Options for the Removal of Cesium and Strontium from Acidic Uranyl Sulfate Solutions from Molybdenum-99 Production:

Part II The Effect of Sodium Carbonate Adjustment to pH 9 on Strontium Removal

E. A. Kyser

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PREFACE OR ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

A small laboratory-scale column process aimed at removing fission products from prototypical acidic sulfate solution wastes from a prototypical Mo-99 recovery process has been operated in a radioactive materials hood at Savannah River National Laboratory. This equipment has been operated with realistic concentrations of uranium (0.4 wt % ^{235}U), plutonium (^{239}Pu), neptunium (^{237}Np), non-radioactive surrogates of common fission products (including Cs and Sr) and two promising absorbents – AMP-PAN and CST R9120-B.

The goal of this work was to demonstrate the removal and concentration of high specific activity isotopes which are expected to dominate the classification of the low-level waste from the production of ^{99}Mo. Both AMP-PAN and CST R9120-B are attractive absorbents for the removal of ^{137}Cs from an acidic sulfate waste stream. They do not provide a solution for the removal of ^{90}Sr from the acidic solutions. CST was shown to be useful at removing both Cs and Sr after adjustment of the acidic sulfate solution with sodium carbonate to pH 9. Limited removal of transuranic species and almost no removal of uranium was observed for CST R9120B absorbent. This could be important due to the relatively large amount of uranium expected to be present in such waste streams. The capacity of these absorbents for ^{137}Cs will likely be dependent on the Cs concentration in the solutions processed but loading in excess of 0.7 mg Cs per gram of CST absorbent while loading 0.14 mg Sr per gram of CST absorbent appears to be achievable from pH 9 carbonate solution.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

A	cross-sectional area of resin bed
AMP-PAN	ammonium molybdophosphate on polyacrylonitrile
ANL	Argonne National Laboratory
BV	bed volume
CST	crystalline silicotitanate
DF	decontamination factor
DI H_2O	deionized water
DOE-NNSA	Department of Energy - National Nuclear Security Administration
FY	fiscal year
HDPE	high density polyethylene
HEU	highly enriched uranium, >20% U-235
h	hour
ID	inner diameter of column
ICPMS	inductively coupled plasma - mass spectroscopy
LEU	low enriched uranium, <20% U-235
Kd	distribution coefficient, mL/g
mda	minimum detection amount
PHA	pulse height analysis
PP	polypropylene
Q	flow rate
SCIX	Small Column Ion Exchange
SHINE	SHINE Medical Technologies LLC (Janesville, Wisconsin)
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCCR	Tank Closure Cesium Removal
TEVA	TEtraValent Actinide resin from Eichrom
Titania	titanium dioxide
TTA	thenoyltrifluoroacetone, a tetravalent specific actinide extractant
ug	microgram, used instead of µg in Excel tables and figures
wt%	weight percent

1.0 Introduction

The U.S. Department of Energy's National Nuclear Security Administration (NNSA) Office of Material Management and Minimization (M^3) manages the Molybdenum-99 (^{99}Mo) Program as part of its mission to minimize the use of highly enriched uranium (HEU) in civilian applications.[1] HEU is a proliferation-sensitive material that, if diverted or stolen, could be used as a component of a nuclear weapon. The ^{99}Mo Program assists global Mo production facilities in converting to non-HEU processes and supports the establishment of domestic supplies of ^{99}Mo without the use of proliferation sensitive HEU.

The U.S. medical community depends on a reliable supply of the radioisotope ^{99}Mo for nuclear medical diagnostic procedures. ^{99}Mo and its decay product, technetium-99m (^{99m}Tc), are used in over 40,000 medical procedures in the United States each day to diagnose heart disease and cancer, to study organ structure and function, and to perform other important medical applications.[1]

In 2012, Congress passed the American Medical Isotopes Production Act (AMIPA), which directed NNSA to establish a technology-neutral program to support the establishment of domestic supplies of ^{99}Mo without the use of HEU. NNSA has implemented this by establishing cooperative agreements with commercial entities and providing funds to the Department of Energy's National Laboratories to support development of low enriched uranium (LEU) ^{99}Mo production technologies. SHINE Medical Technologies, LLC is one of those commercial entities. They plan to use an accelerator to generate neutrons.[2] Those neutrons are focused into an LEU sulfate solution target where ^{235}U atoms fission to produce ^{99}Mo and other isotopes. After approximately a week of irradiation, the uranyl sulfate solution is pumped through an extraction column filled with a titanium-based absorbent (Sachtopore NP). The ^{99}Mo is retained and concentrated on the absorbent. The column is then washed with solutions of dilute sulfuric acid and water prior to recovery of the ^{99}Mo for further purification.

Savannah River National Laboratory (SRNL) has been providing waste processing support to assist in the development of this process technology. In previous studies McCann and Rudisill[3] investigated using crystalline silicotitanate (CST) materials (such as IONSIV R9120, IE-911) to concentrate certain high specific activity fission products in the waste streams which are expected to control the classification of the low-level waste (LLW) from this process. In that work the importance of understanding the amounts of uranium, plutonium, and neptunium that would be present in the wash streams (which require processing as waste) as well as the amounts of these actinides which are retained on the Sachtopore NP absorbent was identified. In later work, Kyser[4] investigated the behavior of the actinides in the ^{99}Mo absorption process under process conditions and how much of each actinide was likely to be present in the waste streams.

1.1 Literature Review

CST originated out of work done by Texas A&M and Sandia National Laboratory.[5,6] CST is currently being manufactured by Honeywell UOP as a Cs absorbent. Cs distribution coefficients ranging from 250 mL/g at 1 M acid to 80,000 mL/g at 2.5 M base were measured by Zheng et al.[6] Batches of CST IE-911 and R9120-B

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[1] https://www.energy.gov/nnsa/nnsa-s-molybdenum-99-program-establishing-reliable-domestic-supply-mo-99-produced-without, accessed May 2021.

[2] http://shinemed.com/demonstrated-technology, accessed May 2021.

[3] K. P. McCann, T. S. Rudisill, "Removal of High Specific Activity Fission Products from Uranyl Sulfate Waste Solutions", SRNL-STI-2020-00199, Savannah River National Laboratory, Aiken, SC 29808, (August 2020).

[4] E. A. Kyser, "Distribution of U, Pu and Np in a Mo-99 Recovery Process using Sachtopore NP (titania based) Absorbent Material", SRNL-STI-2021-00297, Savannah River National Laboratory, Aiken, SC 29808, (July 2021).

[5] R. G. Anthony, R. G. Dosch, D. Gu, C. V. Philip, "Use of Silicotitanates for Removing Cesium and Strontium from Defense Waste", Ind Eng Chem Res 1994, 33, 2702-5.

[6] Z. Zheng, C. V. Philip, R. G. Anthony, J. L Krumhansl, D. E. Trudell, Miller, "Ion Exchange of Group I Metals by Hydrous Crystalline Silicotitanates", Ind Eng Chem. Res. 35 4246-56, (1996).

have been investigated for use in SRS waste processes for many years targeting the high pH region. Venkatesan et al.[7] performed small column testing of CST IE-911 and TAM-5 for Cs removal from 3 M HNO_3. They found Cs capacity on the order of 20 mg Cs/g CST to 1% breakthrough and 50 mg/g to 100% breakthrough. Their test conditions were up to 12.7 mm/min superficial fluid velocity (Q/A= volumetric flowrate/cross sectional area) with a 9-minute residence time in his columns. There have been multiple kinetic studies of CST under caustic conditions. Smith[8] modeled large columns of CST IE-911 for the SRS SCIX design (lead-lag column configuration) where the fluid velocity ranged from 50 to 210 mm/min with a 20 to 40-minute residence time.

McCann and Rudisill[3] performed some initial work and projected that significant removal of ^{137}Cs and ^{90}Sr would be needed for projected SHINE waste to meet Class A limits. The estimated fission product content would require the overall process to achieve 95% removal (DF=20) of ^{137}Cs and 99% removal (DF=100) for ^{90}Sr, as well as 50% removal (DF=2) for ^{144}Ce. McCann and Rudisill[3] performed batch contacts with SRS samples of monosodium titanate (MST) and CST (IE-911 and IONSIV R9120-B) that were available at that time. They also performed a column test using CST IE-911. Differences between the samples of CST were observed that were later attributed to differences between the Na^+ and H^+ forms of the samples used in those tests. Complete conversion of CST is kinetically slow and thus takes significant care to ensure completeness. SRS laboratory procedures recommend the use of 65 BV (bed volume) of 3 M NaOH at a rate of 3 BV/h followed by a soak in 3 M NaOH for 72 h.[9] Rinses with DI water between steps were also specified to remove both fines and precipitates. Similar exhaustive techniques are likely necessary to produce a CST form that does not continue to release sodium ion in acidic solutions. Batch contact tests with weakly acidic solutions are especially sensitive to such effects as the pH of the contact solution should change over time due to the limited amount of acid available. Column tests are likely less affected due to the relatively large amount of acid solution available.

McCann and Rudisill[3] tested a 10x100 mm column which they operated with a superficial velocity of 5 mm/min with a residence time of 20 min (3 BV/h). The column feed solution was pH 1, but no pH measurements were performed to confirm. The feed solution had a total metal concentration ~0.5 g/L. This was a very high feed concentration. Total Cs loading was ~2 mg Cs/g CST, which did not appear to come close to challenging the capacity of the absorbent. Cs and Rb were quantitatively loaded by the CST with partial breakthrough of Pd, Sr, and Ru observed. Sr breakthrough began at ~0.5 mg Sr/g CST. Due to the slow flowrate the column was only operated for 27 BV (or 9 hours total). Note that initially the lanthanides were retained by the absorbent but after 25 BV the cumulative retention dropped to only ~20%.

AMP-PAN (ammonium molybdophosphate on polyacrylonitrile) is an absorbent available from TrisKem (a French company) that is specific for absorbing Cs from acidic solutions. AMP as a powder had earlier usage, but the PAN formulation of AMP was developed by Sebesta et al.[10] in the mid-1990s while at Sandia National Laboratory. Sebesta et al. loaded Cs onto 15 mm diameter columns of AMP-PAN from acidic solutions (1 M HNO_3+1 M $NaNO_3$) at superficial fluid velocities of 110 mm/min (28-114 BV/h) and observed Cs capacity of up to 1.6 g Cs/L absorbent (~1.4 g Cs/g AMP-PAN). The Cs loading kinetics were much faster than CST. Because AMP-PAN had some solubility in 1 M HNO_3, Sebesta et al. noted that AMP- PAN appeared to have higher Cs losses at lower flowrate due to the slow dissolution of the AMP

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[7] K. A. Venkatesan, V. Sukumaran, M. P. Antony, T. G. Srinivasan, Journal of Radioanalytical and Nuclear Chemistry, Vol 280, No 1 129-36, (2009).

[8] F. G. Smith III, "Modeling CST Ion-Exchange for Cesium Removal from SCIX Batches 1-4", SRNL-STI-2011-00181, Savannah River National Laboratory, 2011.

[9] W. D. King, L.L. Hamm, F. F. Fondeur, "CST Ion Exchange Media Pretreatment and Batch Contact Test Results with Tank 10H Supernate to Support TCCR", SRNL-L3100-2017-00149, Savannah River National Laboratory, Aiken SC, December 2017.

[10] F. Sebesta, J. John, A. Motl, "Phase II Report on the Evaluation of Polyacrylonitrile (PAN) as a Binding Polymer for Absorbers used to treat Liquid Radioactive Wastes, SAND96-1088, Sandia National Laboratories, 1996.

which released some of the bound Cs. Marsh et al.[11] also performed Kd tests using AMP-PAN and indicated Cs had a Kd of ~2000 for acidified sludge and supernate. Cerium had double digit retention (Kd as high as 28), but U and Pu retention was observed to be low (0.1 to 2.5).

SrTreat is a sodium titanate-based absorbent currently available from a Finnish company (Selion Oy). It is similar to the monosodium titanate (MST) powder routinely used at SRS for Sr absorption from alkaline solutions. As a powder, MST has been routinely used on analytical samples to remove ^{90}Sr as well as on a tank farm scale for batch removal of Sr, Pu, U, and Np. As a powder form, MST requires filtration for removal and would have too high of a pressure drop for column operations. Calcium, U and other actinides will likely compete for capacity. Lehto et al.[12] has published both Kd and column testing results for SrTreat. They reported Kd's of over 100,000 mL/g for solution of pH 8 to 10. Lehto operated his column at 5 BV/h, which is somewhat faster than the typical CST rate. Lehto also reported a capacity of ~27 mg Sr/cc SrTreat for Sr column breakthrough. This compares to a measured Sr capacity of 2.3 mg Sr/g for MST as reported by Hobbs.[13] Note the McCann and Rudisill[3] also tried to perform some batch contacts with MST and pH 1 sulfuric acid and reported that it was not stable in acid. Lehto does report Sr Kd values of ~0.1 down to pH 1 suggesting that Sr might be stripped from SrTreat by dilute acid solutions.

Under acid conditions there are several products which are touted as being highly specific absorbents for Sr. IBC Advanced Technologies makes several products targeting Sr and Ra (Sr-01, Ra-01, Superlig® 620). Information on these products is very limited from the manufacturer citing intellectual property concerns, but there are some literature references. Verlinde et al.[14] published Kd data for Ra-01 on the order of 100 mL/g for HNO_3/HCL systems. Remenec[15] reported capacity results on the order of 20 mg Sr/g for Sr-01 from 0.1 to 10 M HNO_3. The kinetics of these materials appear to be favorable to use in a column form. DeVol[16] looked at using SuperLig® 620 resin for ^{90}Sr separation for automated process monitoring. Eichrom Technologies also makes a Sr specific resin that is based on a crown ether extractant. Methods[17] from Eichrom recommend loading Sr from multi-molar HNO_3 and elution with 0.05 M HNO_3.

The focus of this was effort was aimed at using highly selectively absorbents to remove ^{137}Cs and ^{90}Sr. However, another option would be to use conventional ion exchange resins. These tend to have low selectivity but there is a lot of historical experience with their use. Conventional cation exchange should readily remove multivalent cationic metal species from pH 1 sulfuric acid solution with a significant capacity. Depending on how much UO_2^{+2} loading is an issue, cation exchange should effectively remove Sr^{+2} and other cationic species. Ang et al. investigated the effectiveness of using cation and anion exchange[18] as well as chelating resins[19] to perform U, Th and lanthanide separations in acidic sulfate media. In pH 2 sulfuric acid Ang showed that UO_2^{+2} was anionic while common lanthanides were cationic, suggesting that the use

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[11] S. F. Marsh, Z. V. Svitra, S. M. Bowen, "Distributions of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY", LA-12654, Los Alamos National Laboratory, 1994.

[12] J. Lehto, L. Brodkin, R. Harjula, E. Tusa, "Separation of Radioactive Strontium from Alkaline Nuclear Waste Solutions with the Highly Effective Ion Exchanger SrTreat", Nuclear Technology, Vol 127, 81-7, (1999).

[13] D. T. Hobbs, "Properties and Uses of Sodium Titanates and Peroxotitanates", J. SC Acad. of Sci., 9(1), [2011].

[14] M. Verlinde, J. Gorny, Gilles Montavon, S Khalfallah, B Boulet, et al. "A new rapid protocol for 226Ra separation and preconcentration in natural water samples using molecular recognition technology for ICP-MS analysis." Journal of Environmental Radioactivity, Elsevier, 2019, 2020, pp.1-7. hal-02391116.

[15] B. Remenec, "The Selective Separation of 99Sr and 99Tc in Nuclear Waste using Molecular Recognition Technology Products", Czechoslovak Journal of Physics, Vol. 56, (2006), Suppl. D D645-D651.

[16] T. DeVol, J. Clements, A. Farawila, M. O'Hara, O. Egorov, J. Grate, "Characterization and application of SuperLig®620 solid phase extraction resin for automated process monitoring of 90Sr", J Radioanal Nucl Chem, Vol 282:623-628, (2009)

[17] https://www.eichrom.com/eichrom/products/sr-resin/, accessed August 2022.

[18] K. L. Ang, D. Li, A. Nikoloski, "The effectiveness of ion exchange resins in separating uranium and thorium from rare earth elements in acidic aqueous sulfate media. Part 1. Anionic and cationic resins", Hydrometallurgy, 174, 147-155, (2007).

[19] K. L. Ang, D. Li, A. Nikoloski, "The effectiveness of ion exchange resins in separating uranium and thorium from rare earth elements in acidic aqueous sulfate media. Part 2. Chelating resins", Minerals Engineering, 123, 8-15 (2008).

of cation exchange would recover Sr^{+2} along with the lanthanide elements without retaining excessive amounts of UO_2^{+2}. Ang et al.'s work also indicates that it would be practical to selectively remove (or recover) uranyl sulfate from a pH 1 solution as an anionic complex. Conventional ion exchange was outside the scope of the current SRNL effort, but these options should be kept in mind as multiple absorbents may be needed to accomplish the goal.

During the previous phase of this work, Kyser[20] tested CST R9120B, AMP-PAN and Ra-01 during fiscal year 2022. That testing showed that both CST R9120B and AMP-PAN were effective at selectively removing Cs and Rb (100%) from pH 1 sulfuric acid solutions. U and Np were not significantly retained (<1%) by either AMP-PAN or CST, but some Pu was retained (10-20%) by both absorbents. CST retained some Mo (60%), and AMP retained some Pd (50%) and weakly retained the various lanthanide species (~20%). These column experiments were very small scale, but even at this scale Cs break-though was still not observed. Figure 1 shows the retention of various metals from acidic solutions by CST R9120B. Both AMP and CST appeared to have some tendency to leach into pH 1 sulfuric acid, but this did not affect their usefulness at removing Cs. Unfortunately, Sr was not removed by any of the materials tested from acidic sulfate solutions. The IBC Ra-01 product was not found to be useful for Sr removal. IBC has other products that could be useful for Sr removal; however, the company did not provide sufficient information to warrant further testing.

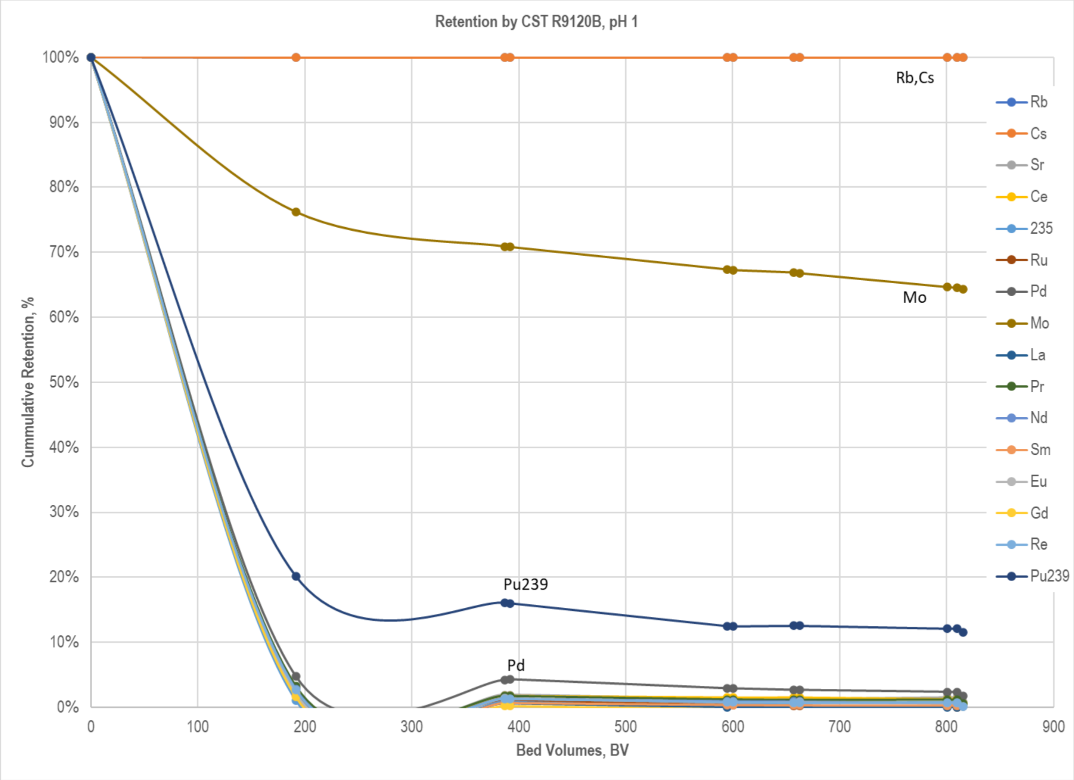

Figure 1. Retention of Metals on CST R9120B from pH 1 Sulfuric Acid Solution.

Based on the SRS experience with CST under highly alkaline conditions and Honeywell UOP literature, the selectivity of CST for Sr was believed to be significantly higher at pH 9 than at pH 1. A pH adjustment from 0.1 M sulfuric acid with sodium carbonate would have limited potential for significant precipitation as the primary metal element species, UO_2^{+2}, has significant solution solubility in a carbonate system

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[20] E. A. Kyser, D. J. Foley, D. P. Diprete, "Options for the Removal of Cesium and Strontium from Acidic Uranyl Sulfate Solutions from Molybdenum-99 Production", SRNL-STI-2022-00365, Savannah River National Laboratory, Aiken, SC 29808, (2022).

(~20 g U/L[21]) due to formation of carbonate complexes. A column experiment was previously attempted in Part I of this study; however, it had to be halted due to excessive gas formation in the absorbent bed. This was presumably due to incomplete conversion of the CST absorbent from the H^+ to the Na^+ ionic form. Conversion had been attempted with pH 9 sodium carbonate solution, but afterwards it was recognized that the total carbonate concentration of the feed solution was considerably higher due to the $UO_2(CO_3)$ that was present. Further review of the SRS pretreatment methodology[9] (65 BV of 3M NaOH followed by 72 hours soak in 3 M NaOH) for complete conversion of CST to the Na^+ form confirmed that the CST was likely still in the H^+ form. These issues occurred late in FY22, and further experimentation at pH 9 was deferred until FY23 as a Part II study.

2.0 Experimental

2.1 Feed Preparation:

The surrogate feed solution is intended to represent the variety of impurities generated when an LEU uranyl sulfate solution is irradiated to produce ^{99}Mo from the fission of ^{235}U. $^{239/240}$Pu and ^{237}Np were added to a uranyl sulfate solution along with a series of representative fission product surrogates (non-radioactive). The commercial ^{99}Mo process makes the heavier radioisotope of Np (^{239}Np), which quickly decays ($t_{½}$ =2.36 days) to ^{239}Pu. Concentrations of the non-radioactive impurities were chosen roughly based on their expected abundance in the future ^{99}Mo process (0.1 to 25 mg/L). The choice of chemical form of the surrogates cannot be certain to match the valence state of the fission product species in the process but was based on both availability and experience. Nitrate salts (ACS reagent grade) dissolved in water or dilute sulfuric acid were used for most elements when available, but molybdenum was added as a molybdate ($Na_2MoO_4 \bullet 2H_2O$) and rhenium as $NaReO_4$ (as a surrogate for technetium).

Uranyl sulfate raffinate solutions from the previous work with titanate were available for use as the source of uranium. The uranyl sulfate solutions were originally prepared by the dissolution of uranium trioxide (UO_3) in a mixture of sulfuric acid and water. A small volume of Pu and Np solution was added (~ 0.5 mg each) to this solution. The nonradioactive surrogates were dissolved and prepared separately for addition to the uranyl sulfate solution. In the previous work[4,20] solubility issues were encountered. Based on that experience, in this work metals, as nitrate salts, were added individually after dissolution in up to 20 mL of DI water. Still, a problem was sometimes observed with what was assumed to be Pd hydrolysis leading to brown solids formation in some feed solutions. Filtration was used to remove these as necessary, but the preference was to remake the feed solution and dissolve the Pd salt in pH 1 sulfuric acid to avoid this issue. Note that barium and strontium sulfate have limited solubility, so these impurities were always added individually as nitrate salts dissolved in water. Also note that multiple lanthanides (cerium especially) have a limited solubility with molybdate. The final solution was filtered using a 0.45-µm cellulose nitrate filter although post precipitation sometimes was observed after filtration. A Hanna handheld pH meter was used to check the pH after preparation of the solutions. This meter was calibrated using off the shelf pH buffer solutions (pH 4, 7, and 10). Typically, fine adjustment of the pH was necessary prior to actual use of the feed solution in the experiment.

Table 1 shows the U/Pu/Np stock solution was prepared by combining 5 mL of uranyl sulfate solution (~2.1 g U) with ~0.5 mg of Pu (94% ^{239}Pu) and ~0.5 mg of ^{237}Np (in 1 mL of 0.1 M sulfuric acid) into 100 mL of 0.1 M sulfuric acid solution. This actinide "spike" solution was pH adjusted separately by the addition of ~6.1 mL of 16 wt% sodium carbonate solution dropwise. The nonradioactive impurities were prepared separately in pH 1 sulfuric acid as shown in Table 2 and sampled for analysis. An aliquot of that impurity feed matrix (50 mL) was diluted to 1 L with pH 1 sulfuric acid solution. A large portion of that diluted impurity matrix (880 mL) was then pH adjusted to pH 9 with addition of ~58 mL of 16 wt% sodium

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[21] W. F. Linke, A Seidell, "Solubilities Inorganic and Metal-Organic Compounds: A compilation of Solubility Data from the Periodical Literature", Volume 2, 4th Ed., D Van Nostrand Company, Princeton, NJ, pg 1601 (1965).

carbonate solution and filtered. A small amount of solids was observed. Lastly, the pH adjusted actinide solution and the pH adjusted impurity matrices were combined, and the final pH was measured as 8.92.

Table 1. Preparation of U/Pu/Np Portion of the Feed Solution for CST R9120-B (Cr393) pH 9.

Description	Vol	U	U	Pu	Pu	Np	Np	H+	HNO3	SO4
	mL	g/L	g	mg/L	mg	mg/L	mg	M	M	M
UO2SO4-A	5	413	2.1					0.100	0.00	0.10
Spike Pu/Np	1.06	0	0	466	0.494	495	0.525	0.186	0.09	0.09
Cr376 Hearts				14100				1.000	0.09	
20 g/L Np						21000		2.500	2.50	
0.1 M sulfuric acid	100							0.100	0.00	0.1
Pu/Np/U Spike 3	106.1	19.5	2.066	5	0.49	5	0.53	0.101	0.0009	0.10

Table 2. Preparation of Feed Solution for CST R9120B (Cr393) pH 9.

Wgt	Description	Vol	Metal Impuritiy		
g		mL		mg	mg/L
0.064	Ru(NO)(NO3)3		Ru	20.3	20.3
0.085	Pd(NO3)2*2H2O	0.001	Pd	33.9	33.9
0.250	Ce(NO3)3*6H2O	0.003	Ce	80.7	80.7
0.019	Cs(NO3)		Cs	13.0	12.96
0.062	Sm(NO3)3*6H2O	0.001	Sm	21.0	21.0
0.237	Nd(NO3)3*6H2O	0.003	Nd	78.0	78.0
0.007	Eu(NO3)3*5H2O	0.000	Eu	2.5	2.48
0.062	La(NO3)3*6H2O	0.001	La	19.9	19.9
0.010	Gd(NO3)3*6H2O	0.000	Gd	3.5	3.5
0.063	Pr(NO3)3*6H2O	0.001	Pr	20.4	20.4
0.019	Rb(NO3)	0.000	Rb	11.0	11.0
0.034	NaReO4	0	Re	23.2	23.2
0.004	Sr(NO3)2	0.000	Sr	1.7	1.66
0.004	Na2MoO4*2H2O	0.0001	Mo	1.6	1.6
2.500	8.1 g Zr/L in H2O	2.500	Zr	20.3	20.2
	98% Conc Sulfuric acid	5.5			
	DI H2O	992			
	Cr393 Impurities	1000		351	

Due to concern of the effect of concentration on the saturation capacity of CST, the concentrations of Cs, Rb, and Sr (which are targeted for retention by CST) were reduced ~10x from the concentrations used in the Phase I experiments. Other fission product metal concentrations targeted final concentrations of 0.1, 1 or 4 mg/L based on the expected abundance in the process solutions.

2.3 Equipment for Column Experiments

A photo of the equipment used for the column experiment with CST R9120B is shown in Figure 2. The process starts with a feed bottle connected to a peristaltic pump. The pump transfers the feed solution to a modified addition funnel installed on the top of small Biorad Econo-column with ~1 cc of wetted absorbent material carefully packed to avoid air bubbles or other voids. The bottom of the column has a stopcock to stop flow. Tubing from this bottom stopcock is fastened by a clamp at approximately the same elevation as the anticipated level in the bottom of the additional funnel. This was done to ensure that the column cannot siphon dry and prevent the liquid head difference between the discharge point and the liquid level in the addition funnel from significantly affecting the flowrate through the column. Figure 2 shows a photo of the equipment prior to the start of the loading for experiment Cr387. The same configuration was used for the current experiment with a new sample of absorbent. Masterflex® peristaltic pump tubing and Luer Lok fittings supplied by Cole-Parmer® were used to make connections between the various components. Pump tubing of various sizes was used depending on the desired flowrate (tubing sizes from -10, -26, -48, corresponding ID's of 0.19, 0.89, 2.79 mm). The cap of the feed bottle was drilled out and a quick-connect was installed in the feed bottle cap. A length of HDPE tubing (~1/16 in. ID) was installed on the barb fitting inside the cap and extended to the bottom of the feed bottle to allow the bottle to be pumped empty. This quick connect fitting allowed easy change between condition, feed, and wash solutions. The tubing inner diameter and pump speed determined the flow rate. The addition funnel on the top of the column was customized by the installation of threaded Luer Lok PP fittings epoxied into place. This funnel was operated sealed (with the cap in place) to allow pressure driven flow through column. A digital manometer connected to the top of the addition funnel was initially used to monitor pressure drops through the column. The relatively large gas volume in the addition funnel provided a safety factor as low pump flowrates did not pressurize the system rapidly, which allowed time for any flow issues to be detected and corrected. In the event of a failure to recognize flow blockage, the large cap on the addition funnel would lose its seal at approximately 0.5 psig. A wire harness was installed to prevent the cap from falling out of the hood in the event the addition funnel was pressurized excessively. Normal operating pressures of 0.02 to 0.1 psig were observed, depending on the absorbent and flowrate. This equipment was generally operated unattended for hours or even overnight.

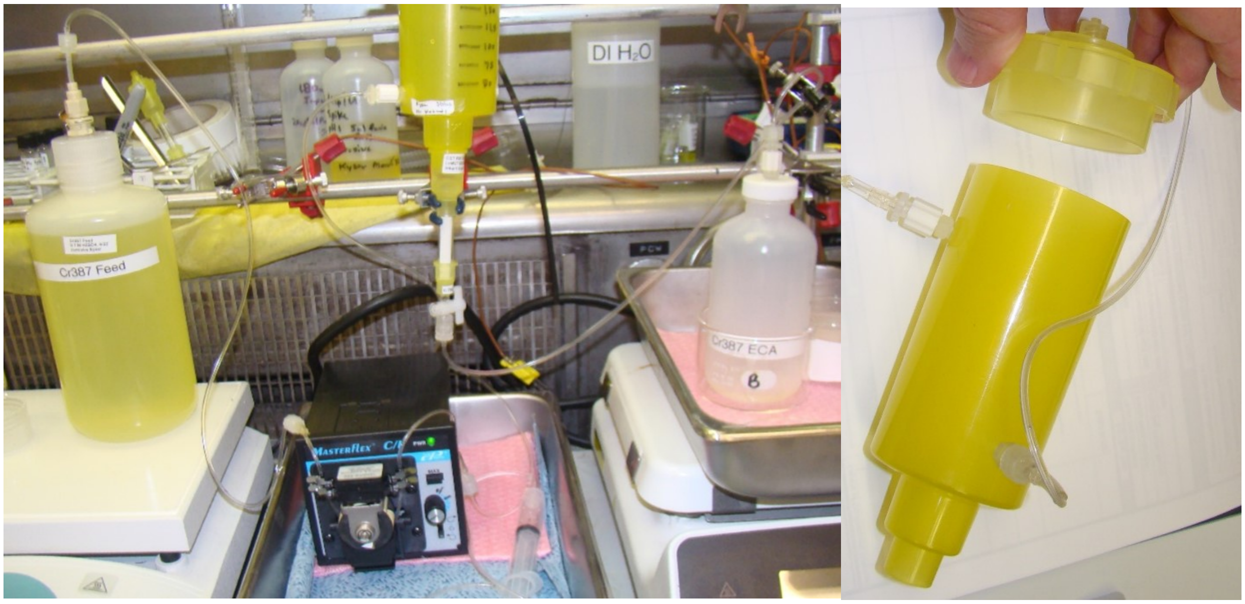

Figure 2. CST Column Setup with Customized Addition Funnel.

2.4 Column Experiments:

Column loading experiments were performed for absorbent materials as follows. Note that in the previous work, pH 9 sodium carbonate was used to convert the CST from the H^+ to the Na^+ ionic form but was found to be incomplete, and the experiment had been aborted due to gas bubble formation in the resin bed.[20] Review of the SRS pretreatment methodology[9] confirmed the need for a more robust treatment of the CST to eliminate all the residual H^+ loading sites. For this work a weighed sample of CST R9120B was converted by flowing 65 BV of 3M NaOH through the bed, followed by a 72-hour soak in 3 M NaOH. The excess 3 M NaOH was removed, and a final soak in pH 9 sodium carbonate was performed. A bed of absorbent ~40 mm tall (or ~0.8 cc volume) was used as in the previous work. After conditioning, any gas bubbles were removed by backflushing the bed with a 10-mL Luer Lok syringe using conditioning solution.

This experiment involved a run time of over 100 hrs spread out over 6 days and was set-up for unattended overnight operation. Due to the small size of the column, the targeted flowrate was 0.1 mL/min. After passing through the column, the raffinate was collected as either a raffinate cut or a sample in a prelabeled, pre-weighed bottle. At the end of the experiment each bottle was weighed (prior to sampling) and the density of solutions determined to obtain both the weight and the volume in each bottle. Samples were taken and ICPMS analyses were performed (as appropriate). Most non-rad impurities were measured by ICPMS. In the Part I study U, Pu and Np were quantified by customized gamma/alpha counting methods, but these analyses were not performed in the Part II study. There was an assumption that the actinide species likely have limited solubility at pH 9, and there were limited funds available to deal with the complications that would involve.

Column operating conditions and capacities were determined based on the literature review and what was practical for testing purposes. Rather small columns (5 mm ID x 50 mm) were used due to the estimated capacity of the absorbents and to limit the overall solution volumes due to handling constraints in the hood where the work was performed.

Absorbent materials were available "in-house" for testing from past and current SRNL work. The CST R9120B was an SRNL sample from a large batch purchased from Honeywell UOP for SRS use in 2020 (batch number 2102020757, Drum #5).

2.4 Analytical Methods:

Most metal ions present in the feed solution were planned to be in the 1-20 mg/L concentration range. U however is present at 2-6 g U/L. ICPMS has been shown to have detection limits of 1 µg/L for most of the metal ions of interest including U. Pu and Np were added to the feed solutions at the 0.5 mg/L concentration level. No additional radiochemical analyses were performed for this portion of the study due to limited funds available for this work.

3.0 Results:

3.1 Adjustment of pH from 1 to 9 with sodium carbonate:

A 20-mL sample of the feed from the previous work was pH adjusted and was analyzed as part of the current effort to identify precipitation effects. Due to the presence of 6 g U/L, more carbonate was required to reach pH 9 than that required to neutralize the 0.1 M sulfuric acid alone, but the amount of carbonate used was not tracked on this initial attempt (which throws off the material balance). The U appeared to remain in solution and no visible solids were apparent. The ICPMS analyses (see Table 3) showed almost quantitative precipitation of the lanthanides included in the feed matrix and possibly some precipitation of Pd. It is noted that the Pu and Np did not appear to precipitate significantly although based on UV-Vis spectra, the Pu appears to form Pu polymer at pH 1 prior to the addition of carbonate solution.

Table 3. Analyzed Concentrations and Mass Balance for Cr388 Feed Preparation and pH Adjustment.

Cr388	LW26230 Feed pH 1 ug/L	LW28998 Feed pH 9 ug/L	LW26230 Feed pH 1 ug/btl	LW28998 Feed pH 9 ug/btl	Percent Mass of pH 1 Impurities
Rb	1282	954	25.6	19.1	74%
Cs	6542	4719	130.8	94.4	72%
Sr	5193	3942	103.9	78.8	76%
Ce	21616	809	432.3	16.2	3.7%
235	23941	17575	478.8	351.5	73%
238	5812459	4217974	116249.2	84359.5	73%
Ru	7008	4797	140.2	95.9	68%
Pd	1786	939	35.7	18.8	53%
Zr	1002	826	20.0	16.5	82%
Mo	25	21	0.5	0.4	84%
La	1249	3	25.0	0.1	0.2%
Pr	2436	8	48.7	0.2	0.3%
Nd	11634	47	232.7	0.9	0.4%
Sm	1219	8	24.4	0.2	0.7%
Eu	1307	14	26.1	0.3	1.1%
Gd	1974	20	39.5	0.4	1.0%
Re	4362	3441	87.2	68.8	79%
234	153	104	3.1	2.1	68%
236	116	77	2.3	1.5	66%
237	446	313	8.9	6.3	70%
239	582	603	11.6	12.1	104%

Note: Yellow highlighted cells are lanthanide elements that appear to have precipitated during pH adjustment.
Note: The amount of carbonate used in the pH adjustment was not tracked. Based on the analytical results, the dilution appears to be 20-30%.

The radioactive components of the feed solution for the current experiment were prepared and pH adjusted separately from the non-radioactive components. In order to parallel the proposed process, initially 0.1 M sulfuric acid solutions were prepared. A 20x concentration acidic impurity matrix was prepared (and sampled) which was then diluted and pH adjusted (and sampled again). It was anticipated that some precipitation might occur. Lastly the radioactive (U/Pu/Np) addition was made. Filtration of the feed was performed multiple times to avoid the complications in analysis. Table 4 shows a material balance for the preparation of the feed solution as analyzed by ICPMS. As in the previous test, the yellow color of the U in solution was not affected by the pH adjustment, and no visible evidence of solids was observed in the solutions after adjustment. A small amount of brown solids was later observed in the acidic impurity matrix bottle thought likely to be associated with Pd. As seen previously, nearly all the lanthanide elements used (98-99.7%) precipitated during the pH adjustment with carbonate. Significant Pd appeared to be precipitated during the pH adjustment. The final concentrations of most lanthanides (other than Ce and Nd) were near to the detection limit of our ICPMS method. The actinides (U,Pu,Np) appeared to be present at the planned concentrations suggesting that the actinides did not precipitate to a significant extent, but an independent analysis of the actinide portion of the feed prior to pH adjustment was not performed.. Because of the much lower U concentration present in the solution (over those tested in Part I), the amount of interference of ^{238}U onto the adjacent 237 and 239 mass channels appears to be much less significant.

Table 4. Analyzed Concentrations and Mass Balance for Cr393 Feed Preparation and pH Adjustment.

	LW28999	LW29000	LW29001	LW28999	LW29000	LW29001	LW29000
	Impurities	Impurities	Feed	Impurities	Impurities	Feed	Percent after
	pH 1 20x	pH 9	pH 9	pH1	pH 9	pH 9	pH 1 to pH 9
Cr393	ug/L	ug/L	ug/L	ug/btl	ug/btl	ug/btl	Adjustment
Rb	12259	656	581	613	577	581	94%
Cs	14310	732	645	715	644	645	90%
Sr	3130	144	131	157	127	131	81%
Ce	87412	108	105	4371	95	105	2%
235			3514			3514	
238			1737360			1737360	
Ru	25058	1336	1155	1253	1176	1155	94%
Pd	31090	1126	1017	1554	991	1017	64%
Zr	17966	1079	955	898	949	955	106%
Mo	1714	92	90	86	81	90	95%
La	21585	3	5	1079	3	5	0.3%
Pr	20879	5	8	1044	4	8	0.4%
Nd	85896	23	24	4295	20	24	0.5%
Sm	21824	10	10	1091	9	10	0.8%
Eu	3015	2	3	151	2	3	1.1%
Gd	4755	3	4	238	3	4	1.2%
Re	20723	1492	1332	1036	1313	1332	127%
237			723			723	
239			636			636	
			Vol, mL	50	880	1000	

Note: Yellow highlighted cells are lanthanide elements that appear to have precipitated during pH adjustment.

3.3 CST R9120-B Column from pH 9 Solution (Cr393):

CST R9120-B 30x60 absorbent was tested as a column after adjustment of the feed solution to pH 9. Due to the slow reported kinetics for CST this experiment was planned to run at a flowrate of 6.6 mL/h, taking 110.4 h to pass 821.7 mL of feed (or 1046.7 BV) through the bed. This flowrate is somewhat faster than the historical 3 BV/h used in the SRS tank farm related work. Table 5 shows a detailed breakdown of the volume, time, and flowrate data for this experiment. During the collection of the ECA and ECB samples, significant difficulty was experienced with control of the flowrate. The flowrate was adjusted many times and proved more difficult to control that in the past experiments. For short periods of time the flowrate was far higher than desired but after adjustment it was too slow. During the 2nd day of operation, elevation adjustment of the discharge tube made the flowrate easier to control but it still trended to higher than planned flowrate. These difficulties did not dramatically affect the results but had to limit performance at the beginning of the experiment.

Table 5. Experimental Conditions for Column Operation with CST R9120B Absorbent pH 9.

	Net wgt	Density	Wgt Vol	Total Vol	Time		Elapsed				Date
	g	g/cc	mL	mL	start	finish	Time	min	mL/min	BV	finished
Feed											
ECA	56.10	1.010	55.5	55.5	9:11	16:56	7:45	465	0.119	70.7	26-Jan
ECB	214.56	1.010	212.4	267.9	7:54	10:35	2:41	1601	0.133	341.2	31-Jan
ECC	194.19	1.010	192.2	460.1	10:35	10:45	23:50	1450	0.133	586.1	1-Feb
EG1	7.04	1.010	7.0	467.0	10:45	11:41	0:56	56	0.124	595.0	1-Feb
ECD	175.95	1.010	174.1	641.2	11:41	12:15	0:34	1474	0.118	816.8	2-Feb
EG2	8.21	1.010	8.1	649.3	12:15	13:40	1:25	85	0.096	827.1	2-Feb
ECE	168.78	1.010	167.0	816.3	13:40	13:15	23:35	1415	0.118	1039.9	3-Feb
EG3	5.405	1.010	5.3	821.7	13:15	14:30	1:15	75	0.071	1046.7	3-Feb

Note: Column: 0.759 g CST R9120B packed into a 5 mm ID column, 0.196 cm^2 cross sectional area, Bed height 40 mm.
Note: Feed:1.7 g U/L, 0.6 mg Cs/L, 0.13 mg Sr/L in 0.1 M sulfuric acid, adjusted to pH 9 with sodium carbonate.
Note: BV = 0.785 cm^3, Q/A = 2.546 mL/min/cm^2, ~15.7 µg Sr/min/cm^2, density=1.010 g/cc.
Note: Density was calculated based on 2 g U/L and 0.1 M sulfate. Measured density (via balance and pipet) lacked precision but average was comparable to calculated value.
Note: Sample designation EC refers to “Effluent Composite” sample which a sample of a bottle of the effluent from the column over an extended period, nominally 23-25 hrs. Sample designation EG refers to “Effluent Grab” sample where the entire sample was submitted for analysis. Due to the low flowrate, Grab samples were collected for a nominal 1-hour time period.

Upon passing through the resin bed, Rb and Cs were at or below the ICPMS detection limit (see Table 6) as had been observed for the similar experiment from pH 1 feed solution. Sr was just above the detection limit in all the raffinate samples resulting in a overall retention of 99.5%. A mass balance was calculated for each species and the cumulative retention is shown as Figure 3 as well as the cumulative percent retention in Figure 4. Elements which are nearly completely retained (Cs and Rb) by CST show a linear slope in Figure 3 with a cumulative retention of close to 100% in Figure 4, similar to the results for AMP-PAN and CST from pH 1 feed solution in the Part I study. In pH 9 carbonate feed, Sr shows nearly as good affinity for CST R9120B as Cs and Rb whereas in pH 1 sulfuric acid, essentially no Sr was retained. Zr, Hf and Nb were all detected in the raffinate samples at far higher concentrations than in the feed solution, suggesting that these elements were leaching out of the CST matrix. Based on the total amounts in solution and the amount of Zr in CST, up to 5 wt% of the CST mass could have dissolved. Similar results were seen in the previous pH 1 sulfuric acid experiment, but it is not clear if sulfate, carbonate or something else was the cause. With these feed concentrations (Cs= 0.6 mg/L, Rb = 0.6 mg/L and Sr= 0.13 mg/L) a Sr loading capacity of greater than 0.14 mg/g CST was demonstrated. Breakthrough of Cs, Rb nor Sr did not occur, so ultimately a significant capacity for Cs and Sr appears to be quite practical.

Table 6. CST R9120-B Column Solution Analyses (ICPMS).

Cr393	Feed	ECA	ECB	ECC	EG1	ECD	EG2	ECE	EG3
Cum. Vol, mL	821.7	55.5	267.9	460.1	467.0	641.2	649.3	816.3	821.7
mL	821.7	55.5	212.4	192.2	7.0	174.1	8.1	167.0	5.3
BV	1046.7	70.7	341.2	586.1	595.0	816.8	827.1	1039.9	1046.7
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Rb	581	0.7	0.4	0.3	0.3	0.3	0.3	0.3	0.4
Cs	645	0.6	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Sr	131	1.2	0.5	0.3	0.4	0.6	0.6	0.9	1.0
Ce	105	24	27	32	32	32	32	35	35
235	3514	3365	3464	3548	3554	3531	3650	3514	3577
238	1737360	1669872	1699217	1746988	1769176	1747563	1788674	1738215	1798026
Ru	1155	999	1097	1094	1099	1094	1096	1103	1106
Pd	1017	193	306	390	412	407	436	435	449
Zr	955	12039	4683	2501	2347	2259	2389	1916	2381
Mo	90	91	91	90	89	89	90	89	91
La	5	1.7	1.1	1.3	1.4	1.2	1.4	1.3	1.4
Pr	8	2.0	1.4	1.5	1.6	1.4	1.6	1.5	1.5
Nd	24	5.5	4.0	4.5	4.4	4.0	4.3	4.4	4.5
Sm	10	1.7	1.5	2.1	1.5	1.7	1.5	1.6	1.6
Eu	3	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Gd	4	1	1	1	1	1	1	1	1
Re	1332	1236	1286	1293	1310	1312	1332	1292	1321
237	723	139	374	534	564	584	614	632	658
239	636	239	337	407	413	419	431	452	454
Hf	20	395	134	69	64	61	66	51	64
Nb	1	716	668	578	571	560	559	508	539

Note: Yellow highlighted cells are evidence of leaching of components from CST.
Note: Light gray highlighted cells are reported at ICPMS detection limit.

The behavior of the lanthanides is affected by the pH adjustment with carbonate. Since most of the mass appeared to precipitate with the addition of carbonate, only a small amount of mass remained, and it appears that a consistent 60 to 80% of the remaining mass was removed by passing through the CST column. The mechanism may be different as there could have been small particles present that were removed by surface phenomena rather than chemical interaction. In any case, a small mass of fine particulate matter should be anticipated. The behavior of Pd also showed it to be moderately removed by CST from pH 9 carbonate/sulfate whereas it had little retention at pH 1 sulfuric acid. U was not retained at either pH.

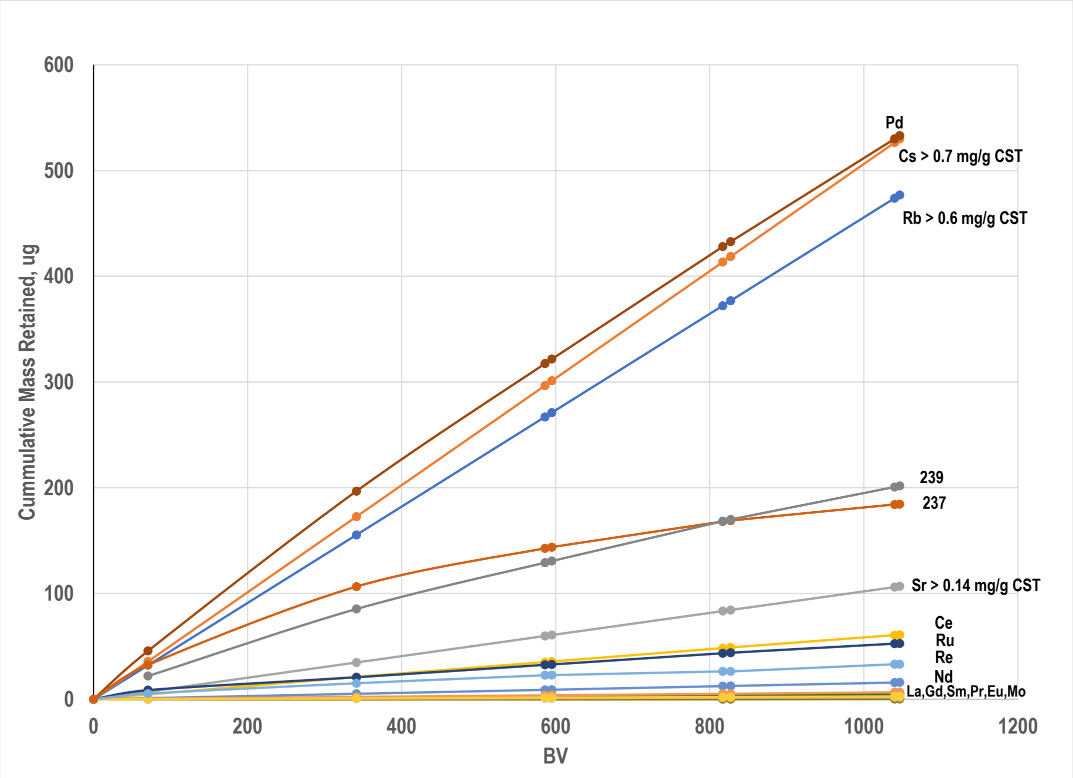

Figure 3. Cumulative Retention of Impurity Mass as a Function of Bed Volume of Raffinate for CST R9120-B Column at pH 9.

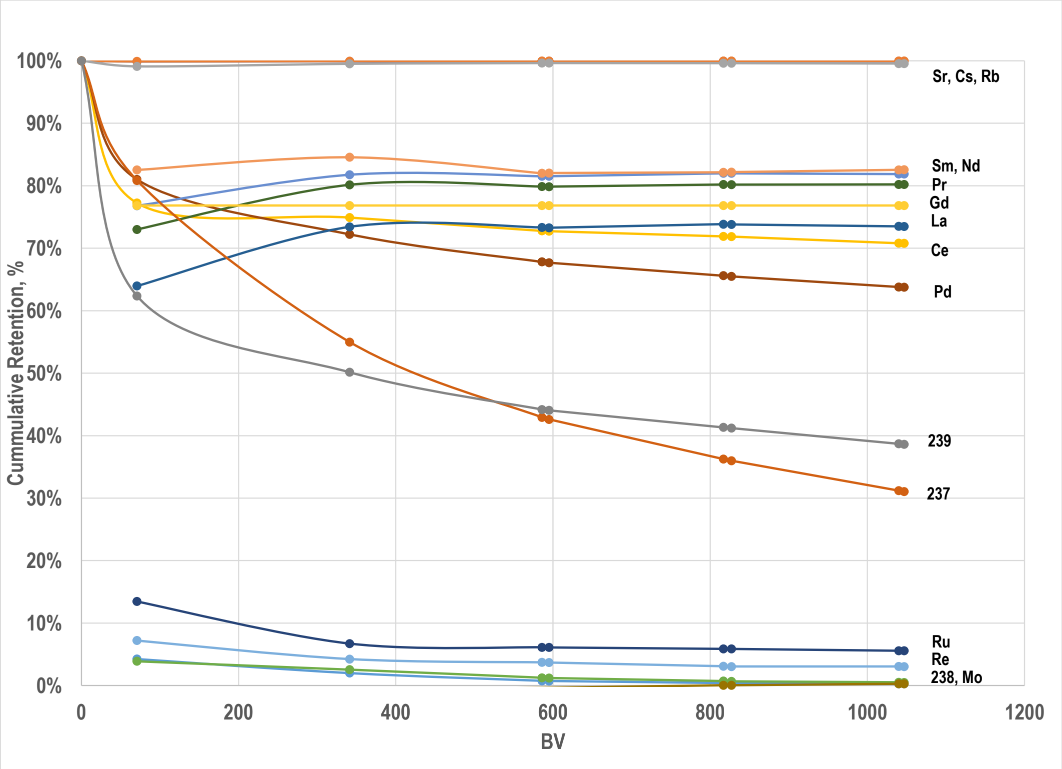

Figure 4. Percent Cumulative Retention as a Function of Bed Volume Fed for CST R9120-B at pH 9.

4.0 Discussion/Recommendations

In this experiment, CST was shown to remove both Cs and Sr at pH 9 without any significant retention of U. The CST absorbent appeared to have released Zr, Nb, and Hf from either pH 1 or pH 9 sulfate solutions (based on the results from this work and the previous experiments), as these elements were found by ICPMS at significantly higher concentrations in the raffinate samples than in the feed sample in both experiments. These elements are reported to be impurities in the CST matrix,[22] and it is almost certain that more significant amounts of Si and Ti were also present in the raffinate samples, but the ICPMS method was not set up to quantify those elements.

Scale-up should be based on keeping the cross-sectional flowrate the same in order to keep the residence time of the solution within the column constant. The resin bed would be expected to have a length of absorbent which is essentially saturated with the species of interest. There will also be a transition zone where the absorbent loading drops from its maximum value to essentially zero. The capacity of the operating production column can then be estimated by a simple two-parameter model utilizing the saturated capacity of the absorbent and the length of resin bed where active mass transfer is taking place. Note that actual breakthrough was never reached in any of these experiments and a very small column was tested. Also, the absorbent capacity will likely be affected by the feed concentration. In these experimental runs the U, Cs, Sr feed concentrations were scaled down to more realistic values from what was previously tested. King et al.[23] published data and modeling which showed that equilibrium Cs loading varied linearly with respect to Cs solution concentration below 5×10^{-5} M Cs. Figure 5 shows Cs equilibrium loading data compared to the ZAM model for CST R9120-B evaluated against CST IE 911. The feed concentrations used in pH 1 portion of this work were biased high in an attempt to determine the saturation concentration of Cs on these materials; however, in light of the data from King, testing at pH 9 was performed at a feed concentration near the expected production concentration. Doing so involves handling somewhat larger volumes of solution, but the results have significantly less uncertainty. However, the behavior with multiple competing absorbing species ends up being much more complicated than Figure 5 would suggest. The current test loaded from pH 9 carbonate was at a feed concentration of ~5×10^{-6} M Cs, which from Figure 5 would be a CST loading of ~0.01 mmol Cs/g CST. In this pH 9

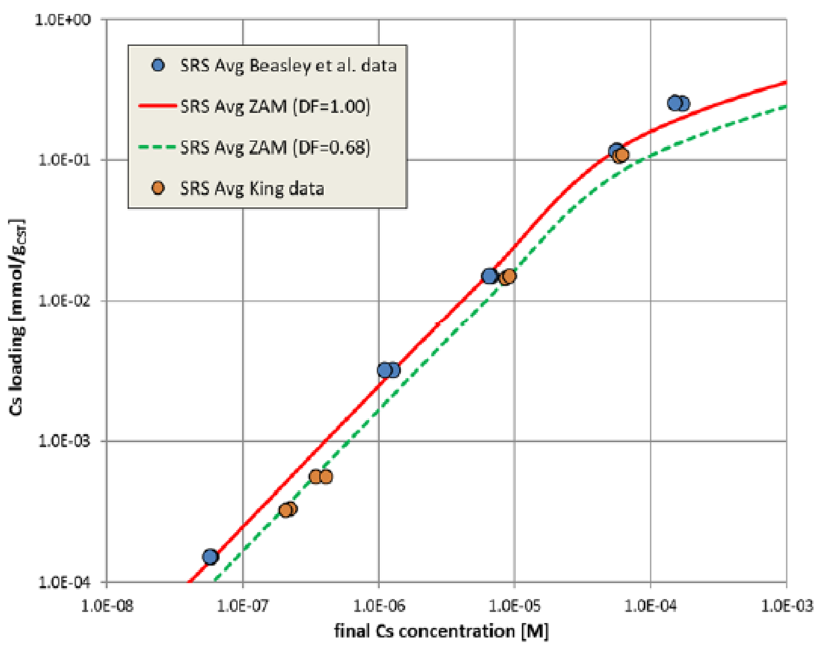

Figure 5. Comparison of Observed and Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and CST at 23 °C.[23]

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[22] E. L. Campbell, A. M. Westesen, F. C/ Colon, D. Boglaienko, T. G. Levitskia, R. A. Peterson, "Elemental Characterization of Crystalline Silicotitanate following Hanford Tank Waste Processing", Sep Sci and Tech, 56:6 1457-65, 2021.

[23] W. D. King, L. L. Hamm, C. J. Coleman, F. F. Fondeur, S. H. Reboul, "Crystalline Silicotitanate (CST) Ion Exchange Media Performance Evaluations in SRS Average Supernate Simulant and Tank 10H Waste Solution to Support TCCR", SRNL-STI-2018-00277, Savannah River National Laboratory, Aiken SC, December 2017.

experiment the total Cs+Rb+Sr loading exceeded 0.015 mmol/g CST without breakthrough.

Table 7 represents an attempt to scale up from small-scale column testing of the current work for CST R9120-B at pH 9. The first line in the table represents the tested lab condition. Note that this column had both a short length and a small diameter. These choices were necessary to limit the amount of solution to be processed to fit the hood space available and to still have chance of loading the column to near capacity. Due to the short length of the lab column configuration, it is advisable to either install a second "guard" column and/or to increase the length of the initial column. For illustration purposes, the last line in Table 7 shows a possible production scale column for processing 1000 L of solution. In this case it will also result in a column that has a more favorable aspect ratio (which is less likely to encounter issues). Increasing the flowrate could hurt performance but since the overall residence time is somewhat increased, this configuration could be just as effective as observed in the initial laboratory test. Due to the significant uncertainties, experimental confirmation is warranted at a larger scale to ensure acceptable performance but a 15-cm ID column filled to a depth of 7 to 8 cm of CST R9120-B would be a reasonable column to retain 600 mg Cs and 60 mg Sr (with capacity for the associated Rb). This proposed flowrate was not tested and could encounter kinetic limitations. Alternatively, a 20-cm ID column filled to a depth of 4 cm of CST R9120-B would also have adequate capacity if the flow can be uniformly distributed across the cross-section of the bed. The loading time of 100 hr was arbitrary, chosen with the goal of processing 1000 L of waste solution within a week.

Table 7. Scaling of the Cs/Sr Loading onto a Column of CST R9120-B from pH 9 Solution.

ID	H	BV	A	Q	Q/A	Residence	Cs	BT	Sr	BT	Time	Vol	mass	mass
cm	cm	cc	cm2	mL/min	cm/min	Time, min	mg/L	mg Cs/g	mg/L	mg Sr/g	hr	L	Cs, mg	Sr, mg
0.5	4	0.785	0.1963	0.11	0.56	7.1	0.645	0.6	0.131	0.141	110	0.822	0.53	0.108
5	4	78.5	19.63	11	0.56	7.1	0.645	0.6	0.06	0.065	100	66	43	4.0
10	4	314	78.5	44	0.56	7.1	0.645	0.6	0.06	0.065	100	264	170	16
15	4	707	177	99	0.56	7.1	0.645	0.6	0.06	0.065	100	594	383	36
20	4	1257	314	176	0.56	7.1	0.6	0.56	0.06	0.065	100	1056	634	63
15	8	1414	177	178	1.0	7.9	0.6	0.56	0.06	0.065	100	1069	642	64

Note: Scale the breakthrough (BT) capacity based on the reduction of the Cs feed concentration.
Recommendation: Double the bed depth but increase the Q by 80% to improve aspect ratio of bed.

5.0 Conclusions

The U retention was shown to not be a significant concern for CST R9120B column experiments from either pH 1 sulfuric acid or pH 9 sulfate solution adjusted with carbonate. Cs was removed to below ICPMS detection limits by both AMP-PAN and CST R9120B from pH 1 sulfuric acid and by CST R9120B from pH 9 sulfate/carbonate solution. Sr was removed to near the ICPMS detection limit from pH 9 sulfate/carbonate solution although it appears that lanthanide precipitation generated fine particles that were too small to observe at the scale this work was performed. It appears that a ~1.5-liter column of CST R9120B would be capable of removing 99.5% of the Sr and 99.9% of the Cs from the SHINE waste stream after adjustment with sodium carbonate. Greater than 95% of the lanthanides (including Ce) can be filtered out as solids with much of the remainder (70%) retained by an adjustment to pH 9 with sodium carbonate. If the precipitated solids cause excessive difficulty, then an alternate option would be to use a combination of strong acid cation resin to remove sufficient Sr and lanthanides from the acidic sulfate stream and the Cs (which would not be retained by the cation resin) could then be removed by a 1-L CST R9120-B column.

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