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EVALUATION OF POTENTIAL ELUANTS FOR NON-ACID ELUTION OF CESIUM FROM RESORCINOL-FORMALDEHYDE RESIN

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Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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EVALUATION OF POTENTIAL ELUANTS FOR NON-ACID ELUTION OF CESIUM FROM RESORCINOL-FORMALDEHYDE RESIN

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C_f	Final cesium concentration
C_i	Initial cesium concentration
CMC	Critical micelle concentration
dC	Change in solution cesium concentration i.e., initial minus final cesium concentration
DSA	Documented Safety Analysis
E&CPT	Environmental & Chemical Process Technology
F-factor	Ratio of the vacuum-dried mass to the damp mass of the resin
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
K_d	Sorption distribution coefficient
LAW	Low-activity waste
m	Mass of damp resin
PES	Polyethersulfone
RSD	Relative standard deviation
S	Cesium sorbed
SCIX	Small-column ion exchange
sRF	Spherical resorcinol-formaldehyde
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
T_i	Target initial cesium concentration
V	Volume of solution
WAC	Weak acid cation
WTP	Waste Treatment and Immobilization Plant

SUMMARY

Small-column ion exchange (SCIX) units installed in high-level waste tanks to remove Cs-137 from highly alkaline salt solutions are among the waste treatment plans in the DOE-complex. Spherical Resorcinol-Formaldehyde (sRF) is the ion exchange resin selected for use in the Hanford Waste Treatment and Immobilization Plant (WTP). It is also the primary ion exchange material under consideration for SCIX at the Hanford site. The elution step of the multi-step ion exchange process is typically done with 0.5 M nitric acid. An acid eluant is a potential hazard in the event of a spill, leak, etc. because the high-level waste tanks are made of carbon steel. Corrosion and associated structural damage may ensue.

A study has been conducted to explore non-acid elution as an alternative. Batch contact sorption equilibrium screening tests have been conducted with 36 potential non-acid eluants. The sorption tests involve equilibrating each cesium-containing eluant solution with the sRF resin for 48 hours at 25 ^{o}C in a shaker oven. In the sorption tests, an eluant is deemed to have a high cesium elution potential if it minimizes cesium sorption onto the sRF resin. The top candidates (based on lowest cesium sorption distribution coefficients) include ammonium carbonate, ammonium carbonate/ammonium hydroxide, ammonium bicarbonate, rubidium carbonate, ammonium acetate, ammonium acetate/ammonium hydroxide, ammonium bicarbonate/ammonium hydroxide, calcium chloride, and magnesium chloride.

A select few of the top candidate eluants from the screening tests were subjected to actual sorption (loading) and elution tests to confirm their elution ability. The actual sorption (loading) and elution tests mimicked the typical sRF-cesium ion exchange process (i.e., sorption or loading, caustic wash, water rinse, and elution) via batch contact sorption and quasi column caustic wash/water rinse/elution. The eluants tested included ammonium carbonate, ammonium acetate, calcium acetate, magnesium acetate, and nitric acid. Calcium acetate and magnesium acetate were substitutes for calcium chloride and magnesium chloride respectively due to corrosion concerns. Nitric acid was selected for benchmarking since it is the baseline cesium eluant for sRF resin.

The cesium elution performance of ammonium carbonate and ammonium acetate was approximately the same as the benchmark eluant, nitric acid. Ninety-seven (97), 94, and 100% percent of the cesium sorbed or loaded were eluted by ammonium carbonate, ammonium acetate, and nitric acid was respectively. The performance of calcium acetate and magnesium acetate, on the other hand, was mediocre. Percent elution was 16 and 8 respectively.

1.0 INTRODUCTION

Plans are underway to use small-column ion exchange (SCIX) units installed in high-level waste tanks to remove Cs-137 from highly alkaline salt solutions. Spherical Resorcinol-Formaldehyde (sRF) ion exchange resin, known for its high selectivity for cesium in highly alkaline radioactive wastes, is the baseline material under consideration for the Hanford site.[1] It is a weak acid cation (WAC) exchange resin and as a result has a high affinity for hydrogen ions. Therefore, it is easily eluted with acid solutions. Nitric acid is used most frequently.

Tanks containing highly alkaline radioactive waste are made of carbon steel. Use of an acid eluant may pose a hazard to the tank integrity (corrosion and associated structural damage) in the event of a spill, leak, etc. It will also impact the Documented Safety Analysis (DSA) in that a Criticality Safety Evaluation Report will be required because of potential effect on fissile material "form" and "distribution".[2] In addition, criticality limits for transfers from non-tank farm facilities (if the supplemental pretreatment facility is so designated) require pH of source waste to be at least 8.[3]

A non-acid eluant may be a viable alternative. It will eliminate the need for special acid handling requirements within the tank farms. Further, non-acid elution will fit in quite well if low-activity waste (LAW) processing is initiated at the Hanford site prior to the completion of the Waste Treatment and Immobilization Plant (WTP).[4] This is because early LAW treatment will require design and implementation of interim pretreatment operations (either in-tank or near-tank) at the tank farm.

The objectives of this study were:

1. To evaluate (via batch contact sorption screening tests) the cesium elution potential from sRF resin using non-acid compounds identified in an earlier literature review.[5] Specifically, cesium sorption distribution coefficients (K_d) on sRF resin from cesium-containing eluants were measured. A lower cesium K_d indicates high elution potential.

2. To confirm the elution ability of a few of the most promising eluants with actual sorption and elution tests.

The work was done per the test plan issued earlier.[6] This report is an update or revision to the preliminary report.[7] The preliminary report did not include the actual sorption and elution (confirmatory) tests.

2.0 EXPERIMENTAL

2.1 MATERIALS

2.1.1 Chemicals

All the chemicals used were reagent grade. They were from various sources or manufacturers. The list of chemicals and their manufacturers are as follows.

1. Ammonium acetate - Fisher Scientific, Pittsburgh, Pennsylvania.
2. Ammonium bicarbonate - MP Biomedicals, Solon, Ohio.
3. Ammonium carbonate - Fisher Scientific, Pittsburgh, Pennsylvania.
4. Ammonium hydroxide - LabChem Inc., Pittsburgh, Pennsylvania
5. Calcium Acetate Monohydrate - Sigma-Aldrich Corporation, St. Louis, Missouri.
6. Calcium chloride - Alfa Aesar, Ward Hill, Massachusetts.
7. Cesium nitrate - GFS Chemicals, Inc., Columbus, Ohio
8. Hexadecyltrimethylammonium chloride - Fisher Scientific, Pittsburgh, Pennsylvania.
9. Lithium chloride - Fisher Scientific, Pittsburgh, Pennsylvania.
10. Lithium hydroxide - Fisher Scientific, Pittsburgh, Pennsylvania.
11. Lithium sulfate - Sigma-Aldrich Corporation, St. Louis, Missouri.
12. Magnesium Acetate Tetrahydrate - Sigma-Aldrich Corporation, St. Louis, Missouri.
13. Magnesium chloride hexahydrate - Fisher Scientific, Pittsburgh, Pennsylvania.
14. Magnesium sulfate - Fisher Scientific, Pittsburgh, Pennsylvania.
15. Nitric acid - Fisher Scientific, Pittsburgh, Pennsylvania.
16. Potassium bicarbonate - Fisher Scientific, Pittsburgh, Pennsylvania.
17. Potassium carbonate - Fisher Scientific, Pittsburgh, Pennsylvania.
18. Potassium hydroxide - Fisher Scientific, Pittsburgh, Pennsylvania.
19. Rubidium carbonate - Sigma-Aldrich Corporation, St. Louis, Missouri.
20. Sodium bicarbonate - Fisher Scientific, Pittsburgh, Pennsylvania.
21. Sodium carbonate - Fisher Scientific, Pittsburgh, Pennsylvania.
22. Sodium hydroxide - Fisher Scientific, Pittsburgh, Pennsylvania.
23. Tetrabutylphosphonium hydroxide - Sigma-Aldrich Corporation, St. Louis, Missouri.
24. Tetramethylammonium chloride - Sigma-Aldrich Corporation, St. Louis, Missouri.
25. Tetramethylammonium hydroxide - Sigma-Aldrich Corporation, St. Louis, Missouri.
26. Tetramethylphosphonium bromide - Sigma-Aldrich Corporation, St. Louis, Missouri.

2.1.2 Simulant Solution

A portion of the supernate simulant (SRS Tank 2F) that was used for the SCIX testing was used for these tests.[8,9] Table 1 gives the target and measured concentrations of the constituents in the Tank 2F supernate simulant.[8]

This supernate simulant will be referred to as “as-received or regular” Tank 2F simulant solution. The concentration of cesium (2.45 mg/L) in the as-received simulant measured during the kinetics test is close to the measured value in Table 1. The concentration of cesium in a portion of the as-received 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 later in the report.

The as-received simulant was used to check the quality of the resin in terms degradation. The spiked simulant was used to establish a benchmark for the eluant cesium sorption tests (subsection 2.2) and for the sorption portion of the true sorption and elution tests (subsection 2.3).

Table 1. Concentration of the Constituents in SRS Tank 2F Supernate Simulant.

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)
Br^-	n/a	< 250 (< 0.003)
$(HCOO)^-$	n/a	< 250 (< 0.006)
$(C_2O_4)^{2-}$	n/a	540 (< 0.006)
Al	6,980 (0.26)	8,600 (0.32)
B	n/a	< 1.19 (< 1.10×10^{-4})
Ba	n/a	< 0.28 (< 2.0×10^{-6})
Ca	n/a	< 1.56 (< 2.50×10^{-8})
Cd	n/a	< 0.353 (< 3.10×10^{-6})
Cr	n/a	< 0.38 (< 7.30×10^{-6})
Cs	2.26 (1.70×10^{-5})	2.25 (1.69×10^{-5})
Cu	n/a	< 1.4 (< 2.20×10^{-5})
Fe	n/a	< 2.0 (< 3.58×10^{-5})
K	274 (0.007)	296 (0.0076)
Li	n/a	< 0.45 (< 1.44×10^{-4})
Mo	n/a	< 2.53 (< 2.64×10^{-5})
Na	137,900 (6.00)	144,000 (6.26)
Ni	n/a	< 1.07 (< 1.82×10^{-5})
P	384 (0.012)	164 (0.005)
Pb	n/a	< 3.02 (< 1.46×10^{-5})
Rb	0.535 (6.30×10^{-6})	0.0098 (1.0×10^{-7})
S	1,023 (0.032)	1,170 (0.036)
Si	n/a	< 7.7 (< 2.74×10^{-4})
Zn	n/a	< 1.1 (< 1.68×10^{-5})
pH	14	14

n/a = not applicable
nm = not measured

2.1.3 Resin Preconditioning and F-Factor Determination

About 400 grams of moist H-form resin (Lot # 5E-370/641) was used for the study. The resin was manufactured by Microbeads AS in Skedsmokorset, Norway. The resin is stable as long as it is stored in deionized water with an inert gas headspace. Even though this batch of resin is five years old, periodic checks via testing on its quality (regarding degradation) indicate its quality is still intact.[8,10-12] The resin was preconditioned using protocols developed by Savannah River National Laboratory (SRNL) in 2004.[13,14]

Resin preconditioning involves taking the resin through deionized water, NaOH (1 M), deionized water, HNO_3 (0.5 M), and deionized water steps at room temperature. The preconditioning protocol was extended by two additional steps [i.e., NaOH (1 M) and deionized water] in order to bring the resin to the Na-form. It was more appropriate to have the resin in Na-form for the tests because the resin (being a weak acid cation resin) has a strong affinity for the hydrogen ion. The resin is in Cs/K/Rb/Na-form (with Na being the predominant cation) in the actual column elution ion exchange step. There is an instance in the literature when cesium sorption or loading onto H-form resin was marginal compared to loading onto Na-form resin.[15]

The F-factor of the damp or moist preconditioned Na-form resin was determined by drying roughly 0.5-gram samples to a constant weight under vacuum at 50 ^{o}C. The F-factor is the solids fraction remaining after the vacuum drying. The F-factor was measured in duplicate. The F-factor of the damp preconditioned H-form resin was also measured in a similar manner prior to the extended steps mentioned earlier.

Damp resin is defined as a preconditioned resin whose water has been drained to the lowest content practical through use of filter pads and minimal vacuum drying at ambient temperature such that it will be devoid of free liquid (i.e., surface or excess water).

2.1.4 Preparation of Eluant/Other Relevant Solutions

Desired concentrations of the solution of each eluant and other relevant compounds (e.g., NaOH, and HNO_3) were prepared. Each preparation involved weighing a predetermined amount of the eluant chemical(s) and adding it/them to a required volume of deionized water followed by stirring at room temperature. Cesium in the form of cesium nitrate was added to each eluant solution (used for the sorption tests in subsection 2.2) when the dissolution of the eluant compound(s) was complete. It was again followed by stirring until the cesium nitrate completely dissolved.

A few of the eluants, namely, ammonium bicarbonate, ammonium carbonate, lithium hydroxide, and potassium bicarbonate, did not completely dissolve. Hence, they were filtered under vacuum using 0.45 µm nylon Nalgene (Rochester, New York) filter units prior to the addition of the cesium nitrate. The undissolved constituents seem to be impurities because the amounts of the compounds added were below their respective solubilities at room temperature. An approximate symbol precedes the concentration of the eluants that did not completely dissolve (see Tables 2-10).

To avoid unnecessary delays and excessive analytical costs, confirmatory analysis of the prepared solutions was not done. The associated risks are low because the exact concentration of the eluants was not critical for the tests.

2.2 NON-ACID ELUTION VIA SORPTION TESTS

As mentioned earlier, the cesium-elution ability (from the sRF resin) of the eluants was assessed via batch contact sorption tests. Both the cesium and the cation of the eluant compete for the soprtion sites on the sRF resin. The extent to which cesium sorption is suppressed describes the relative elution strength of the eluant. Cesium K_d's were measured and used as a determinant of the elution potential of the eluants.

This elution via sorption approach (as a screening tool) is in line with the cardinal ion exchange principle i.e., ion exchange is by and large a reversible process much like the chemical reactions that occur in solutions. It is also in line with the known elutability characteristic of the sRF resin. Generally in ion exchange, 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 principle mentioned above regardless of whether it is sorption/loading, elution, or regeneration. In other words, the resin does not know whether it is sorption/loading, elution, or regeneration.

The equation below depicts a typical ion exchange reversible reaction where ion A on the resin (denoted by underline) is exchanged for ion B in solution. It must be emphasized that equilibrium can be approached from either direction.

$$\underline{RA}^+ + B^+Y^- \Leftrightarrow \underline{RB}^+ + AY^-$$

This elution via sorption approach was used at SRS in 1980.[16] The batch contact cesium sorption results were in agreement with the elution results from the true cesium column loading and elution tests.

The batch contact test procedure described below pertains to both the kinetics and the equilibrium screening tests (see subsections 2.2.1 and 2.2.2). The specifics for each test are given in their respective subsections.

A batch contact test entails the following. Twelve milliliters of cesium-containing eluant (or simulant solution) with known concentrations of eluant and cesium was added to 1.5840 grams of damp sRF resin in 20-mL polypropylene vials equipped with polypropylene screw caps (Chasma Scientific, Inc., Cambridge, Massachusetts). The sRF resin (of known F-factor) was in the Na-form. The resin-eluant (or simulant) mixture was equilibrated for a predetermined time. See Tables 2 and 3 in the results and discussion section (section 3) for all the concentrations, equilibration times, and volume of solution/mass of resin ratios (i.e., phase ratios).

As a precautionary measure on resin degradation, the headspace of the vial containing the resin-eluant (or simulant) mixture was purged with nitrogen prior to capping. The equilibration was done in a Refrigerated Incubator Shaker (model Innova® 4230, New Brunswick Scientific Company, Inc., Edison, New Jersey) equipped with test tube or vial racks at a shaking speed of 200 rpm and a temperature of 25 ± 0.1 °C. A Mettler-Toledo (Columbus, Ohio) analytical balance (model AE 240) with an accuracy of ± 0.0001 g was used to weigh the materials. Figure 1 is a picture of the vials used for the batch contact sorption tests.

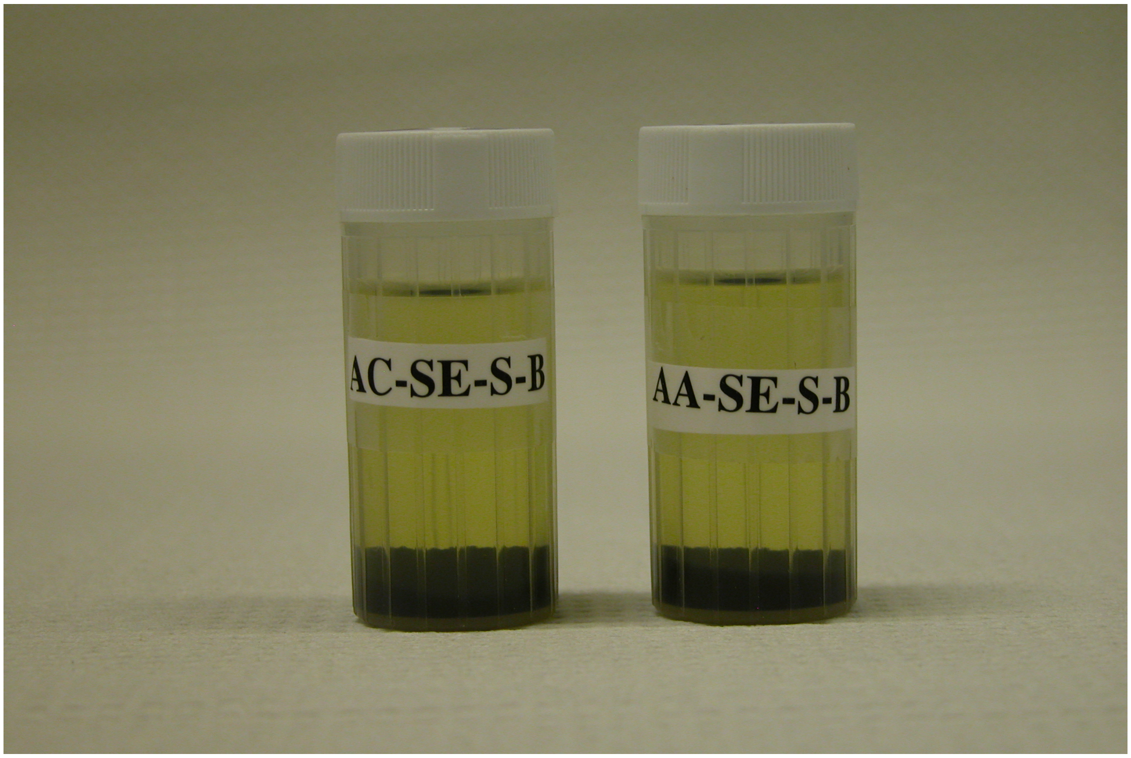

Figure 1. Batch Contact Sorption Test Vials Containing the sRF Resin (Bottom) and the Simulant Solution**.**

Control tests were conducted along with and in the same manner as the sorption test described above. A control is a cesium-containing eluant (or simulant solution) with no solids or resin. It is utilized to determine the initial solution concentration of the desired constituent (i.e., cesium). All the sorption tests were conducted in duplicate.

At the end of the predetermined equilibration period, about 3-mL sample of the solution was withdrawn using a syringe-syringe filter (0.45 μm nylon; Whatman, Inc., Florham Park, New Jersey) assembly equipped with stainless steel needle (Popper & Sons, Inc., New Hyde Park, New York) for analysis of cesium by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The sampling vials were 7-mL polypropylene vials equipped with polypropylene screw caps (Chasma Scientific, Inc., Cambridge, Massachusetts). The amount of cesium sorbed was determined from the initial and final concentrations of cesium in solution.

The temperature of the resin-solution mixture was monitored periodically during the tests using a standard laboratory organic-filled glass thermometer to measure the temperature of deionized water in a polypropylene vial placed in the Refrigerated Incubator Shaker along with the testing vials. The average temperature of the bottled water was $25.7 \pm 0.6\ ^{o}C$ throughout the entire testing period. Note that the water-filled vial was taken out of the oven before the temperature was quickly measured. As a result, the temperature was a little higher because of the relatively high room temperature.

2.2.1 Sorption Kinetics Test

The sorption kinetics test was conducted to determine the sorption equilibrium time needed for the equilibrium screening tests (see next subsection). The sorption method described earlier was followed. Sampling (one per specified equilibration time per vial) occurred at the end of 4, 7, 24, 48, 72, 96, and 192 hours.

Ammonium carbonate was used for the kinetics test. Its selection was based on its fairly wide use as a successfully cesium-eluant from other resins in both plant operation setting and laboratory tests.[15-22]

To instill confidence or give validity to the eluant testing data, a sorption test was performed along with the kinetics test using the as-received Tank 2F simulant (cesium concentration = 2.45 mg/L) mentioned earlier in subsection 2.1.2. This is because the cesium sorption data from a previous test using the same simulant are available for comparison.[8] Comparable results also reaffirm the quality of the resin in terms of degradation even though the resin's quality is not in doubt.

In addition, another sorption test was conducted with the spiked Tank 2F simulant (cesium concentration = 458 mg/L). As mentioned previously, the cesium concentration in the spiked Tank 2F simulant was the same as the cesium concentration in the eluants. The cesium sorption data of the spiked Tank 2F simulant served as a benchmark in the evaluation of the eluant cesium sorption data as discussed later in subsection 3.2. The equilibration period for both tests was 192 hours.

2.2.2 Sorption Equilibrium Screening Tests

The sorption equilibrium screening tests commenced once the equilibrium time was determined from the sorption kinetics test. Again, the batch contact method described earlier was followed.

2.3 SORPTION (LOADING) AND ELUTION TESTS

A select few of the eluants screened using the sorption approach (subsection 2.2.2) were subjected to true sorption (or loading) and elution tests. The tests were performed to confirm the results of the previous subsection (2.2.2). They were designed to mimic the typical flow-through multi-step column sRF-cesium ion exchange process i.e., loading, caustic wash, water rinse, and elution. The tests involved the following steps in sequential order.

1. Sorption or loading of cesium onto the sRF resin from the spiked Tank 2F simulant solution per the batch contact method described in subsection 2.2. The sorption equilibration time (48 hours) was the same as before. To make these sorption tests the same as the previous sorption equilibrium screening tests, aliquots were withdrawn for cesium analysis by ICP-MS before the next step.

2. Vacuum filtration to separate the cesium-laden resin from the simulant solution at room temperature (~25 ^{o}C) using 0.45 µm nylon 150-mL Nalgene filter unit. The headspace of the filter cup was purged with nitrogen and capped just before the vacuum was turned on i.e., the start of the filtration. For the nitric acid eluant, 0.45 µm polyethersulfone (PES) 150-mL Nalgene filter unit was used because of potential incompatibility of nylon with nitric acid.

3. Simultaneous washing and vacuum filtration of the cesium-laden resin with 20 mL of 0.1 M NaOH solution using a new filtrate flask at room temperature. This action displaces the simulant solution left in the resin with NaOH solution. Again, the headspace of the filter cup was purged with nitrogen prior to the start of the filtration.

4. Simultaneous rinsing and vacuum filtration of the cesium-laden resin with 20 mL of deionized water using a new filtrate flask at room temperature. This step displaces the NaOH solution in the resin with water. Purging of the headspace of the filter cup mentioned in the previous steps was also done here.

5. Elution of the cesium-laden resin with 120 mL of eluant solution using a new filtrate flask at room temperature. The headspace of the filter cup was purged with nitrogen and capped just after pouring the eluant solution into the filter cup. It must be noted that no vacuum or pumping was applied. The eluant solution was allowed to percolate through the filter membrane by gravity.

   The duration of the elution was approximately a day. The residual eluant solution in the filter cup was filtered under vacuum to finish off the elution step. As was done before, the headspace of the filter cup was purged with nitrogen prior to the start of the vacuum filtration.

Aliquots of the filtrates from the caustic wash, water rinse, and elution steps (i.e., step 3, 4, and 5 above) were withdrawn for cesium analysis by ICP-MS. A picture of the vials containing the resin and simulant solution used for the batch contact sorption step (step 1 above) were shown earlier in Figure 1. Figure 2 is a picture of the filter units used for the quasi-column steps (i.e., steps 2 to 5 above).

Figure 2. Filter Units Used for the Resin/Solution Separation, Caustic Wash, Water Rinse, and Elution Steps.

3.0 RESULTS AND DISCUSSION

3.1 RESIN F-FACTOR

The F-factor of the preconditioned Na-form resin equals 0.3157 [percent relative standard deviation (RSD) = 1.08]. The F-factor of the preconditioned H-form resin prior to conversion to Na-form equals 0.2893 (percent RSD = 3.46). The ratio of dry Na-form/dry H-form resin equals 1.28.

All the data given in this section are on a Na-form basis. The ratio or H-form resin F-factor is provided to facilitate meaningful comparison with other sRF cesium sorption and elution data.

3.2 SORPTION KINETICS

Figure 3 shows a plot of the cesium sorption kinetics data for ~2 M ammonium carbonate solution and sRF resin at 25 °C in terms of cesium concentration in solution versus equilibration time.

The cesium sorption is fast initially and flattens around 24 to 48 hours, then rises between 48 and 72 hours and finally tapers off as sorption proceeds. Similar cesium sorption kinetics behavior (dip/rise) has been observed for sRF in several simulants.[23,24] The dip/rise is within the error ($\pm$ 20%) in the analysis (see error bars on Figure 3). The fluctuations are relatively small. The average ratio of the 48-hour concentration to each of the concentrations of the last three data points (i.e., 72, 96, and 192 hours) is 0.87. In addition, the average of the concentrations at 7, 24, 48, 72, 96, and 192 hours is 289 mg/L with percent RSD of 8. For all practical purposes, equilibrium is attained in 48 hours. Hence, 48-hour equilibration time was used for the sorption equilibrium screening tests (see next subsection).

Table 2 gives the cesium sorption kinetics data for ~2 M ammonium carbonate solution along with the data for cesium sorption from the spiked Tank 2F simulant solution and the as-received or regular Tank 2F simulant solution at 192 hours of equilibration.

The sorption distribution coefficient, K_d, was determined with the equation below.

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

C_i is initial cesium concentration, C_f is final cesium concentration, V is the volume of solution, m is the mass of damp resin, and F is the F-factor of the damp resin. Note that V/(mF) is the phase ratio given in the Table. Note further that the initial cesium concentration has been corrected for the dilution that ensues from the water in the damp resin.

The data for the as-received Tank 2F simulant solution compare reasonably well with those obtained from previous testing using the same simulant.[8] This instills confidence in the eluant testing data. It also reaffirms that the quality of the preconditioned sRF resin used for this study is good as far as degradation is concerned.

The data for the spiked Tank 2F simulant solution serve as a benchmark for the non-acid elution via sorption tests. Since the sRF resin is designed to have high cesium sorption affinity (or K_d's) from highly alkaline solutions, the K_d value of 212 L/kg for the spiked Tank 2F simulant solution is roughly the demarcation or cutoff value for the sorption screening tests. A K_d value < 212 L/kg from the eluant cesium sorption equilibrium screening test means the eluant has a relatively high/moderate cesium elution potential while a K_d value > 212 L/kg implies an eluant with a low cesium elution potential.

A comparison of the 192-hour data for ~2 M ammonium carbonate solution with the corresponding data for the spiked Tank 2F simulant solution (i.e., the two rows in bold) indicates ~2 M ammonium carbonate solution holds promise for cesium elution (K_d of 10.9 versus 212 L/kg). The percent RSD for the K_d's of all the replicates are < 19 – An indication of good replications.

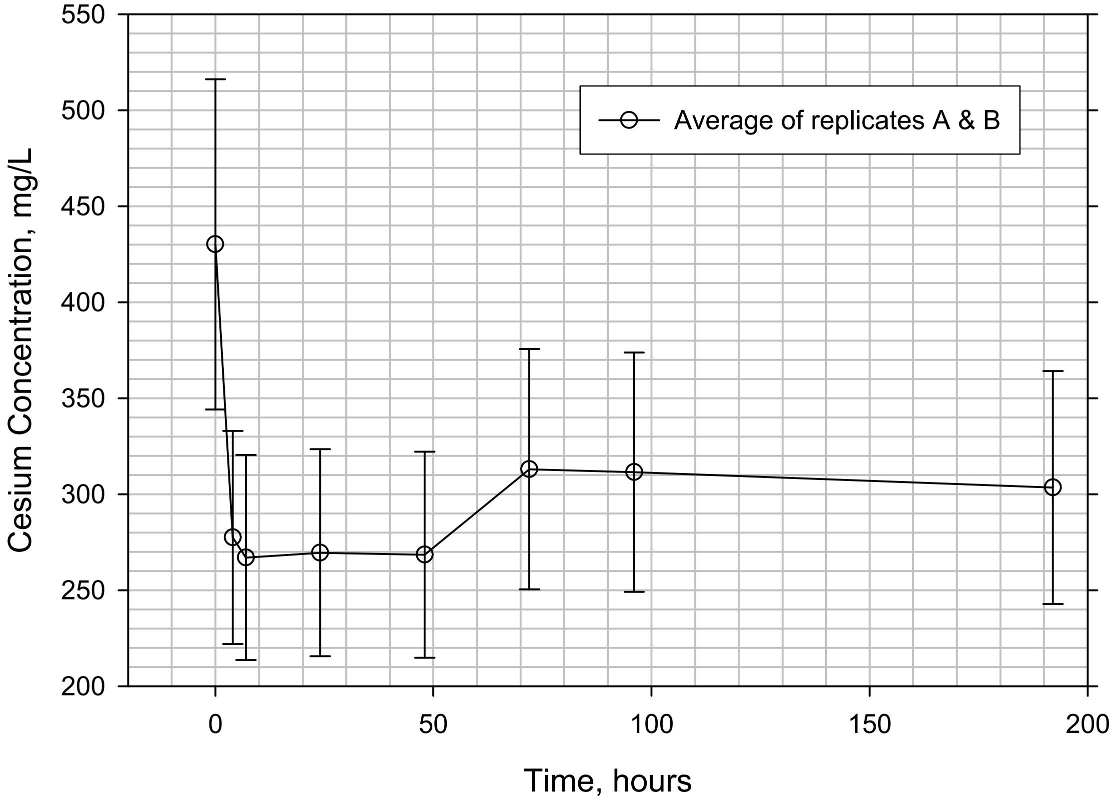

Figure 3. Cesium Sorption Kinetics for ~2 M Ammonium Carbonate Solution and sRF Resin.

Table 2. Cesium Sorption Kinetics for ~2 M Ammonium Carbonate 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**
As-Received 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

3.3 SORPTION EQUILIBRIUM SCREENING TESTS

Table 3 shows the cesium sorption data from the equilibrium screening tests along with the data for the spiked Tank 2F simulant solution (192-hour equilibration time) for comparison. Recall, the 192-hour spiked Tank 2F simulant solution sorption data is the benchmark. The cesium sorption equilibrium time for sRF/simulant solutions is typically 48 hours.[23] Hence, the 48-hour sorption data are not expected to be significantly different from the 192-hour sorption data.

The following general comments on Table 3 are in order prior to discussing its specifics.

- The sorption equilibrium screening tests were done in three sets or batches.

- Some tests involved two compounds, specifically the hydroxides of the cation of the eluant. They were attempts to see if the hydroxides enhanced the elution potential of the eluants.

- 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).

It is not clear why the initial cesium concentration of ~1.8 M ammonium bicarbonate/1M ammonium hydroxide solution (Equilibrium Test – Set 3) was very low even though the K_d seems fairly credible when compared with the K_d for ~1.8 M ammonium bicarbonate solution (Equilibrium Test – Set 2). Same comment also applies to 3 M rubidium carbonate solution (Equilibrium Test – Set 1) which is on the high side.

The relatively low initial cesium concentration of 1 M tetrabutylphosphonium hydroxide (Equilibrium Test – Set 1); and 1 M, 0.1 M, and 0.03 M tetramethylammonium hydroxide (Equilibrium Test – Sets 1, 2, and 2) solutions may be due to the fact that they may be above their respective critical micelle concentrations (CMC). Above the CMC, micelle or colloid formation prevails which may have skewed the cesium concentration to the low side. It is quite possible colloidal particles (micelles) with cesium attached or embedded in them may have deposited in the syringe filter membrane and on the walls of the vials, etc.

Even though the CMC of the above compounds are unknown, CMC values typically range in the fraction of a millimolar to several millimolar. Along the same lines, micelle formation may have obscured evaluation of their elution potential even though it will be shown later (Table 8) that generally high pH's (> 11) seem not to favor cesium elution from sRF i.e., result in relatively high K_d's. The fairly high initial cesium concentrations of the other surfactants used (i.e., all the remaining organics tested) lend some support to the above claim because their concentrations are generally low.

With the exception of a few eluants, the percent RSD of the K_d's are reasonably low. However, comparison of the 48-hour kinetics (Table 2) and the 48-hour equilibrium (Table 3, Equilibrium Test – Set 2) K_d values for ~2 M ammonium carbonate solution shows some disparity (15.7 versus 2.62 L/kg). It may be due to difference in initial concentration which may be from difference in their preparation. Recall, it was mentioned in subsection 2.1.4 that the concentration of the ammonium carbonate solution is approximate because of lack of complete dissolution during preparation. During filtration of the first ammonium carbonate solution (i.e., for the 48-hour kinetics test), the undissolved solids were captured to roughly determine their amount. It led to the rinsing of the volumetric flask with deionized water to get all the solids out. The rinsing may have resulted in more dilution for the solution used for the 48-hour kinetics test.

Because some of the initial cesium concentrations of the eluant solutions were significantly lower (or higher in the case of rubidium carbonate) than their respective target initial cesium concentrations, what-if scenario K_d calculations were done for those eluants to make sure the K_d comparisons are made on an equal-concentration basis. This ensures no eluant whose elution potential is high is missed.

The what-if scenario data are given in Tables 4 to 7. The first two columns in each table give the actual sorption data from the tests as given in Table 3. The remaining columns give the what-if scenario calculations. The calculations assume various values for the change in cesium concentration in solution (dC) and calculate C_f, S (cesium sorbed), and K_d sequentially. The bottom of Table 4 has the definitions and the equations used. The symbols that are not defined were defined earlier in subsection 3.2.

Only the ratio of the initial cesium concentration to the target initial cesium concentration is given for the eluants whose initial cesium concentrations were not significantly different from the target initial cesium concentrations. For ~1.8 M ammonium bicarbonate/1 M ammonium hydroxide solution (Table 6, Equilibrium Test – Set 3), a what-if scenario calculation was not done. The initial cesium concentration was extremely low (1.11 and 1.10 mg/L for the two replicates versus a target of 459 mg/L) that the results will not be practical.

As an example, 3 M rubidium carbonate solution (Table 4, Equilibrium Test – Set 1) has an initial cesium concentration that is about 1.3 times higher than the target initial cesium concentration. However, the what-if scenario K_d values indicate the K_d's would have been still fairly low (a range of 2 to 7 L/kg) had the initial cesium concentration been close to the target. This approach therefore erases any doubts as to the high elution potential of 3 M rubidium carbonate solution.

Table 8 gives a ranking of the eluant solutions tested along with their pre-test or as-prepared pH and elution potential category. The rankings are based solely on the average K_d values without consideration of the downstream impacts. The ranks of the eluants are given in decreasing order of cesium elution potential (i.e., increasing K_d values). Three K_d values (average, low, and high) are given for the eluants whose replicate values are significantly different even though the ranks are based on the average values. Apparently, the low and high K_d values had minimal impact on the ranking. Note that two values for a pH imply it was measured twice for that particular eluant over a course of several days to weeks as a confirmation.

In Table 8, an eluant is deemed to have a high cesium elution potential if its K_d value is < ~100 L/kg. A K_d value of between ~100 to ~200 L/kg puts the eluant in the moderate cesium elution potential category. A low cesium elution potential designation is given to an eluant with a K_d value > ~200 L/kg. Note that the above categories are not hard-and-fast. They were based on using the K_d value of the spiked Tank 2F simulant (i.e., 212 L/kg) as a benchmark or the cutoff K_d value as was previously mentioned in subsections 2.2.1 and 3.2.

The elution potential categories are based mainly on the average K_d values and in some instances also on the range of the what-if scenario K_d values. The range of the what-if scenario K_d values are given in the "cesium elution potential" column (i.e., last column), if applicable. For example, for 1 M tetramethylammonium hydroxide (21st rank), the K_d value of 364 L/kg puts it in the low elution potential category. However, the low end of the what-if scenario K_d range (105-249 L/kg) puts it in the moderate elution potential category as well. Therefore, it is assigned a low/moderate classification.

The ammonium compounds, as a group, clearly stand out as the most promising eluants with rubidium carbonate, calcium chloride, magnesium chloride hexahydrate solutions among the top ten overall. The organic and sodium compounds are generally at the bottom half of the ranking. As alluded to earlier, ammonium compounds, especially ammonium carbonate have been used successfully in the past to elute cesium from other organic and inorganic ion exchange resins/materials.[15-22]

On the whole, high pH (i.e., pH > 12) eluant solutions had mediocre performance except potassium compounds. Put differently, eluants with pH's 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. Supporting evidence is the fact that most of the hydroxides (except potassium hydroxide) are at the bottom of the ranking because they are high pH solutions. The sRF resin was designed to have high affinity for cesium (and unavoidably or inadvertently for potassium and possibly rubidium because they are also in group I of the periodic table) in high pH (i.e., > 11) media or solutions.[23] The data in Table 8 appear to suggest for the other cations to be effective (or to suppress cesium sorption) the pH of their eluant solutions has to be between ~5 and ~10. This is shown by the top nine performers and certainly by the ammonium compounds. It is worth emphasizing that the pH measurements were performed with pH indicator strips (colorpHast pH test strips - EMD Chemicals, Gibbstown, New Jersey).

For 3 M potassium carbonate, ~1.7 M potassium bicarbonate, and 0.03 M tetramethylammonium chloride solutions; addition of their respective hydroxides tends to enhance the elution potential. For the potassium compounds, this is consistent with the statement made earlier that the sRF resin works best at high pH for potassium, cesium, and possibly rubidium despite the fact that the percent RSD of the K_d value for the 3 M potassium carbonate/0.5 M potassium hydroxide solution is fairly high.

For 2 M ammonium acetate, ~1.8 M ammonium bicarbonate, ~2 M ammonium carbonate, 2 M lithium chloride, and 1.8 M lithium sulfate solutions; addition of their respective hydroxides did not enhance the elution potential. Again, the percent RSD of the K_d value for the ~2 M ammonium carbonate/1 M ammonium hydroxide solution is fairly high. Also, the K_d value for 2 M ammonium acetate and 2 M ammonium acetate/1.5 M ammonium hydroxide solutions are close. As mentioned earlier, ammonium hydroxide enhanced the elution potential of ammonium carbonate for other resins. It seems the hydroxide enhancement is resin-specific.

The overall data suggest the following speculations are in order. For 2 M ammonium acetate/1.5 M ammonium hydroxide solution, reducing the ammonium hydroxide concentration to bring the pH of the solution to about 9 may boost the elution potential. Same comment holds for 2 M lithium chloride/~1 M lithium hydroxide and 1.8 M lithium sulfate/~0.5 M lithium hydroxide; and to a lesser degree (because their elution ability is generally low) for 0.75 M sodium bicarbonate/0.5 M sodium hydroxide and 0.03 M tetramethylammonium chloride/0.03 M tetramethylammonium hydroxide. Similarly, boosting the pH of 2 M calcium chloride and 3 M magnesium chloride hexahydrate to about 9 may enhance their elution potential.

The foregoing provides strong incentive for studies on optimization of eluant concentration and pH among others.

3.3.1 Eluants Selected for the True Sorption and Elution Tests

The eluants selected from the screening tests for the true sorption and elution tests were ammonium carbonate, ammonium acetate, calcium acetate, magnesium acetate, nitric acid, and ammonium hydroxide.

Due to corrosion concerns, calcium chloride and magnesium chloride were replaced with calcium acetate and magnesium acetate respectively. Nitric acid is the benchmark eluant. Ammonium hydroxide, as a stand-alone eluant, was not tested. However, the data seem to suggest it may be a viable candidate even though it is a weak base.

Ammonium bicarbonate is basically in the same chemical family as ammonium carbonate. Hence, its exclusion from the eluants selected for the sorption and elution tests despite its high elution potential. Similarly, rubidium carbonate is not among the eluants selected. From operational standpoint, cesium-laden rubidium carbonate eluate from an ion exchange elution process will end up being stored at the tank farm prior to treatment through the WTP. Any potential cross-contamination of this eluate with an untreated cesium-containing tank waste implies the untreated waste will be cesium/rubidium-containing tank waste. Rubidium is a competitor to cesium in the sRF ion exchange loading process. As a result, less cesium will be removed for a given sRF column because rubidium will be removed as well. The same argument holds for potassium compound eluants.

Table 3. Cesium Sorption Equilibrium Screening Tests at 25 ^{o}C – Sets 1, 2 & 3.

	Replicates		**Replicates**		**Replicates**		**Replicates**		**Replicates**		**Average**	**Percent RSD**
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**		
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 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
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

	Replicates		**Replicates**		**Replicates**		**Replicates**		**Replicates**		**Average**	**Percent RSD**
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**		
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 Cont'd												
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
Benchmark from Kinetics Test												
Spiked Tank 2F Simulant[a]	424	425	43.5	49.9	26.1	26.1	9,914	9,786	228	196	212	10.6

Equilibration time = 48 hours except Spiked Tank 2F Simulant.

[a] Equilibration time = 192 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).

The molar concentration of the cations of the carbonate compounds is twice the molar concentration of the respective carbonate compound given above.

Table 4. What-If Scenarios for Initial Cesium Concentration (Sorption Equilibrium Screening 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
3 M Potassium Carbonate						
Initial cesium concentration/Target initial cesium concentration Ratio = 1.051					T_i = 459	
3 M Potassium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 1.030					T_i = 459	
3 M Sodium Carbonate						
Initial cesium concentration/Target initial cesium concentration Ratio = 1.031					T_i = 458	
3 M Sodium Hydroxide						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.994					T_i = 459	

C_i = Initial cesium concentration, mg/L
C_f = Final cesium concentration, mg/L
dC = Change in solution cesium concentration, mg/L = $C_i - C_f$
S = Cesium sorbed, mg/kg = (dC)V/mF
K_d = Sorption distribution coefficient, L/kg = S/C_f = $(dC)V/mFC_f$
T_i = Target initial cesium concentration, mg/L

Table 5. What-If Scenarios for Initial Cesium Concentration (Sorption Equilibrium Screening 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
2 M Ammonium Acetate						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.968					T_i = 459	
~1.8 M Ammonium Bicarbonate						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.946					T_i = 459	
~2 M Ammonium Carbonate						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.951					T_i = 459	
2 M Calcium Chloride						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.947					T_i = 459	
0.03 M Hexadecyltrimethylammonium Chloride						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.966					T_i = 459	
2 M Lithium Chloride						
Initial cesium concentration/Target initial cesium concentration Ratio = 0.932					T_i = 459	

Table 5 Cont'd. What-If Scenarios for Initial Cesium Concentration (Sorption Equilibrium Screening Test – Set 2).

~2.7 M Lithium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.913	$T_i = 459$
1.8 M Lithium Sulfate	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.935	$T_i = 459$
1.8 M Magnesium Sulfate	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.947	$T_i = 459$
~1.7 M Potassium Bicarbonate	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.979	$T_i = 459$
0.75 M Sodium Bicarbonate	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.960	$T_i = 459$

Table 6. What-If Scenarios for Initial Cesium Concentration (Sorption Equilibrium Screening Test – Set 3).

2 M Ammonium Acetate/1.5 M Ammonium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.899	$T_i = 459$
~1.8 M Ammonium Bicarbonate/1 M Ammonium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.002	$T_i = 459$
0.05 M Hexadecyltrimethylammonium Chloride	
Initial Cs concentration/Target Initial Cs concentration Ratio = 0.954	$T_i = 459$
2 M Lithium Chloride/~1 M Lithium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.927	$T_i = 459$
1.8 M Lithium Sulfate/~0.5 M Lithium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.983	$T_i = 459$
~1.7 M Potassium Bicarbonate/0.5 M Potassium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.888	$T_i = 459$
3 M Potassium Carbonate/0.5 M Potassium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.971	$T_i = 459$
0.75 M Sodium Bicarbonate/0.5 M Sodium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.999	$T_i = 459$
1.5 M Sodium Carbonate/0.5 M Sodium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.956	$T_i = 459$
0.03 M Tetrabutylphosphonium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.968	$T_i = 459$
0.05 M Tetrabutylphosphonium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.908	$T_i = 459$
0.03 M Tetramethylammonium Chloride	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.901	$T_i = 459$
0.03 M Tetramethylammonium Chloride/0.03 M Tetramethylammonium Hydroxide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.953	$T_i = 459$
0.03 M Tetramethylphosphonium Bromide	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.917	$T_i = 459$

Table 7. What-If Scenarios for Initial Cesium Concentration (Sorption Kinetics Test).

~2 M Ammonium Carbonate	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.938	$T_i = 459$
Spiked Tank 2F Simulant	
Initial cesium concentration/Target initial cesium concentration Ratio = 0.925	$T_i = 458$

Table 8. Ranking of Eluants from the Cesium Sorption Equilibrium Screening Tests (Sets 1, 2 & 3).

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

3.4 SORPTION (LOADING) AND ELUTION TESTS

The top and bottom portions of Table 9 give the cesium sorption (loading) and elution data respectively. The sorption tests can be considered as 12 replicates since they all used the same mass of resin and same volume of spiked simulant solution. The various percent RSD values of all the A and B (or 12 replicates) replicates indicate good overall reproducibility. Further, the amount of cesium sorbed for the 192-hour equilibration tests (see Table 2) agrees well with the corresponding values for these 48-hour equilibration tests. This confirms that equilibrium is reached in 48 hours for the simulant solution. The initial cesium concentration of each simulant solution for tests 1-6 is close to the target initial cesium concentration (459 mg/L). The ratio of the actual to the target ranged from 0.956 to 1.026.

The elution data show that for 2 M ammonium acetate, ~2 M ammonium carbonate, and 0.5 M nitric acid, virtually all the cesium sorbed or loaded onto the resin was eluted. The average percent elution is at least 94. Since the cesium elution performance of ammonium acetate and ammonium carbonate is roughly equivalent to nitric acid, the benchmark eluant, all indication points to them being potentially effective cesium eluants. It also confirms the effectiveness of the indirect sorption method used to screen the eluants.

Note that the "cesium sorbed" in the sorption or top portion of Table 9 is equivalent to the "cesium sorbed on resin" in the elution or bottom portion of Table 9. The nominal dry mass of resin used for each test = damp mass of resin x F-factor = 1.584 x 0.3157 = 0.5 gram. To obtain the "cesium sorbed" in the top portion of Table 9 on a 0.5-gram resin mass basis, multiply the value by (0.5/1000) or 0.0005.

The pH (in parentheses beside the eluant name) of the 2 M ammonium acetate solution is roughly 6 (measured by pH indicator strips). However, it could be boosted to the minimum of 8 value required for the Tank Farm operations by adding, for example, ammonium hydroxide and/or probably decreasing the concentration as long as the elution performance is not severely affected. The sorption screening data for 2 M ammonium acetate and 2 M ammonium acetate/1.5 M ammonium hydroxide (see Table 8, ranks 5 and 6) indicate the potential effect on elution performance would be minimal. Again, optimization studies regarding eluant concentration and pH will be important going forward.

On the flip side, the cesium elution performance of 1 M ammonium hydroxide, 1.5 M calcium acetate monohydrate, and 2 M magnesium acetate tetrahydrate was not as effective. Unfortunately, no batch contact sorption equilibrium tests were done on them. Hence, their cesium sorption K_d values were not available for K_d performance comparisons. Recall, calcium acetate and magnesium acetate were substitutes for calcium chloride and magnesium chloride respectively because of corrosion concerns.

Ammonium hydroxide was tested because it was felt the data at the end of the sorption screening tests indicated it may be a potential eluant. It is believed that ammonium hydroxide did not work well because the amount that ionizes at a concentration of 1 molar is small. Literature indicates that only 0.42% of the ammonia is in ionized (present as ammonium ion) at 1 molar.[25]

Even though the cesium elution performance of calcium acetate and magnesium acetate was relatively low, it is quite possible their performance may improve in two scenarios.

1. At lower resin cesium loading levels: The cesium loading values (~10,000 mg/kg) in these tests are atypical (or worst-case scenarios) because the cesium concentrations in high-level waste tanks are much lower than that the corresponding equilibrium or final cesium concentrations (average of 73 ± 14 mg/L or a range of 53 - 99 mg/L) obtained here (see top portion of Table 9). In fact, all but two of the Hanford site high-level waste tanks have cesium concentrations less than 8.5 mg/L which is about one-ninth of the average final concentration obtained for the sorption tests. Tanks AZ-101 and AZ-102 have cesium concentrations of 62 and 57 mg/L respectively.[26] These values are still about 20 to 30% lower than the average final cesium concentration obtained here. SCIX is a supplementary pretreatment system. As a result, there will be some flexibility to pick and choose which wastes to treat.

2. A boost of their pH's to around 9/10: This was alluded to earlier in subsection 3.3.

To complete the data set for the sorption and elution tests, data for the pre-elution caustic wash and water rinse steps are provided in Table 10. Again, the tests can be considered as 12 replicates. Based on the percent RSD's, reproducibility is generally good.

Table 9. Cesium Sorption at 25 °C and Elution from sRF Resin at Room Temperature (~25 °C).

SORPTION										
	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	471	471	83.4	79.6	26.2	26.2	**10,151**	**10,233**	**10,192**	0.57
Spiked Tank 2F Simulant – Test 4	456	456	65.0	58.1	26.1	26.2	**10,186**	**10,416**	**10,301**	1.58
Spiked Tank 2F Simulant – Test 5	459	459	79.9	86.9	26.2	26.2	**9,932**	**9,732**	**9,832**	1.44
Spiked Tank 2F Simulant – Test 6	457	457	58.7	53.2	26.2	26.2	**10,435**	**10,580**	**10,508**	0.97
Average of all A & B replicates	456[a]		73.0		26.2		**10,017**			
Percent RSD of all A & B replicates	2.27[a]		19.0		0.17		4.80			
ELUTION										
	Replicates		**Replicates**		**Replicates**		**Replicates**			**% RSD**
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**Average**	
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 M Ammonium Hydroxide (11) – Test 3	1.98	1.81	0.238	0.217	5.073	5.118	**4.68**	**4.24**	**4.46**	6.96
1.5 M Calcium Acetate Monohydrate (8) – Test 4	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 5	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 6	42.8	44.7	5.136	5.364	5.210	5.287	**98.6**	**101**	**100**	2.04

Sorption equilibration time = 48 hours
All the sorption and elution calculations are based on Na-form resin.
[a] Average and percent RSD for six controls. Only one control was done for each duplicate set.
Elution time = ~ 1 day
Volume of eluant solution = 120 mL

Table 10. Caustic Washing and Water Rinsing of the Cesium-Laden sRF Resin at Room Temperature (~25 ^{o}C).

	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	5.84	5.59	0.1168	0.1118	0.981	0.845	0.0196	0.0169
Test 4	4.52	2.64	0.0904	0.0528	0.748	0.535	0.0150	0.0107
Test 5	5.08	6.20	0.1016	0.124	0.936	0.879	0.0187	0.0176
Test 6	4.31	3.97	0.0862	0.0794	0.673	0.610	0.0135	0.0122
Average of all A & B replicates	5.01		0.1001		0.769		0.0154	
Percent RSD of all A & B replicates	20.7		20.7		23.1		23.1	

Volume of Caustic Wash Solution = 20 mL
Volume of Water Rinse Solution = 20 mL

4.0 CONCLUSIONS

Out of the 36 non-acid eluants screened, nine stand out as the most promising with ammonium compounds being the dominant eluants in general. They are as follows in order of decreasing elution potential (based on lowest cesium sorption distribution coefficients).

~ 2 M Ammonium carbonate
2 M Ammonium carbonate/1 M ammonium hydroxide
~1.8 M Ammonium bicarbonate
3 M Rubidium carbonate
2 M Ammonium acetate
2 M Ammonium acetate/1.5 M ammonium hydroxide
~1.8 M Ammonium bicarbonate/1 M ammonium hydroxide
2 M Calcium chloride
3 M Magnesium chloride hexahydrate

The confirmatory (or true sorption and elution) tests indicated ~ 2 M ammonium carbonate and 2 M ammonium acetate are viable eluants for cesium. Their elution performance was roughly comparable to the benchmark or baseline eluant (0.5 M nitric acid). The percent cesium eluted for ammonium carbonate, ammonium acetate, and nitric acid was 97, 94, and 100 respectively.

The cesium elution performance of 1.5 M calcium acetate monohydrate and 2 M magnesium acetate tetrahydrate was lackluster. The percent cesium eluted was 16 and 8 respectively. Relatively lower resin cesium loadings and/or increase of their pH may enhance their elution potential.

5.0 PATH FORWARD

1. Perform elution optimization studies on eluant concentration, pH, and temperature among others using mini-columns (2 to 5-mL).

2. Develop regeneration schemes using mini-columns.

3. Confirm the process with a typical laboratory multi-step small column (10 to 12-mL) ion exchange unit.

All the above will be performed with simulant solutions.

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