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Distribution of U, Pu and Np in a Mo-99 Recovery Process using Sachtopore NP (titania based) Absorbent Material

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PREFACE OR ACKNOWLEDGEMENTS

I need to acknowledge extensive participation in this work by David Diprete. He has endured my continual requests for assistance and questioning of analytical results. Many of the radiochemical analytical results reported in this work are present at low levels with lots of opportunity for interferences resulting in challenges. David went the extra mile to get the job done.

I also need to thank Anita Poore for providing the conduit between the SRNL, SHINE, and NNSA organizations.

Lastly, I need to acknowledge the funding provided by NNSA Office of Defense Nuclear Nonproliferation, Materials Management and Minimization, NA-231 Mo-99 Programs office.

EXEUTIVE SUMMARY

A laboratory scale mockup of 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 (U-238), plutonium (94% Pu-239), neptunium (Np-237), and non-radioisotopes of common fission products (including Mo).

The goal of this work was to determine the amounts of U, Pu, and Np in the liquid waste streams created by the wash streams for the production process. The key question was how the initial acid wash volume will be handled, as this solution contains residual raffinate which amounted to ~ 3% of the mass of the feed solution in this experiment. If the initial 1.9 bed volumes (BV) of acid wash were recycled as in this experiment then the combined wash solutions can be expected to contain 0.4 g U/L, 2.7 µg Pu/L and < 14 µg Np/L. If, on the other extreme, the entire acid wash solution was discarded as waste, then the combined wash solutions can be expected to contain 11 g U/L, 3.8 µg Pu/L and ~ 80 µg Np/L.

The Sachtopore NP absorbent (for Mo-99 recovery) retains a minuscule fraction of the U (2.3 mg U per g titania or 0.03% of the U in the feed). The uncertainties are too large to determine how close the absorbent is to saturation with U. Less mass but a higher fraction of the total Np was retained by the absorbent (0.7 µg Np per g titania or ~2% of the Np in the feed). As has been reported elsewhere, a large fraction of the Pu fed to the titania bed was retained by the absorbent (92% of Pu in the feed or 20 µg per g titania).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AHA	aceto-hydroxamic acid
ANL	Argonne National Laboratory
CST	crystalline silicotitanate
DI H_2O	deionized water
DOE-NNSA	Department of Energy - National Nuclear Security Administration
DTPA	diethylenetriaminepentaacetic acid
HAS	hydroxylamine sulfate
HEU	highly enriched uranium, > 20% U-235
LEU	low enriched uranium, < 20% U-235
Titania	titanium dioxide
Mda	minimum detection amount
PHA	pulse height analysis
SHINE	SHINE Medical Technologies LLC (Janesville, Wisconsin)
SRNL	Savannah River National Laboratory
TTA	thenoyltrifluoroacetone, a tetravalent specific actinide extractant

1.0 Introduction

The U.S. Department of Energy's National Nuclear Security Administration (NNSA) Office of Material Management and Minimization (M3) manages the Molybdenum-99 (Mo-99) 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 Mo-99 Program assists global Mo-99 production facilities in converting to non-HEU processes and supports the establishment of domestic supplies of Mo-99 without the use of proliferation-sensitive HEU.

The U.S. medical community depends on a reliable supply of the radioisotope Mo-99 for nuclear medical diagnostic procedures. Mo-99 and its decay product, technetium-99m (Tc-99m), 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 import 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 Mo-99 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) Mo-99 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 target solution where U-235 atoms fission to produce Mo-99 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 Mo-99 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 Mo-99 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 work McCann 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.[3] 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 amount of these actinides which are retained on the Sachtopore absorbent. The current work was aimed at determining the behavior of the actinides in the Mo-99 absorption process under process conditions.

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 Mo-99 from the fission of U-235. Pu-239 and Np-237 were added to a uranyl sulfate solution along with a series of representative fission product surrogates (all of which were non-radioactive). The commercial Mo-99 process has the heavier radioisotope of Np (Np-239), which quickly decays ($t_{½}$ =2.36 days) to Pu-239. Concentrations of the non-radioactive impurities were larger than the expected concentrations of the impurities made in the commercial production Mo-99. This was done to avoid analytical error associated with detection limitations of the analytical methods available. The

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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).

Pu and Np concentrations were limited (activity was comparable to that from the depleted uranium in the feed solution, < 0.5 µCi/mL) to control the contamination risk for performing this work in a hood. (Performing this work in an SRNL glovebox would have resulted in excessive cross-contamination risk for Pu/Np.) 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 past experience. Nitrate salts dissolved in water were used where those compounds were available, but several elements were dissolved as oxides into a small amount of concentrated sulfuric acid.

Uranium trioxide (UO_3) was dissolved in a mixture of sulfuric acid and water. This solution was filtered as a precaution but there was no evidence of residual solids. 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. Multiple solubility issues were encountered, and changes were made to the order of preparation to limit the problems. (1) Barium and strontium sulfate have limited solubility, so these impurities were added individually as nitrate salts dissolved in water. (2) Multiple lanthanides (cerium in particular) have a limited solubility with molybdate. Therefore, the molybdate was dissolved in water and kept separate until added to the bulk solution. (3) Zirconyl oxynitrate, tin dioxide, and antimony trioxide were dissolved in a small volume of sulfuric acid. This solution was repeatedly filtered but solids continued to reform after each filtration. In hindsight, the consideration of an alternate source of these metal species should be considered in the future. (4) There was concern for the solubility of sodium perrhenate ($NaReO_4$), so it was dissolved in sulfuric acid and kept separate until addition to the bulk uranyl sulfate solution. However, no issue was observed with $NaReO_4$ solubility during this study and there was no specific basis for that concern.

The remainder of the surrogates were added as nitrate salts dissolved in water as a single solution. The palladium turned the uranyl sulfate solution from yellow to brown (see Figure 1). Brown solids formed in this final solution within a few days after all the solutions were combined. The solution was filtered with a 0.45-µm cellulose nitrate filter several days prior to use. Noticeable additional solids did not reform after filtration. These solids were not analyzed but the brown appearance, as seen in Figure 2, is consistent with the presence of palladium. The ICPMS analysis of the feed solution showed that the palladium concentration was lower than expected (as well as Zr, Sn, Sb, and Ba). The relatively high uranium concentration in the feed solution meant that the uranium flow through the system could be visually followed and the initial acid wash containing the bulk of the residual uranium was collected and analyzed separately.

Figure 1. Color of Feed Solution.

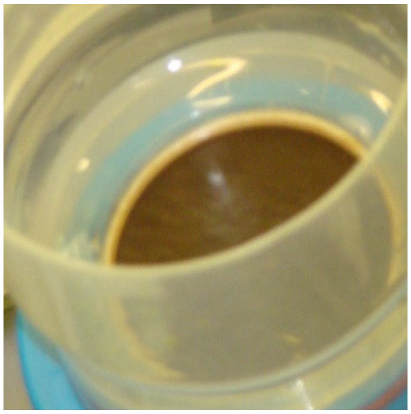

Figure 2. Solids Filtered from Feed Solution.

2.2 Equipment and Process Description:

The uranyl sulfate feed solution and washes were heated to 60-80 °C prior to loading on the Sachtopore column. The solutions were heated on a hotplate and pumped with a peristaltic pump through an empty jacketed glass column used as a preheater prior to entering the titania column through a two-valve manifold on the bottom of the column. After flowing through the Sachtopore bed (up-flow) the solution temperature was measured by a type K thermocouple installed in the tubing and positioned just above the bed. After exiting the column, the solution passed through another multiple-valve manifold where it could be directed to one of several collection bottles. The Sachtopore column and preheater were both jacketed and were heated with hot water (~ 90 °C) from a 1-L beaker of water on a separate hotplate. The jackets of both columns were connected in series with the Sachtopore column being the first in a hot-water heating loop which used a centrifugal lab pump with a capacity of up to 2 gal/min to recirculate the hot water through the column jackets. The hot water was heated to ~ 90 °C with a temperature drop of 5 to 10 °C in the heating loop. Standard Tygon tubing is not rated for this temperature range so C-Flex tubing (rating > 25 psig, 135 °C) was obtained to make heated connections. The jacketed glass columns were purchased from Bio-Rad (Econo-column glass columns, 1-cm ID, 15-cm length). A BioRad Flow Adapter was also used on the titania column to retain the titania in the column during up-flow operation. Sachtopore NP 110-µm, 60-Å pore titania was used as the absorbent material. Figure 3 shows a simplified schematic of the experimental setup. Figure 4 is a photograph of the experimental equipment setup in the radioactive hood where the experiment was performed.

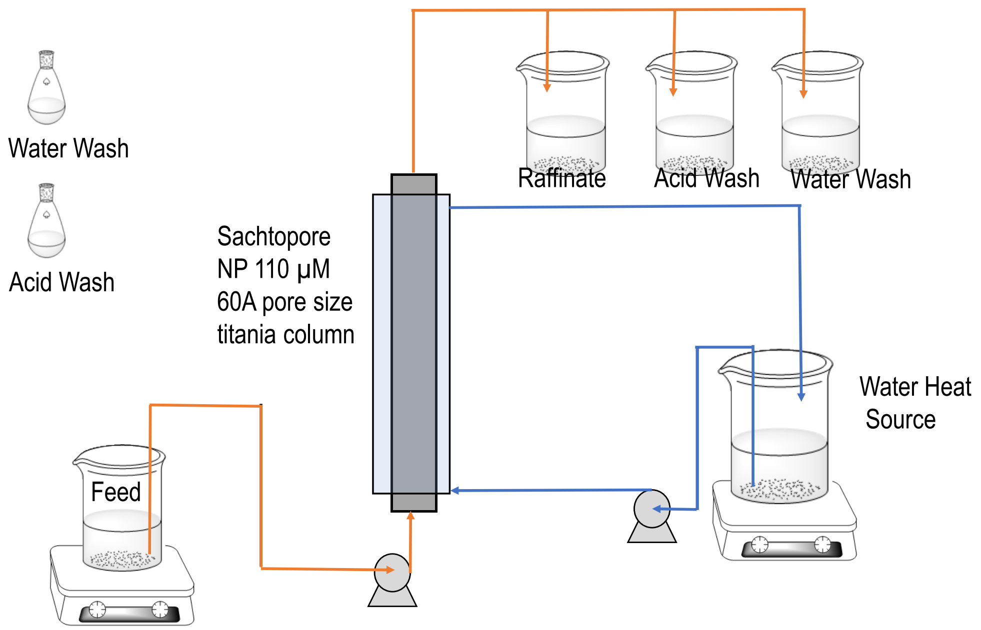

Figure 3. Schematic of Experimental Setup.

Figure 4. Experimental setup in Rad Hood.

Due to the small size of the absorbent particles in the titania column and the relatively high desired flowrates, there is a modest pressure drop across the titania bed. During equipment testing a digital pressure manometer was installed at the top of the preheater column and the pressure was monitored. This equipment was intended to be operated at pressures up to 15 psig. The feed pump was rated to generate a maximum backpressure of 15 psig.

Extensive water testing established that this equipment setup could be operated at temperature at maximum flowrate without leaks. Additionally, the valve manifolds below and above the column were plumbed such that it could be switched from up-flow operation to downflow operation without any tubing connection changes. This avoided contamination concerns during the switchover from up-flow washing to downflow elution. This also allowed the rinse/flush of the preheater and tubing so that a step change in fluid composition to the column could be better achieved. Further photos and sketches of these configurations are included in the appendix.

Temperature monitoring during water testing established that the recirculating heating loop operating at a high flowrate (there was no adjustment capability) could raise the temperature of the feed by ~ 30 °C or more. This allowed the switchover between feed/wash/elution bottles without a lengthy waiting time for the next solution to be fully heated to the operating temperature. Once the solution had been preheated on the hotplate to at least 50 °C, the next step started. This was established during water testing. During radioactive operation, the hot water source beaker was preheated to ~ 90 °C before the start of feed pump, and the feed/wash/elution solution was confirmed to be 50 - 70 °C prior to the initiation of flow through the column. Additional temperature readings were not monitored due to the complexity of the operation of the equipment. Similarly, the column pressure and flowrates were monitored extensively during testing but during the operation of the column with radioactive feed, pressure drop readings were not monitored and the flowrates were calculated later.

2.3 Laboratory flowsheet:

Table 1 is the laboratory flowsheet with realistic process conditions for the Sachtopore column operation. The intent was to scale the flowrate to obtain a cross-sectional velocity for the solution flow through the column comparable to that of a proposed production process. Deionized water was used for the water washes and for the preparations of all wash and elution solutions throughout the experimental work. Due to laboratory solution volume handling constraints, fewer bed volumes (BVs) of uranyl sulfate feed solution were used than proposed for a production process. A shorter titania column was prepared, and a higher Mo concentration was used, both of which would significantly reduce the Mo recovery over that of a production process.

Table 1. Proposed Laboratory Flowsheet for Sachtopore Column.

	Vol, mL*	Q, mL/min*	Time min	Total min	mL/min/cm2			BV
Conditioning pH 1	20	1						2.5
Feed, pH 1, 170 g U/L	400	22.58	17.7	17.7	28.75	80C	upflow	50.9
0.1M H2SO4 Wash	8	22.58	0.4	18.1	28.75	80C	upflow	1.0
0.1M H2SO4 Wash	70	22.58	3.1	21.2	28.75	80C	upflow	8.9
Water Wash	85	22.58	3.8	24.9	28.75	80C	upflow	10.8
1M NaOH	25	7.70	3.2	28.2	9.80	80C	downflow	3.2
0.1M NaOH	135	7.70	17.5	45.7	9.80	80C	downflow	17.2
Water Rinse	100						downflow	10
Remove H2O in Bed							downflow	
Sachtopore-NP titania, 110 micron particles, 60Å pores								
packed into 1 cm diameter, 10 cm height column				7.85	mL BV	10.2 g		
	0.785	cm2 cross sectional area		100	scale down factor			

*Planned flowrates and volumes are shown. The actual operating conditions were measured (see Table 2).

The heated solution (feed, wash, or elution) was pumped into the top of an empty feed preheater column. The preheater restored the solution heat lost to the feed lines before it entered the Sachtopore NP titania column. For each solution source change (feed, acid wash, water wash, pre-elution, and elution), the feed line was pumped empty and then flushed with a small volume of new solution to the waste bottle, (along with any air bubbles). The manifold configuration was adjusted to allow up-flow operation of the column with the raffinate discharged through the top of the column. A thermocouple was sealed in place with epoxy into the "tee" fitting at the top of the column to allow measurement of the solution temperature exiting the column. A small volume of residual solution was "holdup" in the line between the top of the column and the discharge point. A larger volume of residual solution (~ 5 mL) was holdup in the void space within the column. The use of small diameter (1.588 mm) tubing minimized the dilution effect of the holdup in the lines but the holdup in the void space within the Sachtopore bed could not be reduced.

After the elution step, the column was rinsed with water in preparation for disposal. After several weeks it was decided to measure the retained radioisotopes on the resin bed. At that time, air was sucked through the bed using a vacuum source and left overnight to remove as much water as practical. The entire bed of Sachtopore was then poured into a clean sample bottle and analyzed by gamma pulse height analysis (PHA). The entire sample was gamma counted in multiple petri dishes to obtain a geometry of known calibration.

While Table 1 represented the scaled flowsheet, the actual flowrates and volumes of solution only approximated those conditions. Table 2 details the actual flowrates achieved and the measured volumes for each phase of the experiment. The sampling volumes and flushing sequence are also documented in detail. The pump was paused for each change of feed solution for ~ 10 min. This allowed time for the new solution to be preheated by the hotplate. Temperature was monitored at the top of the Sachtopore column.

During the feed and wash steps this was the solution temperature leaving the column. During the elution steps, this temperature was the solution temperature entering the column. The temperature at the bottom of the column was not measured. The pressure readings are dominated by the differential pressure across the Sachtopore column and was measured in the jacketed preheater column.

Table 2. Column Operating Conditions for Sachtopore Column.

	Vol mL	BV	Flowrate mL/min	Conc.		Temp. C	dP psig
Load Feed	380	48	18	170 g U/L	upflow	71.3	6.5
	3	0.4			sample		
					flushed feed line		
Acid Wash	15	1.9	18	0.1 M H_2SO_4	upflow, displace raffinate	71.7	5.6
	74	9.4			bulk acid wash		
	3	0.4			sample		
					flushed feed line		
Water Wash	80	10.2	21	DI H_2O	upflow	70.6	6.1
	3	0.4			sample		
					flushed feed line		
Pre-Elution	26	3.3	7	1 M NaOH	downflow	40.7	
					flushed feed line		
Elution	130	16.6	12	0.1 M NaOH	downflow	52.5	2.8
Flush	100	12.7		DI H_2O	flushed feed line		
				Air	air dried column		

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.

3.0 Results and Discussion

3.1 ICPMS Results

All samples were analyzed using ICPMS and the results are shown in Table 3. Non-radioactive species were designated by elemental symbol based on naturally occurring isotopic distribution, but radioactive isotopes were shown as isotopic mass. Due to the large mass of U-238 present, the masses in channels 239 and 237 were biased high, particularly the mass 239 number. Resolving the mass with 10^5 difference in concentrations was expected to be an issue and the plan always was to obtain values for Pu and Np by gamma PHA rather than ICPMS. Thus, values for Pu-239 and Np-237 are not shown in Table 3. Due to the low solubility of Sn, Sb and Ba, those values are assumed not particularly reliable and are also not shown. The elements Zr and Pd came out about 30% of the targeted concentration. Issues with Pd solubility during dissolution were suspected due to the appearance of brown solids after all impurity solutions had been added to the uranyl sulfate solution. The results also show that Cs and Sr analyzed at 33% and 20%, respectively, lower than expected. Mo analyzed at over 200% of the targeted value. No evidence has been uncovered for that discrepancy, but a preparation error seems most likely. The results for Zr in Table 3 have a somewhat erratic trend in the wash samples which may be due to continued issues with Zr solids. The metals Ru and Pd appear to have some retention on the titania, which has been reported in other research.[4,5]

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[4] A. Youker, “Accelerator-Driver Production of Fission 99Mo”, Mo-99 Topical Meeting on Molybdenum-99 Technological Development, Argonne National Laboratory, September 14, 2016.

[5] A. Youker, et al, “Compendium of Phase-1 mini-SHINE Experiments”, ANL/NE-16/39, September 2016.

The product element Mo was well retained by the titania with only 3% of the mass in the feed passing through the column and 105% found in the elution samples. Table 4 shows the material balance calculated from the volumes and the ICPMS results. The consistency between the raffinate and feed analysis was poor with raffinate analyzing at 16% higher than the feed concentration (but that is within the stated 20% one-sigma uncertainty). The behavior of Zr, Sn, Sb, and Ba were somewhat erratic (Sn, Sb, and Ba were not shown as values because they were less than 2% of the targeted value). This erratic behavior is suspected to be due to fine residual solids still present after filtration. The initial 1.9 BV of acid wash contained ~2.7% of the feed mass at ~ 54% of the feed concentration due to residual raffinate which remained in the column at the beginning of the wash step and must be flushed out. Similarly, in the production process, a similar volume of raffinate containing a significant amount of radioactivity can be segregated and either or discarded without affecting the larger volume of wash solutions. Due to equipment design differences, the BV value in the production equipment will differ from the laboratory equipment. The ability to split the wash by observation of the color of U in solution will not be readily accomplished in the production environment. This split will need to be optimized by trial and error based on volume transferred or elapsed time unless instrumentation is installed (such as a spectrophotometer or colorimeter).

Table 3. ICPMS Results for Nonradioactive Simulants and U.

Element or m/z	Feed Percent of Target	Target Feed Conc. ug/L	Feed ug/L	Raffinate ug/L	Raffinate Grab Sample ug/L	Acid Wash 1st 1.9 BV ug/L	Acid Wash ug/L	Acid Wash Grab sample ug/L	Water Wash ug/L	Water Wash Grab sample ug/L	1 M NaOH Elution ug/L	0.1 M NaOH Elution ug/L
238	102%	1.72E+08	1.75E+08	2.03E+08	2.23E+08	1.22E+08	7.73E+05	1.58E+05	39248	2219	10614	1096
235	104%	688684	714060	826862	900552	494470	3173	632	162	9	44	5
Ru	108%	183040	197269	223848	247335	116220	8306	4046	1389	61	7273	1232
Cs	67%	290551	195521	228122	250037	159147	586	75	43	7	79	15
Ce	103%	178183	184075	213718	234577	132067	1344	81	36	5	6	1
Nd	101%	108015	109492	128419	139563	78866	692	50	20	2	4	1
Sr	80%	94506	75862	87843	95302	53341	171	41	22	21	27	5
Pr	100%	73235	73542	85273	94167	50383	490	32	14	1.4	2.2	1.0
Gd	113%	38626	43821	51668	56580	31153	165	17	6	1.0	1.6	1.0
Mo	223%	18099	40346	1156	1322	486	20	23	6	17	576077	9257
Eu	97%	39358	38177	44839	48668	27246	167	17	7	1.0	1.3	1.0
La	93%	38357	35518	41343	45272	25507	251	15	6	1.0	1.4	1.0
Rb	88%	39057	34288	39933	42964	27603	77	21	16	7	34	6
Sm	102%	32358	33154	39171	42924	24449	170	15	7	1.0	1.4	1.0
Re	99%	26671	26537	30554	32929	16027	98	45	19	17	12	6
Zr	34%	24871	8542	4708	5070	1791	129	71	5	1	18	5
Pd	28%	21706	6036	6850	7641	4580	903	472	70	1	311	96
		Vol, mL	383	380	3	15	74	3	80	3	26	130

Table 4. Material Balance based on ICPMS Results.

Element or m/z	Feed	Raffinate	1.9 BV Acid Wash	Washes	Elution
	% of mass compared to feed solution				
238	100%	116%	2.7%	0.09%	0.0006%
235	100%	116%	2.7%	0.09%	0.0006%
Ru	100%	114%	2.3%	1.0%	0.5%
Cs	100%	117%	3.2%	0.06%	0.005%
Ce	100%	116%	2.8%	0.15%	0.0004%
Nd	100%	117%	2.8%	0.13%	0.001%
Sr	100%	116%	2.8%	0.05%	0.004%
Pr	100%	116%	2.7%	0.13%	0.001%
Gd	100%	118%	2.8%	0.08%	0.001%
Mo	100%	3%	0.05%	0.01%	105%
Eu	100%	118%	2.8%	0.09%	0.001%
La	100%	116%	2.8%	0.14%	0.001%
Rb	100%	117%	3.2%	0.05%	0.013%
Sm	100%	118%	2.9%	0.10%	0.001%
Re	100%	115%	2.4%	0.09%	0.01%
Zr	100%	55%	0.8%	0.3%	0.04%
Pd	100%	114%	3.0%	3.2%	0.9%

3.2 Gamma Analysis of Titania Absorbent:

During the performance of this work, the importance of determining the amounts of radioisotopes on the titania absorbent was recognized. The column was rinsed with water to remove the residual NaOH solution, and then the titania absorbent was dried by drawing air through the bed overnight using the house vacuum system. The entire titania bed was then poured into a sample bottle and submitted for a gamma PHA analysis. This was performed by dividing the absorbent sample approximately equally between two covered petri dishes which were gamma counted using a standard geometry. Two counts were performed: the first about five weeks after the separation was performed and the second count approximately two weeks later to allow decay corrections for the isotopes with short half-lives (Pa-233, Pa-234m and Th-234). The consolidated results of that analysis are shown in Table 5. The short-lived isotopes are decay corrected back to the date of separation and the values for the multiple measurements averaged to a single value, but the one sigma uncertainty for Pa-233, Pa-234m and Th-234 are those reported for a single sample. An alternate peak fitting program[6] on the Np-237 86 keV peak was used to determine the total Np-237 content of the titania absorbent. The uncertainty is somewhat high (20%) but the fraction of Np-237 retained by the titania is small. On the other hand, the amount of Pu-239 is high relative to the total amount of Pu that was used in the test. Comparatively, much more U absorbed on the titania in an absolute sense but considering that there was ~ 100,000 times more U used in the test than Pu or Np, this is still a tiny fraction of the U.

Table 5. Gamma PHA Analysis of Titania Absorbent.

Sample ID Radionuclide	20896 dpm	Uncertainty	uCi total	uCi/g	ug	ug/g
Pu-239	2.56E+07	5%	11.5	1.18	186	19
Pu-241	2.83E+07	5%	12.7	1.30	0.1	0.013
Am-241	11800	5%	0.0053	0.0005	0.002	0.0002
Pa-233	1.85E+05	5%	0.08	0.0085		
Pa-234m	7.26E+06	5%	3.27	0.33		
Th-234	6.09E+06	20%	2.74	0.28		
U-235	449	10%	0.0002	0.0000	94	9.6
U-237	1000	5%	0.0005	0.0000		
Np237	11416	20%	0.0051	0.0005	7	0.7
U-238	17025		0.0077		23007	2346

Total dry sample mass = 9.808 g
Pa and Th isotopes were counted two weeks apart and decay corrected to the date of separation.
Values for Pa and Th are the average values from multiple determinations.
Np-237 peak refit using PeakEasy software and 86 keV peak.
U-238 values calculated from U-235 value and 0.41% isotopic ratio from ICPMS.
Pu source was 94% Pu-239. Total Pu mass was 197 µg Pu with loading of 20 µg Pu/g titania.

3.3 Gamma/Alpha PHA Analysis of Solutions:

Solution samples were also sent for radiochemical analysis of the radioisotopes. The high pH elution solutions were not analyzed by these methods due to concerns over low solubility. The focus of this work was on the recycle/waste streams and it was assumed that minimal concentrations of actinides would be present in the elution solutions. Table 6 shows the tabulation of the gamma PHA results. The U-238 results were available from ICPMS analysis and were also included with the gamma PHA results. The actinides in the samples past the initial acid wash "displacement" were mostly below the minimum detectable amount (mda) value for most gamma emitters. Due to delays in analysis, these samples had returned to secular equilibrium prior to the analysis and the Pa-233 and Pa-234m had mostly returned to secular equilibrium

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[6] PeakEasy Version 4.86 was used rather than the production Genie2K peak fitting software normally used by SRNL AD.

with the long-lived parent isotopes, Np-237 and U-238. The only observation of note from the solution gamma analyses was difficulty with the Np-237 analyses and the recommendation to consider an initial separation to isolate the Np-237 in the future.

Table 6. Material Balance from Gamma PHA Analysis of Solutions.

	Feed	Raffinate	Raffinate Grab sample	Acid Wash 1.9 BV	Acid Wash	Acid Wash Grab sample	Water Wash	Water Wash Grab sample	1 M Eluate	0.1 M Eluate	Titania
Volume, mL	383	380	3	15	74	3	80	3	26	130	9.808 g
Sample ID	20286	20287	20288	20289	20290	20291	20292	20293	20294	20295	20896
Pa-234m, dpm/mL	136000	136000	90700	169000	31200	23000	3090	735			
one-sigma	5%	5%	5%	5%	5%	5%	9%	mda			
Am-241, dpm/mL	535	455	487	532	210	187	80	52			
one-sigma	6.7%	8.0%	7.2%	7.2%	mda	mda	mda	mda			
Np-237, dpm/mL	1810	1940	2160	1200	21	205	15	14			
one-sigma	5.6%	5%	5%	5%	mda	mda	mda	mda			
U-235, dpm/mL	2780	3180	3430	2120	13	8	8	8			
	5%	5%	5%	5%	mda	mda	mda	mda			
U-238, g/L from ICPMS	175	203	223	122	0.77	0.158	0.039	0.002	0.011	0.001	
U, g	67	77	0.7	1.8	0.057	0.00047	0.0031	6.7E-06	2.8E-04	1.4E-04	0.023
Np-237, ug/L	1160	1244	1385	769	14	131	9	9			
Np-237, ug	444	473	4.2	11.5	1.0	0.4	0.8	0.03			7
U, % of feed mass	100%	115%	1.0%	2.7%	0.09%	0.001%	0.005%	0.00001%	0.0004%	0.0002%	0.0343%
Np-237, % of feed mass	100%	106%	0.9%	2.6%	0.23%	0.09%	0.17%	0.01%			1.6%

Grey shaded cells indicate result below mda limit.

The original analytical plan was to analyze the solutions by gamma PHA and then to perform an extraction if needed to quantify the Pu. The SRNL Pu thenoyltrifluoroacetone (TTA) extraction method involves adjustment of the Pu to the tetravalent state and then extraction into a TTA extractant in a low boiling solvent, followed by preparation of alpha plates and measurement by alpha PHA. All solution samples were analyzed by both gamma and Pu TTA methods to obtain values for Np and Pu. The results of the TTA analyses are shown in Table 7. The significant result from this analysis was the confirmation of the Pu feed concentration meaning that almost all (92%) the Pu from the feed solution was retained as the solution passed through the Sachtopore bed. Based on the sample from the end of the raffinate, it appears that the bed was not saturated with Pu and would likely continue to load Pu if additional feed volume had been used.

Table 7. Material Balance from Pu TTA Analysis of Solutions.

	Feed	Raffinate	Raffinate Grab sample	Acid Wash 1.9 BV	Acid Wash	Acid Wash Grab sample	Water Wash	Water Wash Grab sample	Titania
Volume, mL	383	380	3	15	74	3	80	3	9.808 g
Sample ID	20286	20287	20288	20289	20290	20291	20292	20293	20896
Pu-239/240, dpm/mL	89300	6580	7930	2420	800	808	87.4	8.8	
one-sigma	6.8%	6.0%	6.4%	7.7%	5.7%	5.1%	8.3%	14%	
Pu-238, dpm/mL	8460	619	857	179	79	79	9.6	1.3	
one-sigma	7.4%	13%	11%	34%	7.6%	6.7%	23%	MDA	
Pu-239/40, ug	214	16	0.1	0.2	0.4	0.02	0.04	0.0002	197
Pu, ug/L	558	41	50	15	5	5	1	0.1	
% mass	100%	7.3%	0.07%	0.11%	0.17%	0.01%	0.02%	0.0001%	92%
% conc	100%	7.4%	8.9%	2.7%	0.9%	0.9%	0.10%	0.010%	

3.4 U, Pu, Np Material Balance:

Lastly, the results from the ICPMS, gamma, and alpha analyses were combined to perform an overall material balance on the actinides included in this experiment, compiled in Table 8. Despite the unexpected lack of agreement between the feed and raffinate solutions, only minor amounts of actinides should be expected to be found in the wash solutions depending on the handling of the residual raffinate contained in the void space of the column and the piping. There will also be a similar volume of dilute acid solution which will dilute the recycled U raffinate which would be recycled most of the time. The switch between waste to recycled raffinate and back to wash/waste was performed in the laboratory equipment by visual means but this will be more difficult in production equipment operating in a shielded facility with limited instrumentation.

The retention of Pu on the titania column will likely be a waste disposal issue as almost all the Pu in the feed solution was deposited on the Sachtopore absorbent. ANL has investigated the retention of Pu on titania as a function of acid concentration and temperature and suggested increasing the wash acid concentration to strip the Pu.[7] There is also an opportunity to use similar chemical means to remove the Pu after the Mo-99 has been recovered, but that would involve additional process steps and the associated processing time and waste cost. There may be chemical methods to prevent Pu from being retained by the absorbent, but the effects on Mo-99 recovery and rejection of other fission products must be investigated. The inorganic absorbent might make a good waste form, but the regulatory issues will have to be overcome and it may involve significant additional cost if this material must be discarded as TRU waste.

Table 8. Combined Material Balance for Actinides.

	Feed	Raffinate	1.9 BV Acid Wash	Acid Wash	Water Wash	Eluate	Titania
Volume, mL	383	383	15	77	80	156	9.808 g
Sample ID	20286	20287/8	20289	20290/1	20292/3	20294/5	20896
U, g	67	78	1.8	0.06	0.003	0.0004	0.023
Pu, ug	214	16	0.23	0.39	0.044	-	197
Np, ug	444	477	11.5	1.4	0.8	-	7
Pa-233, uCi	0.31						0.083
Pa-234m, uCi	22						3.3
Th-234, uCi	22						2.8
U, %	100%	116%	2.7%	0.09%	0.005%	0.001%	0.03%
Pu, %	100%	7%	0.1%	0.18%	0.02%		92%
Np, %	100%	107%	2.6%	0.32%	0.18%		2%
Pa-233 %	100%						27%
Pa-234m, %	100%						15%
Th-234 %	100%						12%

*Values for Pa and Th from solution analyses are not decay corrected and are not included.
Feed activity for Pa and Th calculated from U and Np measurements assuming secular equilibrium.
Activity for Pa and Th measured on titania absorbent, and decay corrected to date of separation.
Values in grey are mda values.
Radiochemical analyses were not performed on elution samples due to the high pH.
Material Balance Closure: U -19%, Pu +0.2%, Np -12%.

3.5 Process Application:

The thrust of this work was to determine the amounts of U, Pu and Np that might be in the liquid waste streams from the acid and water washes. The magnitude of the amount of U and Np that goes to the waste streams will depend on how the initial volume of the acid wash is handled. In this lab experiment, the initial 1.9 BV of acid wash contained residual raffinate which amounted to ~ 3% of the mass of non-absorbing species including U and Np at approximately half the raffinate concentration. The recycle of this initial

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[7] A. J. Youker, M. A. Brown, T.A. Heltemes, G. F. Vandegrift, "Controlling Pu behavior on Titania: Implications for LEU Fission-Based Mo-99 Production", Industrial and Engineering Chemistry Research, 2017, 56, 11612-7.

acid wash solution in the process would greatly reduce the amount of U, Np-239 and Pu-239 which goes in the waste stream. However, recycle tends to dilute the U concentration in the process which is also reduced by the fission of U-235. The discussion of these issues is beyond the intended scope of this report. In this work the volume of feed solution was limited to ~ 50 BV whereas a production process might use ~ 200 BV of feed solution. Thus, all values in this report that are scaled as the feed mass may be high by as much as a factor of four when a full 200 BV of feed is used.

Once the initial residual raffinate was removed, the remainder of the wash solutions contained 0.09% of the U, 0.2% of the Pu and < 0.7% of the Np in the feed solution. Assuming that the initial acid wash is recycled similarly, the combined wash solutions can be expected to contain 0.4 g U/L, 2.7 µg Pu/L and < 14 µg Np/L. Due to the relatively short half-life of Np-239 (2.36 days), 95% of the Np-239 decays to Pu-239 within one week. Therefore, depending on when the wash solutions are treated, there is a tradeoff between the amount of Np-239 and Pu-239 remaining.

On the other extreme, if the residual raffinate in the initial acid wash were to be discarded to waste, the combined wash solutions would be 11 g U/L, 3.8 µg Pu/L, and ~ 80 µg Np/L. Again, if the wash solutions were to be treated more than two weeks later, then virtually all the Np-239 will have decayed to Pu-239.

If adjustments are made to keep the Pu from being retained by the titania, then additional amounts of Pu will be present in the waste solutions. Several different approaches may be taken to reduce the retention of Pu on the titania. ANL[7] has performed work on the use of increased sulfuric acid concentration in the acid wash or the reduction in the wash temperature as reducing the retention of the Pu on the titania. Based on the observed retention of Pa and Th isotopes in the current work, the use of a reductant or complexant has been suggested, but the effect on Mo-99, Np-239 recovery, and fission product rejection would require investigation. A key area to investigate is the speciation of Pu and Np under process concentrations and conditions.

4.0 Conclusions.

The goal of this work was to determine the amounts of U, Pu and Np that might be in the liquid waste streams created by the wash streams. The key question is how the initial acid wash volume is handled as this solution contains residual raffinate which amounted to ~ 3% of the mass of the feed solution in this experiment. If the initial 1.9 BV of acid wash were recycled as in this experiment then the combined wash solutions can be expected to contain 0.4 g U/L, 2.7 µg Pu/L, and < 14 µg Np/L. If on the other extreme the entire acid wash solution was discarded as waste, then the combined wash solutions can be expected to contain 11 g U/L, 3.8 µg Pu/L, and < 80 µg Np/L.

The titania retains only a very small fraction of the U (0.03% or 2.3 mg U/g titania). It cannot be concluded from the data if the titania is saturated with U as the analytical uncertainties are too large. Less mass but a higher fraction of the total Np was retained by the titania (~ 2% or 0.7 µg Np/g titania). As has been reported elsewhere,[7] a large fraction of the Pu fed to the titania bed will be retained (92% or 20 µg Pu/g titania).

5.0 Recommendations.

The primary recommendation is to evaluate these results with the overall waste handling strategy. The titania absorbent retains sufficient Pu to be concerned that the waste will likely be TRU waste. It is possible to wash the Pu out of the titania after the Mo-99 has been recovered at the cost of additional volume of waste and processing time, but the Pu would still need a disposition path. Alternatively, it would be possible to manipulate the Pu prior to loading on the absorbent, but the effect on both the Mo-99 recovery and the behavior of the other fission products will have to be considered. The use of a reductant or complexant (such as hydroxylamine sulfate (HAS), diethylenetriaminepentaacetic acid (DTPA), or aceto-hydroxamic acid (AHA)) to keep the Pu from being absorbed onto the titania may be possible, but the opportunity for negative effects on either Mo-99 recovery or the behavior of other fission products (or Np) is significant. Also, any organic complexant/reductant must have a sufficient lifetime in the highly radioactive dose field to accomplish its purpose, and the degradation products must be compatible with the process during recycling. If the titania were reused, that could reduce the cost impact, but the generation of some TRU waste would be hard to avoid. Additional understanding on the speciation of Pu (and Np) under process conditions could prove enlightening on the mechanism which controls such a high retention of Pu by the titania.

A secondary recommendation is to consider the use of a fiber optic flow cell to control the switch between high U-containing raffinate and flush/wash. Fiber optic components should be tolerant of the radiation dose and, when outfitted with a modern colorimeter or UV/vis spectrometer, could allow precise control between the U recycle stream and the non-U containing solution.

Appendix A.

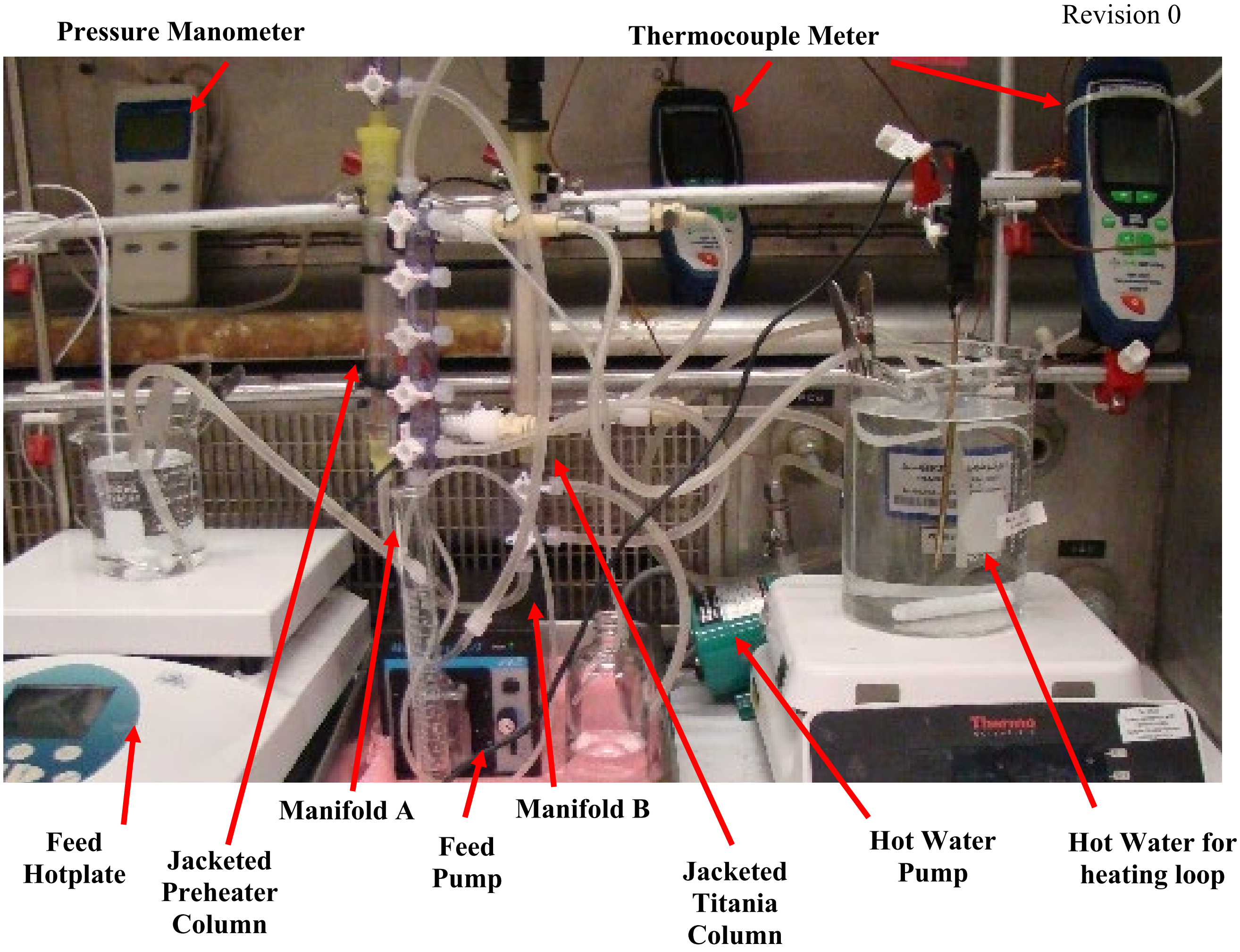

Figure 5. Close up of Experimental Apparatus.

This appendix shows the full experimental setup (Figure 2) with detailed configurations for the valve positions for each phase of the column operation. Valve positions for Flushing during up-flow operation (Figure 6), Up-flow loading/washing (Figure 7), Downflow flushing (Figure 8) and Downflow elution (Figure 9) are shown in the following illustrations. Valve manifolds are labeled A and B with individual valves numbered from the top to bottom of the manifold (A1, A2 or B1, B2, B3, B4, B5). These polycarbonate manifold fittings with luer lock connections were purchased from the Cole Parmer (see part numbers EW-06464-83, -85, -87 or similar).

Figure 6. Valve Configuration for Flush/Rinse during Up-flow operation.

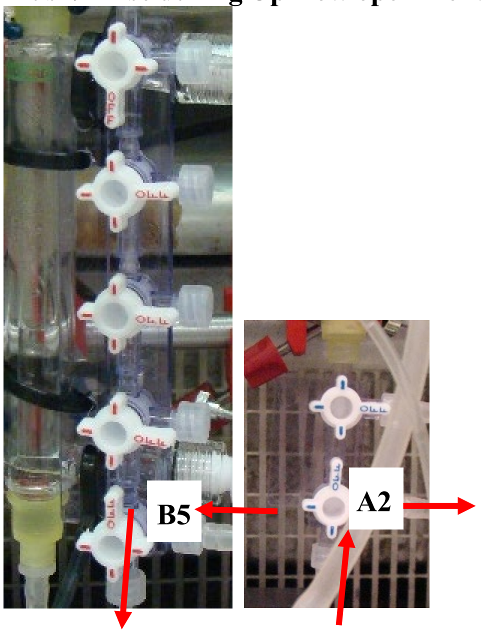

Figure 7. Valve Configuration for Loading/Washing Up-flow.

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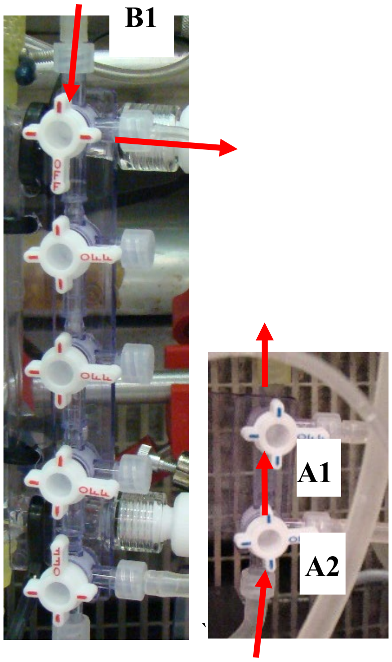

Figure 8. Valve Configuration for Flush/Rinse feed line during Downflow operation.

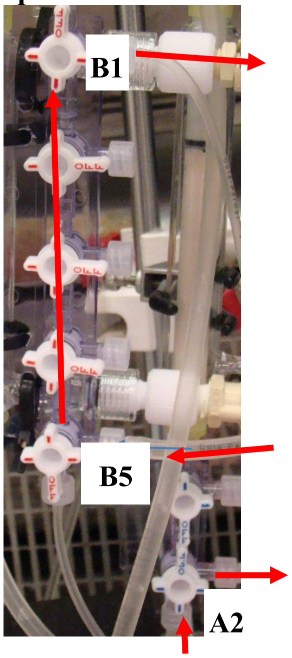

Figure 9. Valve Configuration for Elution Downflow Operation.

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