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

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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 R91290-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, but CST should be investigated at a higher pH. Limited removal of transuranic species and almost no removal of uranium was observed in this testing. 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 the range of 0.2 to 5 mg Cs per gram of absorbent appears to be achievable.

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

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 were 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, 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 Rudisil[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/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). An alternate presentation of McCann and Rudisill's results is shown as Figure 1. 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).

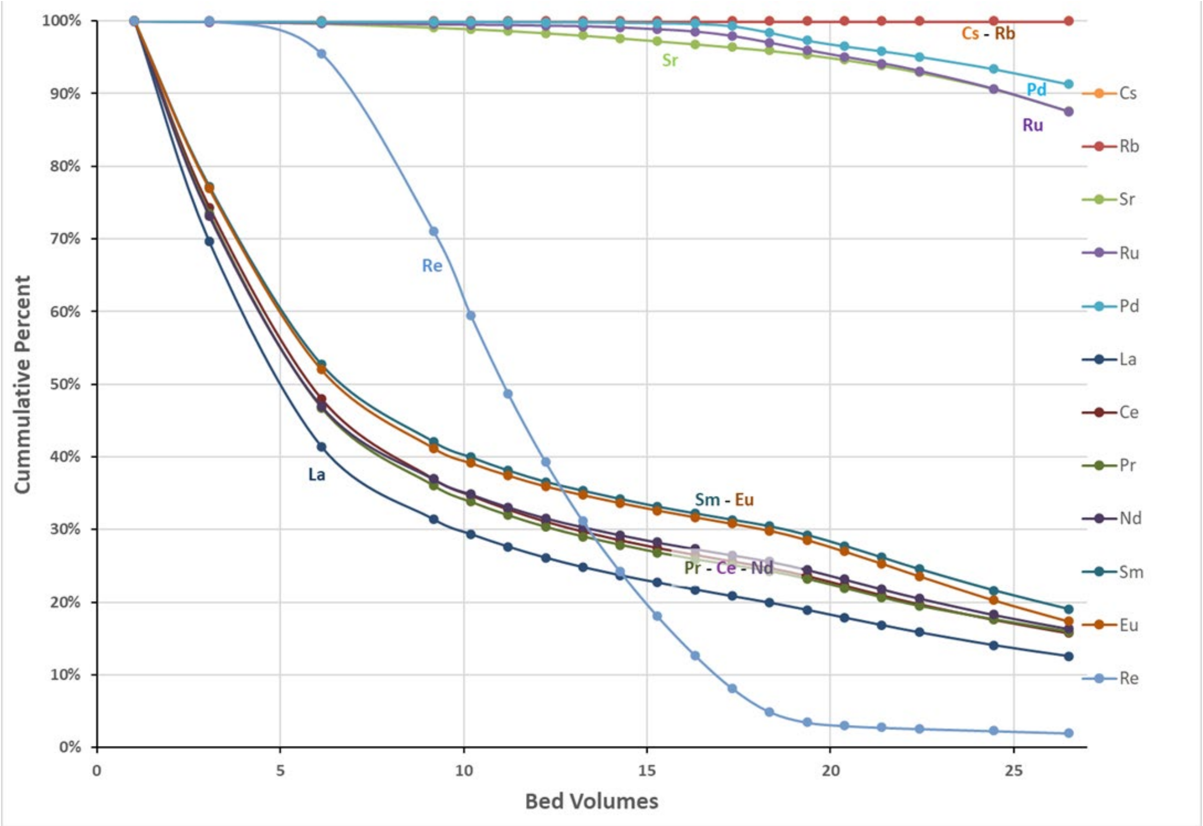

Figure 1. Retention of Metals on CST IE-911.

SrTreat is a sodium titanate-based absorbent currently available from a Finnish company (Selion Oy). It seems like 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.

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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].

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 of 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 appears 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 multimolar HNO_3 and elution with 0.05 M HNO_3.

This work was aimed at using highly selectively absorbents to remove ^{137}Cs and ^{90}Sr. Conventional ion exchange resins might also be applied but these tend to have low selectivity. Conventional cation exchange should readily remove multivalent cationic metal species from pH 1 sulfuric acid solution with a significant capacity. 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. Ang et al.'s work indicates that it may be practical to selectively remove uranyl sulfate from a pH 1 solution as anionic complex.

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*$2H_2O$) 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] 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.

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[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).

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 typically filtered using a 0.45-µm cellulose nitrate filter although this may not have been performed on every feed solution. 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 makeup of the feed solutions for the AMP-PAN (Cr386) and CST R9120-B (Cr387) column experiments. Since some impurities were present in sufficient concentration in the uranyl sulfate solution only a few impurities were added. A U/Pu/Np stock solution was prepared by adding ~0.5 mg of Pu (94% ^{239}Pu) and 0.5 mg of ^{237}Np (in 1 mL of 0.1 M sulfuric acid) to 54 mL of Cr383EC solution (~200 g U/L) from the previous work and then diluting that with 0.1 M sulfuric acid solution to 200 mL. The AMP-PAN column feed was prepared by combining 20 mL of the U/Pu/Np stock solution with 180 mL of the Cr386/8 impurity matrix. The CST R9120-B feed was prepared by combining 100 mL of the U/Pu/Np stock solution with 900 mL of the Cr386/7 impurity matrix. Table 2 shows the makeup of the feed solution for the Ra-01 column run. No radioactive species were used for that experiment.

Table 1. Preparation of Feed Solutions for AMP-PAN (Cr386) and CST R9120-B (Cr387) pH 1.

Wgt	Description	Vol	Metal			H+	SO4
g		mL	Impurity	mg	mg/L	M	M
	Cs(NO3)		Cs				
	Ru(NO)(NO3)3		Ru				
0.092	Ce(NO3)3*6H2O	0	Ce	29.7	16.5		
0.045	Nd(NO3)3*6H2O	0	Nd	14.8	8.2		
0.012	Sr(NO3)2	0	Sr	5.0	2.8		
	Pr(NO3)3*6H2O		Pr				
	Gd(NO3)3*6H2O		Gd				
	Eu(NO3)3*5H2O		Eu				
	La(NO3)3*6H2O		La				
	Rb(NO3)		Rb				
	Sm(NO3)3*6H2O		Sm				
0.009	NaReO4		Re	6.1	3.4		
0.008	Pd(NO3)2*2H2O	0	Pd	3.2	1.8		
0.22	Zr(IV) nitrate soln	0.22	Zr	1.8	1.0		
	Na2MoO4*2H2O		Mo				
17.9	98% conc. H2SO4	10				18	9
	DI H2O	as needed					
	Cr386/7 Impurity	1800		60.6	33.7	0.10	0.10

	Cr383EC	Target	Source
	mg/L	mg/L	
U238	202588	5,500	UO3 dissolved into H2SO4
Cs	228.1	5	Cs(NO3)
Ru	223.8	5	Ru(NO)(NO3)3
Ce	213.7	20	Ce(NO3)3*6H2O
Nd	128.4	10	Nd(NO3)3*6H2O
Sr	87.8	3	Sr(NO3)2
Pr	85.3	2	Pr(NO3)3*6H2O
Gd	51.7		Gd(NO3)3*6H2O
Eu	44.8		Eu(NO3)3*5H2O
La	41.3		La(NO3)3*6H2O
Rb	39.9	1	Rb(NO3)
Sm	39.2	1	Sm(NO3)3*6H2O
Re	30.6	5	NaReO4
Pd	6.9	1	Pd(NO3)2*2H2O
Zr	4.7	1	Zr(NO3)4 in H2O
Ti	2.0		
Sn	1.6		
Mo	1.2		Na2MoO4*2H2O
Fe	1.0		
Np237	1.0	1	SRNL *
Ba	0.3		
Sb	0.2		
Y	0.1		
Pu239	0.04	1	SRNL *

* Pu/Np spike in pH 1 sulfuric acid added to 200mL of Cr383EC solution to increase Np & Pu content of U solution

200 mL of U/Pu/Np solution added to 800 mL of Cr386/7 Impurities

pH adjustment and filtration completed preparation

Table 2. Preparation of Feed Solution for Ra-01 (Cr390) pH 1.

MW	EW	Target Wgt	Wgt	Description	Vol	H+	HNO3	SO4	Metal Impuritiy			Analy zed
		g	g		mL	M	M	M		mg	mg/L	mg/L
318.10	101.07	0.070	0.010	Ru(NO)(NO3)3					Ru	3.2	0.8	1.0
266.46	106.42	0.010	0.010	Pd(NO3)2*2H2O					Pd	4.0	1.0	1.0
434.22	140.12	0.25	0.296	Ce(NO3)3*6H2O					Ce	95.5	23.8	24.0
194.91	132.91	0.030	0.047	Cs(NO3)					Cs	32.0	8.0	8.0
444.47	150.36	0.012	0.014	Sm(NO3)3*6H2O					Sm	4.7	1.2	1.2
438.35	144.24	0.122	0.126	Nd(NO3)3*6H2O					Nd	41.5	10.3	10.5
428.06	151.96	0.002	0.010	Eu(NO3)3*5H2O					Eu	3.5	0.9	0.9
433.01	138.91	0.012	0.020	La(NO3)3*6H2O					La	6.4	1.6	1.5
451.36	157.25	0.002	0.004	Gd(NO3)3*6H2O					Gd	1.4	0.3	1.6
435.01	140.91	0.025	0.028	Pr(NO3)3*6H2O					Pr	9.1	2.3	2.2
147.47	85.468	0.007	0.014	Rb(NO3)					Rb	8.1	2.0	2.3
273.19	186.21	0.029	0.033	NaReO4					Re	22.5	5.6	5.3
211.63	87.62	0.020	0.022	Sr(NO3)2					Sr	9.1	2.3	2.4
242	95.94	0.002	0.008	Na2MoO4*2H2O					Mo	3.2	0.8	0.8
339.24	91.22	0.015	0.015	Zr(IV) nitrate]	0.015				Zr	4.0	1.0	0.9
98.079		40.3	18.2	98% Conc Sulfuric aci	22	18		9				
		3986		DI H2O	3992							
		4000		Cr390 Impurities	4014	0.099	0.001	0.099		248.284		

2.2 Batch Contact:

Batch contact screening experiments were performed by contacting samples of AMP-PAN, CST IE-911 (SRS SCIX), CST Ionsiv R9120-B (SRS TCCR) and Eichrom MnO_2 with EU solutions that had been irradiated in the SRNL neutron source. Since the irradiated EU solution was in HNO_3, it was converted to dilute sulfate by evaporating to dryness and then redissolved in 0.05 M H_2SO_4. The CST samples used in these tests were converted to the H-form (acid) by vortex mixing 12-g samples with 30 mL of 1 M H_2SO_4 for 10 seconds and soaking for 10 minutes. In hindsight, the CST samples may not have been completely converted. After filtering the absorbent solids, they were rinsed with DI water prior to use. Each candidate absorbent was tested in duplicate using a ratio of 4 mL of tracer feed solution per 0.8 g absorbent. Contact between each absorbent sample was performed by vortex mixing for 30 seconds followed by gravity settling for 10 seconds. This mixing-settling cycle was performed three times for one set of samples and then six times for a second set of samples to capture kinetic effects. The filtrate from each test for each absorbent was gamma counted (in triplicate) and compared to the count of the raw irradiated feed solution. The raw irradiated feed solution was 0.33 mg U/mL. There were many short-lived isotopes present with these samples and each count was decay corrected to the same point in time.

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 also 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. 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 top of the addition funnel was initially used to monitor pressure drops through 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.

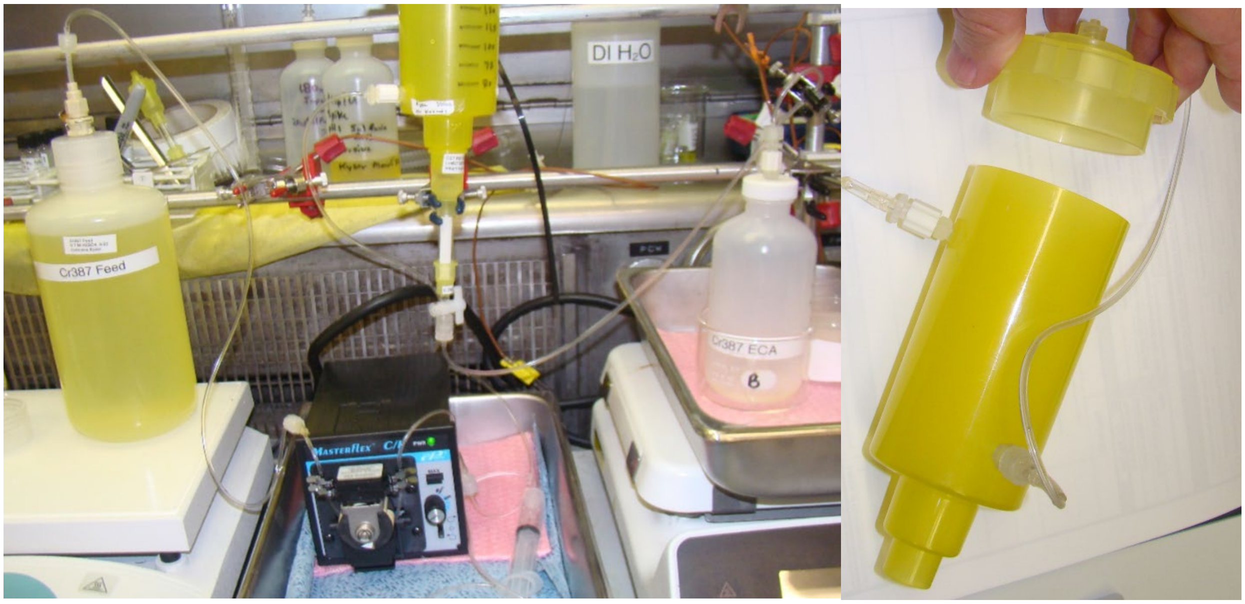


Figure 2. CST Column Setup with Customized Addition Funnel.

2.4 Column Tests:

Column loading tests were performed for absorbent materials as follows. A weighed quantity of absorbent was pre-wetted by soaking in pH 1 sulfuric acid matrix and then fully conditioned after loading into a small Biorad Econo-column with sufficient volume of pH 1 sulfuric acid (except where otherwise stated) until the raffinate coming out of the column was essentially the same as the conditioning solution. Typically, a 5 mm by 50 mm column with a bottom frit was used unless otherwise noted. A plug of glass wool was used to retain the absorbent at the top of the bed, but since all experiments were performed “down-flow”, this was omitted in the later experiments. A bed of absorbent ~40 mm tall or ~0.8 cc volume was used in each experiment. After conditioning, any gas bubbles were removed by backflushing the bed with a 10-mL Luer Lok syringe using conditioning solution.

The volume of feed solution for each column experiment was different depending on the planned flowrate and length of time planned for the experiment. Some of these experiments involved run times of multiple days and were set-up for unattended overnight operation. Experiment plans for flow conditions and sampling frequency for each resin tested are provided as Tables 3, 4, and 5. 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, ICPES, Gamma PHA, Pu by TTA, and Np by TEVA analyses were performed (as appropriate). Most non-rad impurities were measured by ICPMS with the U, Pu and Np quantified by customized gamma/alpha counting methods. When radioactive materials were included in the feed, the absorbent was rinsed with a small amount of conditioning solution (typically pH 1 sulfuric acid and/or water) and then vacuum dried prior to being quantitatively transferred to a sample vial for gamma counting to determine the amounts of U, Pu and Np retained by the absorbent.

Table 3. Experimental Plan for Column Operation with AMP-PAN Absorbent

	Vol	Total	Q	Time	Total		BT	BV
	mL	mL	mL/min	min	hr	mg Cs fed	mg/g	
Acid Condition			0.5	0.00	0.0	0	0	0.0
Cr386 ECA	10	10	0.5	20.0	0.33	0.062	0.14	13.4
Cr386 ECB	30	40	0.5	60.0	1.33	0.246	0.55	53.6
Cr386 ECC	30	70	0.5	60.0	2.33	0.431	0.96	93.8
Cr386 ECD	30	100	0.5	60.0	3.33	0.616	1.38	134.0
Cr386 ECE	30	130	0.5	60.0	4.33	0.801	1.79	174.2
Cr386 ECF	30	160	0.5	60.0	5.33	0.986	2.20	214.4
Cr386 ECG	16	176	0.5	32.0	5.87	1.084	2.43	235.9
Acid Wash	10	186	0.5	20.0	6.20			
Water Rinse	10	196	0.5	20.0	6.53			

Note: Column: 0.447 g AMP-PAN packed into a 5 mm ID column, 0.196 cm^2 cross sectional area, Bed height 38 mm.
Note: Feed: 6.5 mg Cs/L in 0.1 M sulfuric acid, 5.5 g U/L, adjusted to pH 1.
Note: BV = 0.746 cm^3, Q/A = 2.546 mL/min/cm^2, 15.7 µg Cs/min/cm^2.

Table 4. Experimental Plan for Column Operation with CST R9120-R Absorbent.

		Vol	Total	Q	Time	Total		BT	
		mL	mL	mL/min	hr	hr	mg Cs fed	mg/g	BV
	Acid Condition	10		0.11	1.5	1.5		0.000	0.0
Day 1	Cr387ECA	164	164	0.11	24.8	26.4	1.010	1.329	208.8
Day 2	Cr387ECB	153	317	0.11	23.2	49.5	1.953	2.569	403.6
	Cr387EG1	5	322	0.11	0.8	50.3	1.984	2.610	410.0
Day 3	Cr387ECC	153	475	0.11	23.2	73.5	2.926	3.850	604.8
	Cr387EG2	5	480	0.11	0.8	74.2	2.957	3.891	611.2
Day 4	Cr387ECD	50	530	0.11	7.6	81.8	3.265	4.296	674.8
	Cr387EG3	5	535	0.11	0.8	82.6	3.296	4.336	681.2
Day 5	Cr387ECE	120	655	0.11	18.2	100.8	4.035	5.309	834.0
	Cr387EG4	5	660	0.11	0.8	101.5	4.066	5.349	840.3
	Acid Wash	5	665	0.11	0.8	102.3		0.000	846.7
	Water Rinse	10	675	0.11	1.5	103.8		0.000	859.4

Note: Column: 0.760 g CST R9120-B packed into a 5 mm ID column, 0.196 cm^2 cross sectional area, Bed height 40 mm.
Note: Feed: 6.5 mg Cs/L in 0.1 M sulfuric acid, 5.5 g U/L, adjusted to pH 1.
Note: BV = 0.746 cm^3, Q/A = 0.560 mL/min/cm^2, 3.4 µg Cs/min/cm^2.

Table 5. Experimental Plan for Column Operation with IBC RA-01 Absorbent.

		Vol	Total	Q	Time	Total		BT	
		mL	mL	mL/min	min	hr	mg Sr fed	mg/g	BV
	Acid Condition			0.5	0	0.0	0	0.000	0.0
Day 1	Cr390ECA	720	720	0.5	1440	24.0	1.440	4.431	965.0
	Cr390EG1	5	725	0.5	10	24.2	1.450	4.462	971.7
Day 2	Cr390ECB	720	1445	0.5	1440	48.2	2.890	8.892	1936.7
	Cr390EG2	5	1450	0.5	10	48.3	2.900	8.923	1943.4
Day 3	Cr390ECC	720	2170	0.5	1440	72.3	4.340	13.354	2908.3
	Cr390EG3	5	2175	0.5	10	72.5	4.350	13.385	2915.1
Day 4	Cr390ECD	720	2895	0.5	1440	96.5	5.790	17.815	3880.0
	Cr390EG4	5	2900	0.5	10	96.7	5.800	17.846	3886.7
Day 5	Cr390ECE	720	3620	0.5	1440	120.7	7.240	22.277	4851.7
	Cr390EG5	5	3625	0.5	10	120.8	7.250	22.308	4858.4
	Water rinse	10	3635	0.5	20	121.2	7.250		

Note: Column: 0.325 g Ra-01 packed into a 5 mm ID column, 0.196 cm^2 cross sectional area, Bed height 38 mm.
Note: Feed: 2.0 mg Sr/L in 0.1 M sulfuric acid, adjusted to pH 1.
Note: BV = 0.746 cm^3, Q/A = 2.546 $mL/min/cm^2$, 15.7 µg $Sr/min/cm^2$.

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 AMP-PAN used was not in a manufacturer’s bottle and was labeled AMP-PAN/SF, 0.3-0.6 mm, 85.6 wt% AMP, C. Nash. It may have been a BioRad product. The CST R9120-B was an SRNL sample from a large batch purchased for SRS in 2020 (batch number 2102020757, Drum #5). The IBC AnaLig® RA-01 Si had previously been used in radioanalytical separations (Lot # 190311DZ159G).

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. Due to concerns about interference from the overwhelming mass of ^{238}U in the solutions, Pu and Np were analyzed by SRNL radiochemical methods. Pu was separated using a TTA extraction method and quantified by the ^{239,240}Pu peaks in an alpha pulse height analysis (PHA). ^{237}Np was concentrated by TEVA extraction chromatography resin and then analyzed by gamma counting. The used absorbents were water rinsed, air dried, weighed and then gamma counted to determine the mass of U, Pu, and Np retained by the absorbents at the end of each experiment.

3.0 Results:

3.1 Batch Contacts:

Due to the large number of spectral lines and the need to decay correct, processing of the batch contact data took more effort than expected. While the concentrations in the batch contact were very different than those expected in the process, the results show all four materials absorbed a significant fraction of each of the isotopes where data was processed. The isotopes other than U in this experiment involved only trace mass of each isotope. The U concentration was ~0.33 mg U/mL with 1.6 mg U per gram absorbent. Of particular concern was the apparent affinity observed for U due to the large concentration that is expected in the process waste solutions. Limited differences were observed between the replicate samples, so these results were averaged and reported as a single value in Table 6. Uranium Kd values of 4 to 10 were calculated for AMP and CST whereas a Kd value of ~800 was calculated for MnO_2. It was concluded that column testing would be needed to determine the effect of U on the loading of Cs and Sr onto AMP or CST.

Table 6. Summary of Batch Contact Results showing Average of each Isotope Retained by Absorbent.

	AMP	CST R9120-B	CST IE-911	MnO2		
U-235	47%	61%	66%	99%		< 3% remaining in solution
Zr-95	95%	98%	100%	98%		4 to 25% remaining in solution
Np-239	43%	54%	74%	83%		> 25% remaining in solution
I-131	52%	82%	89%	98%		
Ce-144	91%	62%	75%	88%		
Ru-103	49%	66%	71%	99%		
	Percent retained by Absorbent					

3.2 Column Results for AMP-PAN from pH 1 Solution:

The initial absorbent tested in a column was AMP-PAN. The faster reported kinetics allowed for higher flowrates and a shorter operating time so that this experiment was completed in a single shift. The analytical results from the solution samples are shown in Table 7. Upon passing through the resin bed, Rb and Cs were essentially at or below the ICPMS detection limit. A mass balance was calculated for each species; the cumulative retention is shown as Figure 3 and a cumulative percent retention is shown as Figure 4. Elements that are completely retained (Cs and Rb) by the absorbent show a linear slope in Figure 3 and show the cumulative retention as 100% in Figure 4. Lanthanides that are moderately absorbed show initial retention in Figure 3, followed by a “plateau” after 50-100 BV and finally a drop as the wash step removed some of the mass from the bed. Lanthanides such as Ce and Nd that had a relatively high concentration in the feed solution were mostly retained initially but that retention did not appear to affect the Cs absorption, which eventually grew to be greater than the cumulative Ce and Nd loading (Figure 3). A Cs loading of greater than 2.7 mg Cs/g AMP-PAN was calculated by the material balance (Figure 3). After Cs and Rb, Pd is the next most retained species on a cumulative retention percentage basis even though its concentration in the feed was lower (Figure 4). Figure 3 shows that the mass retention of Cs and Rb were essentially unaffected by the wash step (~250-267 BV). A small mass of Pd was removed and larger amounts of the lanthanides were removed in the wash step due to relative differences in the retention.

Mass 238 (from U) is not shown in Figure 3 as the cumulative analytical uncertainties are far greater than the actual mass retained by any of the other species of interest. Since AMP contains Mo and AMP has a slight solubility in pH 1 sulfuric acid, Mo was measured in all the raffinate samples at far larger concentrations than in the feed solution. Of the 447 mg starting mass of AMP-PAN, 5.8 mg of Mo was measured in the raffinates/wash solutions. Additional Mo likely dissolved in the conditioning solution prior to the start of the feed and some colored residue was observed in the bottom of the column that had separated from the

PAN during air-drying. Some dissolution of the AMP was expected as this was previously reported by Sebesta et al.[10] It had been assumed that ICPMS mass numbers 237 and 239 might be affected by the relatively larger concentration of U (mass 238) and for that reason radiochemical analyses were performed for the $^{239/240}$Pu and ^{237}Np. Figure 5 shows a comparison of the ICPMS mass numbers 237 and 239 with the radiochemical analyses for ^{237}Np and ^{239}Pu. ^{237}Np and mass 237 generally agreed with random variation between the two methods. However, the ICPMS mass 239 value was approximately twice that measured by the $^{239/240}$Pu by TTA method. While the ICPMS values for mass 237 were not affected by the U concentration, it appears likely that the mass 239 values were significantly affected by the presence of ~ 6 g U/L. Results for mass numbers 237 and 239 in the presence of significant ^{238}U will likely be instrument dependent.

Gamma PHA analysis of the spent AMP-PAN absorbent showed retention of 5.9 mg U/g (or 0.2% of the feed, see Table 8), which is minor considering the relatively large mass of U in the feed solution. Pu was the primary actinide retained with 23% of the Pu counted on the absorbent although the actual mass was involved was small. Pa (both ^{231}Pa and ^{233}Pa) also appeared to be preferentially retained by AMP-PAN.

Table 7. AMP-PAN Column Solution Analyses (ICPMS and Gamma Results).

Cr386	Feed	ECA	ECB	ECC	ECD	ECE	ECF	ECG	Wash
Vol, mL	184.5	10.6	29.3	29.3	29.1	29.2	29.3	27.6	15.3
Cum. Vol, mL		10.6	39.9	69.2	98.3	127.6	156.9	184.5	199.7
BV	247.3	14.2	53.5	92.8	131.8	171.0	210.3	247.3	267.7
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Rb	1250	1	1	1	2	2	2	3	1
Cs	6589	1	2	2	3	4	4	5	2
Sr	5147	2115	5063	5203	5099	5086	5015	5027	1304
Ce	21694	1985	7699	14018	18411	20667	21412	21840	5405
235	23995	18889	23879	23938	23597	23683	23901	23555	3824
238	5816011	4565380	5797588	5813581	5748204	5745093	5785915	5739514	921944
Ru	7081	5705	6836	7010	6979	7036	7043	7091	1102
Pd	1775	28	373	676	878	1024	1179	1224	434
Zr	1028	563	793	899	952	990	984	993	226
Mo	110	256986	15719	14187	15115	16191	17066	18169	22157
La	1268	124	482	859	1107	1238	1280	1307	332
Pr	2478	229	847	1565	2057	2340	2451	2514	611
Nd	11992	1071	3971	7399	9859	11190	11605	11879	2930
Sm	1263	121	445	828	1090	1224	1265	1299	313
Eu	1343	146	553	936	1198	1343	1374	1395	355
Gd	2043	207	782	1437	1842	2043	2101	2133	508
Re	4385	3397	4214	4309	4309	4328	4327	4318	776
237	454	407	442	450	456	452	453	449	76
239	615	388	469	509	542	552	564	568	130
Pu239/40 (ug/L)	282	83	132	176	219	225	247	261	67
Np237 ug/L	460	294	438	412	464	542	504	378	38

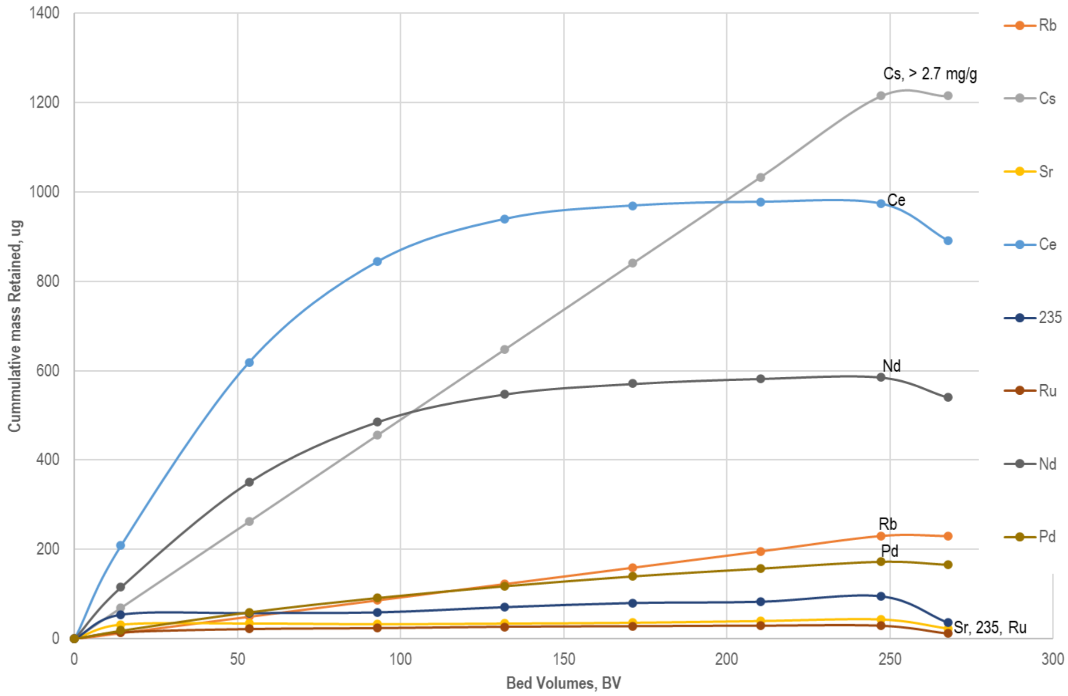


Figure 3. Cumulative Retention of Impurity Mass as a Function of Bed Volume of Raffinate for AMP-PAN Column at pH 1.

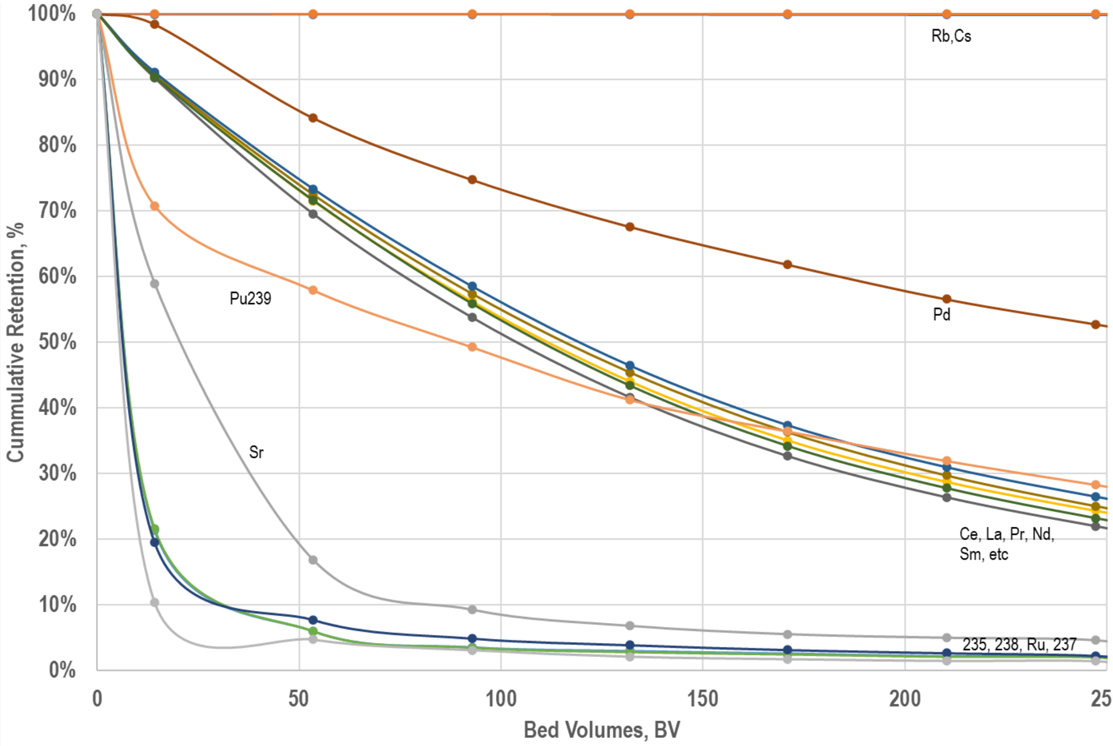


Figure 4. Percent Cumulative Retention as a Function of Bed Volume Fed for AMP-PAN Column.

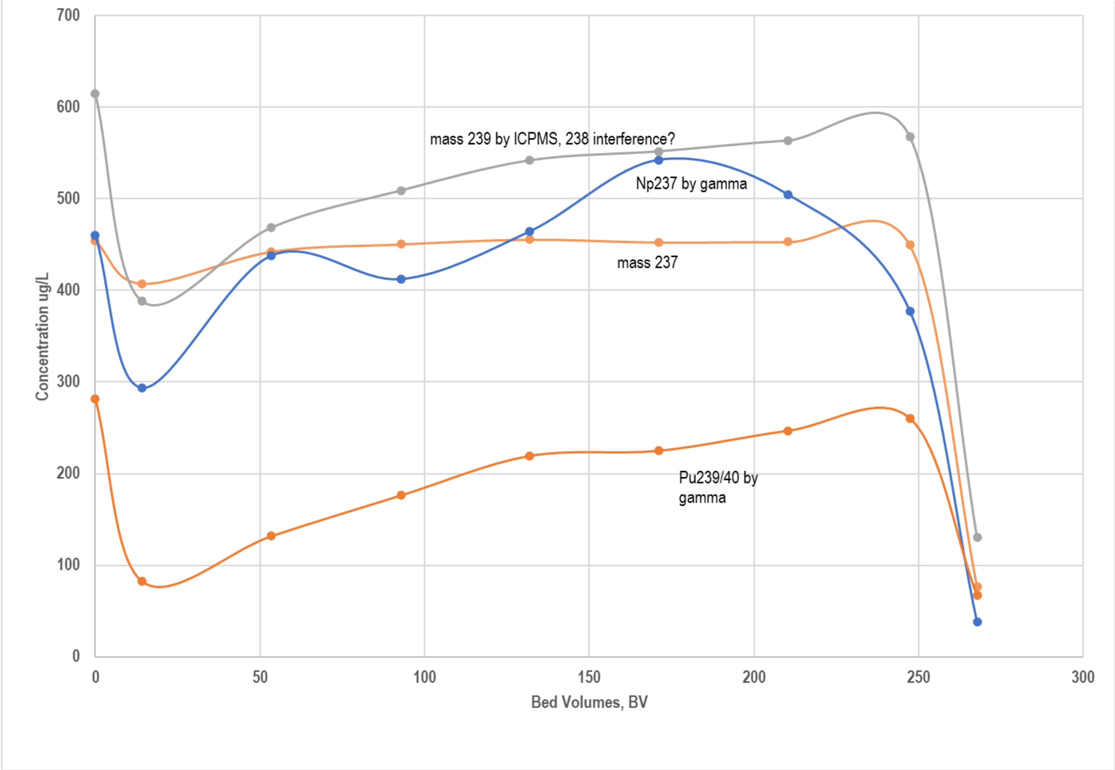


Figure 5. Comparison between Mass 237, 239 values with Radiochemical Results for $^{239/240}$ Pu and ^{237} Np.

Table 8. Mass of U, Pu, Np Retained by AMP-PAN Absorbent measured directly by Gamma PHA.

	AMP-PAN			
	ug	mg/g	% of Feed Mass	
U235	10	0.02	0.2%	
U238	2320	5.9	0.2%	1
Np237	0.04	0.0001	0.1%	
Pu239/40	12	0.029	23%	3
Am241	1.6.E-03	4.0.E-06	-	2

1) Mass of ^{238}U Calculated from the ^{235}U Isotopic from ICPMS.
2) A separate ^{241}Am measurement in the feed was not available.
3) Measured ^{239}Pu but ^{239,240}Pu calculated assuming 94% ^{239}Pu.

3.3 CST R9120-B Column from pH 1 Solution:

CST R9120-B 30x60 absorbent was also tested as a column. Due to the slow reported kinetics for CST this experiment was run at a flowrate of 6.6 mL/h, taking 106 h to pass 636 mL of feed (or 810 BV) through the bed. This flowrate amounts to 7.6 BV/h which is somewhat faster than the historical 3 BV/h used in the SRS tank farm related work. Upon passing through the resin bed, Rb and Cs were at or below the ICPMS detection limit (see Table 9). A mass balance was calculated for each species and the cumulative retention is shown as Figure 6 as well as the cumulative percent retention in Figure 7. Elements which are completely retained (Cs and Rb) by CST show a linear slope in Figure 6 with a cumulative retention of 100% in Figure 7, similar to the results for AMP-PAN. Cs and Rb were not removed by the wash, but Figure 6 shows the mass retained of the weakly absorbing species drops during the wash step. A Cs loading of greater than 5.5 mg Cs/g CST was calculated by the material balance (Figure 6). After Cs and Rb, Mo was the next most retained species on a percentage cumulative retention basis even though its concentration in the feed was lower (Figure 7). Initially, there was some Pu absorption onto CST, but after 800 BV this only amounts to ~12% of the total mass of Pu fed (see Table 10). CST did not absorb significant amounts of U or lanthanides.

Table 9. CST R9120-B Column Solution Analyses (ICPMS and Gamma Results).

Cr387	Feed	ECA	ECB	EG1	ECC	EG2	ECD	EG3	ECE	EC4	WC
Vol, mL	635.8	150.3	153.1	4.3	159.3	4.5	44.3	4.3	108.4	7.2	4.3
Cum. Vol, mL		150.3	303.4	307.8	467.0	471.6	515.9	520.2	628.6	635.8	640.1
BV	809.9	191.5	386.5	392.1	595.0	600.7	657.2	662.7	800.7	809.9	815.4
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Rb	1282	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cs	6542	1	1	1	1	1	1	1	1	1	1
Sr	5193	5049	5137	5130	5192	5161	5142	5096	5056	5161	4625
Ce	21616	21031	21441	21451	21385	21652	21254	21453	21611	21408	19423
235	23941	23677	23752	24169	23953	23776	23573	23890	23625	23733	19956
238	5812459	5673906	5790523	5801298	5799418	5716789	5698041	5811523	5776397	5761469	4873859
Ru	7008	6814	7028	7062	7095	7113	7051	7095	7059	7189	5989
Pd	1786	1701	1723	1550	1782	1775	1780	1748	1769	1820	1594
Zr	1002	27875	19162	18848	16789	15808	15974	15856	16335	16113	17195
Mo	25	5.97	8.62	8.59	9.87	10.65	9.33	11.43	11.45	11.49	9.76
La	1249	1222	1261	1256	1263	1266	1255	1251	1243	1271	1137
Pr	2436	2355	2430	2431	2430	2434	2426	2406	2402	2439	2193
Nd	11634	11303	11645	11830	11611	11691	11578	11668	11740	11699	10543
Sm	1219	1197	1225	1221	1222	1228	1224	1211	1218	1228	1091
Eu	1307	1278	1300	1299	1310	1304	1300	1294	1302	1314	1167
Gd	1974	1941	1996	1996	1997	2004	1983	1981	1978	2009	1781
Re	4362	4243	4368	4345	4364	4394	4386	4369	4322	4373	3573
237	446	433	440	447	443	448	443	440	442	444	416
239	582	518	543	543	539	542	537	529	533	540	479
Cd	1	35	23	23	20	19	19	18	18	20	21
Hf	24	860	557	531	467	434	437	425	431	432	448
Nb	1	354	355	366	372	370	370	369	372	378	374
Pu239/40 (ug/L)	306	244	269	273	289	281	265	270	276	261	267
Np237 ug/L	425	453	433	442	419	440	476	433	464	455	388

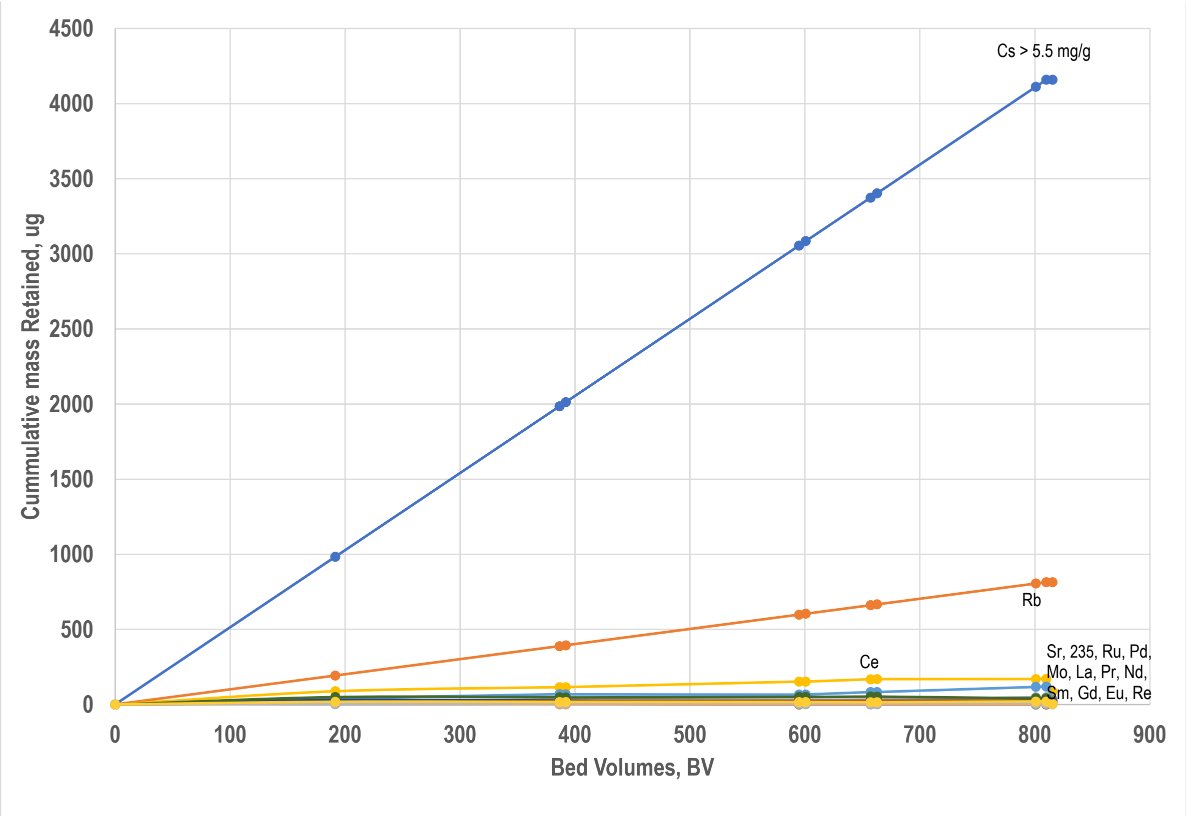
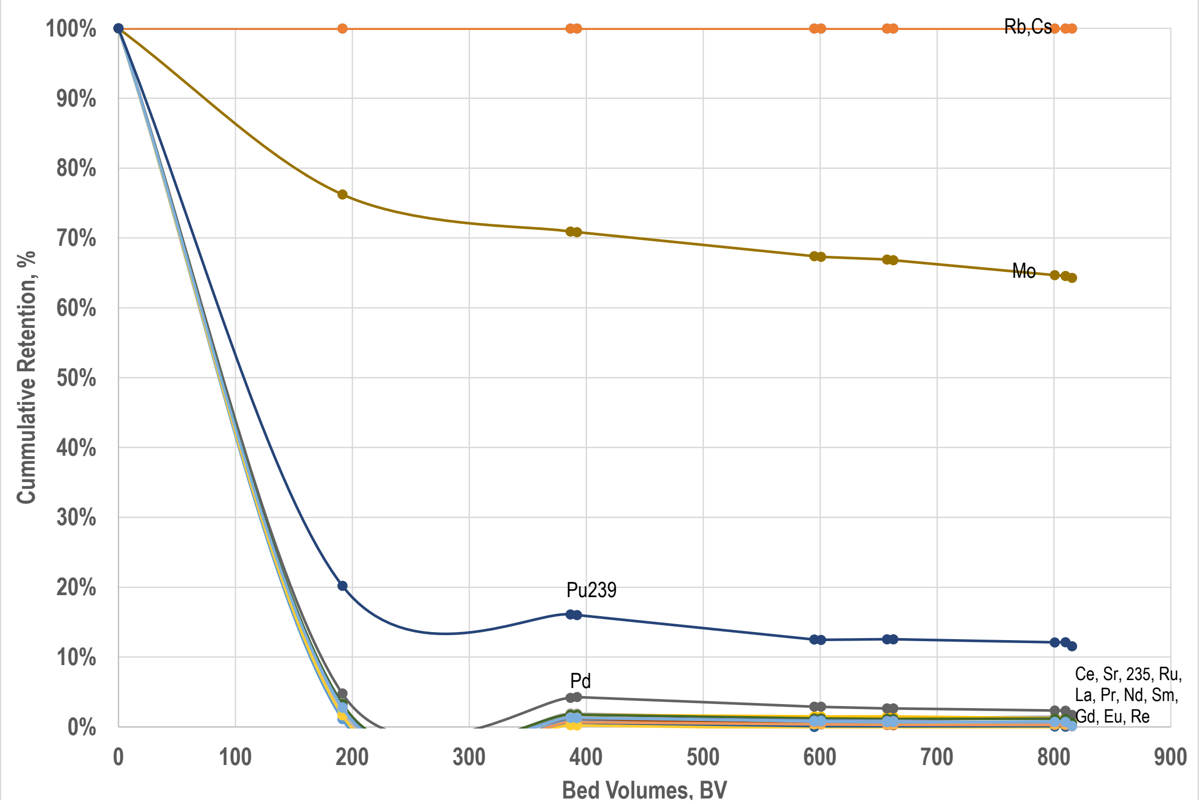


Figure 6. Cumulative Retention of Impurity Mass as a Function of Bed Volume of Raffinate for CST R9120-B Column at pH 1.



Importantly for the SHINE waste treatment, CST did not retain significant amounts of Sr from acidic sulfate solution. The CST absorbent appeared to have released Zr, Nb, Hf, and Cd as these elements were found by ICPMS at significantly higher concentrations in the raffinate samples than in the feed sample. These elements are assumed to be minor impurities in the CST matrix, and it is almost certain that more significant amounts of Si and Ti were also present in the raffinate samples, but the ICPMS method did not quantify those elements. It appears that CST retained smaller amounts of the actinides other than Pu than AMP-PAN.

Table 10. Mass of U, Pu, Np Retained by CST R9120-B Absorbent measured directly by Gamma PHA.

	CST R9120-B			
	ug	mg/g	% of Feed Mass	
U235	6	10	0.04%	
U238	1450	1.9	0.04%	1
Np237	0.12	0.0002	0.0%	
Pu239/40	14	0.018	7%	3
Am241	5.0E-05	6.6.E-08	-	2

1) Mass of ^{238}U Calculated from the ^{235}U Isotopic from ICPMS.
2) A separate ^{241}Am measurement in the feed was not available.
3) Measured ^{239}Pu but ^{239,240}Pu calculated assuming 94% ^{239}Pu.

3.4 CST R9120-B Column from pH 9 Carbonate Solution:

A second CST R9120-B experiment with a pH 9 feedstock was performed. It was thought that Sr would be retained by CST better at high pH. The starting point for this feedstock used a similar recipe to that used for the previous experiments but the acidic solution was pH adjusted to pH 9 with sodium carbonate. Carbonate was used due to the solubility of $UO_2(CO_3)_x$ complexes. The pH adjustment appeared successful due to the absence of U solid precipitation. For a column run at high pH, the CST R9120-B absorbent had to be converted from the H+ to the Na+ ionic form. Initially this was done with pH 9 sodium carbonate solution, but when the pH 9 U feed solution contacted the CST, bubbles of gas were released that disrupted the bed of CST absorbent. The experiment was halted at this point. Attempts to convert the CST in place were unsuccessful. The problem was recognized to be due to the large concentration of carbonate complexed by the U (~0.03 M), which would react with acidic sites on the CST material and release CO_2. 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. Further efforts at performing tests as pH 9 were deferred at that point.

3.5 IBC Ra-01 Column (nonRad) from pH 1 Solution:

Due to the lack of significant uptake of Sr on the AMP-PAN and CST, there still was a need for significant removal of Sr from the acidic waste solutions. IBC Ra-01 is marketed for Ra absorbent but could be effective at retaining Sr. A screening column experiment was performed using a column of Ra-01 resin. Kinetics reported in the literature were more like AMP-PAN, so a flowrate of 30 mL/h was used. The experiment used over 3.5 L of feed solution (4689 BV) over 121 hours. This flowrate was 38.6 BV/h. Table 11 is a tabulation of the ICPMS concentration results for this column experiment. None of the major elements of interest showed any retention by the absorbent. Some removal of Pb and Ba may have occurred, but the concentrations in the feed solution were only slightly above the detection limit. No further work with this material is warranted but some of the other IBC products would likely perform better for Sr removal.

Table 11. IBC Ra-01 Column Solution Analyses (ICPMS).

Cr390	Feed	ECA	EG1	ECB	EG2	ECC	EG3	ECD	EG4	ECE	EG5
Vol, mL	3482.7	687.3	4.6	728.7	5.4	685.7	5.2	675.1	4.9	681.1	4.7
Cum. Vol, mL		687	692	1421	1426	2112	2117	2792	2797	3478	3483
BV	4669	921	928	1904	1912	2831	2838	3743	3749	4662	4669
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Rb	2334	2280	2355	2318	2336	2310	2290	2322	2321	2294	2285
Cs	8045	7892	8134	7990	8187	8003	7927	8029	8056	7987	7909
Sr	2391	2348	2413	2379	2389	2363	2348	2371	2356	2359	2336
Ce	24028	23995	24452	23911	24393	24073	23786	23993	24041	24153	23885
Ru	1034	1017	1041	1033	1041	1026	1026	1029	1032	1036	1015
Pd	1030	1016	946	1015	958	1004	999	1016	991	1041	1024
Zr	918	901	930	913	927	914	908	916	908	910	902
Mo	833	824	849	834	840	833	830	838	832	830	821
La	1512	1507	1530	1496	1512	1502	1495	1516	1501	1504	1485
Pr	2156	2142	2198	2135	2177	2149	2136	2159	2136	2153	2108
Nd	10495	10391	10736	10551	10651	10481	10465	10580	10592	10496	10640
Sm	1180	1169	1206	1173	1179	1168	1161	1174	1183	1180	1157
Eu	887	879	902	879	891	887	873	886	878	883	870
Gd	1593	1572	1604	1575	1599	1581	1571	1597	1612	1626	1604
Re	5313	5336	5457	5421	5434	5312	5305	5297	5332	5409	5346
Ba	38	16	40	39	42	40	41	40	40	40	38
Lu	1	1	1	1	1	1	1	1	1	1	1
Hf	21	20	21	21	21	21	21	21	21	21	21
Pb	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.7	0.5

4.0 Discussion/Recommendations

The U retention observed in the batch contact tests was shown to not be a significant concern for either the AMP-PAN or CST R9120-B column experiments. The total mass of U available in the batch contacts was comparable to the mass of U measured on the AMP-PAN and CST absorbents at the end of the column experiments. Only minor amounts of U were retained by either AMP-PAN or CST R9120-B and both materials proved to have high selectivity and capacity for Cs under the test conditions. Either material could be adapted to remove Cs from acidic sulfate waste streams such as that proposed to be generated by the SHINE process. However, neither material shows any useful capacity for Sr from acid solutions. AMP has faster kinetics than CST for Cs, but the AMP may be more soluble than CST over time. The solubility may not be that obvious in the shorter AMP experiment that was performed. That would be something to watch for more closely in future work.

CST is reported to remove Sr at high pH, and the initial attempt to test CST at pH 9 (carbonate) was aborted due to off-gassing. This was likely due to reaction between the significant amount of carbonate complexed by the U and un-neutralized acid in the CST matrix. Additional work with CST under alkaline carbonate conditions is proposed for testing early next FY. There are other materials which hold promise at removing only Sr from acidic solutions (such as those from Eichrom and IBC Advanced Technologies), but these materials are perceived to be more expensive and were also not available for testing by SRNL during FY22.

4.1 Scaling from Lab Scale to Production Scale:

Scale-up should be based on keeping the cross-sectional flowrate the same to keep the residence time of the solution within the column constant. The resin bed is 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 would 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 in the column experiments with AMP-PAN and CST R9120-B actual Cs breakthrough was never reached. Saturation loading of Cs for AMP-PAN was greater than 2.7 mg Cs/g and for CST-9120-B it was greater than 5.5 mg Cs/g for a Cs feed concentration of 6.5 mg Cs/L. However, the absorbent capacity will likely be affected by the feed concentration. In these experimental runs the U, Cs, Sr feed concentrations were biased high to maintain analytical sensitivity and to limit the solution volume handled. Actual process conditions may involve Cs and Sr feed concentration 10x lower than in these experiments making scaling much more difficult. It is expected that the saturation loading may drop proportionally to the feed concentration. There is precedence for this with CST equilibrium loading from caustic solutions. King et al.[20] 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 8 shows Cs equilibrium loading data compared to the ZAM model for CST R9120-B evaluated against CST IE 911. Based on this graph, one can estimate that a 10x drop in the Cs feed concentration should reduce the Cs saturation value by 10x (below ~5×10^{-5} M Cs). The feed concentrations used in this work were biased high in an attempt to measure the saturation concentration of Cs on these materials; however, in light of the data from King, future testing should be performed at a feed concentration at or lower than the expected production concentration. Doing so will involve handling somewhat larger volumes of solution, but the results will have significantly less uncertainty.

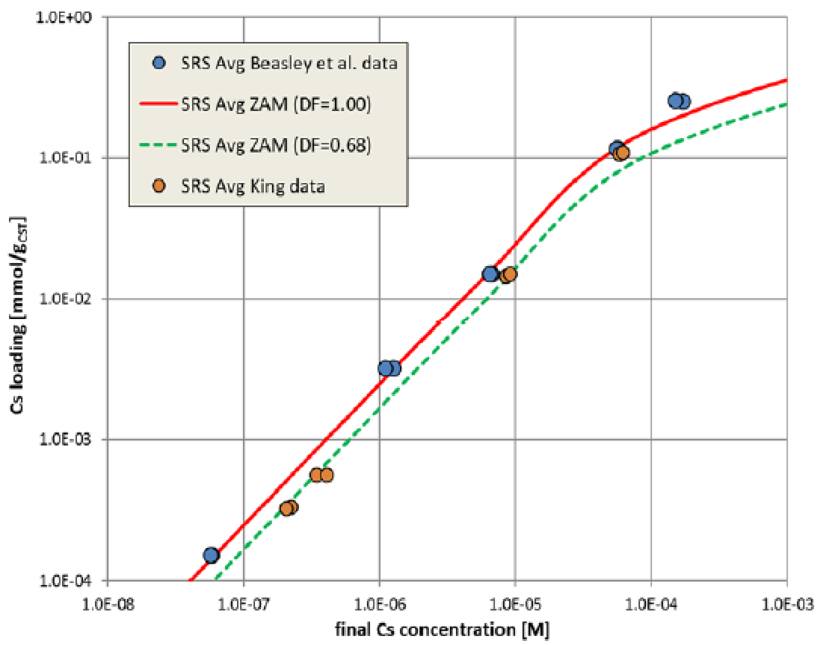


Figure 8. Comparison of Observed and Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and CST at 23 °C.[20]

One can use Figure 8 as a basis to estimate the capacity at a lower Cs feed concentration and then get an estimate for the size and capability for a production scale column. Tables 11 and 12 represent an attempt to scale up from small-scale column testing of the current work for both AMP-PAN and CST R9120-B. The first line in each table represents the tested lab condition. The estimated break-through (BT) Cs capacity is scaled by the Cs feed concentration. For AMP-PAN this reduces the observed loading value (> 2.7 mg Cs/g) to 0.246 mg Cs/g based on an assumed Cs feed concentration of 0.6 mg Cs/L. Similarly for CST R9120-B, the observed loading value (>5.5 mg Cs/g) is reduced to 0.498 mg Cs/g. Due to the short length of the lab

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[20] 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.

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 Tables 11 and 12 show a possible production scale column. In this case it will also result in a column that has a more favorable aspect ratio. 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 to ensure acceptable performance.

Table 12. Scaling of the Cs Loading onto a Column of AMP-PAN.

ID	H	BV	A	Q	Q/A	Cs	BT	Time	Vol	Mass	
mm	mm	cc	cm2	mL/min	cm/min	mg/L	mg Cs/g	hr	L	Cs, mg	
5	38	0.746	0.1963	0.485	2.47	6.5	2.7	6.3	0.183	1.2	
50	38	74.6	19.63	48.5	2.47	0.6	0.25	100	291	175	
75	38	167.9	44.2	109	2.47	0.6	0.25	100	655	393	
100	38	298	78.5	194	2.47	0.6	0.25	100	1164	698	
125	38	466	123	303	2.47	0.6	0.25	100	1819	1091	
150	38	672	177	437	2.47	0.6	0.25	100	2619	1571	
75	76	336	44.2	196	4.45	0.6	0.25	100	1179	707	1

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

Table 13. Scaling of the Cs Loading onto a Column of CST R9120-B.

ID	H	BV	A	Q	Q/A	Cs	BT	Time	Vol	mass	
mm	mm	cc	cm2	mL/min	cm/min	mg/L	mg Cs/g	hr	L	Cs, mg	
5	40	0.785	0.1963	0.11	0.56	6.5	5.4	105.7	0.698	4.5	
50	40	78.5	19.63	11	0.56	0.6	0.50	100	66	40	
100	40	314	78.5	44	0.56	0.6	0.50	100	264	158	
150	40	707	177	99	0.56	0.6	0.50	100	594	356	
200	40	1257	314	176	0.56	0.6	0.50	100	1056	634	
250	40	1963	491	275	0.56	0.6	0.50	100	1650	990	
300	40	2827	707	396	0.56	0.6	0.50	100	2376	1426	
150	80	1414	177	178	1.0	0.6	0.50	100	1069	642	1

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

5.0 Conclusions

AMP-PAN and CST R9120-B were both tested in a column configuration and were found to be effective to selectively remove 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. 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. While there are products on the market that would likely remove Sr from acidic solutions, they tend to be more expensive and involve proprietary extractants. Investigation of the use of CST R9120-B from carbonate adjusted solutions to remove both Cs and Sr at pH 9 (while keeping U in solution) is recommended.

Appendix A. Additional Results

Table 14. Detailed Flowrate Data for AMP-PAN Column Experiment (Cr386).

		Cr386	AMP-PAN 0.447g,3.8 cm tall, 0.5 cm ID, 0.746 cc BV										
	AD	Tare	Final Wgt	Net wgt	Density	Est Vol	Wgt Vol	Time					
	ID	g	g	g	g/cc	mL	mL	start	finish	min	min	mL/min	BV
ECA	26179	7.332	18.030	10.70	1.0120	10.1	10.57	7:59:42	8:21:42	0:22:00	22.00	0.481	14.2
ECB	26180	8.431	38.099	29.67	1.0123	30	29.31	8:22:27	9:21:21	0:58:54	58.90	0.498	53.5
ECC	26181	8.454	38.105	29.65	1.0108	30	29.33	9:22:10	10:22:16	1:00:06	60.10	0.488	92.8
ECD	26182	8.381	37.816	29.44	1.0106	30	29.13	10:22:47	11:22:53	1:00:06	60.10	0.485	131.8
ECE	26183	8.443	38.024	29.58	1.0118	30	29.24	11:23:25	12:22:59	0:59:34	59.57	0.491	171.0
ECF	26184	8.391	38.106	29.72	1.0134	30	29.32	12:23:33	13:24:36	1:01:03	61.05	0.480	210.3
ECG	26185	8.291	36.206	27.92	1.0121	28	27.58	13:25:20	14:23:54	0:58:34	58.57	0.471	247.3
WC	26189	8.312	23.738	15.43	1.0110	18	15.26	14:28:09	14:44:28	0:16:19	24.70	0.618	267.7
Feed	26178					188.1	184.47848				6.34	0.485	

Table 15. Detailed Flowrate Data for CST R9120-B (pH 1) Column Experiment (Cr387).

		Cr387	CST R9120-B, 0.760 g, 4.0 cm tall, 0.5 cm ID, 0.785 cc BV											
	AD	Tare	Final Wgt	Net wgt	Density	Est Vol	Wgt Vol	Time		Elapsed				Date
	ID	g	g	g	g/cc	mL	mL	start	finish	Time	min	mL/min	BV	finished
ECA	26231	34.48	186.8492	152.37	1.0136	155	150.32	8:16:19	8:16	23:59:41	1440.00	0.104	191.4	26-Apr
ECB	26232	35.034	190.1328	155.10	1.0130	160	153.11	8:16	8:20	0:04:00	1444.00	0.106	386.4	27-Apr
EG1	26233	7.322	11.7263	4.40	1.013	5	4.35	8:20	9:05	0:45:00	45.00	0.097	392.0	27-Apr
ECC	26234	34.825	196.7578	161.93	1.0168	168	159.26	9:05	8:15	23:10:00	1439.97	0.111	594.8	28-Apr
EG2	26235	7.297	11.889	4.59	1.013	5	4.53	8:15	8:55	0:40:00	40.00	0.113	600.6	28-Apr
ECD	26236	35.007	79.8846	44.88	1.0126	48	44.32	8:55	15:19	6:24:00	384.00	0.115	657.0	28-Apr
EG3	26237	7.303	11.6537	4.35	1.013	5	4.29	15:19	15:55	0:36:00	36.00	0.119	662.5	29-Apr
ECE	26238	35.125	144.812	109.69	1.0120	105	108.39	15:55	8:17	16:22:00	1439.68	0.075	800.5	29-Apr
EG4	26239	7.286	14.5652	7.28	1.013	8	7.19	8:17	9:32	1:15:00	75.00	0.096	809.7	29-Apr
WC	26240	7.302	11.6821	4.38	1.013	4.5	4.32	9:32	10:25	0:53:00	53.00	0.082	815.2	29-Apr
Feed	26230					659	636	810			105.72745			

Table 16. Detailed Flowrate Data for Ra-01 Column Experiment (Cr390).

		Cr390	RA-01 0.325g , 3.8 cm tall, 0.5 cm ID, 0.746 cc BV											
	AD	Tare	Final Wgt	Net wgt	Density	Est Vol	Wgt Vol	Time		Elapsed			BV	Date
	ID	g	g	g	g/cc,(1)	mL	mL	start	finish	Time	min	mL/min		finished
ECA	26983	101.122	791.95	690.83	1.0051	700	687.32	15:23	14:00	22:37:00	1357	0.507	921	23-Jun
EG1	26984	7.299	11.946	4.65	1.0051	5	4.62	14:00	14:09	0:09:00	9	0.514	928	23-Jun
ECB	26985	101.083	833.52	732.44	1.0051	730	728.72	14:09	14:39	0:30:00	1470	0.496	1905	24-Jun
EG2	26986	7.335	12.782	5.45	1.0051	5	5.42	14:39	14:50	0:11:00	11	0.493	1912	24-Jun
ECC	26987	101.452	790.62	689.17	1.0051	700	685.67	8:16	8:32	0:16:00	1456	0.471	2831	28-Jun
EG3	26988	7.342	12.571	5.23	1.0051	5	5.20	8:32	8:42	0:10:00	10	0.520	2838	28-Jun
ECD	26989	101.1	779.62	678.52	1.0051	700	675.08	8:42	8:44	0:02:00	1442	0.468	3743	29-Jun
EG4	26990	7.327	12.228	4.90	1.0051	5	4.88	8:44	8:54	0:10:00	10	0.488	3750	29-Jun
ECE	26991	101.132	785.73	684.60	1.0051	700	681.12	8:54	9:26	0:32:00	1472	0.463	4663	30-Jun
EG5	26992	7.296	12.032	4.74	1.0051	5	4.71	9:26	9:36	0:10:00	10	0.471	4669	30-Jun
WC	not measured				(1) Measured with Density meter									
Feed	26982					3555	3483				121			

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