Evaluating ^{99}Tc Release from Intact Saltstone Monoliths

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The University of Georgia

Savannah River Ecology Laboratory ®

DEPARTMENT OF ENERGY UNITED STATES OF AMERICA

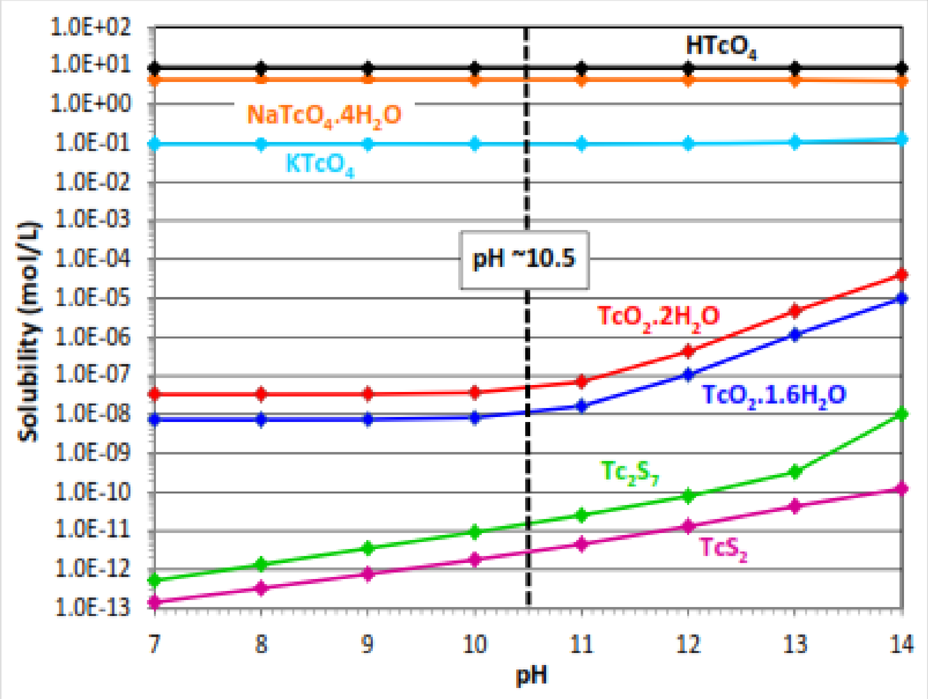
SRR Savannah River Remediation

Technetium (Tc) Characteristics

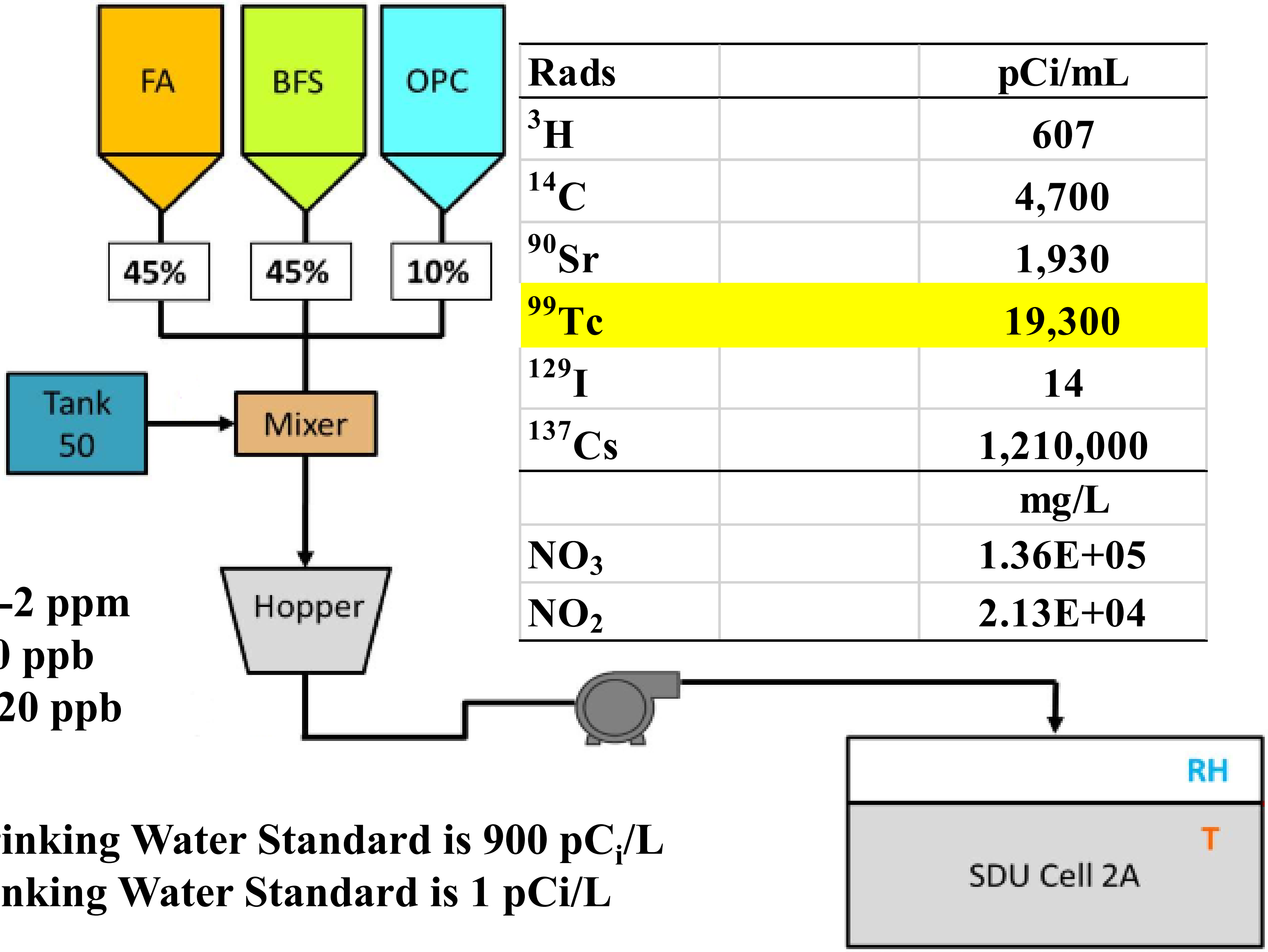
- Reduced form Tc(IV) is less soluble/mobile
- Tc(VII) reduced to Tc(IV) which precipitates as $TcO_2 \cdot nH_2O_{(s)}$ or with S^{2-}

$$TcO_4^- + 4H^+ + 3e^- = TcO_{2(s)} + 2H_2O$$

- Tc(IV) may be oxidized with moderate O_2 exposure
    - dependence on physical and chemical integrity of the waste form



SRS LAW Strategy



Tank 50 Composition

Rads		pCi/mL
^{3}H		607
^{14}C		4,700
^{90}Sr		1,930
^{99}Tc		19,300
^{129}I		14
^{137}Cs		1,210,000
		mg/L
NO_3		1.36E+05
NO_2		2.13E+04

^{99}Tc – 1-2 ppm
^{129}I - 60 ppb
^{137}Cs – 20 ppb

^{99}Tc Drinking Water Standard is 900 pC_i/L
^{129}I Drinking Water Standard is 1 pCi/L

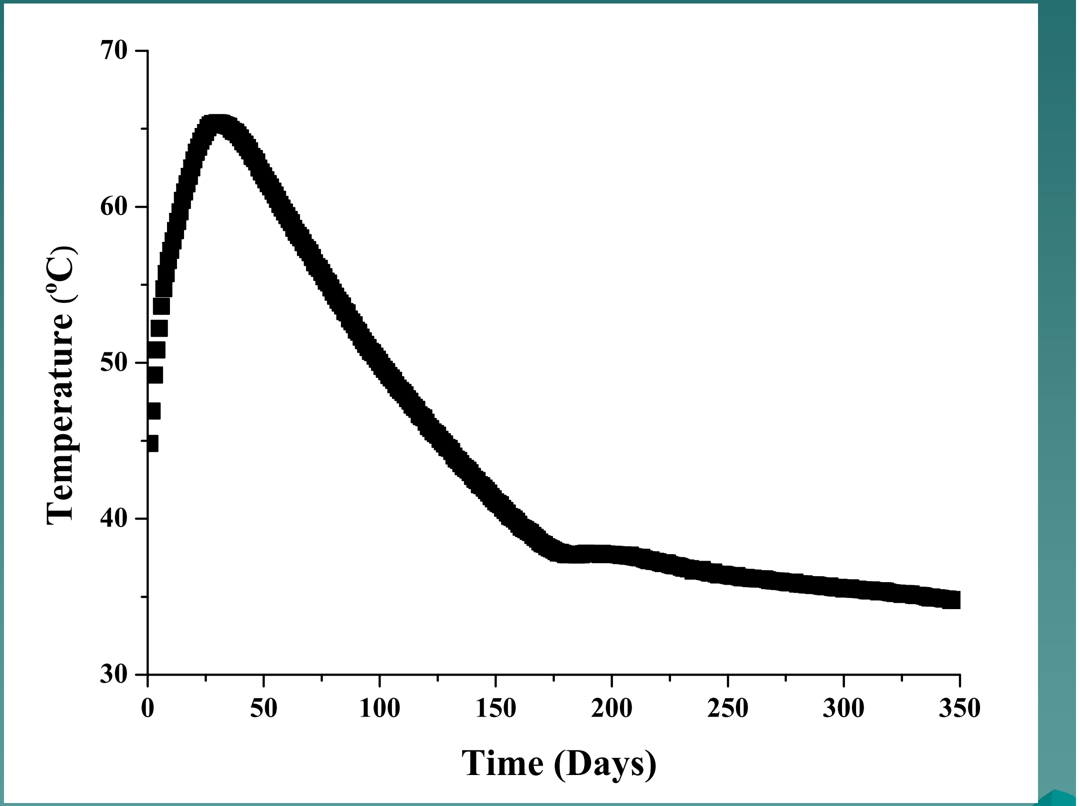
Saltstone Experiments

- **Saltstone Simulants - spiked with ^{127}I, Re or ^{99}Tc**
- **Multiple BFS Sources, i.e., inherent reductive capacity**
- **Curing 6+ months – Temperature regime to matches vaults**
- **Saltstone core samples from SDU2A**
- **EPA 1315: *Mass transfer rates of constituents in Monolithic or Compacted Granular Materials using a Semi-Dynamic Tank Leaching Procedure* (ANS 16.1)**
- **Dynamic Leaching Method (DLM)**
- **Monitor: ^{99}Tc, ^{137}Cs, ^{127}I, ^{129}I (pending), NO_3^- and Re (when added)**

Saltwaste/Saltstone Simulants

Material	ARP/MCU Salt Simulant	
	Molarity (moles/L)	Mass (g/L)
Sodium Hydroxide, NaOH (50 wt.% by weight)	1.594	127.50
Sodium Nitrate, $NaNO_3$	3.159	268.48
Sodium Nitrite, $NaNO_2$	0.368	25.39
Sodium Carbonate, Na_2CO_3	0.176	18.65
Sodium Sulfate, Na_2SO_4	0.059	8.37
Aluminum Nitrate, $Al(NO_3)_4.9H_2O$	0.054	20.33
Sodium Phosphate, $Na_3PO_4.12H_2O$	0.012	4.67

Saltstone Curing Temperature SDU 2A



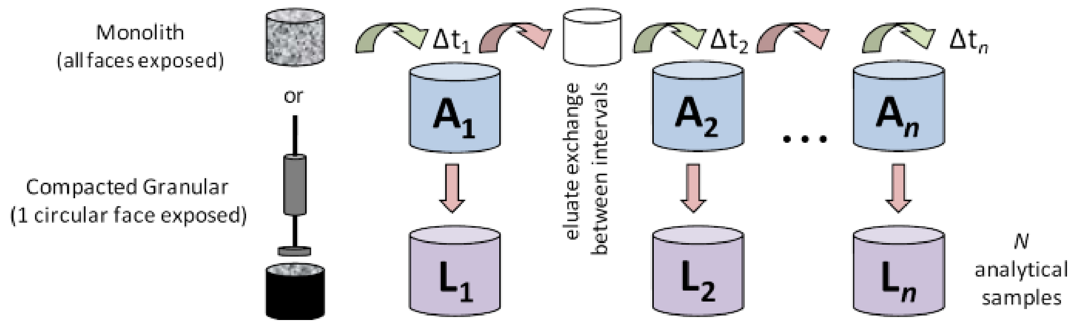
Contaminant Release: EPA 1315

- 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.

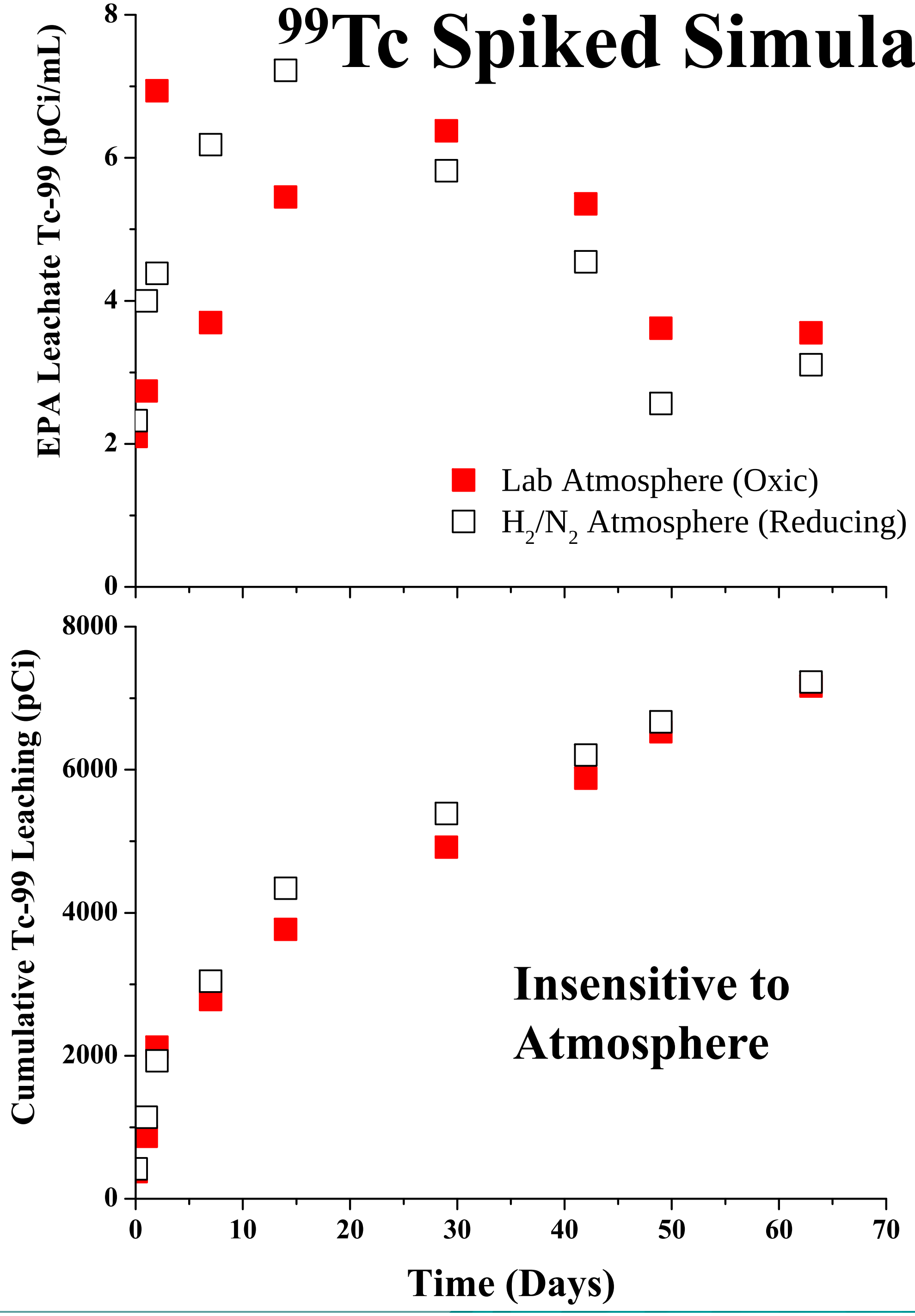
- SDU2A cores and Tc-spiked samples
- ≥ 5cm liquid around sample all exposed surfaces
- Test Monolith Dimensions
    - 5.1 cm diameter
    - 8.0 to 10.5 cm length
- Tested only with leachates equilibrated with air

Contaminant Release: EPA 1315

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
T03	23.0 ± 0.5		2
T04		5.0 ± 0.1	7
T05		7.0 ± 0.1	14
T06		14.0 ± 0.1	28
T07		14.0 ± 0.1	42
T08		7.0 ± 0.1	49
T09		14.0 ± 0.1	63



^{99}Tc Spiked Simulant



Insensitive to Atmosphere

Leaching Data Analysis

Effective Diffusivity

$$De = \pi\left[\frac{a_n/A_o}{\Delta t_n}\right]\left[\frac{V}{S}\right]^2 T$$

Generalized Mean Square Root of Leaching Time

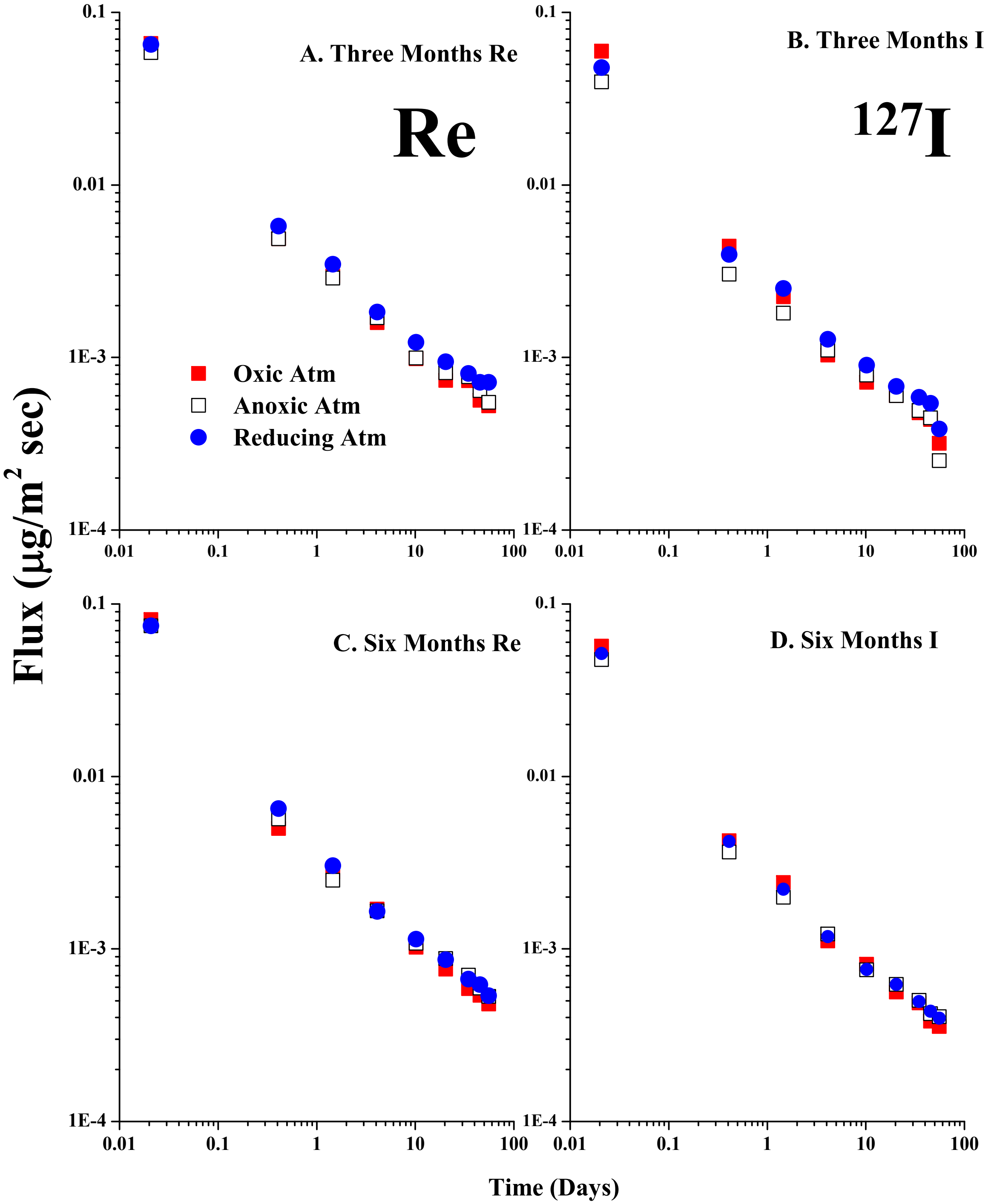
$$T = \left[\frac{\sqrt{t_n} + \sqrt{t_{n-1}}}{2}\right]^2$$

Leaching Index

$$\boxed{LI_n = -\log[D_e]}$$

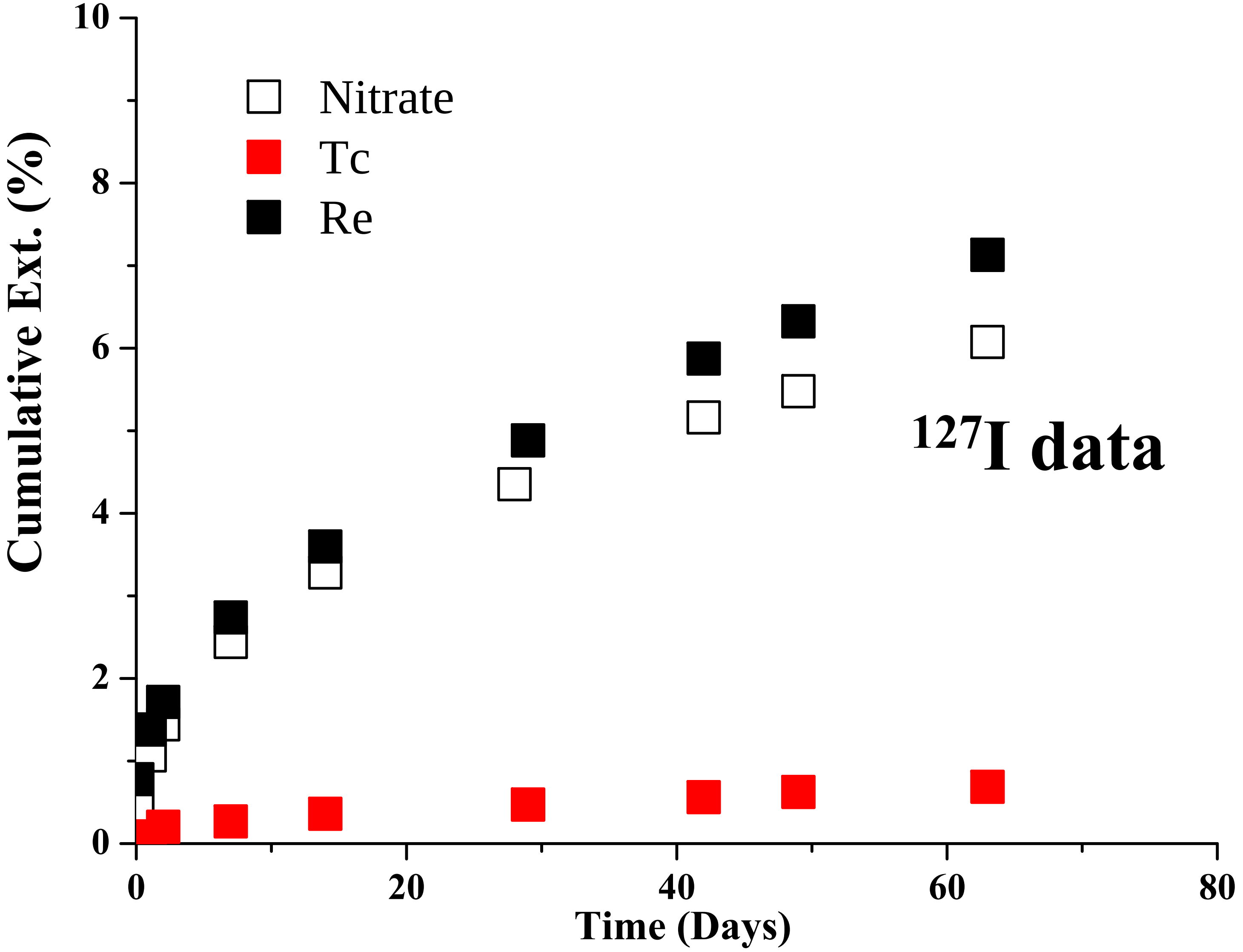
↑ *LI* = slower leaching

↓ *LI* = faster leaching

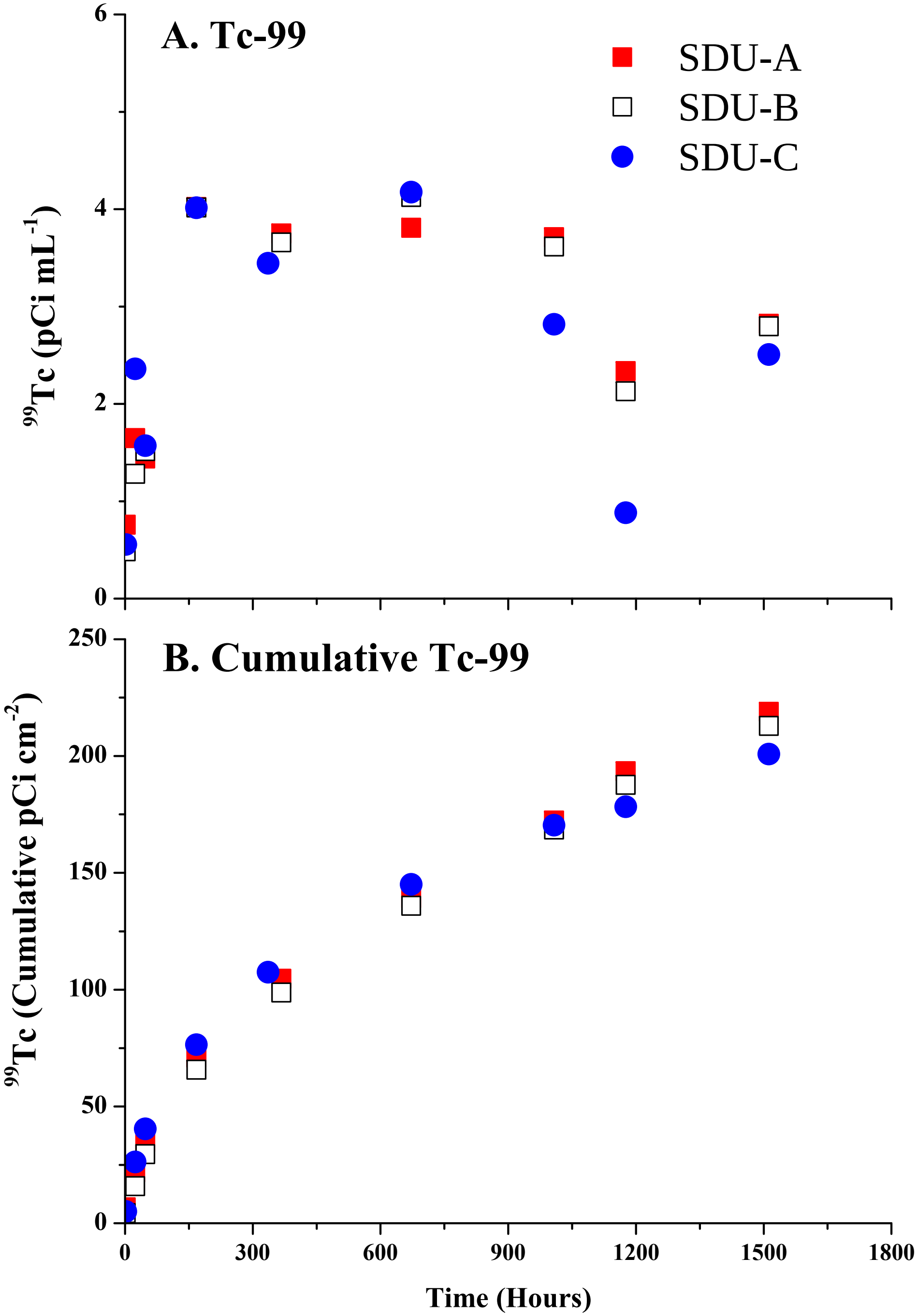

A. Three Months Re
Re
B. Three Months I
^{127}I
C. Six Months Re
D. Six Months I
■ Oxic Atm
□ Anoxic Atm
● Reducing Atm
Flux (µg/m^2 sec)
Time (Days)
0.1
0.01
1E-3
1E-4
0.01
0.1
1
10
100

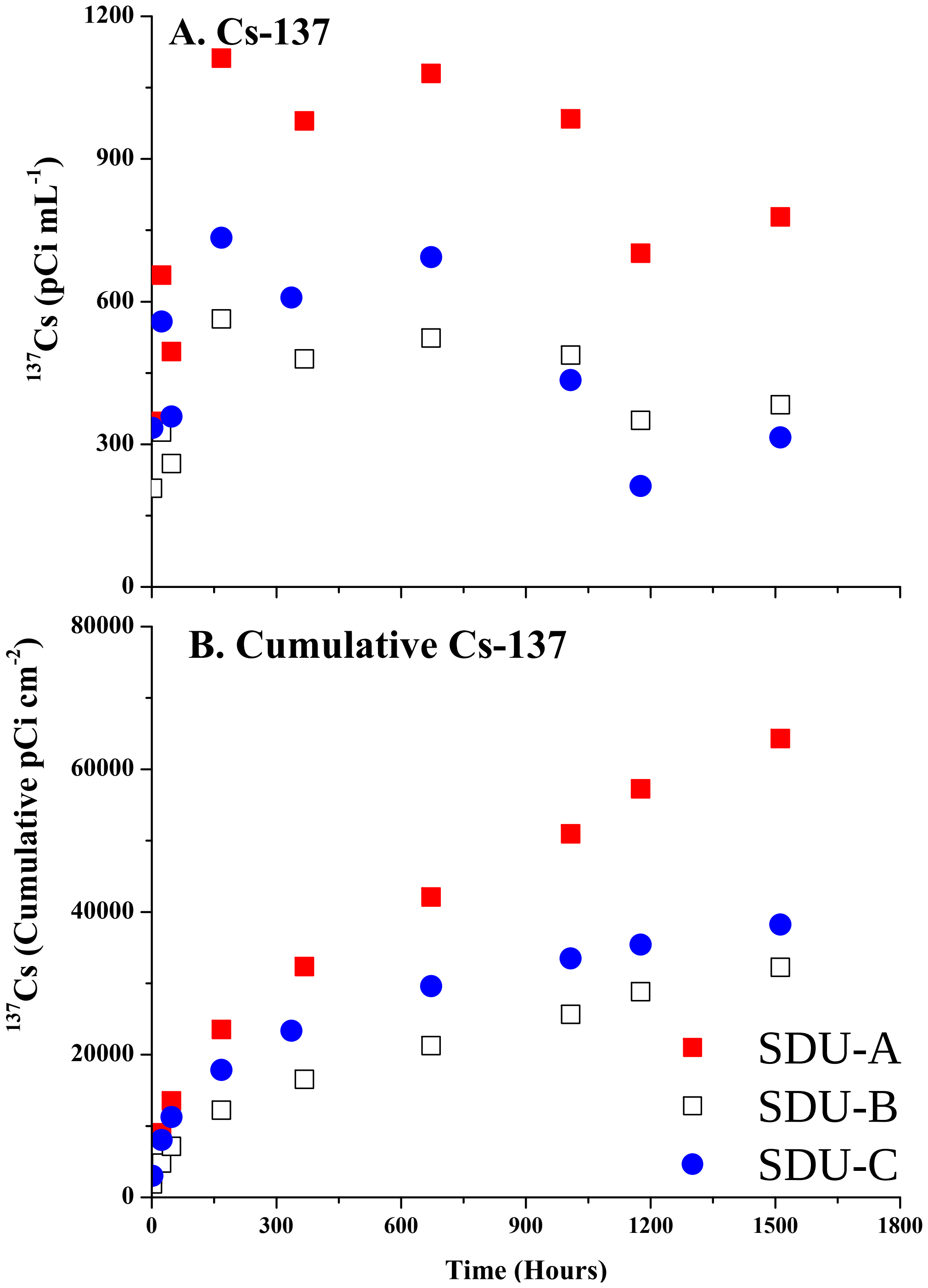
Cumulative % Extracted (1D Test):

^{99}Tc and Re Spiked Simulant Grouts



Three SDU Grout Samples

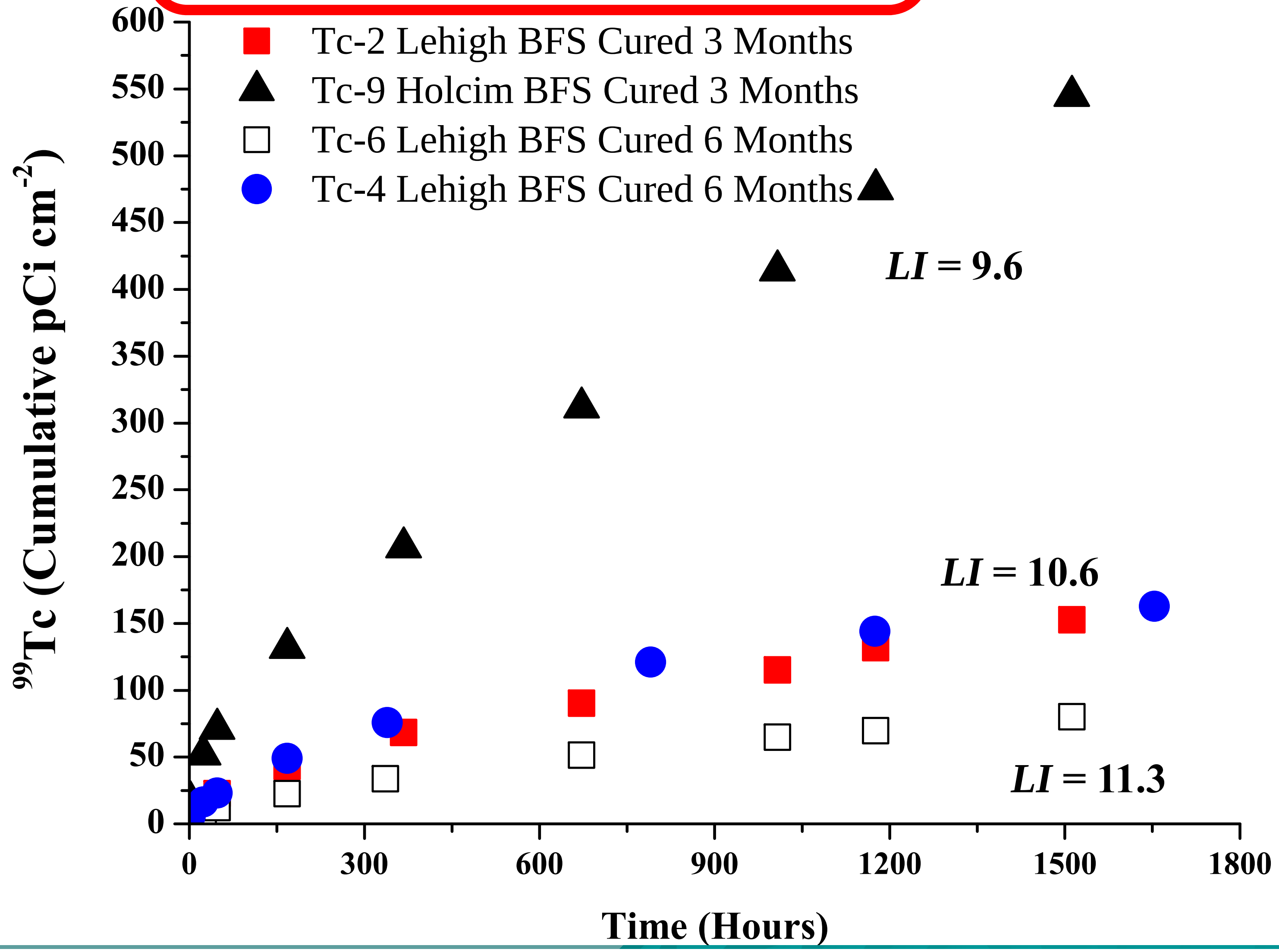




Three SDU Grout Samples

^{99}Tc-Spiked Grout Samples: Impact of BFS Source

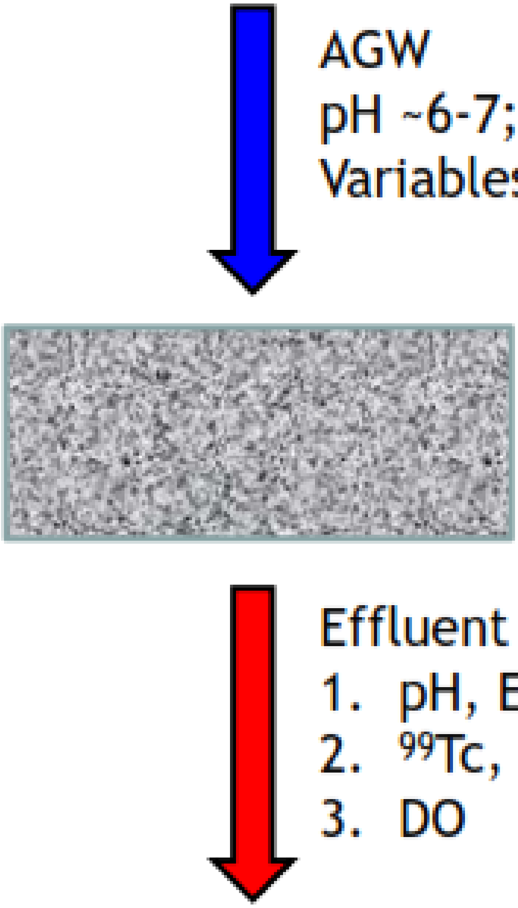
SAMPLE	Reductive Capacity	Fe	S	Ca	Al
	μeq gm^{-1}	mg/kg	mg/kg	mg/kg	mg/kg
Holcim BFS (FY15)	713	1,685	13,934	234,566	18,324
Lehigh BFS (Batch 1)	1600	3,504	23,620	285,232	39,933



EPA 1315 Data Summary: Leachability Indices

		^{99}Tc	Re	^{137}Cs	NO_3	^{127}I
Sample		**LI**	**LI**	**LI**	**LI**	**LI**
FY15 Spiked Saltstone						
	Old BFS (Holcim)	**9.7-9.9**	**7.5-7.7**	**NA**	**7.5-7.9**	**7.6-7.8**
FY16 Spiked Saltstone						^{129}I
	New BFS (Lehigh)	**10.6-11.3**	**NA**	**NA**	**6.7-7.5**	**NA**
	Old BFS (Holcim)	**9.6**	**NA**	**NA**	**7.5**	**NA**
Three SDU Cores						
	Old BFS (Holcim)	**10.2-10.3**	**NA**	**9.4-10.0**	**6.6-8.5**	**pending**

Dynamic Leaching Method Based on K_{sat} FWP



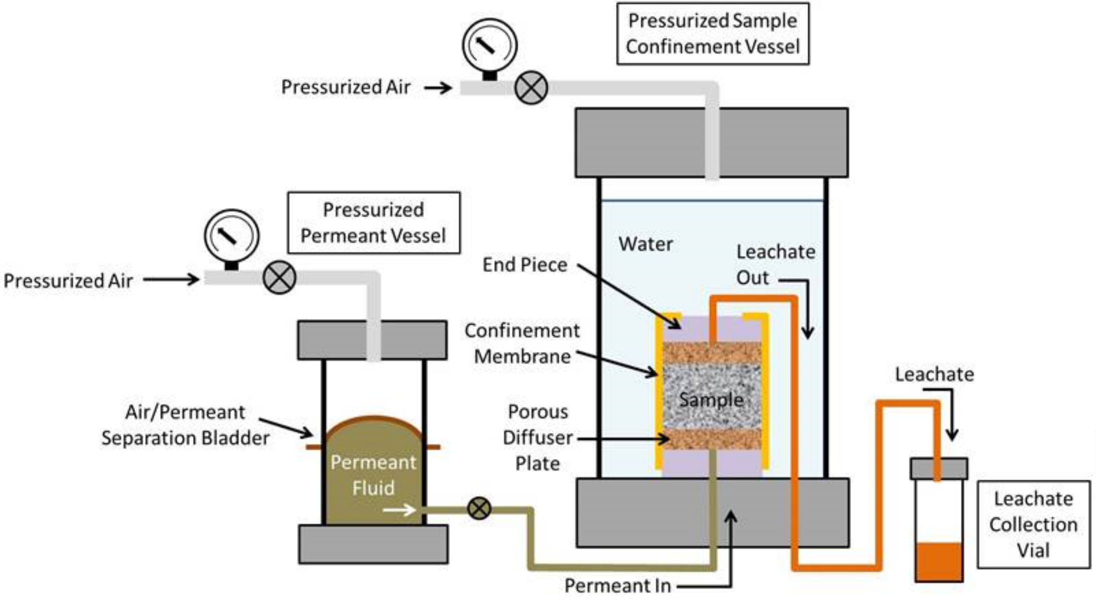
AGW
pH ~6-7; E_h ~600 mV
Variables: (1) DO (0 or 8 ppm)
(2) Added ^{99}Tc as $(TcO_4)^-$

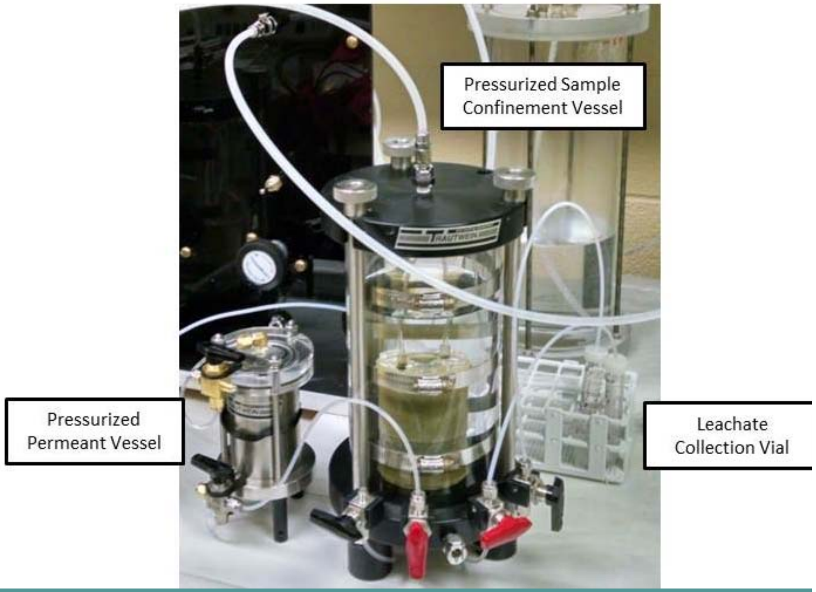
10-20 psi pressure differential

Effluent measurements include:

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

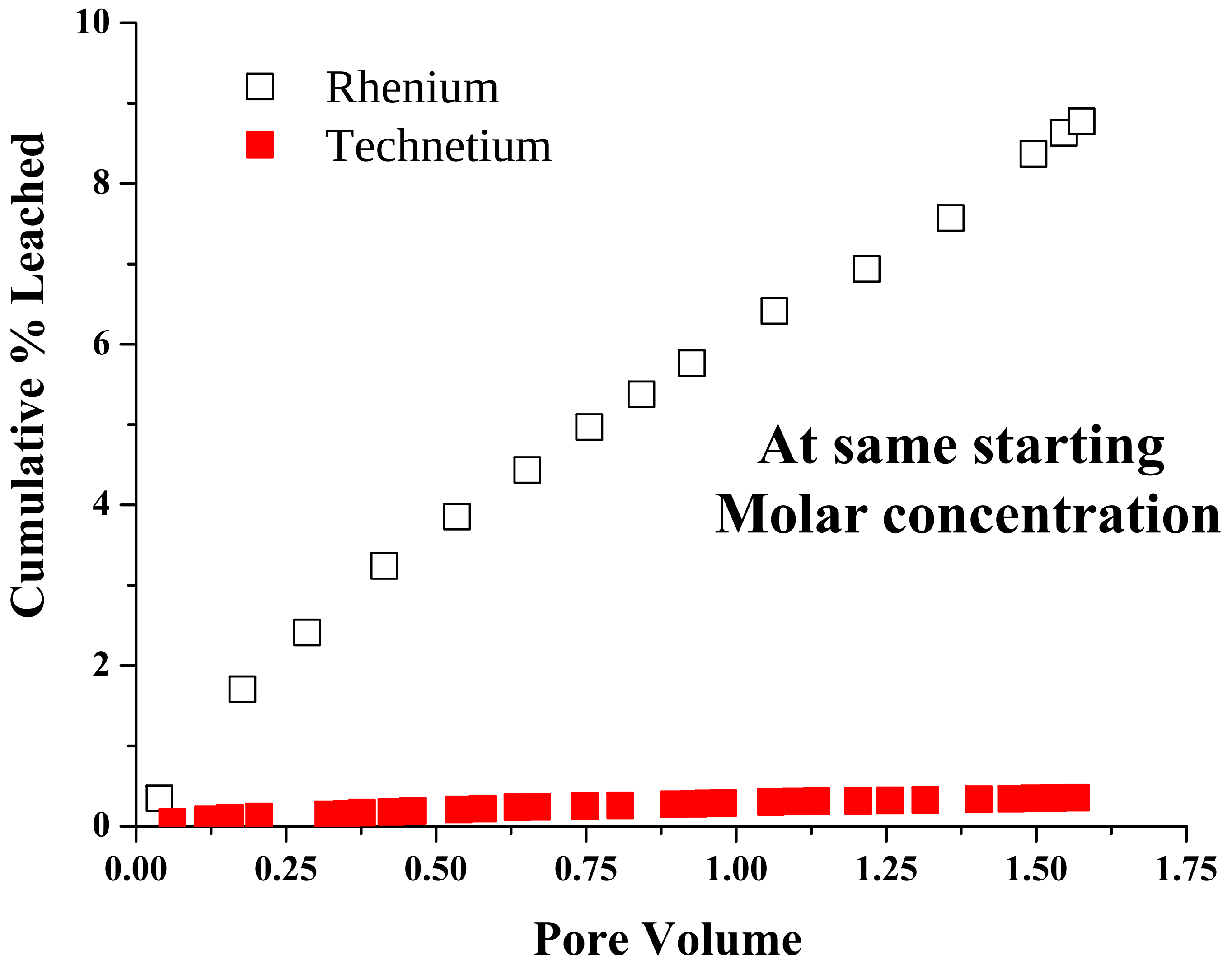
SREL DLM System



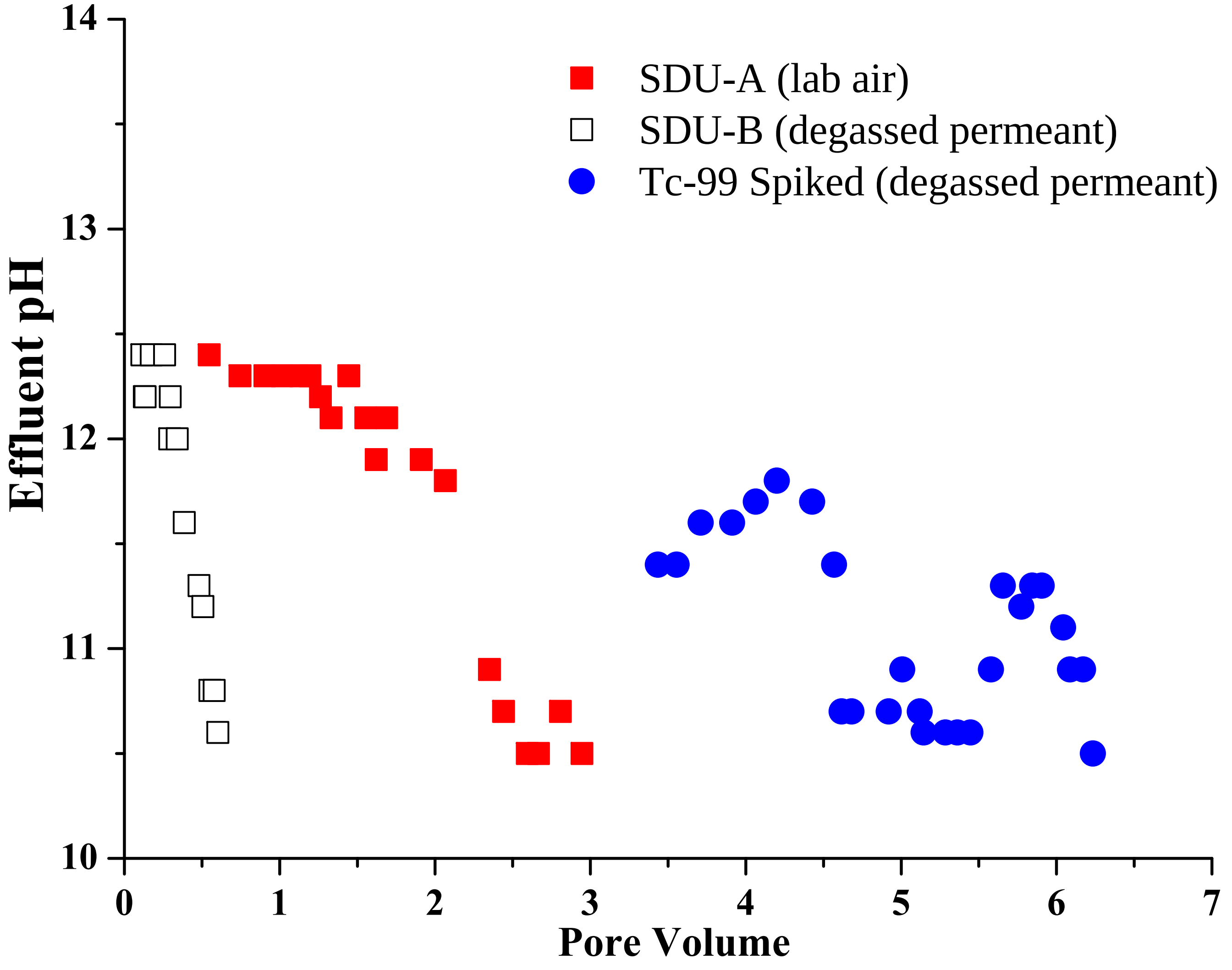


DLM Manifold (3 Sample Capacity)

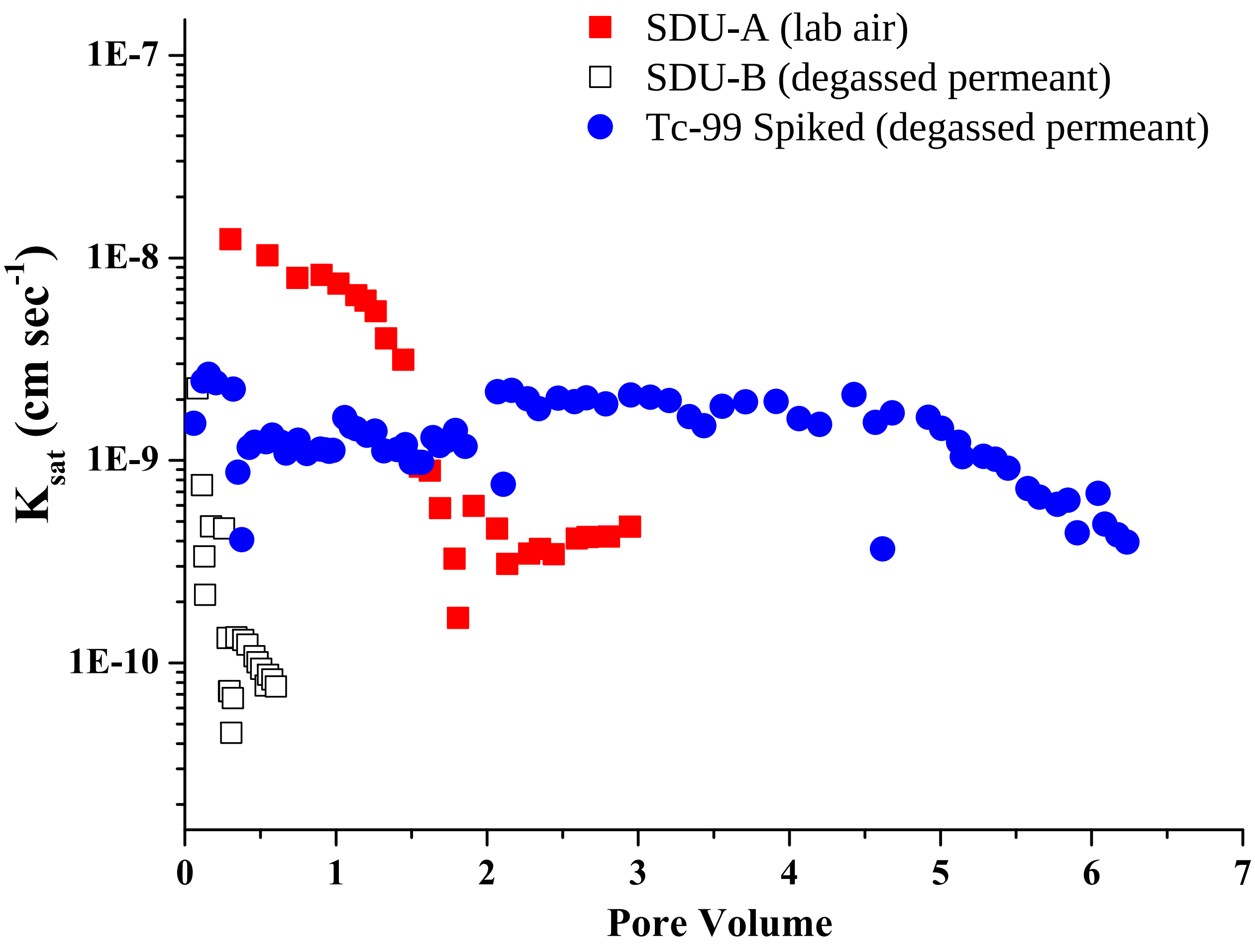
Dynamic Leaching Spiked Grouts: Re vs ^{99}Tc

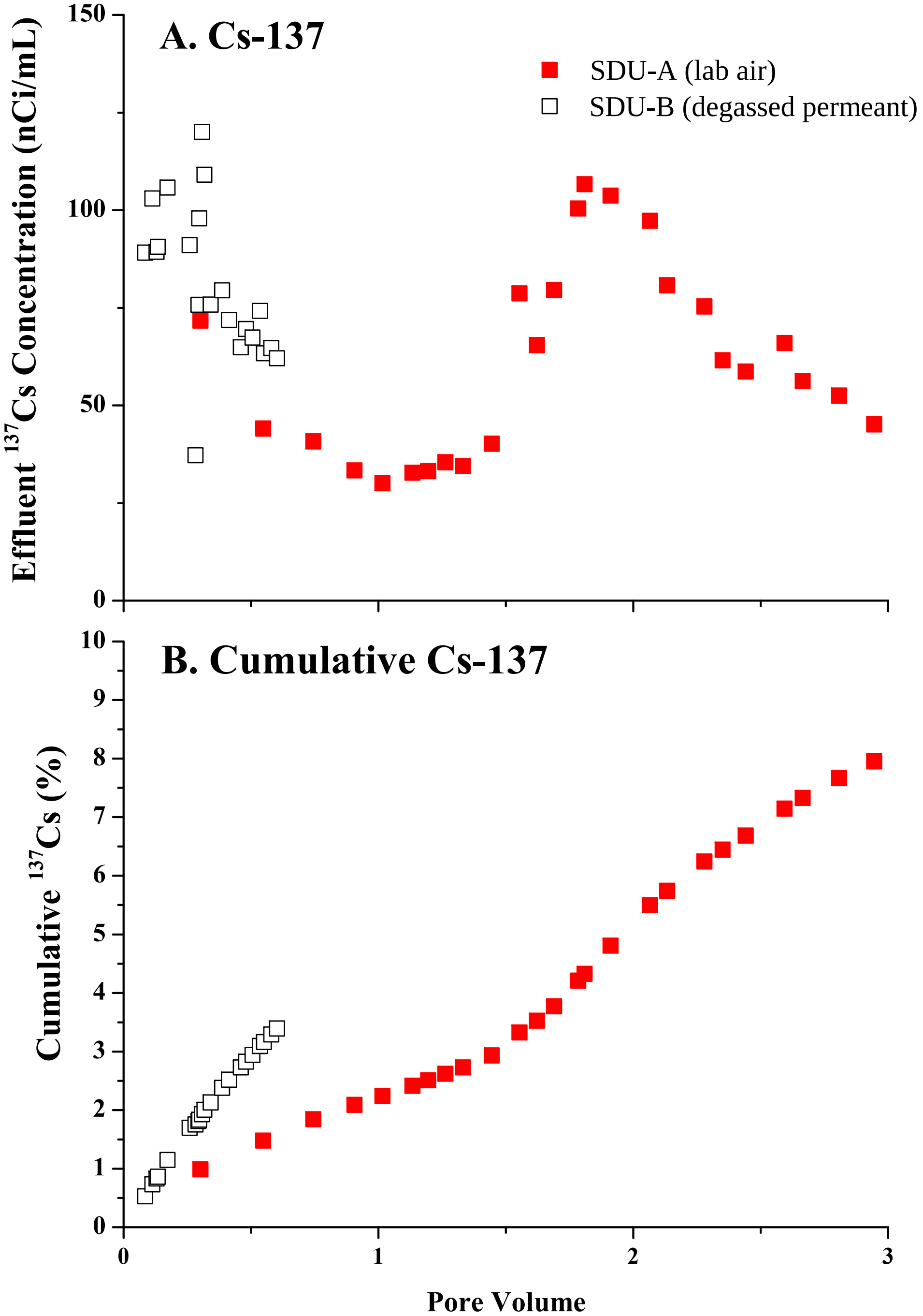


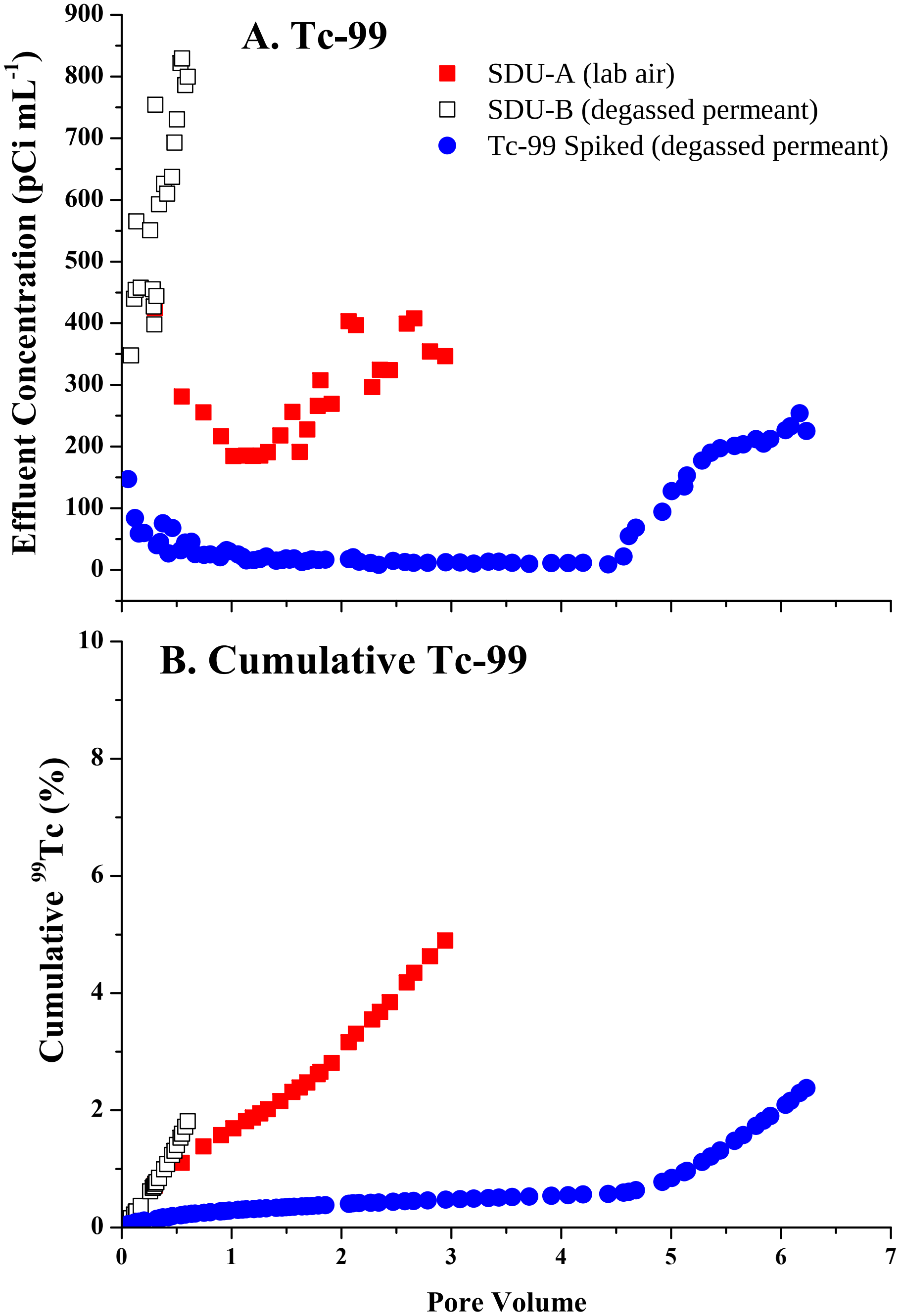
At same starting Molar concentration

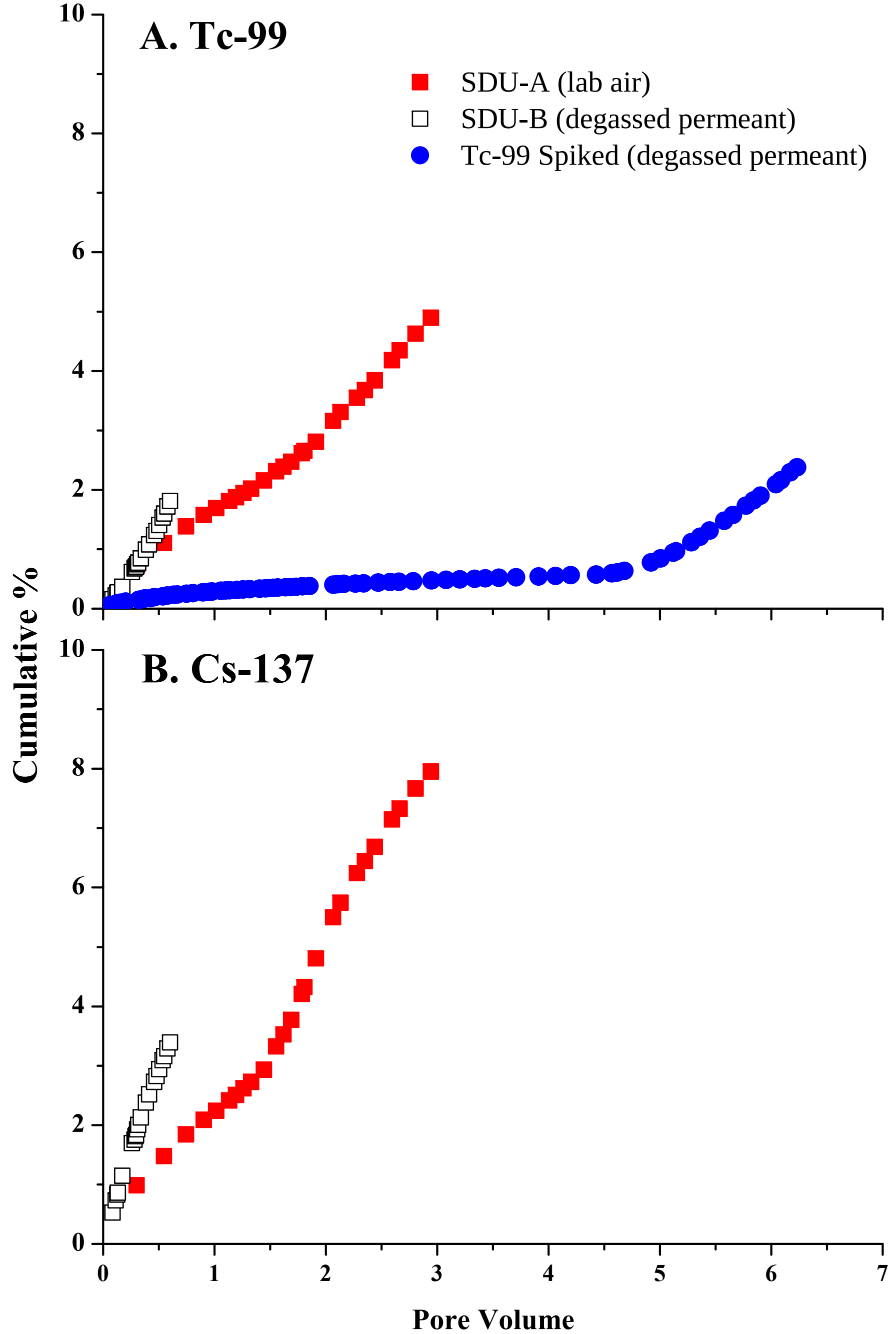

■ SDU-A (lab air)
□ SDU-B (degassed permeant)
● Tc-99 Spiked (degassed permeant)
Effluent pH
14
13
12
11
10
Pore Volume
0
1
2
3
4
5
6
7

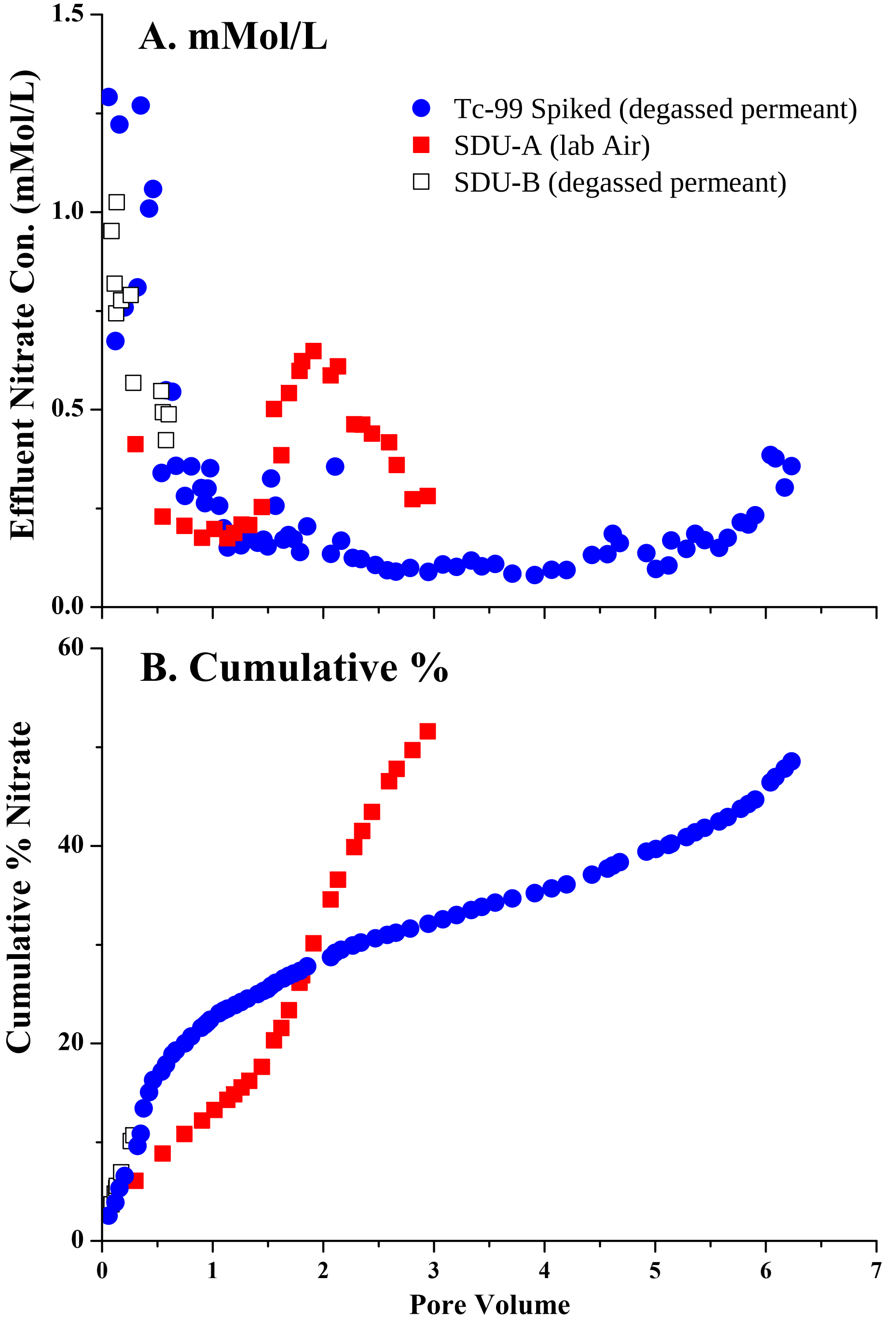
Hydraulic Conductivity (K_{sat})




A. Cs-137
SDU-A (lab air)
SDU-B (degassed permeant)
Effluent ^{137}Cs Concentration (nCi/mL)
0
50
100
150
B. Cumulative Cs-137
Cumulative ^{137}Cs (%)
0
1
2
3
4
5
6
7
8
9
10
0
1
2
3
Pore Volume


A. Tc-99
■ SDU-A (lab air)
□ SDU-B (degassed permeant)
● Tc-99 Spiked (degassed permeant)
Effluent Concentration (pCi mL^{-1})
900
800
700
600
500
400
300
200
100
0
B. Cumulative Tc-99
Cumulative ^{99}Tc (%)
10
8
6
4
2
0
0
1
2
3
4
5
6
7
Pore Volume


A. Tc-99
■ SDU-A (lab air)
□ SDU-B (degassed permeant)
● Tc-99 Spiked (degassed permeant)
B. Cs-137
Cumulative %
Pore Volume
0
2
4
6
8
10
0
1
2
3
4
5
6
7


A. mMol/L
Effluent Nitrate Con. (mMol/L)
1.5
1.0
0.5
0.0
● Tc-99 Spiked (degassed permeant)
■ SDU-A (lab Air)
□ SDU-B (degassed permeant)
B. Cumulative %
Cumulative % Nitrate
60
40
20
0
0
1
2
3
4
5
6
7
Pore Volume

Conclusions I: Spiked Samples

- Re, ^{127}I, and NO_3^- leach at similar rates, i.e., non-reactive (*LI* 7.5-7.9)
- ^{99}Tc leaches at much slower rate than Re (*LI* 9.7-11.3)
- ^{99}Tc results consistent with Hanford Cast Stone results (Westik et al., 2013; Serne et al., 2015)
- Extraction atmosphere didn’t impact Re, Tc, or ^{127}I leaching
  - Re mobile/oxidized (redox potential or Re(IV) solubility)
  - Tc immobilized/reduced
  - ^{129}I tests ongoing

Conclusions II: SDU Cores

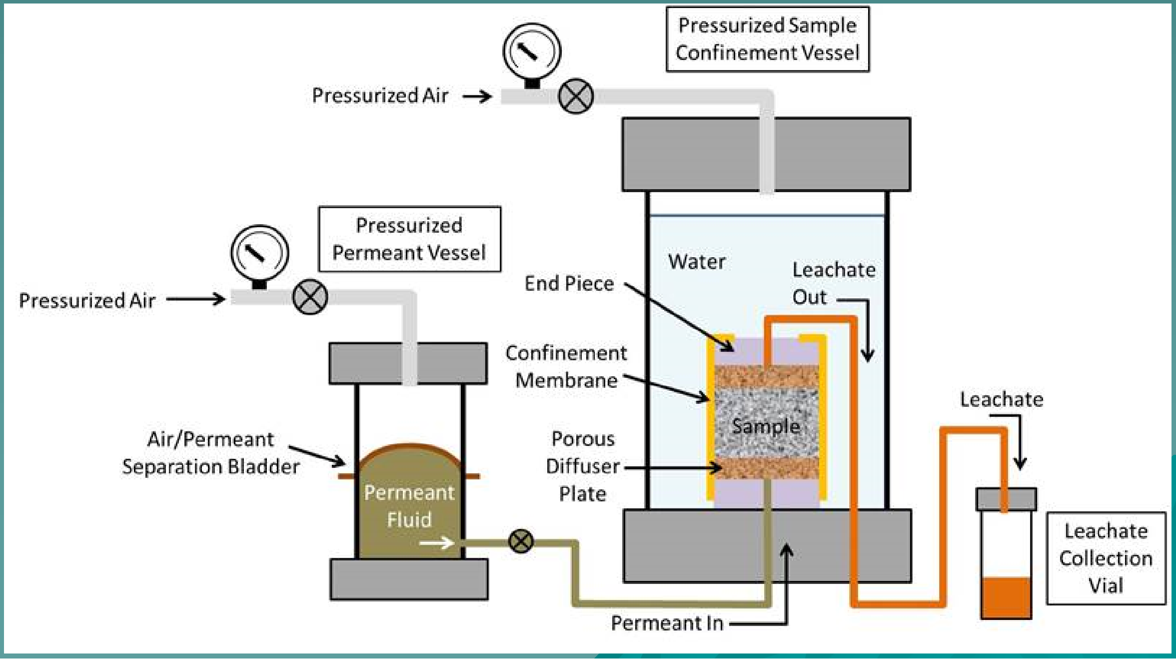
- Similar ^{99}Tc leachability observed for SDU and simulant materials (*LI* 9.6 to 11.3)
- ^{99}Tc leachability dependent on BFS source (reductive capacity) and curing time
  - (*LI* 9.6 vs 11.3)
- ^{137}Cs leaching slower than predicted
  - (*LI* 9.4-9.9)

Conclusions III: DLM Tests

- Variable residence times make comparisons difficult
- K_{sat} Lab Simulants > SDU Cores (i.e., 10^{-9} vs 10^{-10} to 10^{-11} cm s^{-1})
- Rate of leaching: NO_3^- >> ^{137}Cs > ^{99}Tc
- Tc leaching generally consistent with TcO_2 nH_2O

Modified DLM System

- Constant inlet flow rate with monitored backpressure
  - Target ≈ 1+ mL/day
- Automated control of confining pressure (i.e., inlet + 4 PSI)
- Low-volume (50 µL) flow-through sensors (pH, ORP, DO)
  - Reduce leachate exposure to atmosphere
- Controlled backpressure at the outlet (1-2 PSI)
  - Minimize leachate degassing before collection

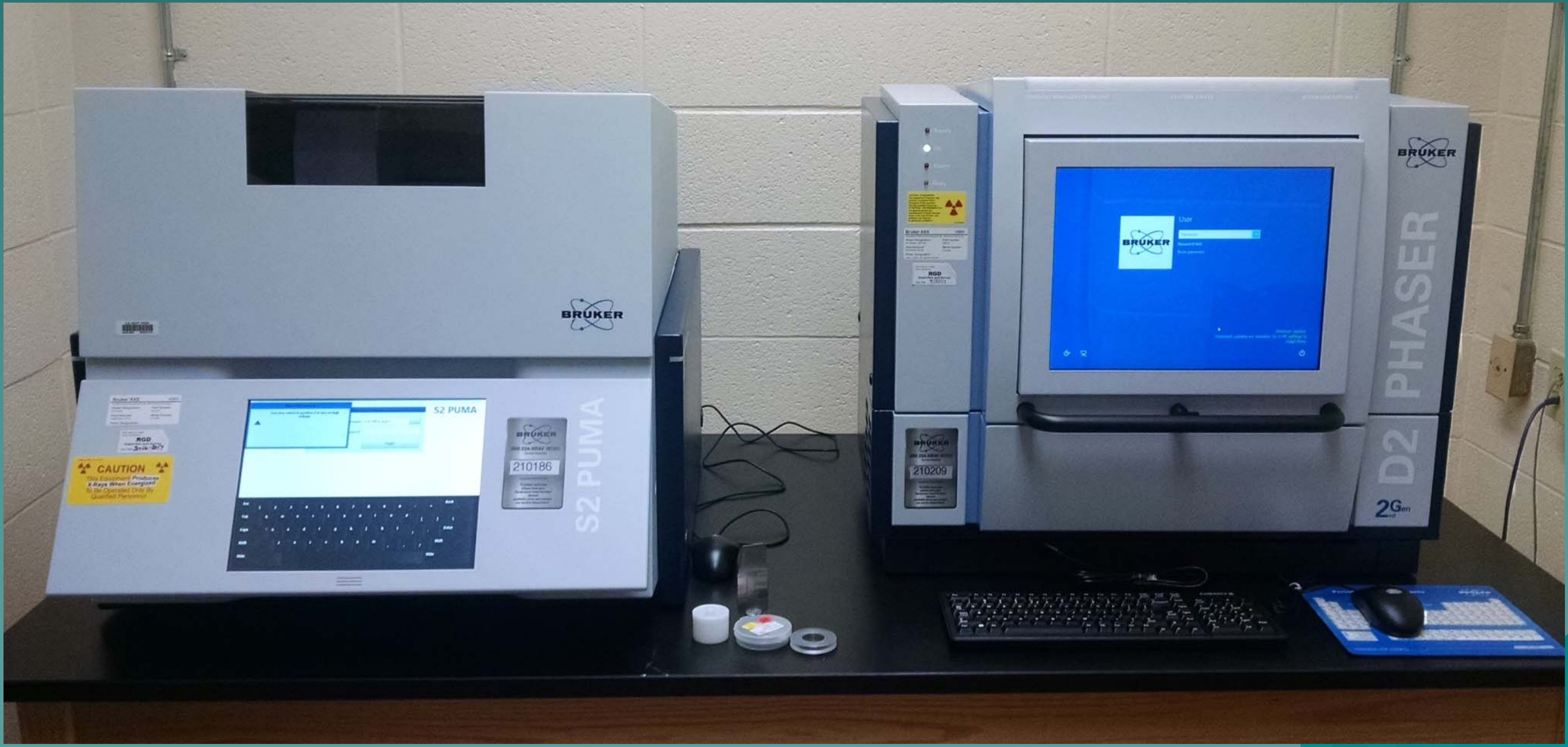


FY17 Testing

- EPA1315 and DLM tests with ^{129}I-spiked saltstone, BFS source materials
- Expanded DLM testing with controlled flow rates (solubility vs kinetic controls)
- Non-reactive tracer (^3H_2O) to estimate conductive porosity

- **Solid phase characterization during curing and leaching tests (XRF, XRD, TGA)**

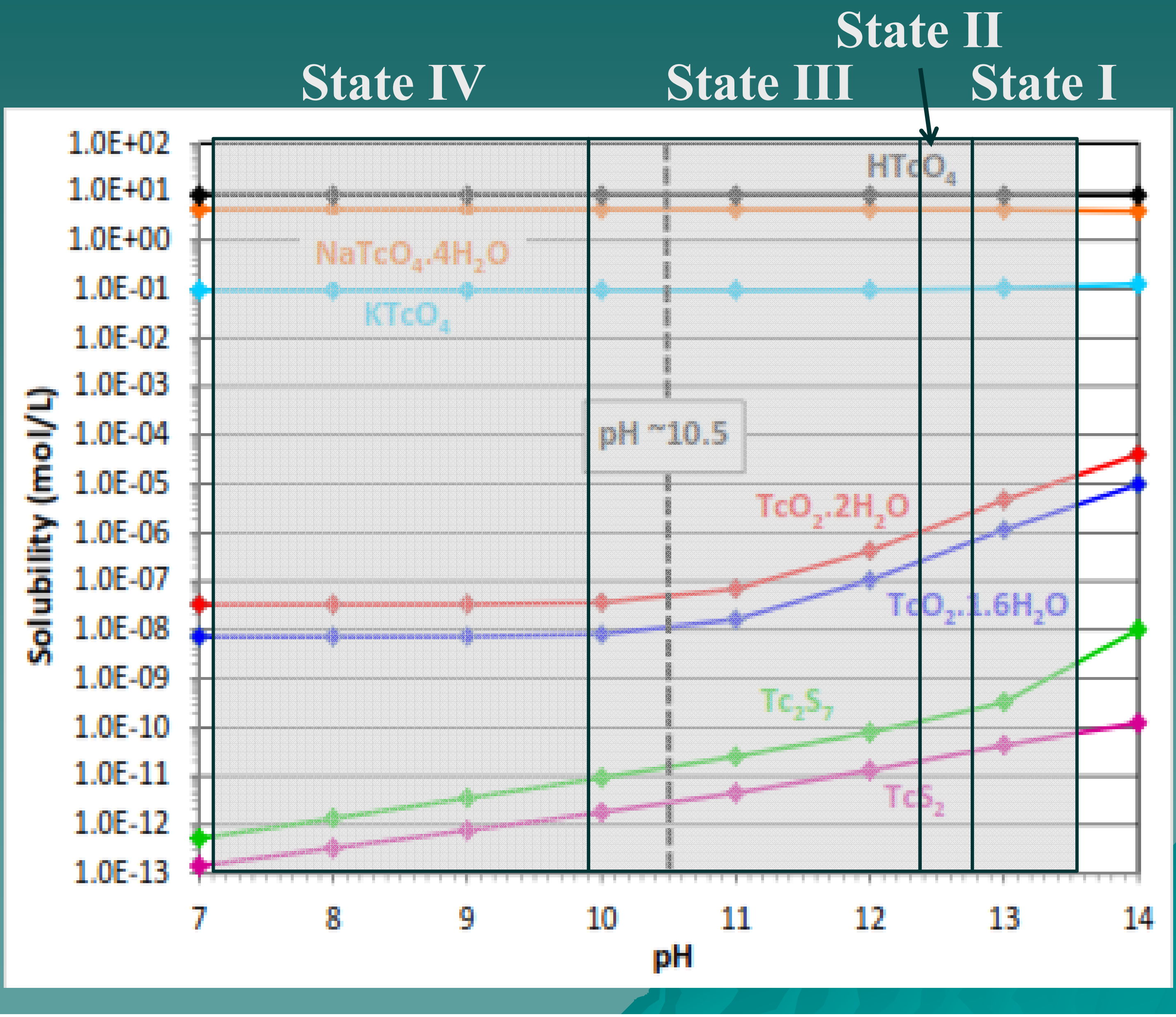
XRF **XRD**



FY17 Testing

- Geochemical Modeling – EPA and DLM data
  - CSH transformations
  - Residual reductive capacity
  - ^{99}Tc phase identification
  - Carbonation
- Calorimetry – Heat Capacity, Heat of Hydration
  - Processing - Curing rates
  - Durability

^{99}Tc Solubility vs Cement Weathering



State IV

State III

State II

State I

Important Redox Reactions

Reaction	$E^\circ, Volt$
1. $ReO^-_{4(aq)} + 4H^+ + 3e^- \leftrightarrow ReO_{2(s)} + 2H_2O_{(l)}$	-0.55
2. $TcO^-_{4(aq)} + 4H^+ + 3e^- \leftrightarrow TcO_{2(s)} + 2H_2O_{(l)}$	-0.36
3. $Fe^{2+} + 2e^- \leftrightarrow Fe_{(S)}$	-0.44
4. $CrO_4^{2-} + 4H_2O + 3e^- \leftrightarrow Cr(OH)_3 + 5OH^-$	-0.13
5. $2H^+ + 2e^- \leftrightarrow H_2$	0.00
6. $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+0.77
7. $\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- \leftrightarrow \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+0.88
8. $Fe(OH)_3 + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O$	+0.98
9. $\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^- \leftrightarrow \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	+1.12
10. $O_{2(g)} + 4H^+ + 4e^- \leftrightarrow 2H_2O$	+1.23
11. $NO_3^- + 6H^+ + 5e^- \leftrightarrow \frac{1}{2}N_2 + 2H_2O$	+1.26

^{99}Tc Analysis by ICP-MS