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Dual Column Tracer Experimental Results

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Dual Column Tracer Experimental Results

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1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting Morgridge Institute for Research (MIR) in their efforts to develop SHINE (Subcritical Hybrid Intense Neutron Emitter), which is an accelerator-driven process that will use a uranyl-sulfate solution for the production of Mo-99. An integral part of the process is the development of a dual column for the recovery of Mo-99 from an irradiated target solution. Argonne has collected data from batch studies and small-scale column experiments to input into VERSE (Versatile Reaction Separation), which was developed by Dr. Linda Wang at Purdue University, to design large-scale separation processes using data obtained on a much smaller scale. Plant-scale column designs have been generated for the initial Mo-recovery column and the concentration column, which has been added to reduce strip volume prior to entry into the LEU-Modified Cintichem purification process. Direct downscale column experiments have been performed using 1 g of linac-irradiated DU (depleted uranium) foils as a spike for a uranyl-sulfate solution. The strip solution from the initial recovery column was used as a spike for a pH 2 sodium nitrate solution, which served as the feed solution for the concentration column.

2 EXPERIMENT

2.1 SORBENTS

A 110-micron particle size pure titania sorbent with 60-Å pores was used for the initial recovery column, which was a 0.66 cm ID (internal diameter) $\times$ 5 cm L (length) column. Approximately 152 mL of a 130 g-U/L uranyl-sulfate solution with a stable Mo concentration of 2.4×10^{-3} mM and 1 g of dissolved linac-irradiated foils was passed through the column at a flow rate of 1.4 mL/min. A 40-micron particle size pure titania sorbent with 60-Å pores was used for the concentration column, which was a 1 cm ID $\times$ 1.5 cm L column. The SHINE concentration column design was tested using the product solution from a downsized Mo-recovery column as a spike because a column small enough to handle 52 mL of solution could not be packed. Approximately 1470 mL of a pH 2 $NaNO_3$ solution containing 2.4×10^{-2} mM stable Mo spiked with 52 mL of strip solution generated from the initial recovery column was loaded onto the column at a flow rate of 24.5 mL/min. Mo was recovered after passing 20 CVs (column volumes) of 1 M NH_4OH heated to 70°C at a flow rate of 4 mL/min through the column.

2.2 FOIL DISSOLUTION

After cooling overnight, the foils were removed from the linac facility. The double-encapsulated Al-clad target was cut open and foils were removed. Three small irradiated-DU foils totaling 1 g of uranium were dissolved in nitric acid. The foils were dissolved in 20 mL of 6 M HNO_3 using a hot water bath and a condenser filled with ice and acetone. Dissolution took approximately 3 h because the nitric acid concentration was kept low to minimize the amount of nitrate left in solution. After dissolution, the uranyl-nitrate solution was brought to dryness to drive off nitrate. The solid uranium was re-dissolved in 250 mL of a 130 g-U/L uranyl-sulfate solution containing 2.4×10^{-3} mM stable Mo with a final pH of ~1. The final solution was used as the feed solution for the initial recovery column. It was passed through the 110-micron particle size titania column over a period of 2 h.

2.3 GAMMA COUNTING

Samples were counted at a distance using a Germanium detector. The U-237 content was very high due to the γ-n reaction on U-238, which makes it difficult to analyze fission products with lower energies. U-237 summation peaks make it difficult to accurately measure activities for certain fission products, so as a result, irradiation of low enriched uranium (LEU) solutions in the future will provide more meaningful sources of tracers planned for use in column experiments and clean-up studies using centrifugal contactors for the entire UREX process.

3 RESULTS AND DISCUSSION

3.1 INITIAL Mo RECOVERY COLUMN

Approximately 152 mL of a 130 g-U/L uranyl-sulfate solution was loaded onto a 0.66 cm ID × 5 cm L titania column in the up-flow direction at a flow rate of 1.3 mL/min. The column was subsequently washed with 10 CVs of 0.1 M H_2SO_4 in the up-flow direction, 5 CVs of H_2O in the up-flow direction, 30 CVs of 0.1 M NH_4OH heated to 70°C in the down-flow direction at 0.7 mL/min, and 5 CVs of H_2O in the up-flow direction. Approximately 260 μCi Mo-99 was produced during irradiation, and 87% Mo was recovered in the strip solution. Iodine was a major contaminant found in the Mo product. Table 1 shows the results for various isotopes produced. Errors associated with these results are ±10%, which is why some of the percentages found in each fraction exceed 100%. Results suggest that almost all of the Sr-91, Ru-103, Rh-105, Ce-141, Ce-143, Nd-147, and Pm-151 produced do not adsorb on titania and are found in the effluent and acid wash, which contains 1 CV of column effluent. SHINE can expect these fission products to be present in the target solution prior to clean-up. Isotopes that essentially remain adsorbed on the titania column after Mo-recovery include Nb, Zr, and Sb isotopes, and

TABLE 1 List of Isotope Activities with Decay Calculations Back to End of Irradiation (March 26, 2013, at 6:00 PM) and Isotopic Distributions after Initial Recovery Column

Isotope	Feed Activity (μCi)	Half-Life (h)	% in Effluent	% in Acid Wash	% in Water Wash #1	% in Strip	% in Water Wash #2	% Remaining on Column
Sr-91	1233.5	9.6	95.1	0.5	0.0	0.0	0.0	4.4
Nb-95	1.0	840.0	10.1	0.0	0.2	0.0	0.1	89.6
Zr-95	9.5	1536.0	3.3	0.1	0.0	0.0	0.0	96.5
Nb-97	40.1	1.2	3.4	0.1	0.0	0.1	0.0	96.3
Zr-97	759.0	16.8	1.7	0.3	0.0	0.4	0.0	97.6
Mo-99	260.9	66.6	0.0	0.0	0.0	87.0	0.2	12.8
Ru-103	3.7	936.0	100.4	3.1	0.6	0.0	0.0	0.0
Rh-105	231.0	4.6	100.2	1.9	0.3	1.8	0.0	0.0
Sb-127	27.4	93.6	3.8	0.3	0.0	13.7	0.1	82.1
Te-131m	89.5	31.2	2.1	3.2	0.6	26.5	0.1	67.5
I-131	25.3	192.0	1.2	0.4	0.2	97.0	0.1	1.1
I-132	101.8	2.4	0.9	1.6	0.5	28.2	0.1	68.7
Te-132	173.3	76.8	2.8	1.9	1.0	53.0	0.1	41.2
I-133	495.0	20.4	0.2	0.0	0.0	109.9	0.1	0.0
Ba-140	64.1	312.0	99.9	1.4	0.1	0.6	0.0	0.0
La-140	37.1	40.8	74.4	1.2	0.1	0.9	0.0	23.5
Ce-141	17.6	768.0	106.6	0.9	0.0	0.0	0.0	0.0
Ce-143	346.6	33.6	107.5	1.0	0.0	0.3	0.0	0.0
Nd-147	18.2	264.0	96.4	1.0	0.0	2.9	0.0	0.0
Pm-151	74.2	288.0	100.8	1.0	0.0	0.0	0.0	0.0

40–60% of Te isotopes remain bound to the titania column. Nearly all of the I-131 and I-133 co-eluted with the Mo-product with an additional 30% I-132. Not all of the I-132 eluted with other iodine isotopes in the Mo-product solution because it is a decay product of Te-132, and ~40% Te-132 remained on the column post Mo-recovery.

Results from the irradiated DU foil experiments suggest that iodine will be a major contaminant in the Mo-product stream. However, additional steps have been added to the LEU-Modified Cintichem process to handle large amounts of iodine. The first step includes an additional contact step with 1 M HNO_3 to promote formation of volatile iodine, which can be trapped, and an isotopic exchange step to convert any iodate or iodine to iodide. These results contradict previous Van de Graaff iodine speciation results, which showed that more than 95% of the iodine was present as iodide after irradiation. Nonetheless, the mini-SHINE experiments will provide vital data under conditions much more representative of the SHINE operation regarding iodine behavior during irradiation, cooling, Mo separation, and Mo recovery.

3.2 CONCENTRATION COLUMN

After a 2-h Mo loading process onto a S110 packed column, and then stripping Mo from the column with 0.1 M NaOH at 70°C, the Mo-product-solution from the initial recovery column is then reduced using a concentration column. Before loading onto the concentration column, the Mo product is acidified, resulting in approximately 24 L of a solution containing 0.1 M $NaNO_3$ and 2.4×10^{-2} mM Mo at pH 2. The column design for concentrating the Mo product is a 4 cm ID × 1.5 cm L column utilizing S40 sorbent.[1] The column was designed to load the product in 60 min at 80°C, resulting in a flow rate of 392 mL/min and velocity of 31.2 cm/min (Stepinski et al. 2012). The details of the concentration column process design are outlined in Table 2. After loading, the column is washed with 10 CVs of 0.01 M HNO_3, followed by 10 CVs of water, and stripped with 1 M NH_4OH at 70°C.

The column process utilized for the concentration-column experiment was a direct scale-down of the design summarized in Table 2. For the lab-scale experiment, a 1 cm ID × 1.5 cm L S40 column was loaded at 31.2 cm/min at 80°C. Details of the lab-scale column process are summarized in Table 3. The feed solution (1470 mL) utilized in this experiment had a composition of 0.1 M $NaNO_3$, 0.0064 M HNO_3 (pH 2.2), and 2.4×10^{-2} mM Mo. The feed

TABLE 2 Concentration Column Design for Loading 99.9% of Mo in 60 min, Utilizing S40 Sorbent

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/Sorbent Mass (Ci/g)	Strip Volume (mL)
4	31.20	1.11	1.5	19	24	0.32	163.45	301.6

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[1] ZirChrom Separations, Inc.

TABLE 3 Direct Scale-Down Concentration Column Design Concentration Column Experiment with the Linac Irradiated Target

Column ID	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Flow Rate (mL/min)	Feed Volume (mL)
1	31.20	1.11	1.50	1.18	1.48	0.32	24.50	1470

solution was loaded using the ÄKTA LC (GE Healthcare Life Sciences) in 60 min at a rate of 24.5 mL/min. Following loading, the column was washed with 11.8 mL (10 BV) of 0.01 M HNO_3 and H_2O at 31.2 cm/min (24.5 mL/min). The column was stripped with 3×14.3 mL (3×12 CV) of 1 M NH_4OH at 70°C at a rate of 5 cm/min (4 mL/min).

3.3 CONCENTRATION COLUMN RESULTS

The gamma counting results indicate that Mo-99 was not present in the effluent or the acid and water washes, suggesting that all the Mo was loaded on the column. The results indicate that 88.5% ± 10% of Mo was stripped from the column. Mo-99 recovery ranged from 103.6% to 87.1% for three different sample counts over a period of 72 h. However, the dead time on strip 1, was >80% for all counts and could affect the results. The results for samples counted on March 19, 2013, 8:00 PM are summarized in Table 4.

Partitioning of actinides and fission products between process streams was determined using gamma counting (Table 5). Iodine partitioned in the strips, along with the Mo product

TABLE 4 Mo Recovery Results, Counted on March 19, 2013, 8:00 PM

Stream	Volume (BV)	Mo-99 (µCi)	Mo-99 (%)
Feed		1.91E+02	
Eluent		ND[a]	
Wash 0.01 M HNO_3	10	ND	
Wash, water	10	ND	
Strip, fraction 1	12	1.56E+02	81.6
Strip, fraction 2	12	1.04E+01	5.5
Strip, fraction 3	12	2.83E+00	1.5
Mo recovered (strips)	36	1.69E+02	88.5

[a]   ND = "not detected."

TABLE 5 Partitioning of U and Fission Products between Concentration Column Process Streams

Isotope	Half-life	Feed	Eluent		Acid Wash		Water Wash		Strip 1		Strip 2		Strip 3		Total	
	days	µCi	µCi	%	µCi	%	µCi	%	µCi	%	µCi	%	µCi	%	µCi	%
I-133	0.9	4.69E+02	8.82E+00	1.9	8.32E-02	0.0	1.68E-02	0.0	1.13E+02	24.1	7.74E+01	16.5	2.83E+01	6.0	2.28E+02	48.6
Sb-127	3.9	3.48E+00	ND		ND		ND		1.50E-01	4.3	1.23E-01	3.5	5.73E-02	1.6	3.30E-01	9.5
Te-131m	1.3	4.44E+01	5.20E+00	11.7	2.37E-02	0.1	2.03E-02	0.0	1.18E+00	2.7	1.31E+00	3.0	4.39E-01	1.0	8.18E+00	18.4
Te-132	3.2	7.70E+01	4.40E+00	5.7	5.27E-02	0.1	2.04E-02	0.0	3.27E+00	4.3	3.17E+00	4.1	1.57E+00	2.0	1.25E+01	16.2
U-237	6.8	ND	1.47E+00		3.00E-02		1.18E-02		ND		ND		ND		1.51E+00	
Zr-97	0.70	3.41E+00	1.53E+00	44.8	6.96E-03	0.2	ND		ND		1.64E-01	4.8	0.00E+00	0.0	1.70E+00	49.9

(~50%) and the remaining iodine, was either lost to the vapor phase or left on the sorbent. Approximately 10% of the antimony was found in the Mo product, and the rest likely remained on the sorbent. Similarly, approximately 10% of the tellurium was found in the Mo product, and >80% likely remained on the sorbent. A large fraction of the zirconium (~45%) was found in the effluent, and ~50% likely remained on the sorbent. U-237 was detected in eluent and washes only; none was detected in the strip fractions.

I-131, I-132, Nb-97, and Xe-135 were detected in the process streams at $t = 64$ h. Their activities were not corrected to $t = 0$ since they are growing in from their parent radionuclides. Only I-131, I-132, and Xe-135 were detected in the Mo product stream; their activities are presented as µCi/mCi Mo-99 at $t = 64$ h (Table 6).

TABLE 6 Radionuclides Detected in the Product Stream at $t = 64$ h

Isotope	Half-life (days)	Parent	Half-life (days)	Total Activity (µCi) at T-count, 64 h	µCi/mCi Mo-99
I-131	8.02	Te-131m	1.25	1.27E+01	76
I-132	0.1	Te-132	3.25	4.05E+00	24
Nb-97	0.05	Zr-97	0.7	ND[a]	
Xe-135	0.38	I-135	0.28	1.91E+01	115

[a]   ND = "not detected."

4 CONCLUSIONS

Results from the dual-column Mo separation and recovery process using linac-irradiated DU foils as a spike show that 87% ± 10% Mo was recovered from the initial recovery column. Iodine was the major contaminant found in the Mo product, and about 15% Sb and 30% Te were found as well. Modifications have been made to the LEU-Modified Cintichem purification process to remove the iodine from the Mo product, and the current process can already handle removal of Sb and Te. The mini-SHINE experiments will provide data that are more representative of the SHINE system, where fission products are generated in solution rather than in a foil; however, these foil experiments suggest that iodine contamination in the Mo product is highly likely.

Verification studies for a 4 cm ID × 1.5 cm L S40 99.9% Mo loading column design for concentration of the Mo product indicate that the all of the Mo in the feed solution was loaded on the column. Approximately 88.5% ± 10% Mo was recovered from the concentration column. However, the dead time for strip 1 was >80%, which could have affected the results. Partitioning of U and fission products between different process streams indicates that a fraction of Te, Sb, and Zr partitions in the Mo product stream, and the majority remains on the sorbent. Approximately 50% of the iodine in feed was found in the Mo product, and the rest was either lost to the vapor phase or left on the sorbent. Uranium was detected in effluent and washes only; none was detected in the Mo product. Overall, this column design achieved excellent loading and provides an additional purification step for Mo product. Stripping results call for additional verification and optimization. Improvements can be made based on the results that we have obtained to date, such as minimizing the dead volume in the system and decreasing the amount of U-237 to reduce gamma counting errors.

5 REFERENCE

Stepinski, D.C., A.J. Youker, and G.F. Vandegrift, 2012, *Plant-scale Concentration Column Designs for SHINE Target Solution*, Argonne National Laboratory, September.