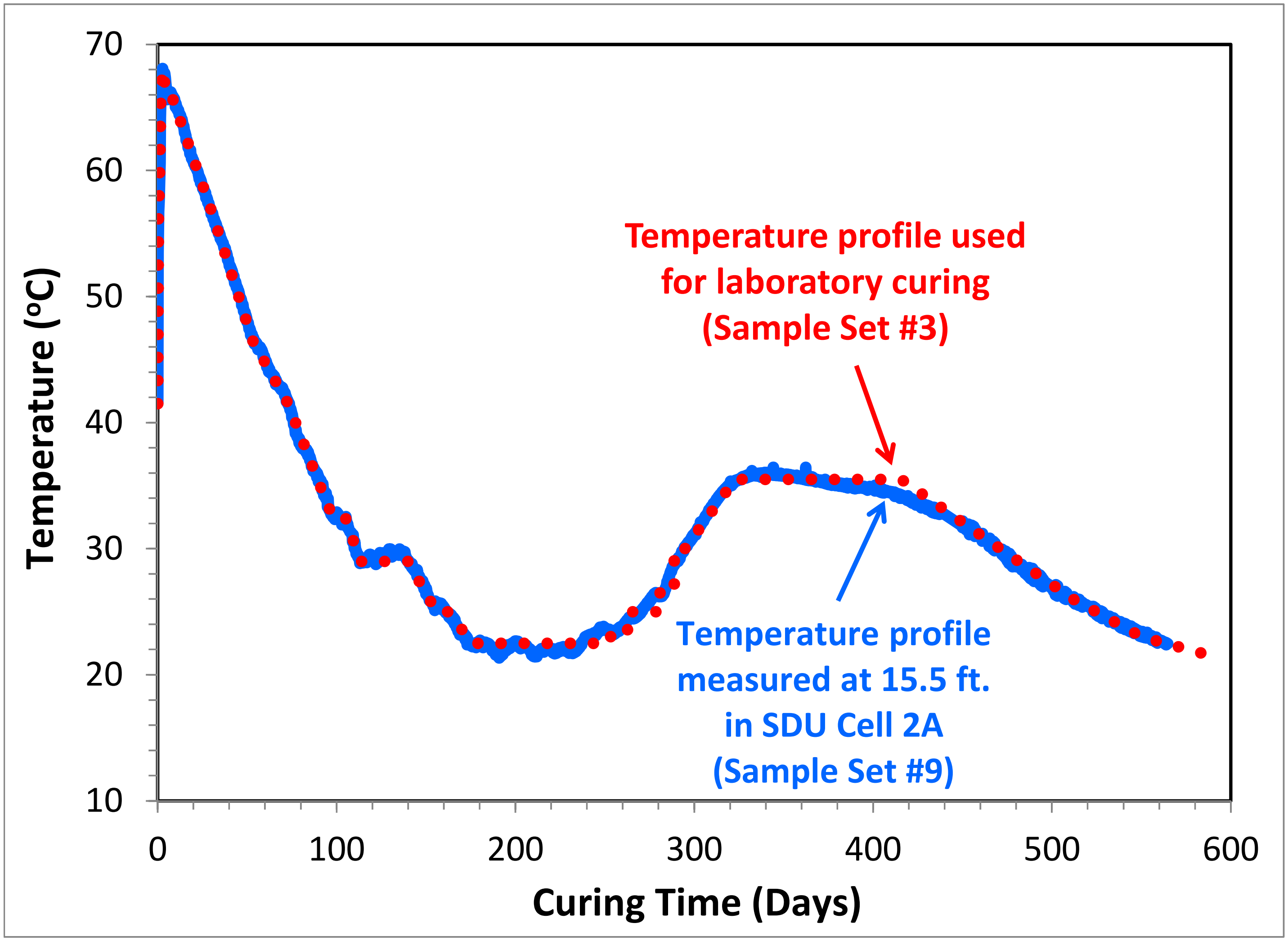
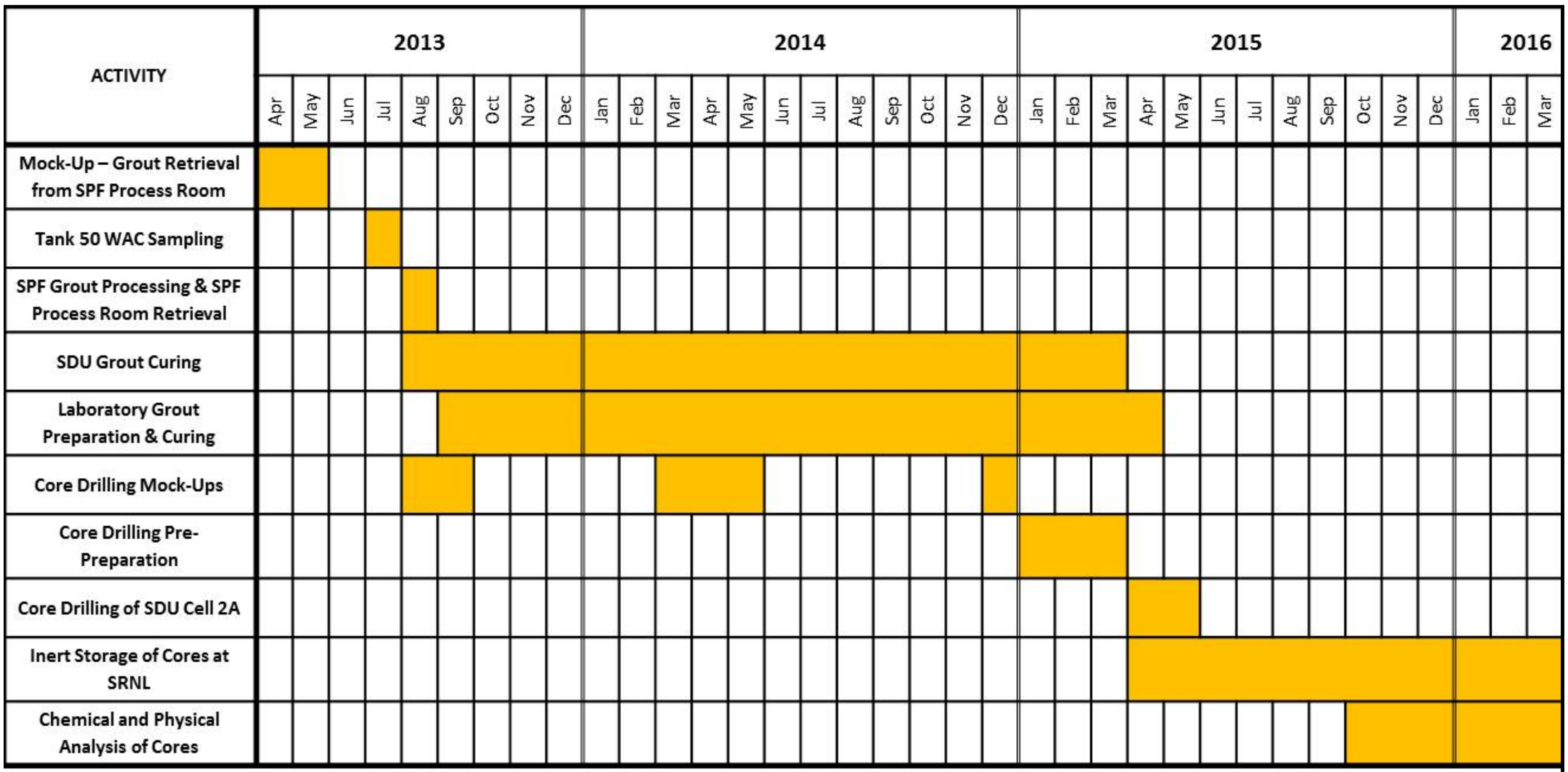


Timeline: SDU2A Core Sampling Strategy

- **Three year endeavor to plan, optimize, extract and analyze cores.**



Sample Extraction and Storage

Cores drilled at 3 SDU ports

~ 7 ft. vertical drill distance: 2 ft. vapor space and 5 ft. grout

Extracted samples maintained in inert environment

Laboratory Anaerobic Chamber

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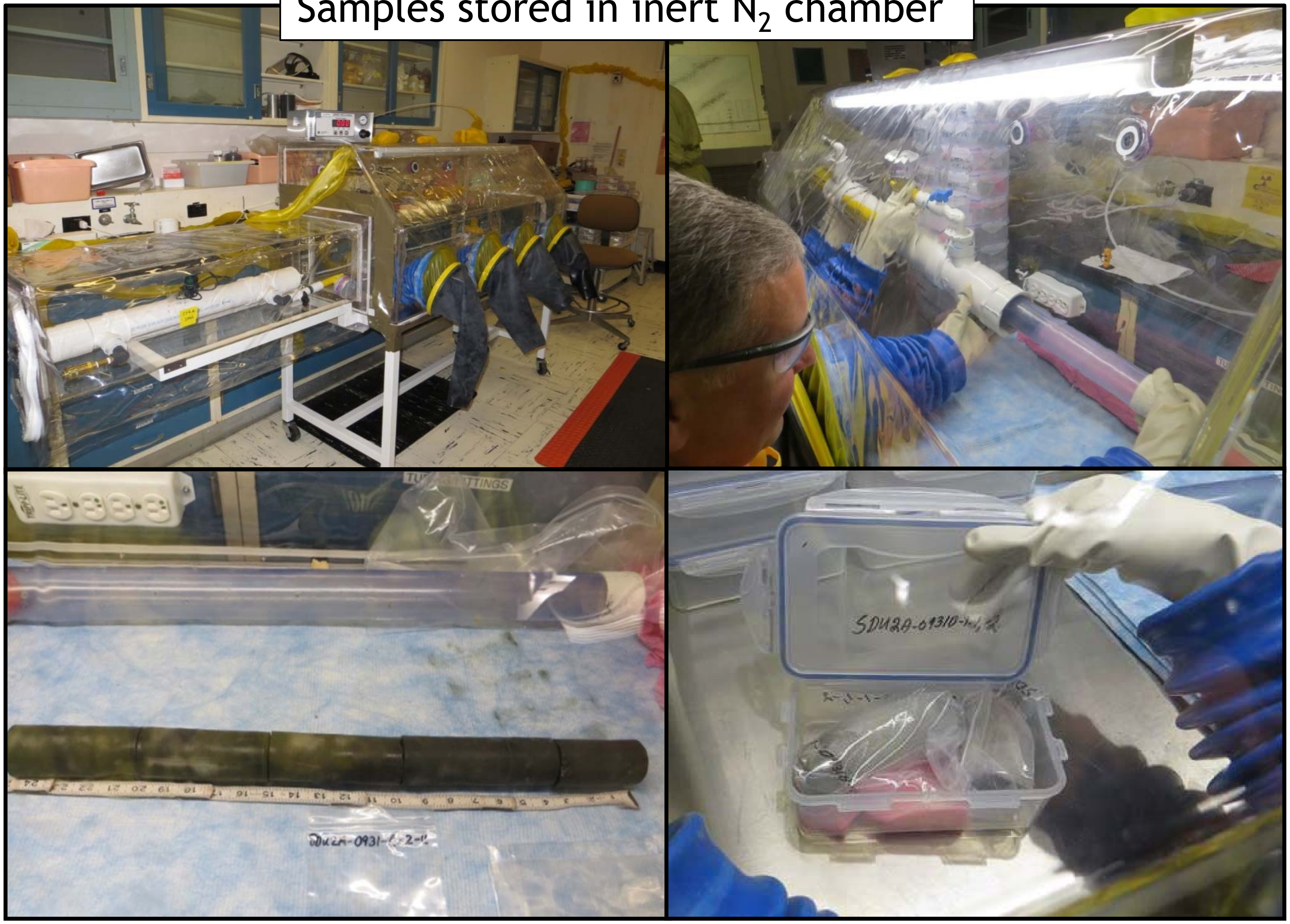
Samples stored in inert N_2 chamber



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Sample Identification

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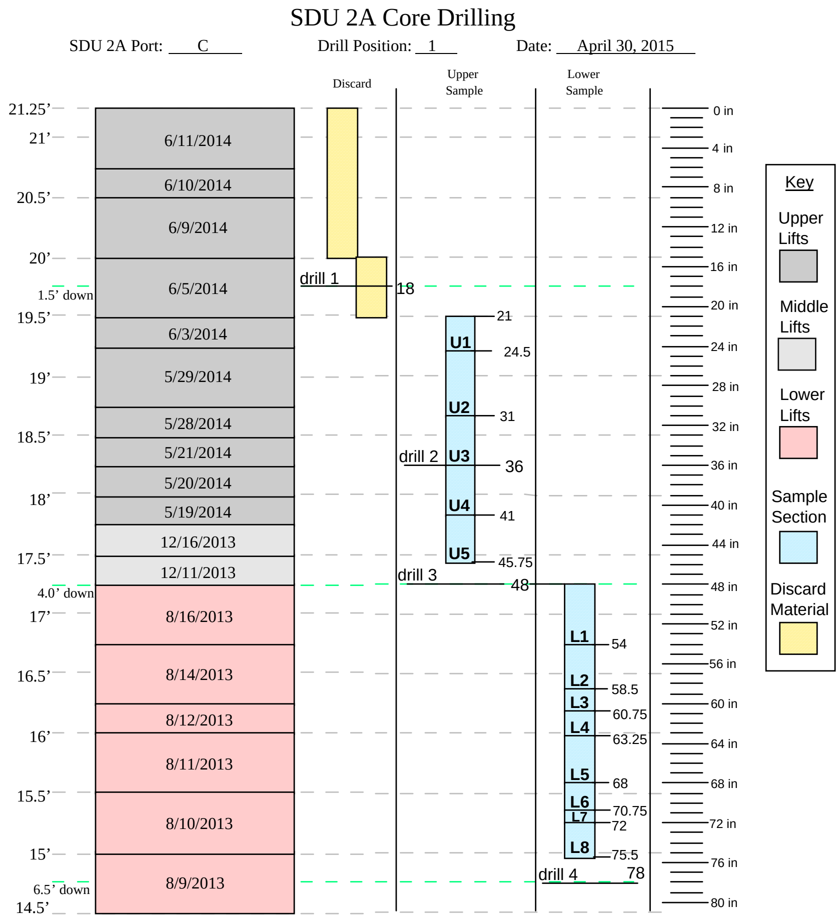
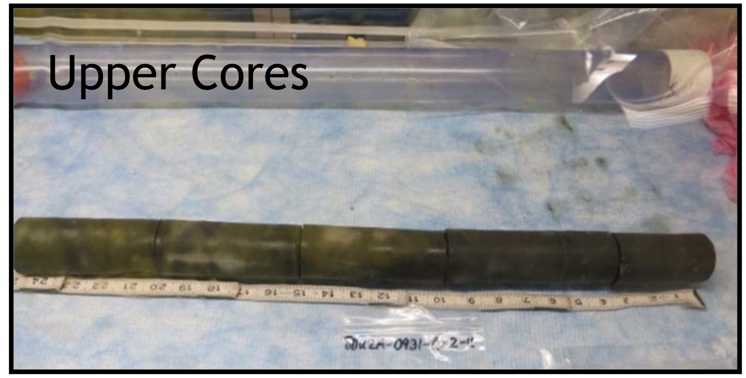


Notes:

Discard	Upper Sample	Lower Sample
First sample section length is 17 inches, hole depth 15 inches. Material has chips (some chips are suspected to have turned in the extraction tube).	Retrieved and discarded additional 6 inches off the top. Upper sample section 24 inches, hole depth 48 inches.	Lower core section length 28.5 inches. Excellent quality. Much like the upper section and clearly better than drill position 1.



- All cores analyzed by SRNL were from lower sections associated with Aug. 10-16th, 2013 pour dates.

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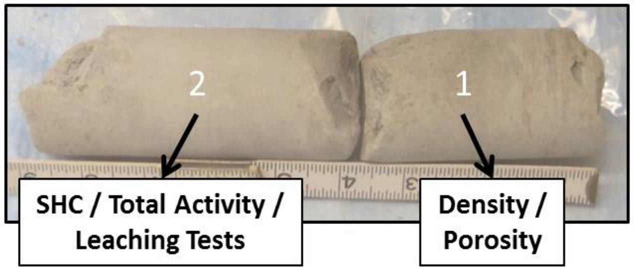
Sample Analyses

PROPERTY	SAMPLE CONFIGURATION	SAMPLE REQUIREMENTS
Density, Porosity, Moisture Content	Fractured samples – exposure to O_2 will not affect data.	Approx. 15 grams
Saturated Hydraulic Conductivity	Cylindrical sample with little or no observable surface damage.	2 in. x 2 in. (D x H)
Total Activity (^{99}Tc, ^{90}Sr, ^{129}I)	Fractured samples – exposure to O_2 will not affect data.	Approx. 45 grams for all isotopes
(^{99}Tc, ^{90}Sr, ^{129}I) leachate concentrations and/or K_d with pH/Eh measurements	Sub-sample removed from interior of intact sample to ensure minimal O_2 exposure – sub-sample ground for measurement. Eh/pH measurements taken on slurry before and after leaching.	Approx. 10 mL for all isotopes – leachate separated for individual isotope measurements

- ^{129}I, ^{79}Se, ^{90}Sr, and ^{99}Tc are designated as radionuclides contained within saltstone that may contribute most significantly to future radiological risks to workers, the public, and the environment.
- In addition, ^{129}I, ^{226}Ra, and ^{99}Tc are the primary contributors with respect to the peak dose to chronic intruders after closure.
- ^{79}Se and ^{226}Ra not evaluated since concentrations consistently <detection limits.

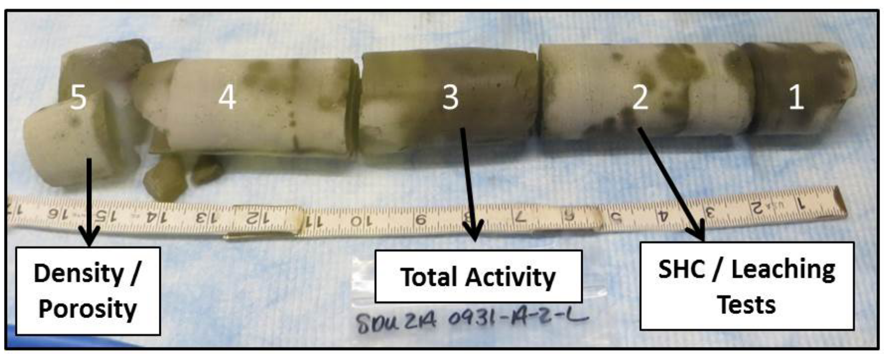
Sample Analyses Designation

SDU2A-0931-B-2-L-1



SDU2A-0931-A-1-L

SDU2A-0931-A-2-L



- All analyses conducted on lower core sections associated with Aug. 2013 pour dates.
- First core extraction attempts were from Port B.
- Due to unexpected drilling difficulties only 2 core pieces were retrieved.
- Two viable cores retrieved from Port A.
- Samples were damaged but intact cores available for SHC.

Sample Analyses Designation

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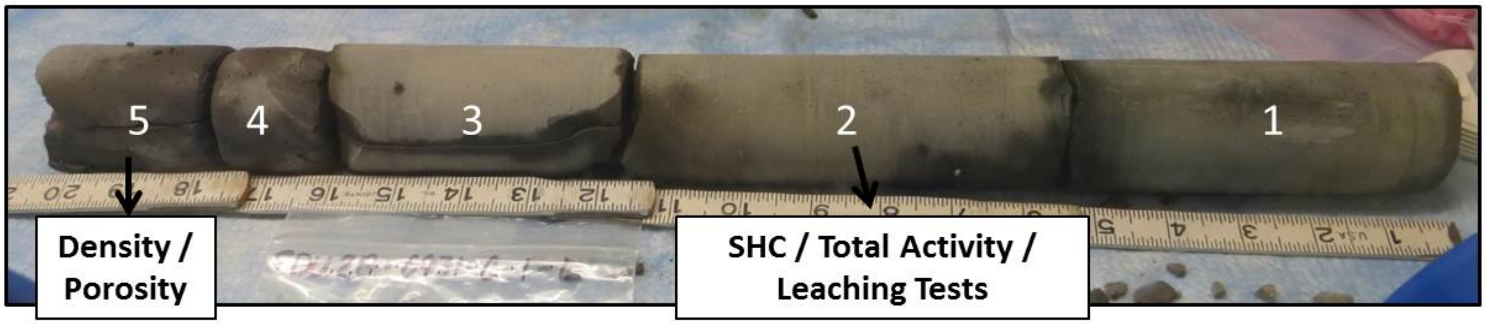
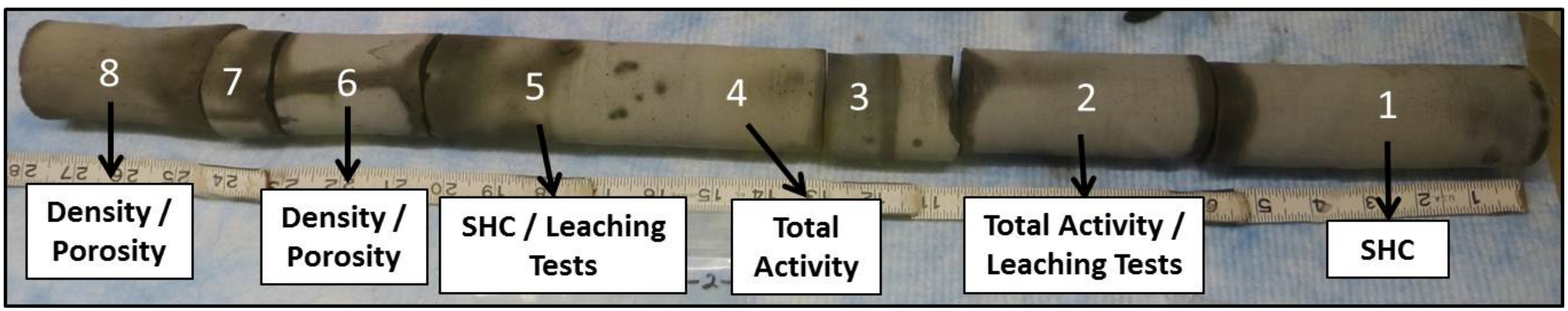
- Optimum cores in terms of physical integrity retrieved from Port C
- Analyses doubled for core from Port C (Hole 2) to compensate for only 1 core extracted form Port B

SDU2A-0931-C-1-L



SDU2A-0931-C-2-L



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Density, Porosity, & Water Content

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Sample ID	Approximate Pour Date and SDU Height	Bulk Density (g/cm^3)	Total Porosity (%)	Permeable Porosity (%)	Water Content (%)
SDU2A-0931-A-1-L-5	08-12-2013 / 16.0 ft	1.72 [0.01]	64.3	45.0 [0.4]	29.8 [0.2]
SDU2A-0931-A-2-L-5	08-12-2013 / 16.0 ft	1.74 [0.00]	63.6	41.9 [0.1]	29.0 [0.2]
SDU2A-0931-B-1-L-1	08-16-2013 / 17.0 ft	1.72 [0.01]	67.3	43.2 [0.2]	31.2 [1.2]
SDU2A-0931-C-1-L-5	08-12-2013 / 16.0 ft	1.76 [0.02]	64.5	42.0 [0.3]	29.1 [0.6]
SDU2A-0931-C-2-L-6	08-11-2013 / 15.5 ft	1.75 [0.04]	66.6	43.3 [1.4]	30.5 [0.9]
SDU2A-0931-C-2-L-8	08-10-2013 / 15.0 ft	1.71 [0.06]	68.8	46.6 [2.1]	32.1 [0.1]
Sample Set 9 (Mean of 18 samples: 6 cores – 3 sub-samples)		**1.73** [0.03]	**65.8** [2.0]	**43.7** [1.8]	**30.3** [1.2]
Sample Set 3 (Mean of 9 samples: 3 cores – 3 sub-samples)		**1.76** [0.01]	**59.8** [0.8]	**40.8** [0.7]	**30.4** [0.1]

- SDU2A cores exhibit sample-to-sample variability.
- Mean density < lab-prepared; mean porosity > lab-prepared.
- Why and what impacts to relevant properties (e.g., higher permeable porosity and effect on SHC)?

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Field vs. Lab Processing

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Parameter	Sample Set #3	Sample Set #9
Dry and Liquid Component Proportions	• Exact mass of each constituent measured in laboratory	• Variable bulk delivery in SPF On 8/12/2013: • Avg. dry feed rate 33.0 ton/hr (± 1%) • Avg. salt soln. feed rate 87.8 GPM (± 2%)
Mixing	• Small scale laboratory batch mixer	• Large scale, continuous mixer
Additional flush Water Added	• Not applicable to laboratory-prepared samples	• Approx. 50 gal. flush water added to clean SPF hopper every 45 min. during processing • Approx. 800-900 gal. flush water added at end of processing
Delivery	• Poured into cylindrical molds from mixing bowl	• Transferred through pipe from SPF to SDU2A via peristaltic pump • Grout allowed to free-fall into SDU2A and spread to extremities
Curing	• All samples cured according to same thermal profile in controlled humidity oven	• Temperature profile of each sample dependent on location in SDU • Prolonged periods between SPF operation may result in water evaporation from monolith surface
Storage	• Samples remained in controlled environment in capped molds until time of prep/testing	• Samples core drilled, extracted from core holes, and stored in inerted transport containers • Upon receipt at SRNL, samples removed from transport containers (inside an inerted N_2, low humidity chamber) and cataloged/photographed prior to placement in sealable containers

SPF Processing Parameters

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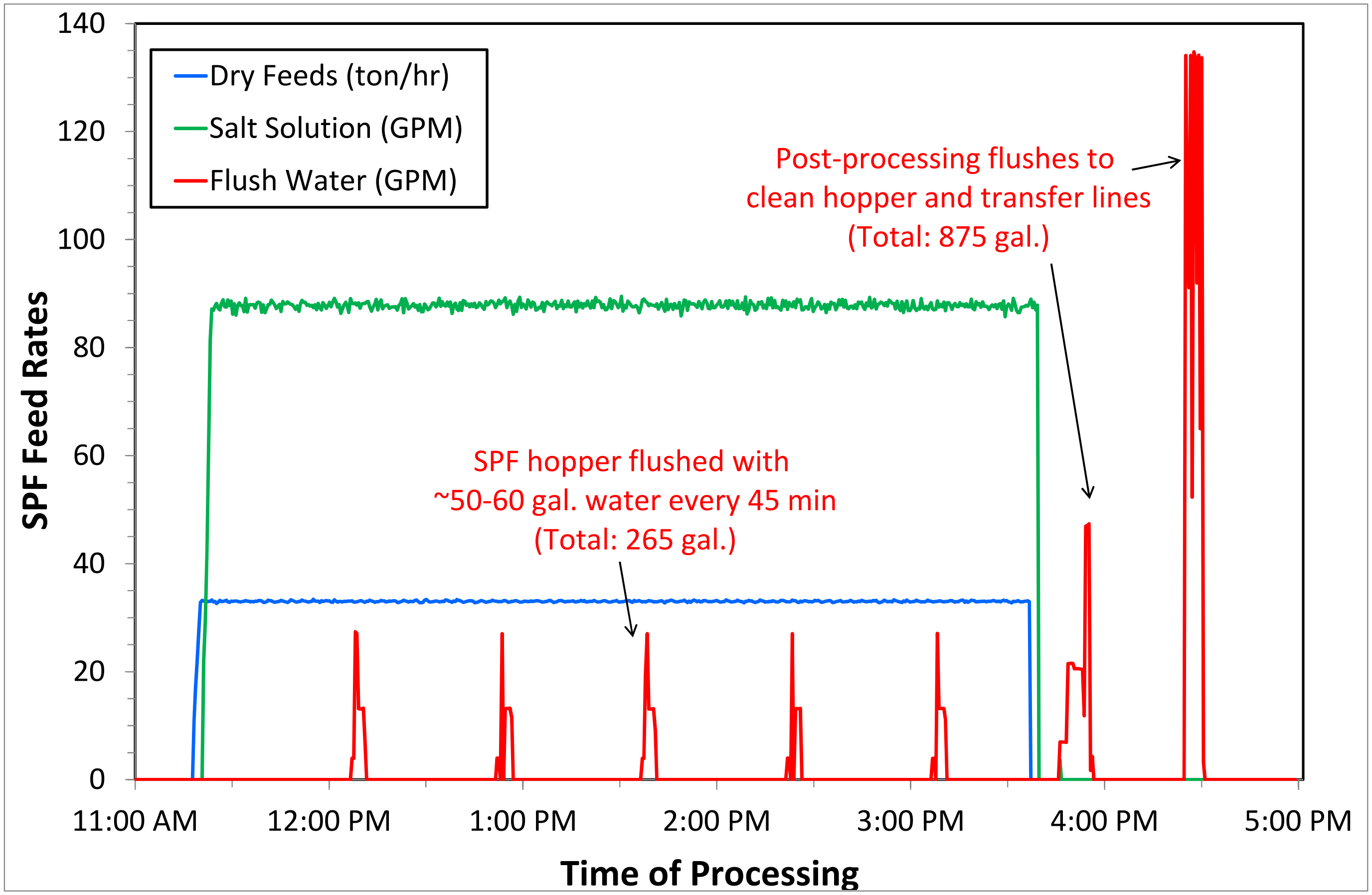

- While some of end-of-day flush water may become incorporated into saltstone much is expected to be removed as drain water or bleed water.

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Saturated Hydraulic Conductivity

Sample ID	Approximate Pour Date and SDU Height	SHC (cm/sec)	Comments on Sample Integrity
SDU2A-0931-A-1-L-3	08-14-2013 / 16.5 ft	1.2E-09	Side defects that could not be excluded when sample sectioned to 2" length
SDU2A-0931-A-2-L-2	08-16-2013 / 17.0 ft	<1.0E-9	No observable surface defects
SDU2A-0931-B-1-L-2	08-14-2013 / 16.5 ft	4.4E-09	Difficult to section without fracturing
SDU2A-0931-C-1-L-2	08-16-2013 / 17.0 ft	<1.0E-9	No observable surface defects
SDU2A-0931-C-2-L-1	08-16-2013 / 17.0 ft	<1.0E-9	No observable surface defects
SDU2A-0931-C-2-L-5	08-11-2013 / 15.5 ft	<1.0E-9	No observable surface defects
Sample Set 9 (Mean of 6 samples)		**<1.6E-09**	4 of 6 samples with no visible surface defects
Sample Set 3 Mean (Mean of 3 samples)		**<1.0E-09**	Demolded samples without surface defects
SDF PA		**6.4E-09**	N/A

- Despite higher permeable porosity for SDU cores impact to SHC is insignificant.
- Cores taken from 3 ports and between 15.5 – 17.0 ft. all demonstrated lower SHC than PA input value.
- Recent SREL data indicates SDU2A core SHCs between 6E-10 and 7E-11 cm/sec.

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Samples used For SHC Testing

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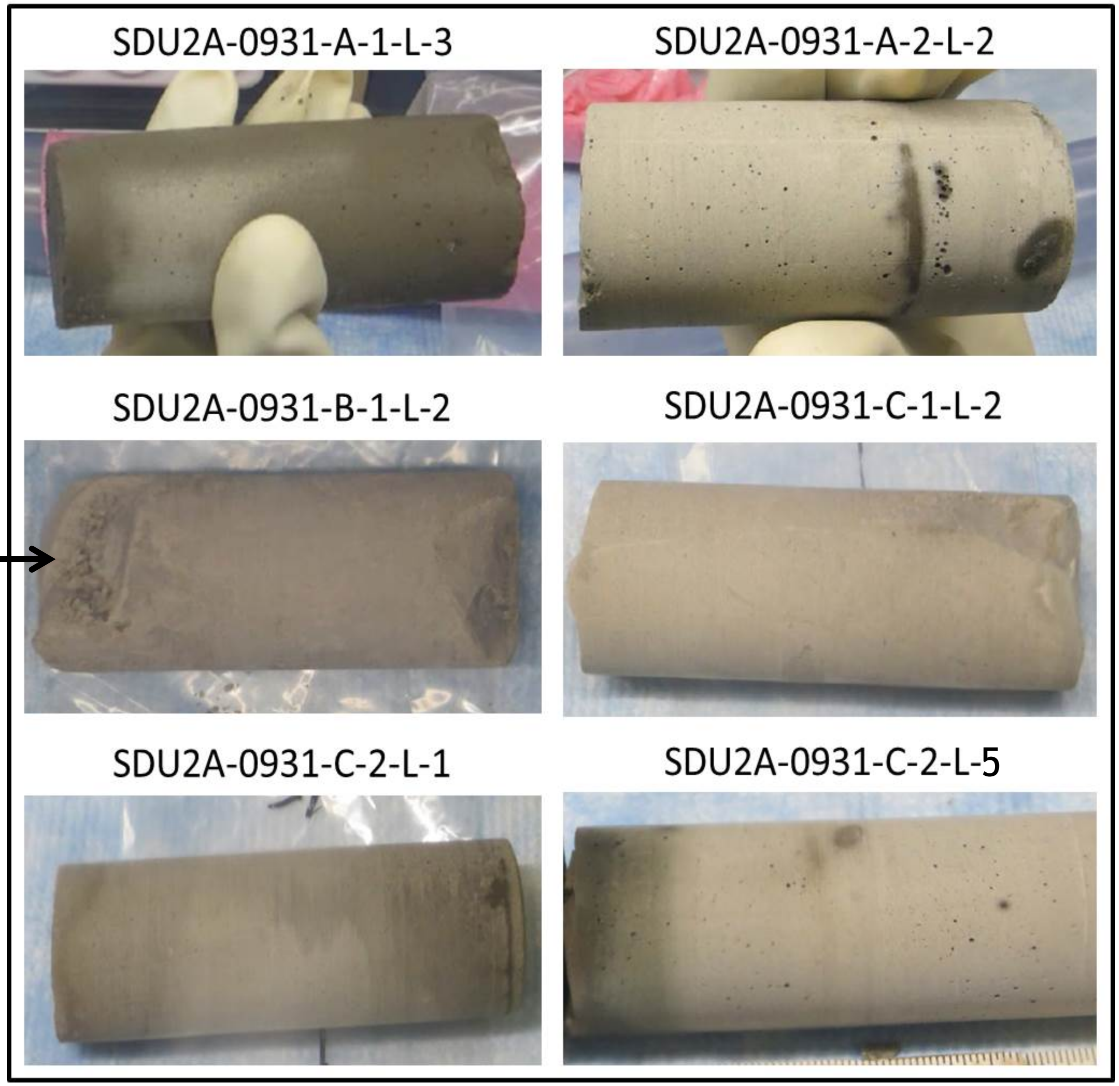
1 useable SHC sample from Port B that spalled/fractured when cutting to 2” length



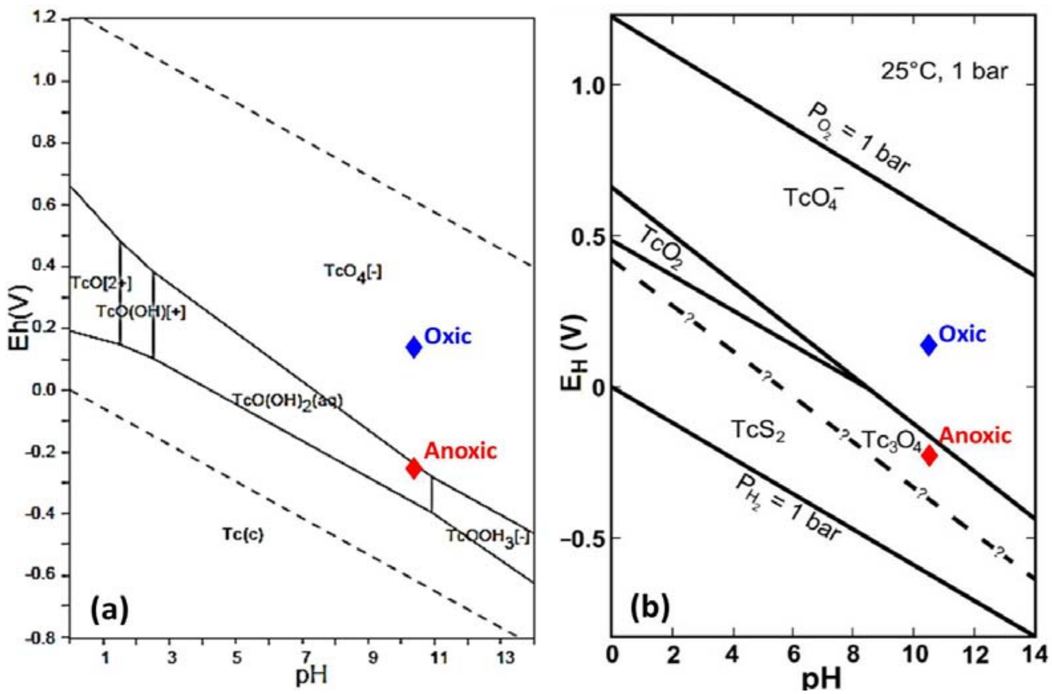
SDU2A Contaminant Leaching Behavior

- Tests involved mixing 1 gram of ground SDU2A core with 10 mL leachate.
- One set of leachates contained (8 ppm - oxic); other set boiled to remove DO (anoxic).
- Samples equilibrated for 7 days and leachates analyzed for ^{99}Tc, ^{90}Sr, ^{129}I, E_h and pH .
- PA transport model:
  - ^{99}Tc assumed to be in reduced, sparingly soluble Tc(IV) form in anoxic, high pH environment ⇨ leaching behavior solubility controlled.
  - In oxic environment Tc(VI) assumed to be transformed to highly soluble Tc(VII) (pertechnetate) ⇨ leaching behavior controlled by adsorption to saltstone particle surfaces environments (liquid-solid partitioning K_d).
  - ^{90}Sr and ^{129}I leaching controlled by adsorption in both oxic and anoxic environments (liquid-solid partitioning K_d).

Tc Solubility

^{99}Tc Solubility - Predicted Tc Species Based on pH-E_h

Sample ID	Approx. Pour Date and SDU Pour Height	Anoxic		Oxic	
		pH	E_h (mV)	pH	E_h (mV)
SDU2A-0931-A-1-L-3	08-14-2013 / 16.5 ft	10.4	-186	10.6	178
SDU2A-0931-A-2-L-2	08-16-2013 / 17.0 ft	10.4	-220	10.8	148
SDU2A-0931-B-1-L-2	08-14-2013 / 16.5 ft	10.4	-222	10.6	146
SDU2A-0931-C-1-L-2	08-16-2013 / 17.0 ft	10.6	-240	10.7	144
SDU2A-0931-C-2-L-2	08-14-2013 / 16.5 ft	10.6	-211	10.8	144
SDU2A-0931-C-2-L-5	08-11-2013 / 15.5 ft	10.5	-220	10.7	170
Sample Set 9 Mean		**10.5**	**-217**	**10.7**	**155**



Tc Solubility Limits

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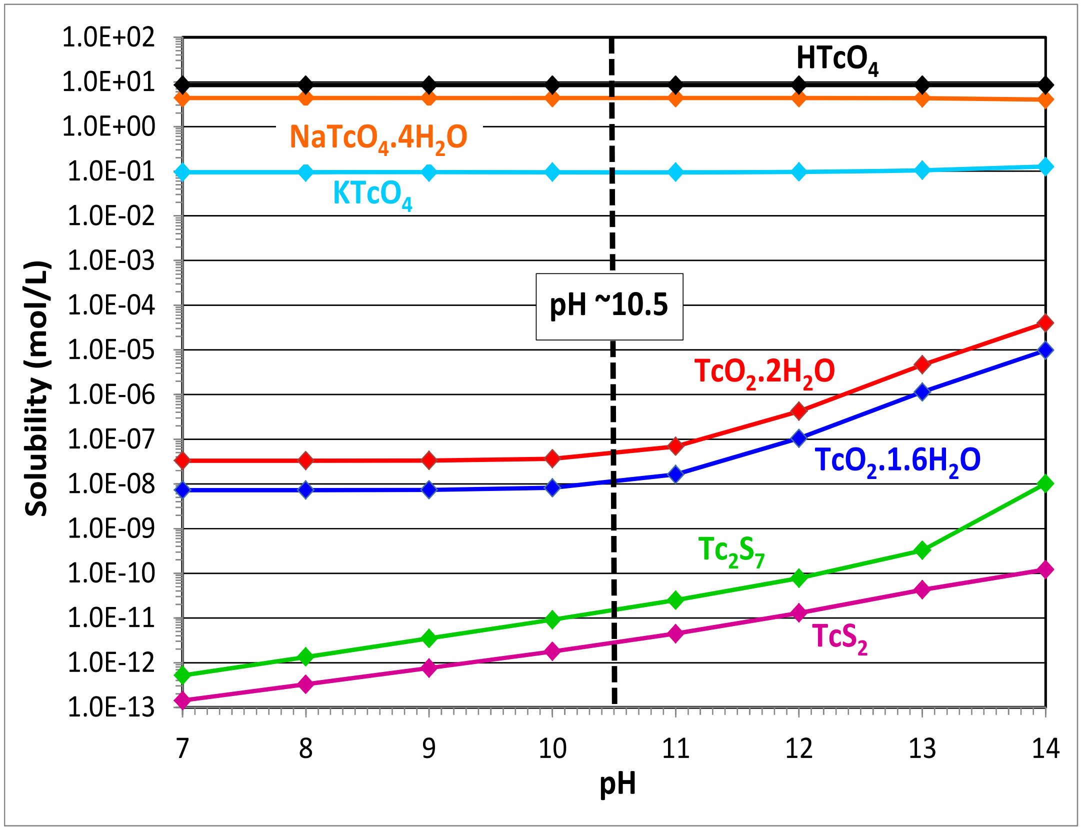


At pH 10.5 Tc species solubility limits are:

TcS_x ⇨ ~3E-12 to 2E-11 mol/L

$TcO_2.xH_2O$ ⇨ ~1E-08 to 6E-08 mol/L

$(TcO_4)^-$ ⇨ ~1E-01 to 1E+01 mol/L

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)).

^{99}Tc Solubility (Anoxic)

Sample ID	Approx. Pour Date & SDU Pour Height	^{99}Tc Conc. (mol/L)	pH	E_h (mV)
SDU2A-0931-A-1-L-3	08-14-2013 / 16.5 ft	<1.16E-08	10.4	-186
SDU2A-0931-A-2-L-2	08-16-2013 / 17.0 ft	3.95E-08	10.4	-220
SDU2A-0931-B-1-L-2	08-14-2013 / 16.5 ft	1.87E-08	10.4	-222
SDU2A-0931-C-1-L-2	08-16-2013 / 17.0 ft	3.32E-08	10.6	-240
SDU2A-0931-C-2-L-2	08-14-2013 / 16.5 ft	2.41E-08	10.6	-211
SDU2A-0931-C-2-L-5	08-11-2013 / 15.5 ft	7.01E-09	10.5	-220
Sample Set 9 Mean		**2.23E-08**	**10.5**	**-217**
SDF PA Transport Model		**1.0E-08**		

- Anoxic ^{99}Tc concentrations ~2.2E-08 mol/L ⇨ suggests leaching behavior is controlled by reduced $TcO_2.xH_2O$ solubility as modeled in PA. Does that mean no pertechnetate $(TcO_4)^-$??
- Number of studies have indicated that 20-30% ^{99}Tc may not be reduced though. **BUT** these studies typically involved spiking with 1-2 orders of magnitude higher proportions of ^{99}Tc to enable XAS analysis.
- For the samples in this study: if, for example, 25% of the ^{99}Tc in the SDU2A cores was soluble $(TcO_4)^-$ the measured ^{99}Tc concentration would be 1E-07 mol/L.
- **Note**: there is not enough ^{99}Tc in the SDU2A cores to challenge the pertechnetate solubility limits.
- PA transport model value factor of 2 less than that measured for SDU2A cores.

^{99}Tc Solubility – Anoxic vs. Oxic

Sample ID	Approx. Pour Date and SDU Pour Height	Anoxic			Oxic		
		^{99}Tc Conc. (mol/L)	pH	E_h (mV)	^{99}Tc Conc. (mol/L)	pH	E_h (mV)
SDU2A-0931-A-1-L-3	08-14-2013 / 16.5 ft	<1.16E-08	10.4	-186	2.62E-08	10.6	178
SDU2A-0931-A-2-L-2	08-16-2013 / 17.0 ft	3.95E-08	10.4	-220	2.53E-08	10.8	148
SDU2A-0931-B-1-L-2	08-14-2013 / 16.5 ft	1.87E-08	10.4	-222	2.03E-08	10.6	146
SDU2A-0931-C-1-L-2	08-16-2013 / 17.0 ft	3.32E-08	10.6	-240	2.27E-08	10.7	144
SDU2A-0931-C-2-L-2	08-14-2013 / 16.5 ft	2.41E-08	10.6	-211	2.16E-08	10.8	144
SDU2A-0931-C-2-L-5	08-11-2013 / 15.5 ft	7.01E-09	10.5	-220	2.42E-08	10.7	170
Sample Set 9 Mean		**2.23E-08**	**10.5**	**-217**	**2.34E-08**	**10.7**	**155**

- ^{99}Tc solubility in oxic conditions equivalent to anoxic conditions; pH-E_h would predict highly soluble $(TcO_4)^-$.
- Suggestive of stable reduced Tc-phase and slow oxidation kinetics in presence of DO.

Liquid-Solid Partitioning (K_d)

Standard (Adsorption) K_d

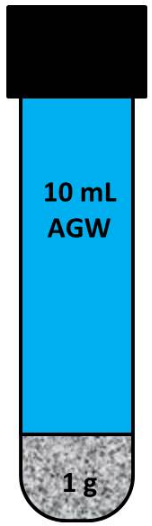
Solid - Liquid "Pseudo" Equilibration: 7 days

START OF TEST

For a standard K_d the total radionuclide activity is associated with the liquid phase at time t = 0

Liquid Phase
- ~10 mL liquid
- An accurately determined amount (X pCi) of Radionuclide A is added to liquid phase

Solid Phase
- ~1 gram ground material
- Measured radionuclide A activity per unit mass = 0 pCi/g



END OF TEST

During solid – liquid equilibration radionuclides may be adsorbed to the solid phase

Liquid Phase
- Measured radionuclide A activity per unit volume: Y pCi/mL
- Total activity = Y pCi/mL x 10 mL = 10Y pCi

Solid Phase
- Calculated radionuclide A activity = (X – 10Y) pCi
- Activity per unit mass:

= (X – 10Y) pCi / 1 gram = (X – 10Y) pCi/g

- $K_d = \dfrac{(X - 10Y)\ \text{pCi/g}}{Y\ \text{pCi/mL}} = \dfrac{(X - 10Y)}{Y}\ \text{mL/g}$

- Accurately known spike amount added to liquid phase.
- Analysis only required to determine radionuclide concentration in post-equilibrated liquid ⇨ inherent analytical uncertainty.

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Reverse (Desorption) K_d

We do the right thing.

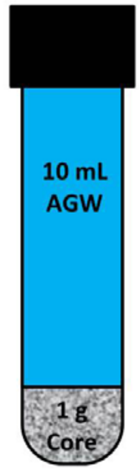
Solid - Liquid "Pseudo" Equilibration: 7 days

START OF TEST

For a reverse K_d the total radionuclide activity is associated with the solid phase at time t = 0

Liquid Phase
- ~10 mL AGW
- Radionuclide A activity per unit volume = 0 pCi/mL

Solid Phase
- ~1 gram ground SDU2A core
- Measured radionuclide A activity per unit mass = X pCi/g
- Total activity = X pCi/g x 1 gram = X pCi



END OF TEST

During solid – liquid equilibration radionuclides may be transferred to the liquid phase

Liquid Phase
- Measured radionuclide A activity per unit volume: Y pCi/mL
- Total activity = Y pCi/mL x 10 mL = 10Y pCi

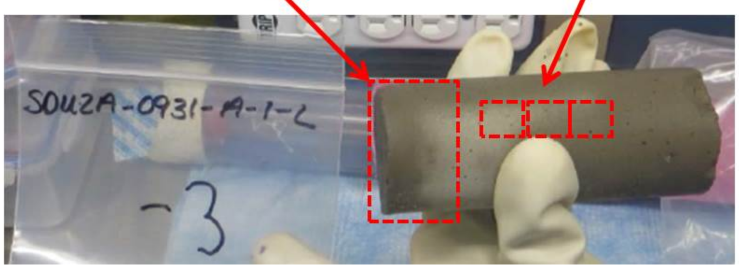
Solid Phase
- Calculated total radionuclide A activity = (X – 10Y) pCi
- Activity per unit mass:

= (X – 10Y) pCi / 1 gram = (X – 10Y) pCi/g

- $K_d = \dfrac{(X - 10Y)\ \text{pCi/g}}{Y\ \text{pCi/mL}} = \dfrac{(X - 10Y)}{Y}\ \text{mL/g}$

Portion of sample used for measuring total activity

3 x 1 gram samples used for K_d measurements



- Analysis required for radionuclide concentration associated with starting SDU2A core material ⇨ inherent analytical uncertainty.
- Analysis also required to determine radionuclide concentration in post-equilibrated liquid ⇨ inherent analytical uncertainty.

SDU2A Cores Total Activity

- To determine the total activity, each radionuclide of interest must be individually separated from the saltstone matrix.
- Process involves acid digestion of ground SDU2A cores followed by selective separation techniques for each radionuclide.

Radionuclide	Measured Total Activity (Mean) ($pCi/g_{saltstone}$)	Tank 50 Salt Soln. Activity ($pCi/mL_{salt\ soln}$)	Predicted Saltstone Activity ($pCi/g_{saltstone}$)	Ratio of Measured / Predicted Activities
^{99}Tc	1.48E+03	1.93E+04	6.43E+03	23%
^{90}Sr	7.74E+02	1.93E+03	6.43E+02	120%
^{129}I	4.13E+00	1.43E+01	4.77E+00	87%

- While the ^{90}Sr and ^{129}I activities in the SDU2A core material are within +/- 20% of the predicted, ^{99}Tc is <25%.
- Tank 50 ^{99}Tc concentration is consistently measured at ~1.9E+04 pCi/mL, and thus possible that ^{99}Tc digestion/separation may not be optimized.
- Discount any mechanism associated with ^{99}Tc loss during coring (e.g., wash out due to water coolant) would also be expected to remove ^{129}I and ^{90}Sr.

Reverse K_d

Sample ID	Reverse K_d (mL/g)					
	^{99}Tc (Anoxic)	^{99}Tc (Oxic)	^{90}Sr (Anoxic)	^{90}Sr (Oxic)	^{129}I (Anoxic)	^{129}I (Oxic)
SDU2A-0931-A-1-L	N/A	32	70	>79	4	2
SDU2A-0931-A-2-L		27	36	>73	-1	-5
SDU2A-0931-B-1-L		31	46	>108	-1	-1
SDU2A-0931-C-1-L		25	65	>119	4	-3
SDU2A-0931-C-2-L		27	>41	>119	1	-1
SDU2A-0931-C-2-L		25	70	>176	-5	-5
Sample Set 9 Mean	**N/A**	**28**	**>55**	**>112**	**0.3**	**-2 (K_d = 0)**
SDF PA Model Input	**N/A**	**0.5**	**15**	**15**	**9**	**15**

- K_d for ^{99}Tc and ^{90}Sr > assumed PA value.
- For ^{129}I lowest feasible K_d is zero – negative K_ds for ^{129}I are associated with:
  - Analytical uncertainty of two radiochemical analyses.
  - Analytical uncertainty same for ^{99}Tc and ^{90}Sr measurements but ^{129}I concentrations in saltstone at least 2 orders of magnitude lower.
  - Implications of lower ^{129}I K_d than used in PA transport model.

SDU2A Core Analysis Summary

- Differences in SDU2A core sample densities and porosities reflect anticipated variability associated with field processing. Variations insignificant with respect to key saltstone properties.
- Higher average permeable (open) porosity for SDU2A cores did not adversely impact SHC which indicated equivalent performance to lab-processed samples.
- SDU2A cores were obtained from 3 different SDU ports, and SDU heights between 15.5 to 17.0 ft. In addition, core drilling extraction method imparted significant physical damage to cores.

  Nonetheless SHC of all samples lower than SDF PA input of 6.4E-09 cm/sec; most samples were characterized as lower than detection (1.0E-09 cm/sec).
- Ongoing studies at SREL with lower detection limit equipment indicate SHCs for SDU2A cores in the range of 6E-10 and 7E-11 cm/sec.

SDU2A Core Analysis Summary

- 7-day liquid-solid partitioning tests indicate:
- Under anoxic conditions the leaching behavior of ^{99}Tc is controlled by the solubility of reduced $TcO_2.xH_2O$ phases as modeled in the SDF PA transport simulation.
- Measured ^{99}Tc solubility of 2.2E-08 mol/L compared to 1.0E-08 mol/L assumed in PA transport model.
- ^{99}Tc leachate concentrations under oxic conditions equivalent to anoxic and suggest stable reduced Tc phases and slow oxidation kinetics in the presence of DO.
- ^{90}Sr Kd higher than modeled in SDF PA transport model.
- ^{129}I $K_d < 1$ ml/g and potentially zero; lower than currently assumed in PA transport model.

PA Transport Model Impacts

Saturated Hydraulic Conductivity

- **Based on SDU 2A Core Analysis, the initial Saturated Hydraulic Conductivity (SHC) is expected to be between the Evaluation Case value (6.4E-09 cm/sec) and the Low SHC Case (i.e., Flow Case 03 = 3.9E-10 cm/sec)**

Source	SHC (cm/sec)
SDU 2A Core Analysis (SRNL)	<1.6E-09
SDU 2A Core Analysis (SREL)	~1.0E-10
FY2014 SDF SA (Evaluation Case)	6.4E-09
FY2014 SDF SA (Low SHC Case)	3.9E-10

Technetium Solubility

- **Based on SDU 2A Core Analysis, the Technetium (Tc) Solubility is expected to be approximately double the value use in the Evaluation Case (2.2E-08 mol/L versus 1.0E-08 mol/L)**

Source	**Tc Solubility (mol/L)**
SDU 2A Core Analysis (SRNL)	2.2E-08
FY2014 SDF SA (Evaluation Case)	1.0E-08

K_ds

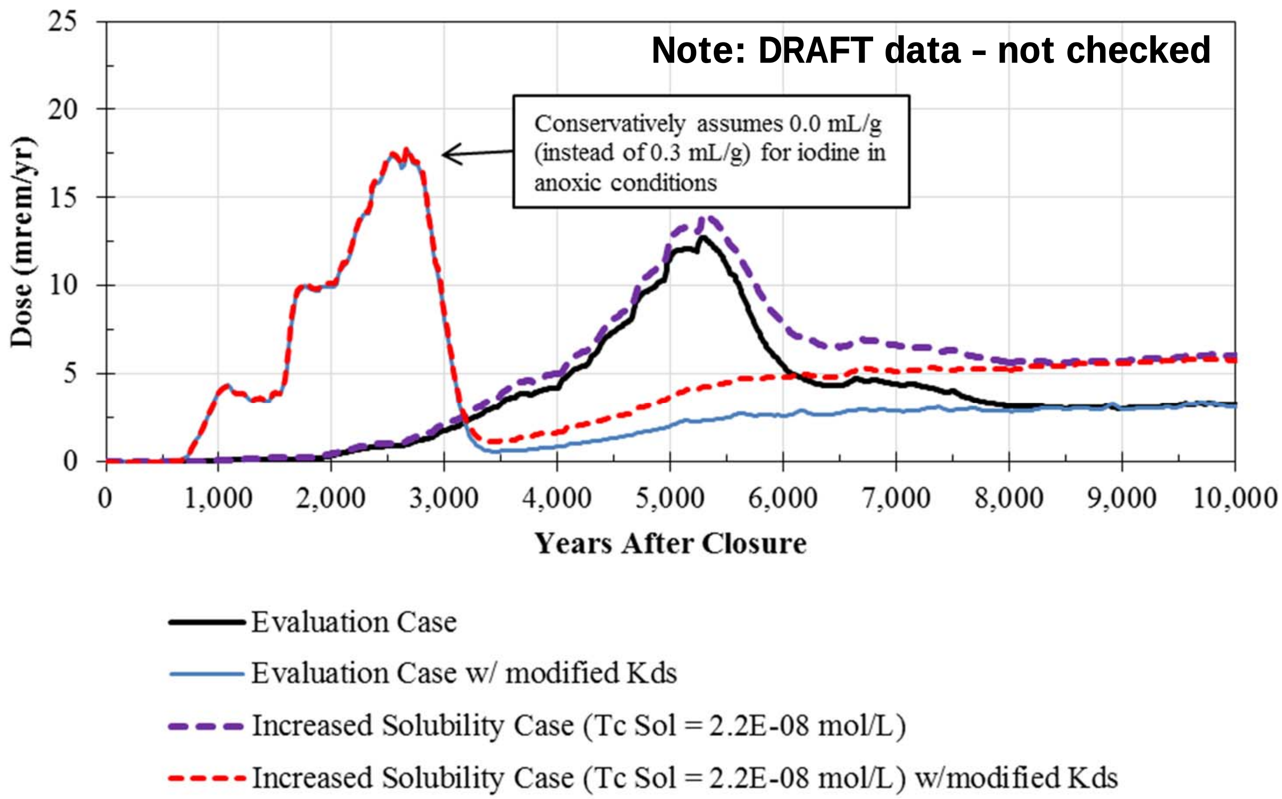
- **Based on SDU 2A Core Analysis, the Kd values for iodine (I), Strontium (Sr), and Tc (under oxidized conditions) are all different than the values assumed in the Evaluation Case**

Source	I K_d (mL/g)	I K_d (mL/g)	Sr K_d (mL/g)	Sr K_d (mL/g)	Tc K_d (mL/g)	Tc K_d (mL/g)
Condition	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic
SDU 2A Core Analysis (SRNL)	0.3*	0	>55	>112	N/A	28
FY2014 SDF SA (Evaluation Case)	9	15	15	15	N/A	0.5

*For conservatism, the anoxic I Kd will be set to 0.0 mL/g

Collective Impacts

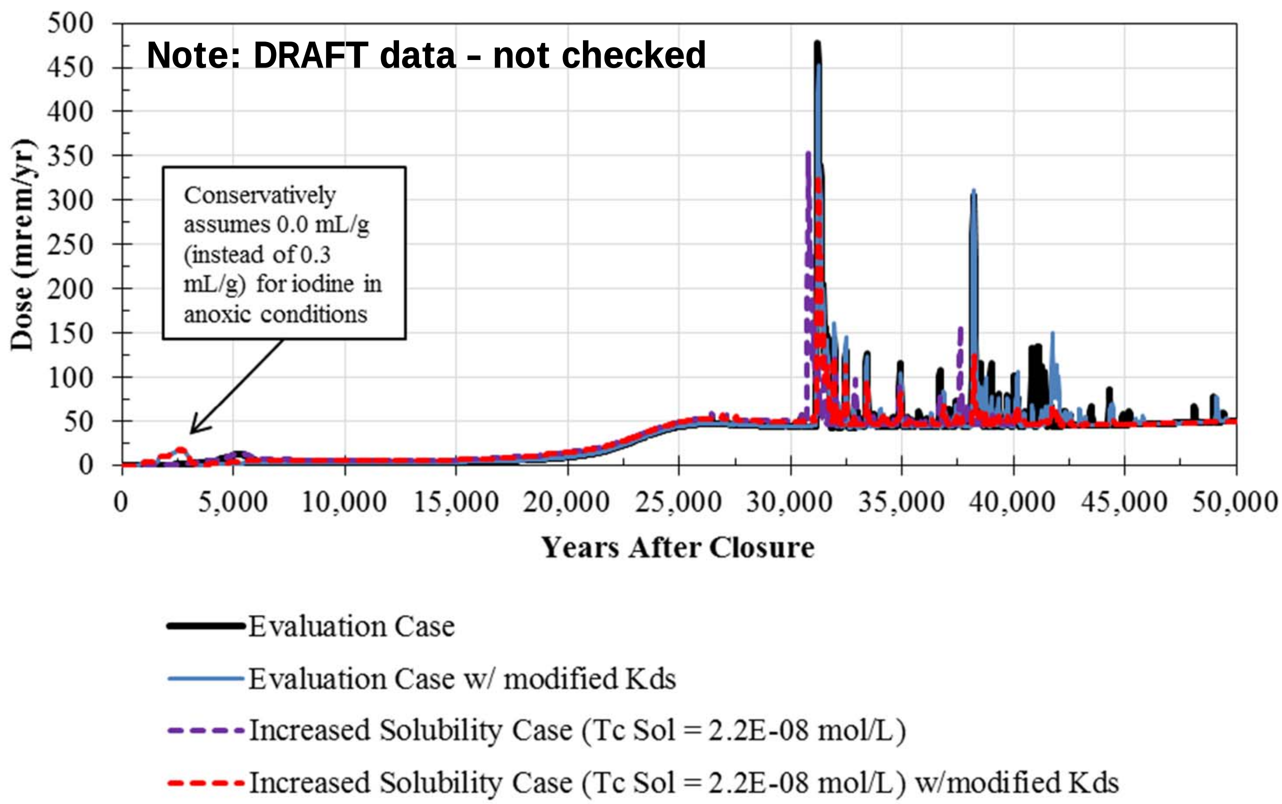
- **Incorporating the results of the SDU 2A Core Sample Analysis gives a higher and earlier I-129 dose peak**



Collective Impacts

We do the right thing.

- **Incorporating the results of the SDU 2A Core Sample Analysis gives a lower and later Tc-99 dose peak**



Collective Impacts

- **With the exception of the modified I K_ds, all of the revised values improve the expected results (or have negligible impacts)**
  - The adverse impacts of the modified I K_ds are expected to be mitigated by the lower SHC
  - Due to the analytical approach used to estimate the I K_ds, there is some uncertainty (i.e., the negative values from the reverse K_d analysis are not realistic)
  - Assuming a value of 0 mL/g is intended to bound this uncertainty

Note: A lower cementitious degradation rate for saltstone within the first 3,000 years after closure would significantly limit the release of I-129

SREL Monolith Leaching Data

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Research Update/Status: Salt Waste Disposal

We do the right thing.

- **SDU2A cores from upper core sections were provided to SREL for leaching analysis.**
- **Leaching behavior of radionuclides from monolithic SDU2A cores and Tc-spiked saltstone simulant (SREL).**
  - *EPA Method 1315* – samples submerged in AGW leachate for 63 days with intermittent leachate analysis for radionuclide concentrations.
  - *Dynamic Leaching* – AGW permeant forced through a monolithic sample and radionuclide concentrations in effluent determined.
  - Leachates associated with SDU2A cores will be analyzed for ^{99}Tc and ^{129}I.
  - Monolithic sample tests are more representative of leaching behavior in the field compared to ground sample (K_d) analysis ⇨ inform ^{129}I leaching behavior.
  - **BUT** leachates not yet analyzed for ^{129}I.

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SREL SDU2A Cores

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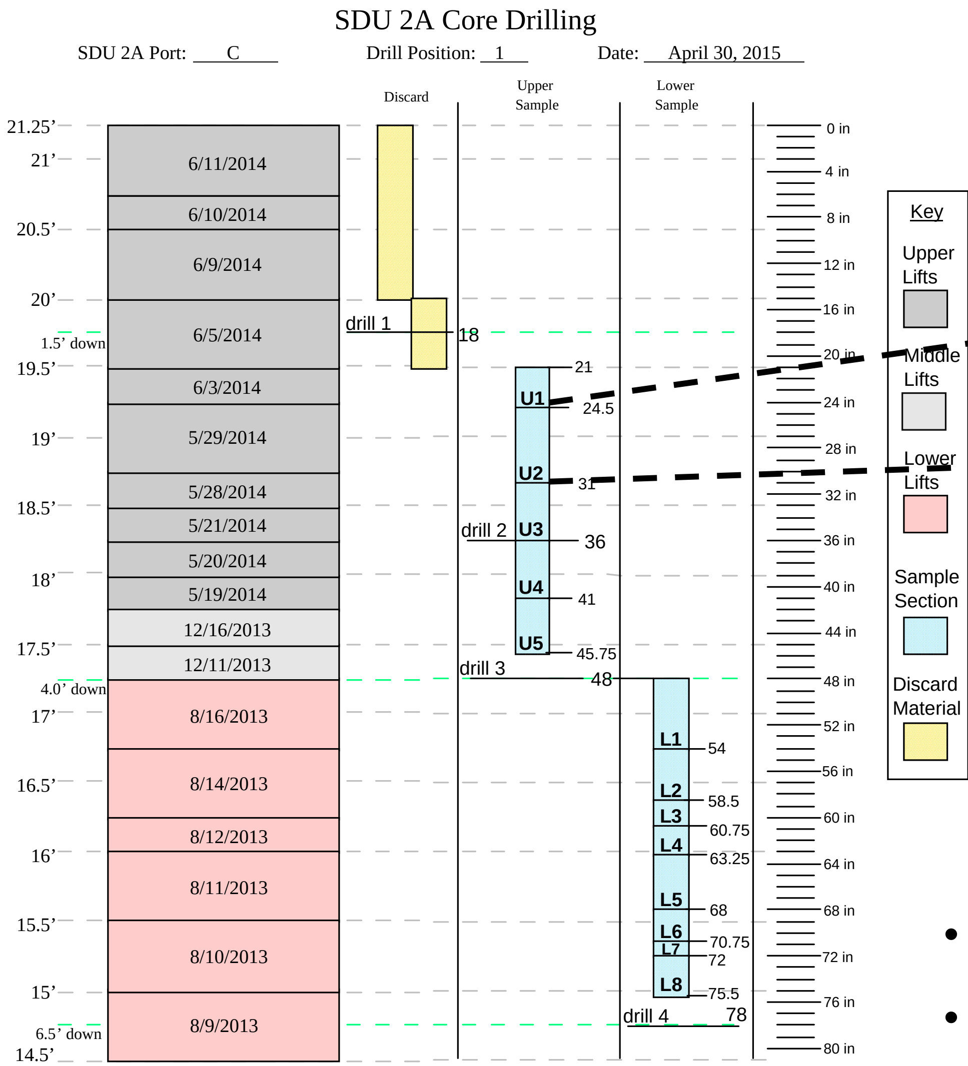
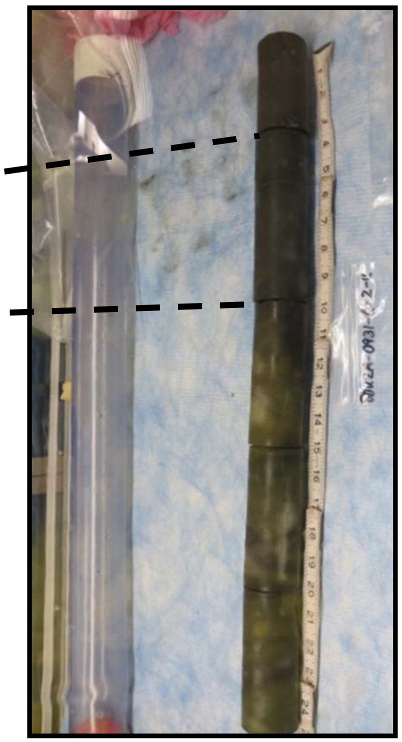




- Upper core samples were utilized
- EPA/DLM samples poured in May 2014 timeframe

EPA 1315 Testing

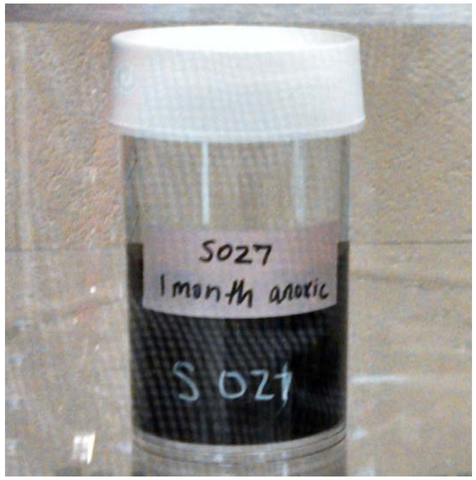
- **Evaluate leaching behavior of monolithic samples; more representative than ground samples.**
- **EPA Method 1315**
  - Samples are submerged in leachate solutions for a period of 63 days.

Interval Label	Interval Duration (h)	Interval Duration (d)	Cumulative Leaching Time (d)
T01	2.0 ± 0.25	–	0.08
T02	23.0 ± 0.5	–	1.0
T03	23.0 ± 0.5	–	2.0
T04	–	5.0 ± 0.1	7.0
T05	–	7.0 ± 0.1	14.0
T06	–	14.0 ± 0.1	28.0
T07	–	14.0 ± 0.1	42.0
T08	–	7.0 ± 0.1	49.0
T09	–	14.0 ± 0.1	63.0

At every test interval the leachate is removed and analyzed and fresh leachate added to the solution.

EPA Method 1315 – Tc/Re-spiked Saltstone

Single Surface Exposed



- Tc/Re-spiked samples
- Test Monolith Dimensions
  - 5.1 cm diameter
  - 5.0 cm length
- ≥ 5cm liquid above exposed surface
- Tested with leachates equilibrated with air, UHP N_2, and N_2-2%H_2.

All Surfaces Exposed

- SDU2A cores and Tc-spiked samples
- ≥ 5cm liquid around sample all exposed surfaces
- Test Monolith Dimensions
  - 5.1 cm diameter
  - 8.0 to 10.5 cm length
- Tested only with leachates equilibrated with air

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Tc-Spiked in Various Environments

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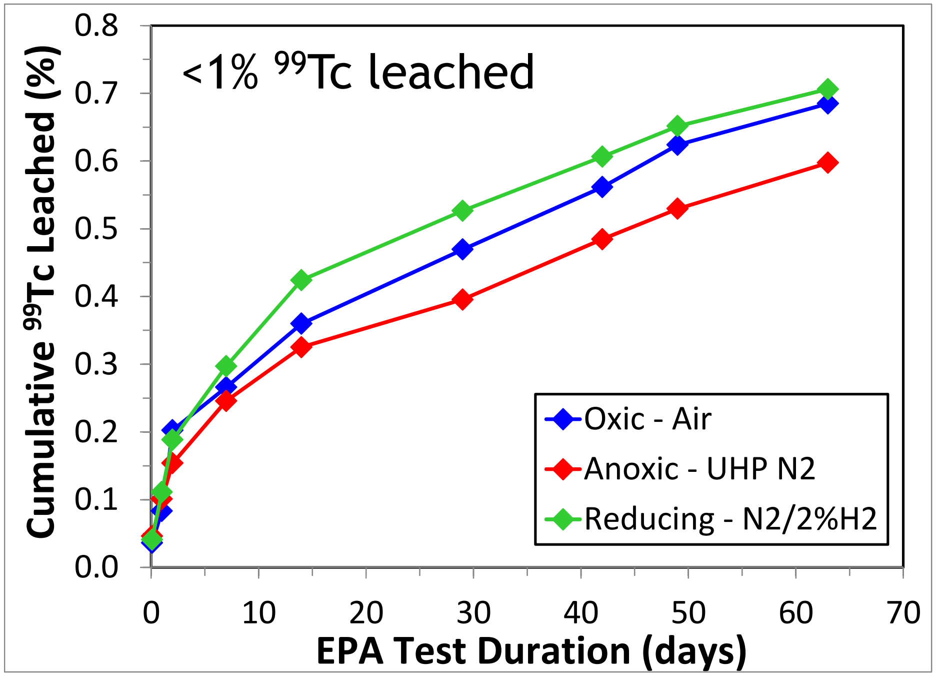
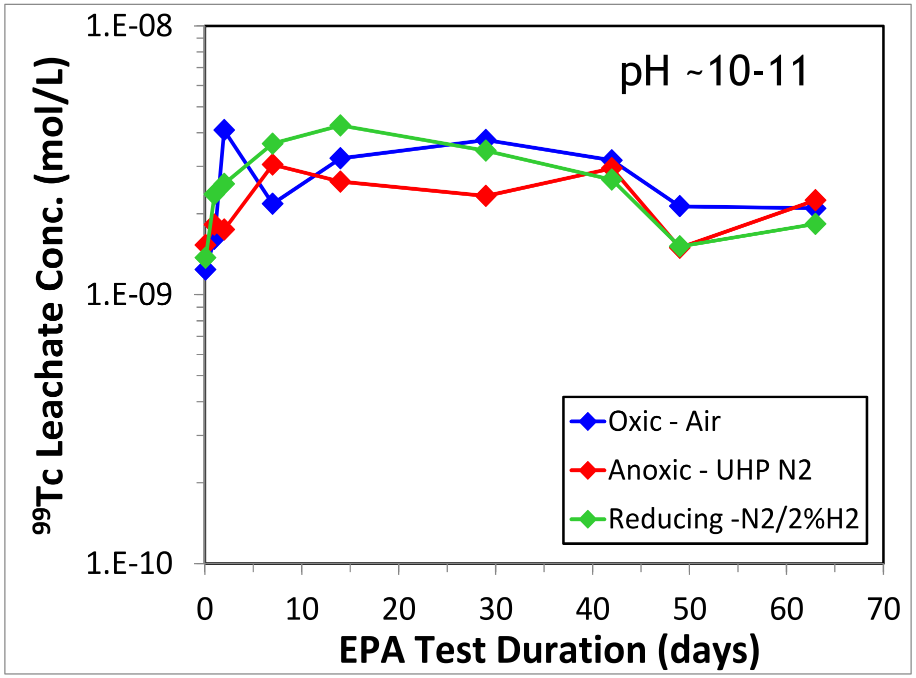
Single Surface Exposed

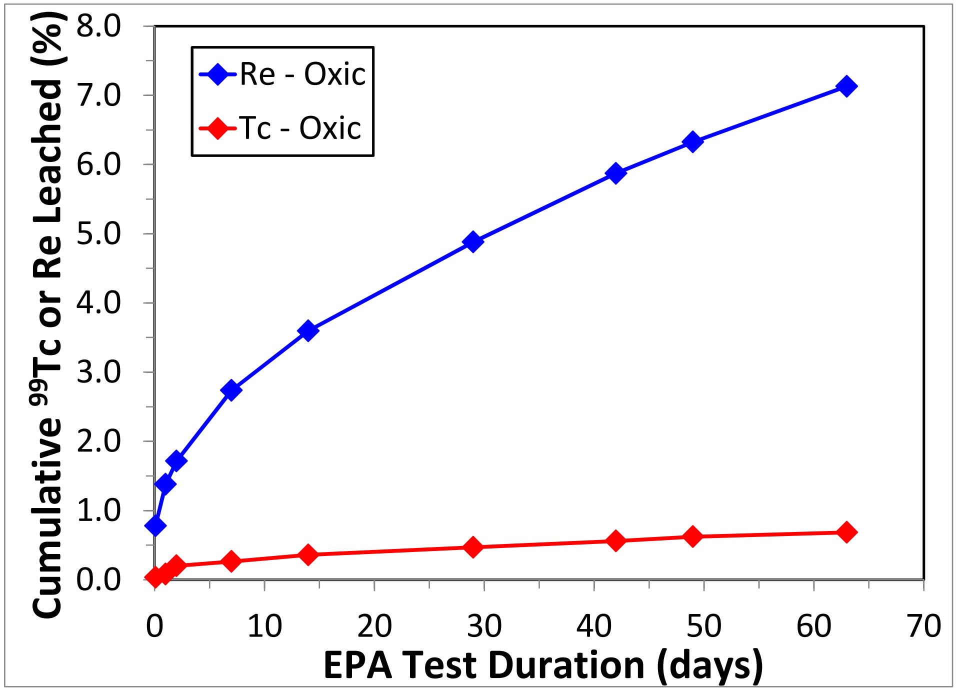




- Lab saltstone samples prepared using salt simulant with ^{99}Tc concentration equivalent to Tank 50 (i.e., 1.93E+04 pCi/mL).
- Data indicates no impact with respect to environment in which tests were conducted.
- As such subsequent testing was limited to equilibration in air.

Tc- or Re-Spiked Saltstone

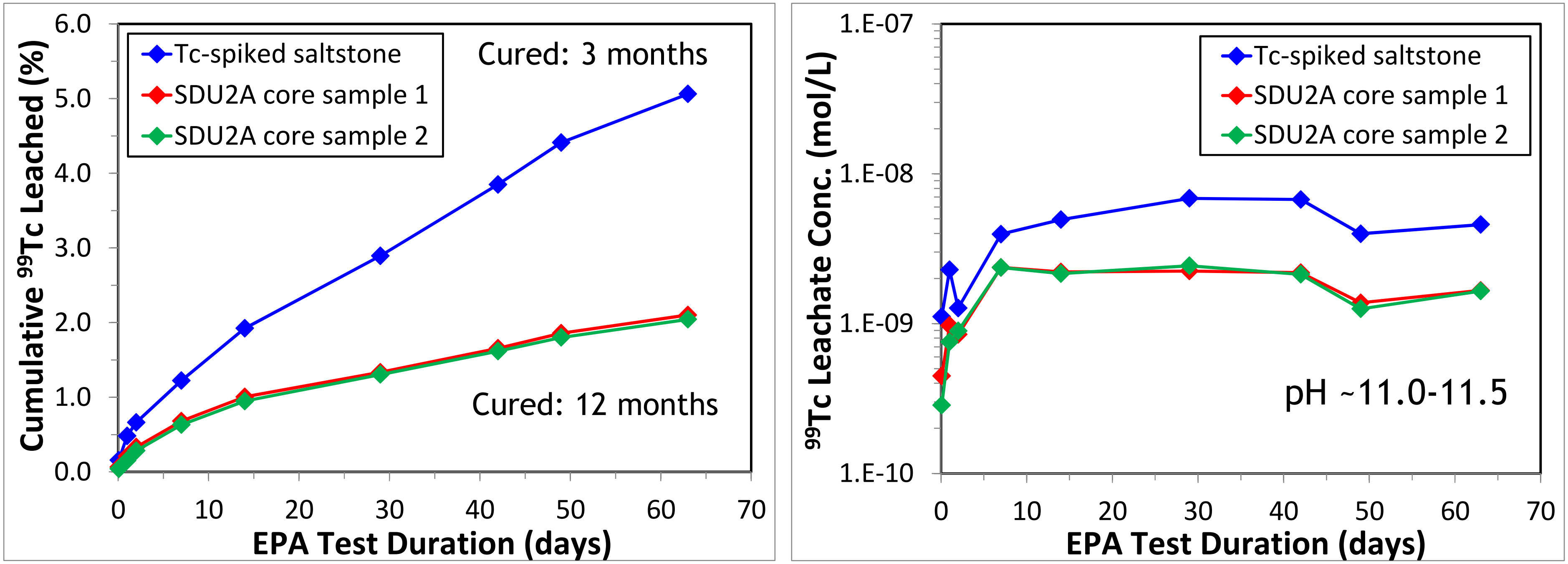
- EPA 1315 (single surface exposed) also conducted on Re-spiked samples.



- Data indicates:
  1. Re is not a good surrogate for Tc in leaching experiments.
  2. Contaminant leaching from the monolith is not artificially impeded with single surface exposed; validates low % ^{99}Tc observed for previous tests.

SDU 2A Cores

All Surfaces Exposed

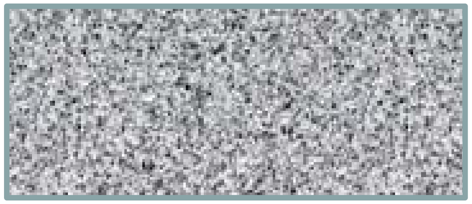


- Data indicates:
  - As expected greater % ^{99}Tc leached when all surfaces exposed.
  - SDU2A cores indicated lower % ^{99}Tc leached compared to Tc-spiked samples – possibly associated with cure time and reduced sample permeability.
  - Leachate concentrations again indicative of $TcO_2.xH_2O$ solubility.

Dynamic Leaching

- Apply a pressure gradient across monolithic saltstone samples (using SHC permeameter equipment) to force AGW permeant through the sample.

AGW
pH ~6-7; E_h ~600 mV
Variables: (1) DO (0 or 8 ppm)
(2) Added ^{99}Tc as $(TcO_4)^-$



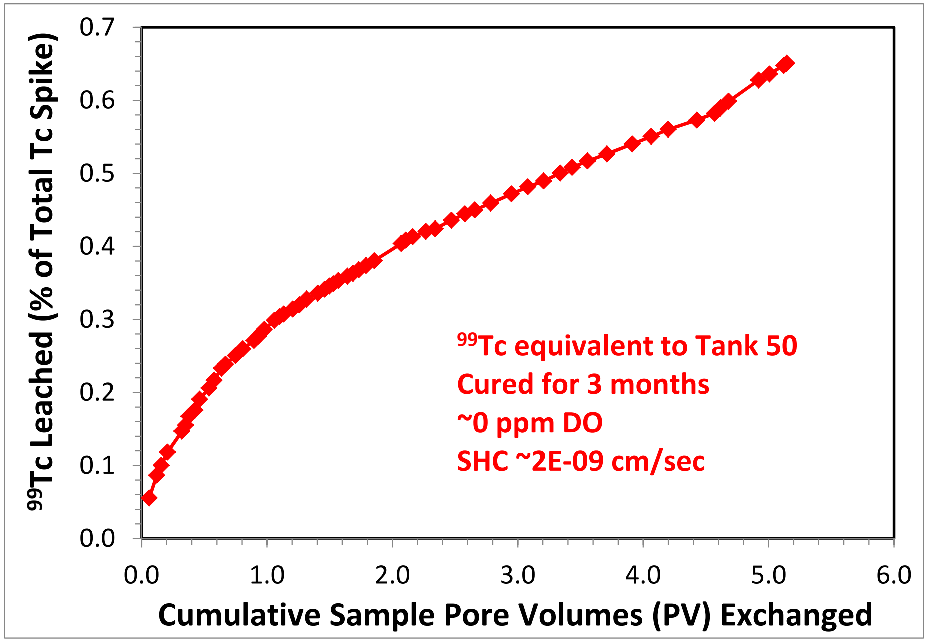
10-20 psi pressure differential

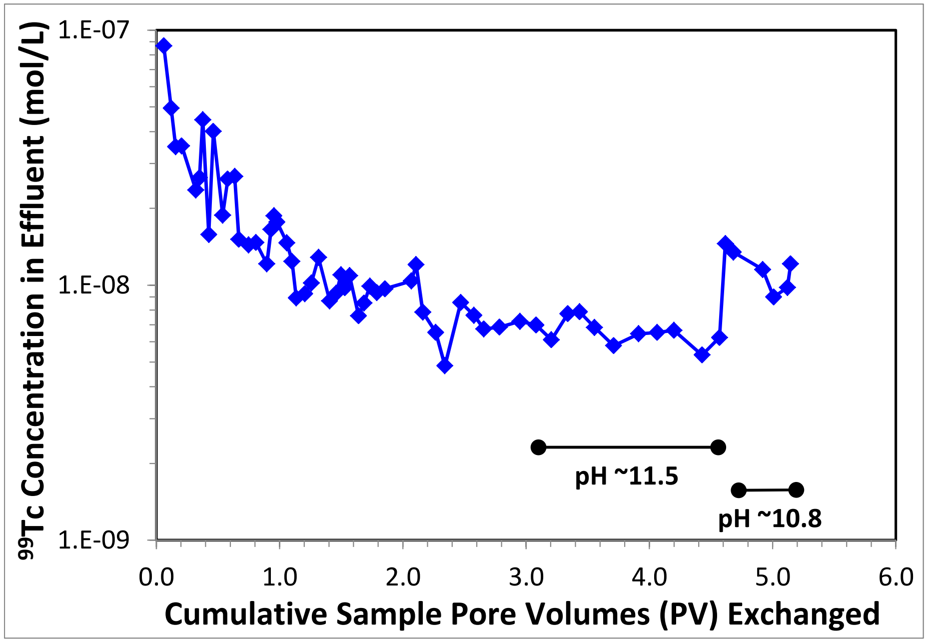
Effluent measurements include:

1. pH, E^h
2. ^{99}Tc, $(NO_3)^{2-}$ (+ ^{129}I, ^{137}Cs for SDU2A cores)
3. DO

Tc-Spiked Sample

- DLM testing of ^{99}Tc-spiked saltstone has been running for ~300 days.
- Approx. 6 pore volumes have been exchanged (assuming 60% total porosity; 9 pore volumes if assume 40% permeable porosity).
- Typical effluent volume per data point ~3 mL.





- Less than 1% of ^{99}Tc spiked into sample has been leached.

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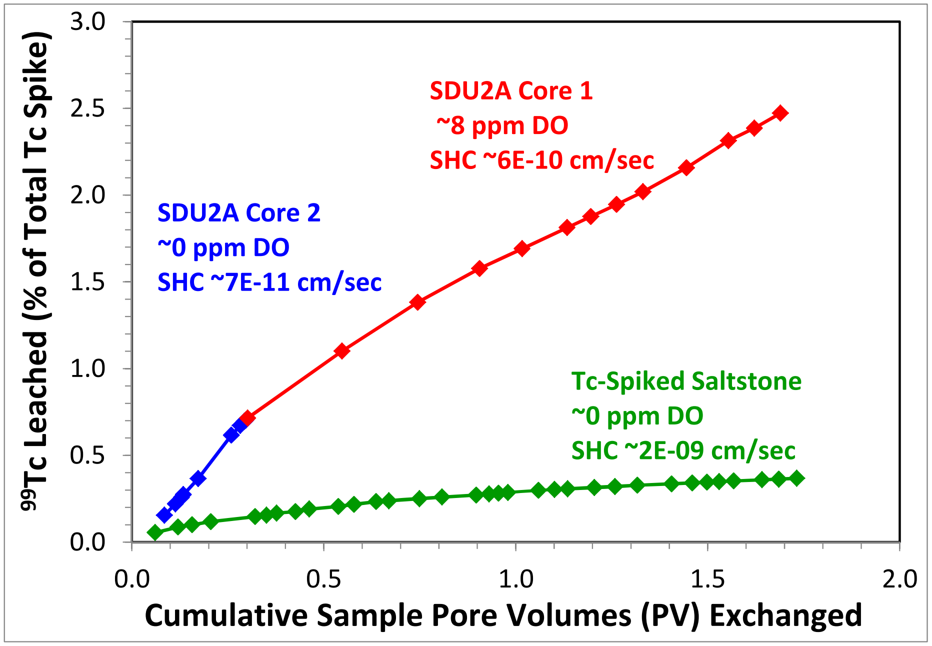
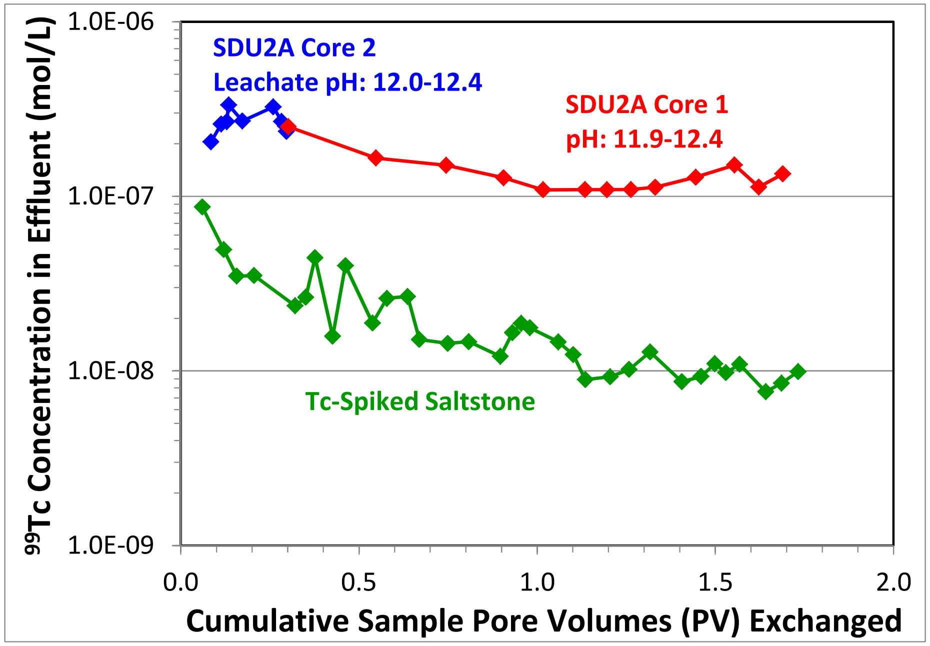
DLM of SDU2A Cores





- 2 SDU2A cores being evaluated (with and without DO).
- Low SHC is slowing the flow through rate in comparison to the Tc-spiked sample.
- % ^{99}Tc leached 5-10 times > than Tc-spiked sample.
- Effluent concentrations for SDU2A cores ~E-07 mol/L compared to ~E-08 mol/L for Tc-spiked samples.

pH-E_h

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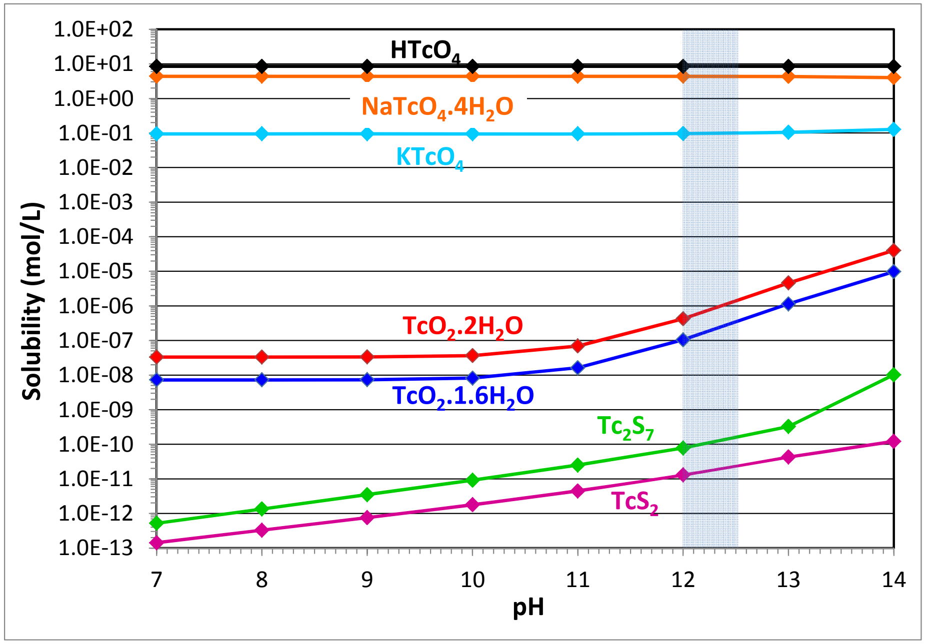

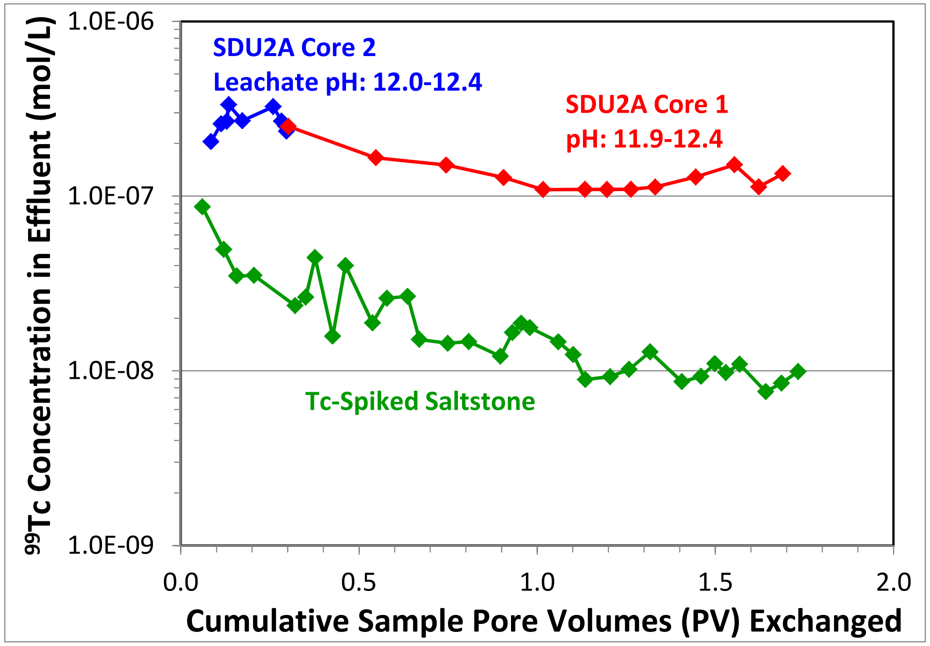

SDU2A Core Environment	Permeant (average)			Effluent (average)		
	pH	*E_h (mV)*	*DO (ppm)*	*pH*	*E_h (mV)*	*DO (ppm)*
Oxic	6.5	+600	8	12.2	-65	3.5
Anoxic	6.5	+600	0	12.3	-70	3.5

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SREL Summary

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- EPA 1315 and DLM leachate tests on monolithic ^{99}Tc-spiked and SDU2A cores confirm leaching behavior controlled by the solubility of reduced $TcO_2.xH_2O$ phases.
- For SDU2A cores pH of leachates is ~12 after the exchange of 1-2 pore volumes ⇨ $TcO_2.xH_2O$ solubility ~1E-07 mol/L.
- As additional pore volumes are exchanged a drop in pH and solubility is predicted.
- May lead to altered PA modeling approach:
  - ⇨ Model ^{99}Tc leaching behavior for initial pore volumes at 1E-07 mol/L $TcO_2.xH_2O$ solubility limit.
  - ⇨ With more pore volumes exchanged pH will decrease and model ^{99}Tc leaching behavior based on 1E-08 mol/L $TcO_2.xH_2O$ solubility limit.
- Studies on-going and method still being developed.