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Alternative Non-Acid Eluants for Spherical Resorcinol-Formaldehyde

Kofi Adu-Wusu
Charles A. Nash & Frank M. Pennebaker
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safety ◆ performance ◆ cleanup ◆ closure

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Outline

- **Background**
- **Objective/Approach**
- **Experimental**
- **Results**
- **Conclusion**
- **Path Forward**

Background

- Small-column ion exchange (SCIX) units installed in or near high-level waste tanks to remove Cs-137 from highly alkaline solutions are among the waste treatment plans in the DOE-complex.
- Spherical Resorcinol-Formaldehyde (sRF) is the ion exchange (IX) resin under consideration for SCIX at the Hanford site.
- The elution step of the multi-step IX process is typically done with nitric acid.
- An acid eluant is a potential hazard in the event of a spill, leak, etc. because the waste tanks are made of carbon steel. Corrosion and associated structural damage may ensue.
- A non-acid eluant may be a viable alternative.
- It will eliminate the need for special acid handling requirements within the tank farms.

Objective/Approach

- **Objective**
  - Evaluate the cesium elution potential from sRF resin using non-acid compounds identified in an earlier literature review.
- **Approach**
  - Use batch contact sorption screening tests.
    - Specifically, measure cesium sorption distribution coefficients (K_d) on sRF resin from cesium-containing eluants.
    - A lower cesium K_d indicates high elution potential.
  - Actual sorption (or loading) and elution tests (confirmatory tests) using a select few of the top candidate eluants.

Rationale for Using Sorption as a Screening Tool

- **It is in line with the cardinal IX principle i.e., IX is by and large a reversible process much like the chemical reactions that occur in solutions.**
  - $\underline{RA}^+ + B^+Y^- \leftrightarrow \underline{RB}^+ + AY^-$
    - Equilibrium can be approached from either direction.
- **It is in line with the elutability characteristic of the sRF resin.**
- **Generally in IX, the resin exchanges its ions for ions in solution as long as conditions are favorable.**
- **The terms sorption/loading, elution, or regeneration are outcomes or expectations based on process manipulations.**
  - The resin's characteristic function is based on the same reversibility principle regardless of whether it is sorption, elution, or regeneration.
  - The resin does not know whether it is sorption, elution, or regeneration.

Simulant Solution

- **SRS Tank 2F simulant (referred to as "regular" Tank 2F simulant solution) was used.**
  - Used to check the quality of the resin in terms degradation by comparing with data from previous test using the same simulant and same batch of sRF resin.
- **The cesium concentration in a portion of the regular simulant was increased (by adding non-radioactive cesium nitrate) to match the cesium concentration (500 mg/L nominal) in the eluants. This is referred to as "spiked" Tank 2F simulant solution.**
  - Used to establish a sorption K_d benchmark for the cesium sorption screening tests.
  - Used for the sorption portion of the actual sorption and elution tests.

Composition of SRS Tank 2F Simulant Solution

Analyte	Target Concentration, mg/L (M)	Measured Concentration, mg/L (M)
Free OH^-	12,920 (0.76)	13,600 (0.80)
CO_3^{2-}	7,800 (0.13)	nm
NO_2^-	6,854 (0.149)	7,850 (0.171)
NO_3^-	259,800 (4.19)	306,800 (4.95)
PO_4^{3-}	475 (0.005)	< 1,000 (< 0.011)
SO_4^{2-}	3,070 (0.032)	3,170 (0.033)
Cl^-	106 (0.003)	< 250 (< 0.007)
F^-	55 (0.003)	< 250 (< 0.013)
Al	6,980 (0.26)	8,600 (0.32)
Cs	2.26 (1.70×10^{-5})	2.25 (1.69×10^{-5})
K	274 (0.007)	296 (0.0076)
Na	137,900 (6.00)	144,000 (6.26)
P	384 (0.012)	164 (0.005)
Rb	0.535 (6.30×10^{-6})	0.0098 (1.0×10^{-7})
S	1,023 (0.032)	1,170 (0.036)
pH	14	14

nm = not measured

Target and measured values are fairly close.

Eluants

- **Sorption kinetics tests and sorption equilibrium screening tests**
  - Eluants containing 500 mg/L cesium (nominal).
  - Cesium nitrate was the source of cesium.
- **Sorption and elution tests (confirmatory tests)**
  - Cesium-free eluants
- **Analysis of the prepared eluants was not done.**

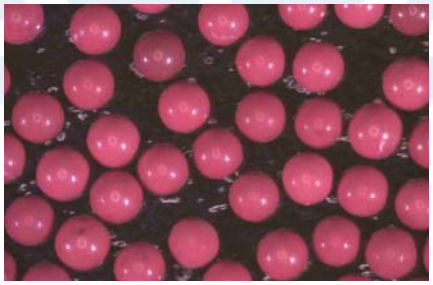
List of Eluants Tested

Ammonium Acetate	Potassium Bicarbonate
Ammonium Acetate/Ammonium Hydroxide	Potassium Bicarbonate/Potassium Hydroxide
Ammonium Bicarbonate	Potassium Carbonate
Ammonium Bicarbonate/Ammonium Hydroxide	Potassium Carbonate/Potassium Hydroxide
Ammonium Carbonate	Potassium Hydroxide
Ammonium Carbonate/Ammonium Hydroxide	Rubidium Carbonate
Calcium Chloride (CC)	Sodium Bicarbonate
Calcium Acetate Monohydrate – Substitute for CC	Sodium Bicarbonate/Sodium Hydroxide
Hexadecyltrimethylammonium Chloride	Sodium Carbonate
Lithium Chloride	Sodium Carbonate/Sodium Hydroxide
Lithium Chloride/Lithium Hydroxide	Sodium Hydroxide
Lithium Hydroxide	Tetrabutylphosphonium Hydroxide
Lithium Sulfate	Tetramethylammonium Chloride
Lithium Sulfate/Lithium Hydroxide	Tetramethylammonium Chloride/Tetramethylammonium Hydroxide
Magnesium Chloride Hexahydrate (MCH)	Tetramethylammonium Hydroxide
Magnesium Acetate Tetrahydrate – Substitute for MCH	Tetramethylphosphonium Bromide
Magnesium Sulfate	Nitric Acid – Benchmark

Selection was based on prior literature review.

Resin Preconditioning and F-Factor Determination

- **Resin preconditioning involves taking the as-received H-form sRF resin through the following steps at room temperature**
  - NaOH (1 M)
  - Deionized water
  - HNO_3 (0.5 M)
  - Deionized water (resin is in H-form)
  - NaOH (1 M)
  - Deionized water (resin is in Na-form and is damp or moist)



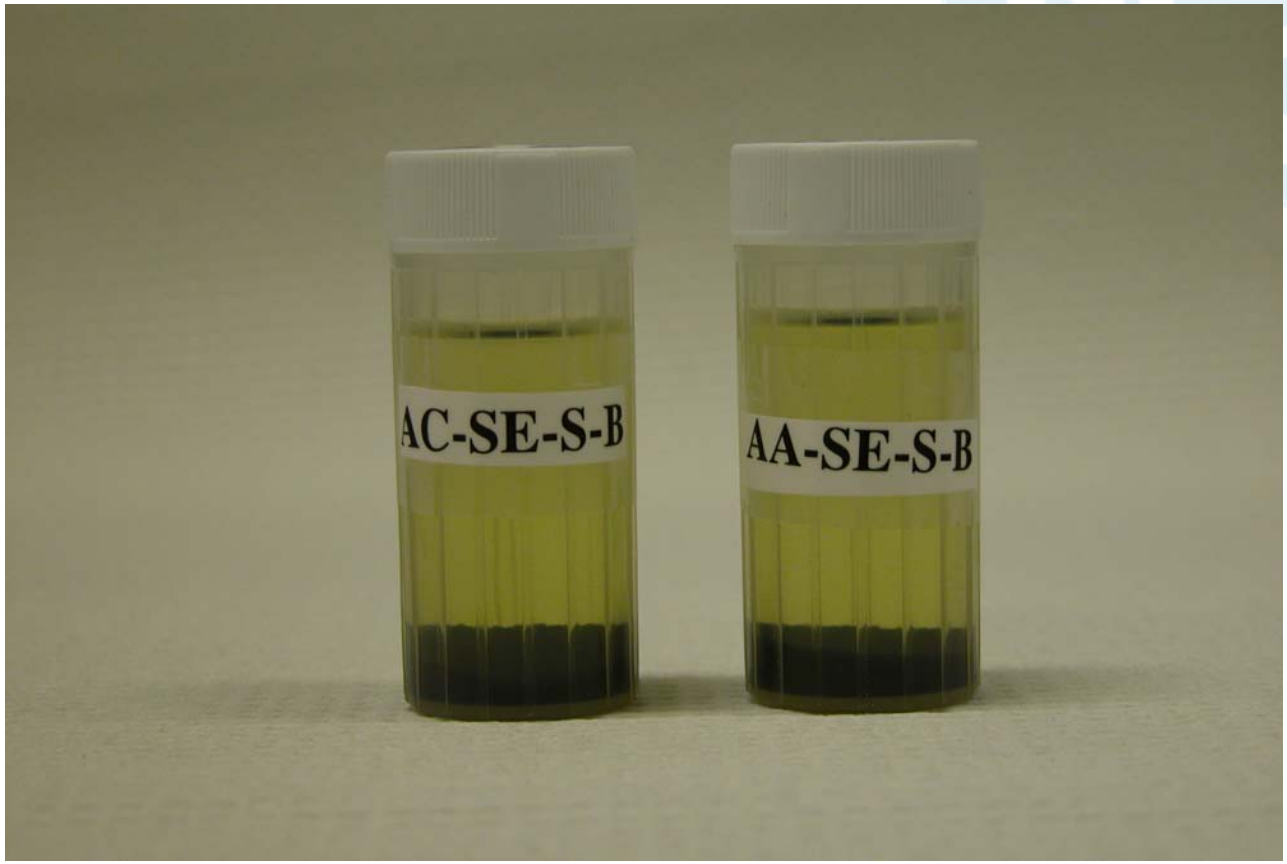
sRF resin in H-form

- **Damp resin is defined as a preconditioned resin whose water has been drained to the lowest content practical.**
- **The F-factor is the solids fraction remaining after vacuum drying samples of the damp preconditioned Na-form or H-form resin to a constant weight at 50 ºC.**
  - F-factor of the Na-form resin = 0.3157 (RSD = 1.08%)
  - F-factor of the H-form resin (prior to conversion to Na-form) = 0.2893 (RSD = 3.46%)
  - Ratio of dry Na-form/dry H-form resin = 1.28

Non-Acid Elution Via Sorption Tests

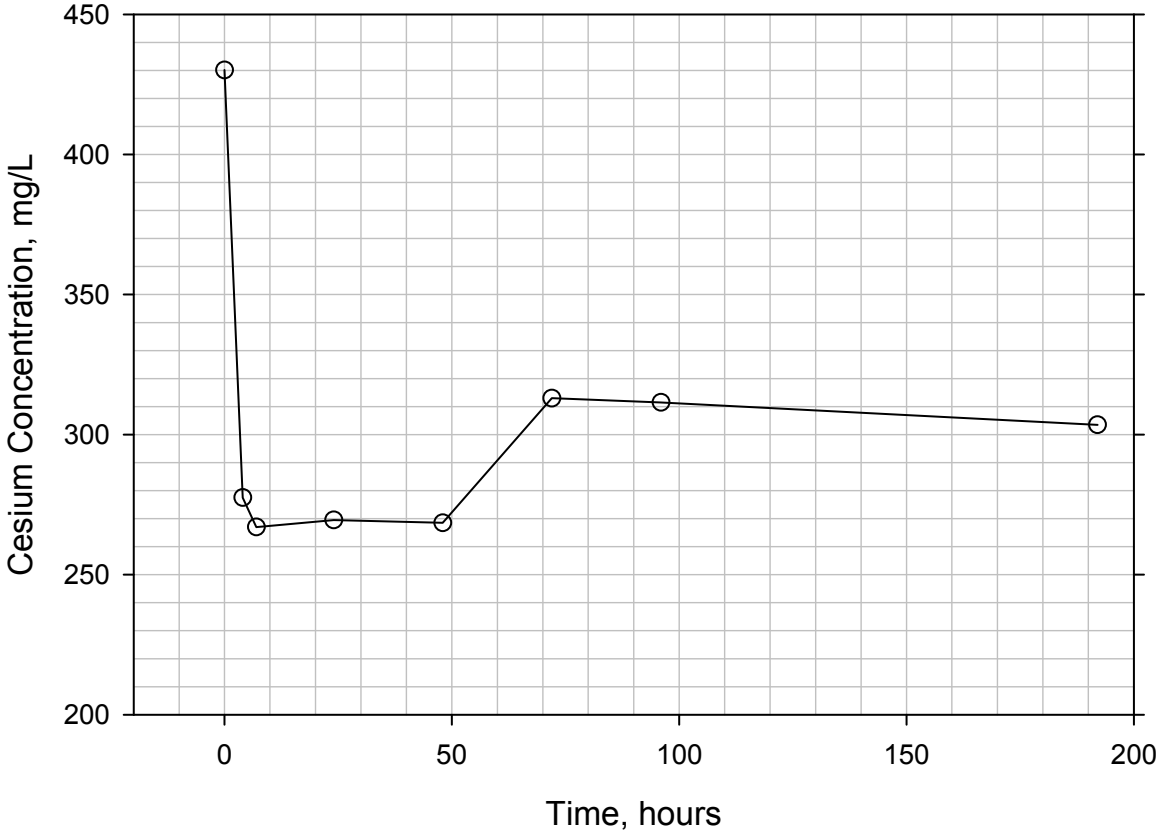
- **Batch contact sorption kinetics test – determination of sorption equilibrium time**
- **Batch contact sorption equilibrium screening tests**
- **Batch contact test entails the following**
  - Mixing 12 mL of cesium-containing eluant (or simulant solution) and 1.5840 grams of damp Na-form resin for a predetermined time at 25 ^{o}C using a shaker oven.
  - Withdrawing about 3-mL of the solution at the end of the equilibration period for analysis of cesium by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).
  - Control is a cesium-containing eluant (or simulant solution) with no solids or resin.
    - It is used to determine the initial cesium concentration.
  - Amount of cesium sorbed – determined from the initial and final concentrations of cesium in solution.

Sorption Test Vials



Sorption Kinetics

- **~2 M Ammonium Carbonate Solution and sRF Resin at 25 ^{o}C**



For all practical purposes, equilibrium is attained in 48 hours.

Sorption Kinetics

- **~2 M Ammonium Carbonate Solution and sRF Resin at 25 °C**

Time	Cesium Conc.	Phase Ratio	Cesium Sorbed	K_d	% RSD - K_d
Hours	mg/L	L/kg	mg/kg	L/kg	%
~2 M Ammonium Carbonate Solution					
0	430	n/a	n/a	n/a	n/a
4	278	26.1	3,982	14.4	5.04
7	267	26.3	4,281	16.1	6.51
24	270	26.1	4,199	15.6	2.01
48	269	26.1	4,223	15.7	0.36
72	313	26.1	3,059	9.78	2.97
96	312	26.1	3,096	10.0	19.1
192	**304**	**26.2**	**3,315**	**10.9**	**13.5**
Spiked Tank 2F Simulant Solution					
0	424	n/a	n/a	n/a	n/a
192	**46.7**	**26.1**	**9,850**	**212**	**10.6**
Regular Tank 2F Simulant Solution					
0	2.24	n/a	n/a	n/a	n/a
192	0.0523	26.1	57.2	1,100	10.4

All the sorption calculations are based on Na-form resin.
n/a = not applicable

- Spiked Tank 2F simulant data is the benchmark for the sorption screening tests.
- K_d = 212 is cutoff value
- Comparison of the 192-hour data for ammonium carbonate with the 192-hour data for the spiked simulant indicates ammonium carbonate holds promise for cesium elution (K_d of 10.9 versus 212).

Sorption Distribution Coefficient (K_d)

$$K_d = \frac{(C_i - C_f)V}{mFC_f}$$

- C_i = initial cesium concentration
- C_f = final cesium concentration
- V = volume of solution
- m = mass of damp resin
- F = F-factor of the damp resin
- V/(mF) = phase ratio

Sorption Equilibrium Screening Tests at 25 °C

Eluant Solution	Initial Cesium Conc.	Final Cesium Conc.	Phase Ratio	Cesium Sorbed	K_d	% RSD - K_d
	mg/L	mg/L	L/kg	mg/kg	L/kg	%
Equilibrium Test – Set 1						
3 M Potassium Carbonate	482	153	26.2	8,612	**57.1**	19.7
3 M Potassium Hydroxide	472	119	26.2	9,253	**78.1**	4.21
3 M Rubidium Carbonate	*602*	499	26.1	2,698	**5.43**	24.2
1.5 M Sodium Carbonate	473	18.9	26.1	11,847	**633**	15.3
3 M Sodium Hydroxide	456	6.09	26.2	11,778	**1,938**	4.03
1 M Tetrabutylphosphonium Hydroxide	*376*	12.7	26.1	9,499	**758**	14.1
1 M Tetramethylammonium Hydroxide	*372*	25.4	26.2	9,078	**364**	21.0
Equilibrium Test – Set 2						
2 M Ammonium Acetate	444	344	26.2	2,612	**7.59**	3.53
~1.8 M Ammonium Bicarbonate	434	360	26.2	1,932	**5.37**	13.3
~2 M Ammonium Carbonate	436	397	26.2	1,037	**2.62**	14.1
~2 M Ammonium Carbonate/1 M Ammonium Hydroxide	*390*	340	26.2	1,328	**3.92**	25.9
2 M Calcium Chloride	434	270	26.2	*4,299*	***16.7***	45.7
0.03 M Hexadecyltrimethylammonium Chloride	443	48.7	26.2	10,319	**212**	7.18
2 M Lithium Chloride	427	*116*	26.2	8,159	***75.0***	39.1
~2.7 M Lithium Hydroxide	419	2.49	26.2	10,891	**4,439**	16.7
1.8 M Lithium Sulfate	429	132	26.2	7,776	**59.1**	1.02
3 M Magnesium Chloride Hexahydrate	*394*	174	26.2	5,770	**33.2**	5.22
1.8 M Magnesium Sulfate	434	109	26.2	8,511	**78.1**	0.98
~1.7 M Potassium Bicarbonate	449	39.2	26.1	10,711	**274**	3.46
0.75 M Sodium Bicarbonate	440	30.0	26.2	10,727	**357**	6.01
0.03 M Tetramethylammonium Hydroxide	*363*	1.91	26.2	9,450	**5,072**	20.7
0.1 M Tetramethylammonium Hydroxide	*321*	6.45	26.2	8,238	**1,282**	8.66

Test Sets 1 & 2

Equilibration time = 48 hours
All the sorption calculations are based on Na-form resin.
Values in italics have either significantly different replicate values or significantly lower/higher initial cesium concentrations than the target values (459 or 458 mg/L).

Sorption Equilibrium Screening Tests at 25 °C

Test Set 3

Eluant Solution	Initial Cesium Conc.	Final Cesium Conc.	Phase Ratio	Cesium Sorbed	K_d	% RSD - K_d
	mg/L	mg/L	L/kg	mg/kg	L/kg	%
Equilibrium Test – Set 3						
2 M Ammonium Acetate/1.5 M Ammonium Hydroxide	412	307	26.2	2,754	**8.97**	2.32
~1.8 M Ammonium Bicarbonate/1M Ammonium Hydroxide	*1.11*	0.759	26.2	9.07	**12.0**	9.75
0.05 M Hexadecyltrimethylammonium Chloride	437	52.2	26.2	10,084	***198***	27.3
2 M Lithium Chloride/~1 M Lithium Hydroxide	425	*12.4*	26.1	10,781	***997***	50.4
1.8 M Lithium Sulfate/~0.5 M Lithium Hydroxide	451	22.3	26.2	11,210	**503**	2.73
~1.7 M Potassium Bicarbonate/0.5 M Potassium Hydroxide	407	*97.3*	26.2	8,109	***87.6***	36.1
3 M Potassium Carbonate/0.5 M Potassium Hydroxide	445	157	26.2	7,548	***49.5***	29.6
0.75 M Sodium Bicarbonate/0.5 M Sodium Hydroxide	458	29.5	26.2	11,217	**382**	6.02
1.5 M Sodium Carbonate/0.5 M Sodium Hydroxide	438	10.0	26.2	11,205	**1,128**	13.9
0.03 M Tetrabutylphosphonium Hydroxide	444	3.67	26.2	11,521	**3,164**	11.2
0.05 M Tetrabutylphosphonium Hydroxide	416	2.76	26.2	10,826	**3,927**	4.42
0.03 M Tetramethylammonium Chloride	413	*24.2*	26.2	10,174	***540***	68.0
0.03 M Tetramethylammonium Chloride/0.03 M Tetramethylammonium Hydroxide	437	26.8	26.2	10,729	**401**	4.10
0.03 M Tetramethylphosphonium Bromide	421	22.5	26.2	10,415	**464**	2.18

Equilibration time = 48 hours
All the sorption calculations are based on Na-form resin.
Values in italics have either significantly different replicate values or significantly lower/higher initial cesium concentrations than the target values (459 or 458 mg/L).

What-If Scenario K_d Calculations for Initial Cesium Concentration

- **Test Set 1**

3 M Rubidium Carbonate						
Initial cesium concentration/Target initial cesium concentration Ratio = 1.313					T_i = 458	
Actual Sorption Data		What-If Scenarios				
C_i =	602	If C_i =	458	458	458	458
dC =	103	and dC =	30	50	80	95
C_f =	499	then C_f =	428	408	378	363
S =	2,698	S =	782	1,304	2,086	2,478
K_d =	5	K_d =	2	3	6	7
1 M Tetrabutylphosphonium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.820					T_i = 459	
Actual Sorption Data		What-If Scenarios				
C_i =	376	If C_i =	459	459	459	459
dC =	363	and dC =	383	403	430	363
C_f =	12.7	then C_f =	76	56	29	96
S =	9,499	S =	10,012	10,534	11,240	9,489
K_d =	758	K_d =	133	190	394	99
1 M Tetramethylammonium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.812					T_i = 459	
Actual Sorption Data		What-If Scenarios				
C_i =	372	If C_i =	459	459	459	459
dC =	347	and dC =	367	387	415	347
C_f =	25.4	then C_f =	92	72	44	112
S =	9,078	S =	9,603	10,126	10,858	9,079
K_d =	364	K_d =	105	141	249	81

C_i = Initial cesium concentration, mg/L
C_f = Final cesium concentration, mg/L
dC = Change in solution cesium concentration i.e., initial minus final cesium concentration, mg/L
S = Cesium sorbed, mg/kg
K_d = Sorption distribution coefficient, L/kg
T_i = Target initial cesium concentration, mg/L

- For eluants with significantly lower or higher initial cesium concentrations than their respective target initial cesium concentrations.
- Affirm the elution potential of an eluant and hence, its ranking.

What-If Scenario K_d Calculations for Initial Cesium Concentration

- **Test Set 2**

~2 M Ammonium Carbonate/1 M Ammonium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.851					T_i = 459	
Actual Sorption Data		What-If Scenarios				
C_i =	390	If C_i =	459	459	459	459
dC =	51	and dC =	65	75	90	51
C_f =	340	then C_f =	394	384	369	408
S =	1,328	S =	1,701	1962	2,355	1,334
K_d =	4	K_d =	4	5	6	3
3 M Magnesium Chloride Hexahydrate						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.860					T_i = 459	
Actual Sorption Data		What-If Scenarios				
C_i =	394	If C_i =	459	459	459	459
dC =	220	and dC =	240	260	295	220
C_f =	174	then C_f =	219	199	164	239
S =	5,770	S =	6,283	6,807	7,723	5,760
K_d =	33	K_d =	29	34	47	24
0.03 M Tetramethylammonium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.792					T_i = 459	
Actual Sorption Data		What-If Scenarios				
C_i =	363	If C_i =	459	459	459	459
dC =	361	and dC =	385	405	430	361
C_f =	1.9	then C_f =	74	54	29	98
S =	9,450	S =	10,072	10,595	11,249	9,444
K_d =	5,072	K_d =	137	198	394	97
0.1 M Tetramethylammonium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.701					T_i = 459	
Actual Sorption Data		What-If Scenarios				
C_i =	321	If C_i =	459	459	459	459
dC =	315	and dC =	365	385	420	315
C_f =	6.5	then C_f =	94	74	39	144
S =	8,238	S =	9,545	10,068	10,983	8,237
K_d =	1,282	K_d =	102	137	285	57

Eluant Rankings/Elution Potential Categories

Eluant Solution	pH	K_d, L/kg	Rank	Cesium Elution Potential
~2 M Ammonium Carbonate	9	2.62	1	High
~2 M Ammonium Carbonate/1 M Ammonium Hydroxide	9	3.92	2	High (what-if scenario K_d range is 4-6)
~1.8 M Ammonium Bicarbonate	9	5.37	3	High
3 M Rubidium Carbonate	10.5	5.43	3	High (what-if scenario K_d range is 2-7)
2 M Ammonium Acetate	7	7.59	5	High
2 M Ammonium Acetate/1.5 M Ammonium Hydroxide	10	8.97	6	High
~1.8 M Ammonium Bicarbonate/1 M Ammonium Hydroxide	9	12.0	7	High
2 M Calcium Chloride	6	16.7/11.3/22.0	8	High
3 M Magnesium Chloride Hexahydrate	5	33.2	9	High (what-if scenario K_d range is 29-47)
3 M Potassium Carbonate/0.5M Potassium Hydroxide	11/14	49.5/39.9/59.9	10	High
3 M Potassium Carbonate	14/14	57.1	11	High
1.8 M Lithium Sulfate	8	59.1	12	High
2 M Lithium Chloride	6	75.0/54.3/95.8	13	High
1.8 M Magnesium Sulfate	7	78.1	14	High
3 M Potassium Hydroxide	14	78.1	14	High
~1.7 M Potassium Bicarbonate/0.5 M Potassium Hydroxide	9/10	87.6/65.3/110	16	High
0.05 M Hexadecyltrimethylammonium Chloride	7	198/160/237	17	Moderate/low
0.03 M Hexadecyltrimethylammonium Chloride	7	212	18	Low
~1.7 M Potassium Bicarbonate	9/11	274	19	Low
0.75 M Sodium Bicarbonate	8	357	20	Low
1 M Tetramethylammonium Hydroxide	13	364	21	Low/moderate based on the what-if scenario K_d range of 105-249
0.75 M Sodium Bicarbonate/0.5 M Sodium Hydroxide	10	382	22	Low
0.03 M Tetramethylammonium Chloride/0.03 M Tetramethylammonium Hydroxide	13	401	23	Low
0.03 M Tetramethylphosphonium Bromide	7	464	24	Low
1.8 M Lithium Sulfate/~0.5 M Lithium Hydroxide	14	503	25	Low
0.03 M Tetramethylammonium Chloride	7	540/280/800	26	Low
1.5 M Sodium Carbonate	14/14	633	27	Low
1 M Tetrabutylphosphonium Hydroxide	13	758	28	Low/moderate based on the what-if scenario K_d range of 133-394
2 M Lithium Chloride/~1 M Lithium Hydroxide	13	997	29	Low
1.5 M Sodium Carbonate/0.5 M Sodium Hydroxide	14	1,128	30	Low
0.1 M Tetramethylammonium Hydroxide	14	1,282	31	Low/moderate based on the what-if scenario K_d range of 102-285
3 M Sodium Hydroxide	14	1,938	32	Low
0.03 M Tetrabutylphosphonium Hydroxide	14	3,164	33	Low
0.05 M Tetrabutylphosphonium Hydroxide	14	3,927	34	Low
~2.7 M Lithium Hydroxide	14	4,439	35	Low
0.03 M Tetramethylammonium Hydroxide	14	5,072	36	Low/moderate based on the what-if-scenario K_d range of 137-394

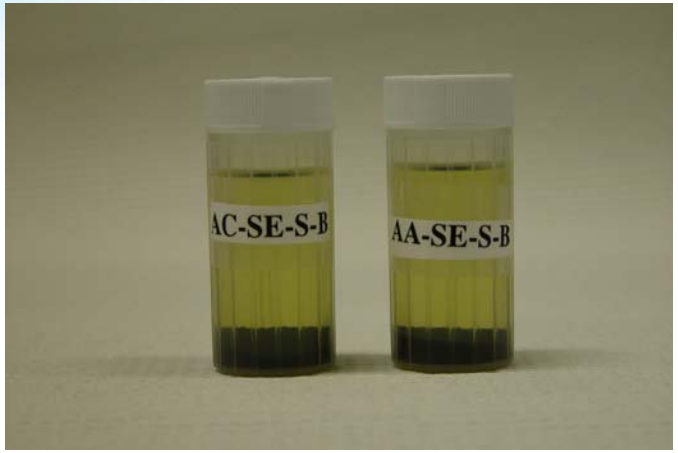
Eluant Rankings/Elution Potential Categories

- **Ammonium compounds, as a group, stand out as the most promising eluants with rubidium carbonate, calcium chloride, magnesium chloride among the top ten overall.**
- **The organic and sodium compounds are generally at the bottom half of the ranking.**
- **High pH (i.e., pH > 12) eluant solutions had mediocre performance except potassium compounds.**
- **Eluants with pH of ≤ 11 had promising performance except some of the organics, 0.75 M sodium bicarbonate, and 0.75 M sodium bicarbonate/0.5M sodium hydroxide solutions.**
- **Elution Potential Categories**
  - K_d < ~100 L/kg: High cesium elution potential
  - ~100 < K_d < ~200 L/kg: Moderate cesium elution potential
  - K_d > ~200 L/kg: Low cesium elution potential

Sorption & Elution Tests (Confirmatory Tests)

- **Mimic the typical sRF-cesium column IX process i.e., loading, caustic wash, water rinse, and elution via the following steps**
  - Batch contact sorption with spiked Tank 2F simulant solution
  - Quasi-column separation of cesium-laden resin from simulant solution – vacuum filtration
  - Quasi-column caustic wash (feed displacement) with 0.1 M NaOH solution – vacuum filtration
  - Quasi-column deionized water rinse – vacuum filtration
  - Quasi-column elution – percolation without vacuum filtration or pumping
- **Sorption, caustic wash, and water rinse solutions; and eluate were analyzed for cesium by ICP-MS.**

Sorption & Elution Tests – Vials and Filter Units



Sorption Step

Quasi-column resin/simulant separation, caustic wash, water rinse, and elution steps

Sorption & Elution Tests (Confirmatory Tests)

- **Sorption/Loading at 25 °C**

Sorption Solution – Test #	Initial Cesium Conc.	Final Cesium Conc.	Phase Ratio	Cesium Sorbed	% RSD – Cs Sorbed
Units	mg/L	mg/L	L/kg	mg/kg	%
Spiked Tank 2F Simulant – Test 1	438	88.9	26.2	**9,147**	4.11
Spiked Tank 2F Simulant – Test 2	454	66.7	26.1	**10,125**	1.66
Spiked Tank 2F Simulant – Test 3	456	61.6	26.1	**10,301**	1.58
Spiked Tank 2F Simulant – Test 4	459	83.4	26.2	**9,832**	1.44
Spiked Tank 2F Simulant – Test 5	457	56.0	26.2	**10,508**	0.97
Average	453	71.3	26.2	**9,983**	
Percent RSD	1.80	19.9	0.14	5.30	

Sorption equilibration time = 48 hours
All the sorption calculations are based on Na-form resin.

- The sorption tests can be considered as 10 replicates.
- Various percent RSDs indicate good overall reproducibility.

Sorption & Elution Tests (Confirmatory Tests)

- **Elution at Room Temperature (~25 °C)**

Eluant Solution (Pre-Test pH) – Test #	Cesium Conc. in Eluate	Cesium in Eluate	Cesium Sorbed on Resin	Percent Cesium Eluted	% RSD – % Cs Eluted
Units	mg/L	mg	mg	%	%
2 M Ammonium Acetate (6) – Test 1	35.8	4.296	4.580	**93.6**	7.23
~2 M Ammonium Carbonate (9) – Test 2	40.8	4.890	5.067	**96.5**	3.44
1.5 M Calcium Acetate Monohydrate (8) – Test 3	6.76	0.811	5.157	**15.7**	13.6
2 M Magnesium Acetate Tetrahydrate (8) – Test 4	2.76	0.331	4.911	**6.73**	3.59
0.5 M Nitric Acid (0) – Test 5	43.8	5.250	5.249	**100**	2.04

Elution time = ~ 1 day
All the elution calculations are based on Na-form resin.
Volume of eluant solution = 120 mL

- High elution performance – ammonium acetate, ammonium carbonate, and nitric acid (benchmark eluant).
  - Confirms the effectiveness of the indirect sorption method used to screen the eluants.
- Marginal elution performance – calcium acetate and magnesium acetate
  - Performance may improve at lower resin cesium loading and/or a boost of pH to 9/10.

Sorption & Elution Tests (Confirmatory Tests)

- **Caustic Wash & Water Rinse at Room Temperature (~25 ºC)**

	CAUSTIC WASH		WATER RINSE	
Test #	**Cesium Conc. in Caustic Wash Solution**	**Cesium in Caustic Wash Solution**	**Cesium Conc. in Water Rinse Solution**	**Cesium in Water Rinse Solution**
Units	mg/L	mg	mg/L	mg
Test 1	5.97	0.1194	0.856	0.0171
Test 2	5.00	0.0999	0.653	0.0131
Test 3	3.58	0.0716	0.642	0.0128
Test 4	5.64	0.1128	0.908	0.0182
Test 5	4.14	0.0828	0.642	0.0128
Average	4.87	0.0973	0.740	0.0148
Percent RSD	20.6	20.6	17.7	17.7

Volume of caustic wash solution = 20 mL
Volume of water rinse solution = 20 mL

Reproducibility is generally good.

Conclusions

- **Ammonium compounds, especially ammonium acetate and ammonium carbonate, stand out (among the 36 eluants screened) as potential non-acid eluants for cesium on sRF resin.**
- **Even though the elution performance of calcium acetate and magnesium acetate was low, their performance may be enhanced**
  - Relatively lower resin cesium loadings
  - Increase of their pH to about 9/10

Path Forward

- **Perform elution optimization studies on eluant concentration, pH, and temperature using mini-columns (2 to 5-mL).**
- **Develop regeneration schemes using mini-columns.**
- **Confirm the process with a typical laboratory multi-step small column (10 to 12-mL) IX unit.**
- **All the above will be performed with simulant solutions.**

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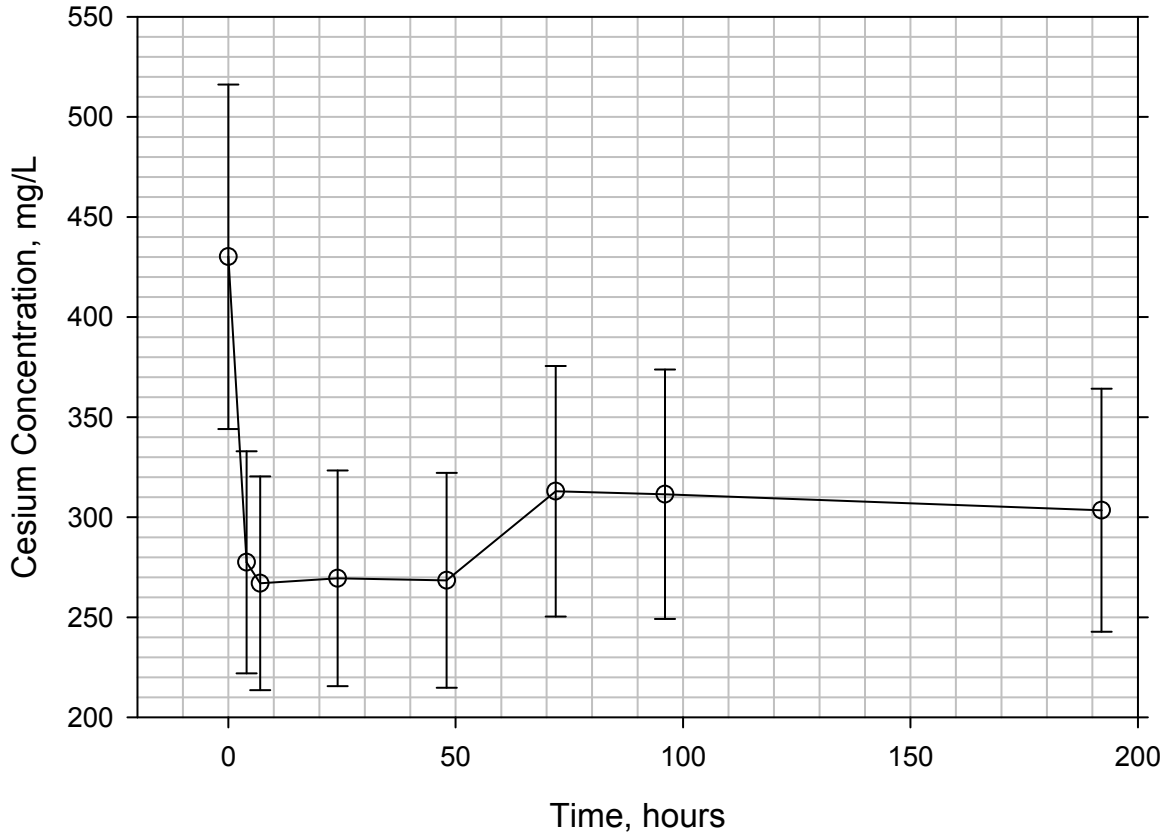
Questions?

- **Contact Information**
  - Kofi Adu-Wusu
  - 803-725-8866
  - kofi.adu-wusu@srnl.doe.gov

Backup Slides

Sorption Kinetics

- **~2 M Ammonium Carbonate Solution and sRF Resin at 25 °C**



For all practical purposes, equilibrium is attained in 48 hours.

Sorption Kinetics

- **~2 M Ammonium Carbonate Solution and sRF Resin at 25 °C**

	Replicate A	Replicate B	Replicate A	Replicate B	Replicate A	Replicate B	Replicate A	Replicate B	Average	Percent RSD
Time	**Cesium Conc.**	**Cesium Conc.**	**Phase Ratio**	**Phase Ratio**	**Cesium Sorbed**	**Cesium Sorbed**	**K_d**	**K_d**	**K_d**	
Hours	mg/L	mg/L	L/kg	L/kg	mg/kg	mg/kg	L/kg	L/kg	L/kg	%
~2 M Ammonium Carbonate Solution										
0	426	435	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
4	271	284	26.1	26.1	4,030	3,933	14.9	13.8	14.4	5.04
7	259	275	26.1	26.4	4,350	4,212	16.8	15.3	16.1	6.51
24	268	271	26.1	26.2	4,115	4,282	15.4	15.8	15.6	2.01
48	266	271	26.2	26.1	4,172	4,272	15.7	15.8	15.7	0.36
72	308	318	26.2	26.1	3,075	3,044	10.0	9.6	9.78	2.97
96	320	303	26.2	26.1	2,761	3432	8.6	11.3	10.0	19.1
192	**309**	**298**	**26.2**	**26.1**	**3,058**	**3,571**	**9.9**	**12.0**	**10.9**	**13.5**
Spiked Tank 2F Simulant Solution										
0	424	425	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
192	**43.5**	**49.9**	**26.1**	**26.1**	**9,914**	**9,786**	**228**	**196**	**212**	**10.6**
Regular Tank 2F Simulant Solution										
0	2.24	2.24	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
192	0.0485	0.056	26.1	26.2	57.3	57.1	1,182	1,019	1,100	10.4

All the sorption calculations are based on Na-form resin.
n/a = not applicable

Sorption Equilibrium Screening Tests at 25 °C

Eluant Solution	Replicates A: Initial Cesium Conc.	Replicates B: Initial Cesium Conc.	Replicates A: Final Cesium Conc.	Replicates B: Final Cesium Conc.	Replicates A: Phase Ratio	Replicates B: Phase Ratio	Replicates A: Cesium Sorbed	Replicates B: Cesium Sorbed	Replicates A: K_d	Replicates B: K_d	Average K_d	Percent RSD
	mg/L	mg/L	mg/L	mg/L	L/kg	L/kg	mg/kg	mg/kg	L/kg	L/kg	L/kg	%
Equilibrium Test – Set 1												
3 M Potassium Carbonate	486	478	169	137	26.2	26.2	8,306	8,918	49.1	65.1	**57.1**	19.7
3 M Potassium Hydroxide	476	469	117	120	26.2	26.1	9,412	9,095	80.4	75.8	**78.1**	4.21
3 M Rubidium Carbonate	*593*	*611*	506	491	26.1	26.1	2,275	3,121	4.50	6.36	**5.43**	24.2
1.5 M Sodium Carbonate	477	469	17.1	20.7	26.1	26.1	12,006	11,689	702	565	**633**	15.3
3 M Sodium Hydroxide	449	463	5.82	6.35	26.2	26.2	11,600	11,955	1,993	1,883	**1,938**	4.03
1 M Tetrabutylphosphonium Hydroxide	*378*	*374*	11.5	13.8	26.2	26.1	9,581	9,416	833	682	**758**	14.1
1 M Tetramethylammonium Hydroxide	*369*	*376*	28.7	22.1	26.2	26.1	8,907	9,249	310	418	**364**	21.0
Equilibrium Test – Set 2												
2 M Ammonium Acetate	431	457	336	352	26.2	26.2	2,487	2,738	7.40	7.78	**7.59**	3.53
~1.8 M Ammonium Bicarbonate	435	433	355	365	26.2	26.2	2,087	1,777	5.88	4.87	**5.37**	13.3
~2 M Ammonium Carbonate	438	434	395	398	26.2	26.2	1,136	938	2.88	2.36	**2.62**	14.1
~2 M Ammonium Carbonate/1 M Ammonium Hydroxide	*386*	*394*	344	335	26.2	26.2	1,102	1,553	3.20	4.64	**3.92**	25.9
2 M Calcium Chloride	439	429	*307*	*233*	26.2	26.2	*3,462*	*5,136*	*11.3*	*22.0*	**16.7**	45.7
0.03 M Hexadecyltrimethylammonium Chloride	439	447	46.1	51.3	26.2	26.2	10,292	10,346	223	201	**212**	7.18
2 M Lithium Chloride	433	422	*141*	*90.5*	26.2	26.2	7,650	8,668	*54.3*	*95.8*	**75.0**	39.1
~2.7 M Lithium Hydroxide	422	415	2.80	2.18	26.2	26.2	10,966	10,816	3,916	4,962	**4,439**	16.7
1.8 M Lithium Sulfate	435	423	134	129	26.2	26.2	7,868	7,685	58.7	59.6	**59.1**	1.02
3 M Magnesium Chloride Hexahydrate	*389*	*400*	168	180	26.2	26.2	5,784	5,756	34.4	32.0	**33.2**	5.22
1.8 M Magnesium Sulfate	437	432	109	109	26.2	26.2	8,570	8,452	78.6	77.5	**78.1**	0.98
~1.7 M Potassium Bicarbonate	453	445	38.6	39.7	26.2	26.2	10,822	10,599	280	267	**274**	3.46
0.75 M Sodium Bicarbonate	418	462	29.7	30.3	26.2	26.2	10,164	11,289	342	373	**357**	6.01
0.03 M Tetramethylammonium Hydroxide	*355*	*371*	1.59	2.23	26.2	26.2	9,242	9,658	5,812	4,331	**5,072**	20.7
0.1 M Tetramethylammonium Hydroxide	*320*	*323*	6.81	6.09	26.2	26.2	8,193	8,283	1,203	1,360	**1,282**	8.66

Test Sets 1 & 2

Equilibration time = 48 hours
All the sorption calculations are based on Na-form resin.
Values in italics have either significantly different replicate values or significantly lower/higher initial cesium concentrations than the target values (459 or 458 mg/L).

Sorption Equilibrium Screening Tests at 25 °C

Test Set 3

	Replicates		Replicates		Replicates		Replicates		Replicates			Percent
	A	B	A	B	A	B	A	B	A	B	Average	RSD
Eluant Solution	**Initial Cesium Conc.**	**Initial Cesium Conc.**	**Final Cesium Conc.**	**Final Cesium Conc.**	**Phase Ratio**	**Phase Ratio**	**Cesium Sorbed**	**Cesium Sorbed**	**K_d**	**K_d**	**K_d**	
	mg/L	mg/L	mg/L	mg/L	L/kg	L/kg	mg/kg	mg/kg	L/kg	L/kg	L/kg	%
Equilibrium Test – Set 3												
2 M Ammonium Acetate/1.5 M Ammonium Hydroxide	415	410	310	304	26.2	26.2	2,735	2,772	8.82	9.12	**8.97**	2.32
~1.8 M Ammonium Bicarbonate/1M Ammonium Hydroxide	*1.11*	*1.10*	0.778	0.739	26.2	26.2	8.68	9.46	11.16	12.81	**12.0**	9.75
0.05 M Hexadecyltrimethylammonium Chloride	419	456	58.9	45.4	26.2	26.2	9,429	10,739	*160*	*237*	**198**	27.3
2 M Lithium Chloride/~1 M Lithium Hydroxide	424	426	*8.02*	*16.7*	26.1	26.12	10,847	10,716	*1,352*	*642*	**997**	50.4
1.8 M Lithium Sulfate/~0.5 M Lithium Hydroxide	467	435	23.5	21.1	26.2	26.2	11,597	10,823	493	513	**503**	2.73
~1.7 M Potassium Bicarbonate/0.5 M Potassium Hydroxide	405	409	*116*	*78.6*	26.2	26.2	7,571	8,647	*65.3*	*110*	**87.6**	36.1
3 M Potassium Carbonate/0.5 M Potassium Hydroxide	444	447	135	179	26.2	26.2	8,087	7,010	*59.9*	*39.2*	**49.5**	29.6
0.75 M Sodium Bicarbonate/0.5 M Sodium Hydroxide	462	454	30.9	28.0	26.2	26.2	11,292	11,143	365	398	**382**	6.02
1.5 M Sodium Carbonate/0.5 M Sodium Hydroxide	443	434	11.1	8.97	26.2	26.2	11,298	11,112	1,018	1,239	**1,128**	13.9
0.03 M Tetrabutylphosphonium Hydroxide	442	446	3.36	3.97	26.2	26.2	11,475	11,567	3,415	2,914	**3,164**	11.2
0.05 M Tetrabutylphosphonium Hydroxide	418	415	2.86	2.66	26.2	26.2	10,881	10,772	3,804	4,050	**3,927**	4.42
0.03 M Tetramethylammonium Chloride	414	413	*13.1*	*35.2*	26.2	26.2	10,475	9,874	*800*	*280*	**540**	68.0
0.03 M Tetramethylammonium Chloride/0.03 M Tetramethylammonium Hydroxide	429	445	27.0	26.5	26.2	26.2	10,518	10,940	390	413	**401**	4.10
0.03 M Tetramethylphosphonium Bromide	426	415	23.1	21.8	26.2	26.2	10,557	10,274	457	471	**464**	2.18

Equilibration time = 48 hours
All the sorption calculations are based on Na-form resin.
Values in italics have either significantly different replicate values or significantly lower/higher initial cesium concentrations than the target values (459 or 458 mg/L).

Sorption & Elution Tests (Confirmatory Tests)

- **Sorption/Loading at 25 °C**

	Replicates		Replicates		Replicates		Replicates			% RSD
	A	B	A	B	A	B	A	B	Average	
Sorption Solution – Test #	**Initial Cesium Conc.**	**Initial Cesium Conc.**	**Final Cesium Conc.**	**Final Cesium Conc.**	**Phase Ratio**	**Phase Ratio**	**Cesium Sorbed**	**Cesium Sorbed**	**Cesium Sorbed**	
Units	mg/L	mg/L	mg/L	mg/L	L/kg	L/kg	mg/kg	mg/kg	mg/kg	%
Spiked Tank 2F Simulant – Test 1	438	438	99.4	78.4	26.2	26.1	**8,880**	**9,413**	**9,147**	4.11
Spiked Tank 2F Simulant – Test 2	454	454	70.9	62.4	26.1	26.2	**10,006**	**10,245**	**10,125**	1.66
Spiked Tank 2F Simulant – Test 3	456	456	65.0	58.1	26.1	26.2	**10,186**	**10,416**	**10,301**	1.58
Spiked Tank 2F Simulant – Test 4	459	459	79.9	86.9	26.2	26.2	**9,932**	**9,732**	**9,832**	1.44
Spiked Tank 2F Simulant – Test 5	457	457	58.7	53.2	26.2	26.2	**10,435**	**10,580**	**10,508**	0.97
Average of all A & B replicates	453*		71.3		26.2		**9,983**			
Percent RSD of all A & B replicates	1.80*		20.6		0.18		5.24			

Sorption equilibration time = 48 hours
All the sorption calculations are based on Na-form resin.
* Average and percent RSD for five controls. Only one control was done for each duplicate set.

- The sorption tests can be considered as 10 replicates.
- Various percent RSDs indicate good overall reproducibility.

Sorption & Elution Tests (Confirmatory Tests)

- **Elution at Room Temperature (~25 °C)**

	Replicates		Replicates		Replicates		Replicates			%
	A	B	A	B	A	B	A	B	Average	RSD
Eluant Solution (Pre-Test pH) – Test #	Cesium Conc. in Eluate	Cesium Conc. in Eluate	Cesium in Eluate	Cesium in Eluate	Cesium Sorbed on Resin	Cesium Sorbed on Resin	Percent Cesium Eluted	Percent Cesium Eluted	Percent Cesium Eluted	
Units	mg/L	mg/L	mg	mg	mg	mg	%	%	%	%
2 M Ammonium Acetate (6) – Test 1	32.9	38.7	3.948	4.644	4.443	4.718	**88.9**	**98.4**	**93.6**	7.23
~2 M Ammonium Carbonate (9) – Test 2	39.3	42.2	4.716	5.064	5.010	5.124	**94.1**	**98.8**	**96.5**	3.44
1.5 M Calcium Acetate Monohydrate (8) – Test 3	7.35	6.17	0.882	0.740	5.111	5.204	**17.3**	**14.2**	**15.7**	13.6
2 M Magnesium Acetate Tetrahydrate (8) – Test 4	2.85	2.66	0.342	0.319	4.955	4.866	**6.90**	**6.56**	**6.73**	3.59
0.5 M Nitric Acid (0) – Test 5	42.8	44.7	5.136	5.364	5.210	5.287	**98.6**	**101**	**100**	2.04

Elution time = ~ 1 day
All the elution calculations are based on Na-form resin.
Volume of eluant solution = 120 mL

- ➢High elution performance – ammonium acetate, ammonium carbonate, and nitric acid (benchmark eluant).
  - Confirms the effectiveness of the indirect sorption method used to screen the eluants.
- ➢Marginal elution performance – calcium acetate and magnesium acetate
  - Performance may improve at lower resin cesium loading and/or a boost of pH to 9/10.

Sorption & Elution Tests (Confirmatory Tests)

- **Caustic Wash & Water Rinse at Room Temperature (~25 ºC)**

	CAUSTIC WASH (0.1 M NaOH Solution)				WATER RINSE			
	Replicates		Replicates		Replicates		Replicates	
	A	B	A	B	A	B	A	B
Test #	Cesium Conc. in Caustic Wash Solution	Cesium Conc. in Caustic Wash Solution	Cesium in Caustic Wash Solution	Cesium in Caustic Wash Solution	Cesium Conc. in Water Rinse Solution	Cesium Conc. in Water Rinse Solution	Cesium in Water Rinse Solution	Cesium in Water Rinse Solution
Units	mg/L	mg/L	mg	mg	mg/L	mg/L	mg	mg
Test 1	5.83	6.11	0.1166	0.1222	1.090	0.622	0.0218	0.0124
Test 2	5.08	4.91	0.1016	0.0982	0.741	0.565	0.0148	0.0113
Test 3	4.52	2.64	0.0904	0.0528	0.748	0.535	0.0150	0.0107
Test 4	5.08	6.20	0.1016	0.124	0.936	0.879	0.0187	0.0176
Test 5	4.31	3.97	0.0862	0.0794	0.673	0.610	0.0135	0.0122
Average of all A & B replicates	4.87		0.0973		0.740		0.0148	
Percent RSD of all A & B replicates	22.2		22.2		24.2		24.2	

Volume of caustic wash solution = 20 mL
Volume of water rinse solution = 20 mL

Reproducibility is generally good.