

Verification of Column Design for Recovery of Mo from Low-Enriched Uranium Target using Irradiated Target Tracer Solution

Chemical Sciences and Engineering Division

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VERIFICATION OF COLUMN DESIGN FOR RECOVERY OF Mo FROM LOW-ENRICHED URANIUM TARGET USING IRRADIATED TARGET TRACER SOLUTION

1 INTRODUCTION

The Conversion Program of the Global Threat Reduction Initiative (GTRI) is developing technology necessary to enable the conversion of civilian facilities using high-enriched uranium (HEU) to low-enriched uranium (LEU) for fuels and targets. The conversion of conventional HEU dispersion targets to LEU for the production of ^{99}Mo requires approximately five times the uranium to maintain the ^{99}Mo yield per target. Under GTRI, Argonne is developing two front-end options to the current processes to allow the use of LEU-foil targets. In both processes, the aim is to produce a product after the front end that will be compatible with current purification operations and that will, with the same number of targets irradiated, provide the same or higher yield of ^{99}Mo at the end of processing. The goal of the front-end process is to deliver a product solution that is of the same or higher Mo purity than the current solution and is of equal or better compatibility with current purification processes.

The two front-end processes under development as part of this project are: (1) the dissolution of irradiated LEU foil (up to 250 g in a single batch) and nickel fission recoil barrier in nitric acid at ambient pressure, followed by Mo recovery on a titania column, and (2) the electrochemical dissolution of LEU foil in a series of steps that produces an alkaline (basic) solution feed for ^{99}Mo purification. This report describes results from recovery of Mo on a 3.5 x 5 cm column containing the Sachtopore titania sorbent S40. The process is designed for a feed solution that contains ~7 mM Mo and ~450 g-U/L, and the nitric acid concentration after dissolution is ~1 M. The volume of solution is assumed to be 500 mL, and the pressure drop (ΔP) constraint is 0.8 atm based on use of vacuum/gravity fluid-transfer system.

The 3.5 x 5 cm column was tested experimentally at 60 °C using a 1 M H^+ solution with 450 g-U/L, 7 mM Mo, and tracer levels of Mo-99 (Stepinski et al., 2012). Loading velocity and column length were kept constant at 2.60 cm/min and 5 cm, respectively, while the column ID and solution volume were reduced to 1 cm and 40.8 mL, respectively. Recovery of Mo was achieved with 0.1 M NaOH by counter-current stripping at 3 cm/min and 25 °C. Also, $99.4 \pm 3\%$ of Mo was loaded on the column, and $99.9 \pm 3\%$ was recovered in strip fractions #2 and #3, six bed volumes (BV) each. The Mo-99 activity in the nitric acid wash (8 BV) and water wash (3 BV) fractions and strip fraction #1 (4 BV) and #4 (14 BV) was below detectable levels.

Based on the results, a Mo recovery process was designed by using a 3.5 x 5 cm column with S40 sorbent (Table 1). In this process, 500 mL of solution is loaded at 60 °C in 20 min at 25 mL/min. The loading is followed by washing with 1 M HNO_3 and H_2O at 48.1 mL/min and 25 °C. The Mo is stripped at 25 °C with 770 mL of 0.1 M NaOH at a flow rate of 28.9 mL/min for 26.7 min. The total process time is 58 min. The calculated pressure drops for the loading, washing, and strip are 0.35, 0.43, and 0.26 atm, respectively.

TABLE 1 Process for Recovery of Mo from LEU Target Solution Using a 3.5 x 5 cm Column and S40 Sorbent

Step	Loading Time (min)	Volume (mL)	Flow Rate (mL/min)	Loading Velocity (cm/min)	Solution Volume (BV)
Load	20	500	25.0	2.60	
Wash, 1 M HNO ₃	8	385	48.1	5	8
Wash, H ₂ O	3	144	48.1	5	3
Strip, 0.1 M NaOH	26.7	770	28.9	3	16

This report describes testing of the 3.5 x 5 cm column design with S40 sorbent and ~0.5 L of 1 M H⁺ solution containing 450 g/L uranyl nitrate and tracer irradiated target. The partitioning of fission products between process streams was monitored by gamma counting, and Mo yield under these conditions was determined.

2 RESULTS AND DISCUSSION

2.1 DESIGN OF COLUMN PROCESS CONDITIONS FOR ALTERNATIVE TARGET SOLUTION VOLUMES

In a previous report (Stepinski et al., 2012), column designs for Sachtopore sorbent S40 with 40- μm particle size, were determined using isotherms parameters for S80 sorbent. In this report we have determined Langmuir isotherm parameters for S40 sorbent and using VERSE simulation program (Purdue University) have estimated intraparticle diffusivity using the updated Langmuir isotherm parameters. Langmuir isotherm parameters for uptake of Mo from 450 g-U/L solution, 1 M H^+ solution on S40 sorbent were obtained using batch equilibrium data for samples equilibrated 24 h at 60 °C as described previously (Stepinski et al., 2012). Langmuir isotherm parameters were fitted using Origin 9.1 and are $a = 347$, $b = 0.5 \text{ mM}^{-1}$ (Figure 1).

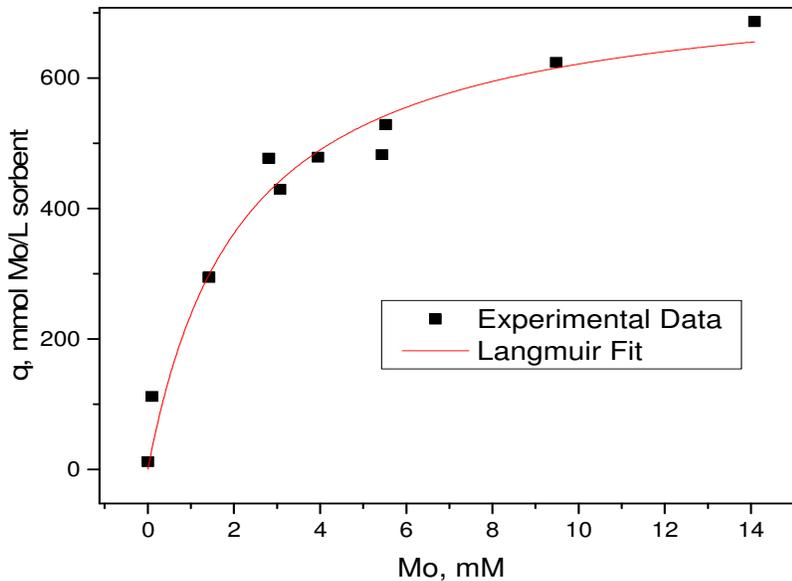


FIGURE 1 Langmuir Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Uptake of Mo on S40 Sorbent

To estimate intraparticle diffusivity using the updated Langmuir isotherm parameters, the results of a breakthrough experiment obtained by loading 150 mL of 450 g-U/L, 6.5 mM Mo and 1 M H^+ solution onto 6.6 x 35 mm S40 column at 3 cm/min at 60 °C, were simulated with VERSE. For the VERSE simulations the axial dispersion coefficient, E_b , was estimated with the Chung and Wen (1968) correlation. The mass transfer coefficient, k_f , was estimated with the Wilson and Geankoplis (1966) correlation. The Brownian diffusivity (D_∞) of HMoO_4^- in aqueous solution at 25 °C used in the simulations was 8.3 cm^2/min (Marcus, 1997). The Stokes-Einstein equation was then used to correct the D_∞ for solution viscosity and temperature effects. At 60 °C, the viscosity of 450 g-U/L $\text{UO}_2(\text{NO}_3)_2$ and 1 M HNO_3 solution was calculated to be 1.40 cp, using a correlation listed in HW-57386 (Krigens, 1968). Therefore, at 60 °C, $D_{\infty, \text{Mo}}$ in 450 g-U/L $\text{UO}_2(\text{NO}_3)_2$ and 1 M HNO_3 solution was calculated to be $5.51 \times 10^{-4} \text{ cm}^2/\text{min}$. The intraparticle

diffusivity was estimated by comparing the experimental Mo breakthrough curve obtained by loading 150 mL of 450 g-U/L, 6.5 mM Mo and 1 M H⁺ solution onto 6.6 x 35 mm S40 column at 3 cm/min at 60 °C, with VERSE simulations. In 450 g-U/L UO₂(NO₃)₂ and 1 M HNO₃ solution, the intraparticle diffusivities of Mo on S40, using $D_{\infty}/D_p = 70$, was estimated to be $D_p = 7.87 \times 10^{-6} \text{ cm}^2/\text{min}$ (Figure 2).

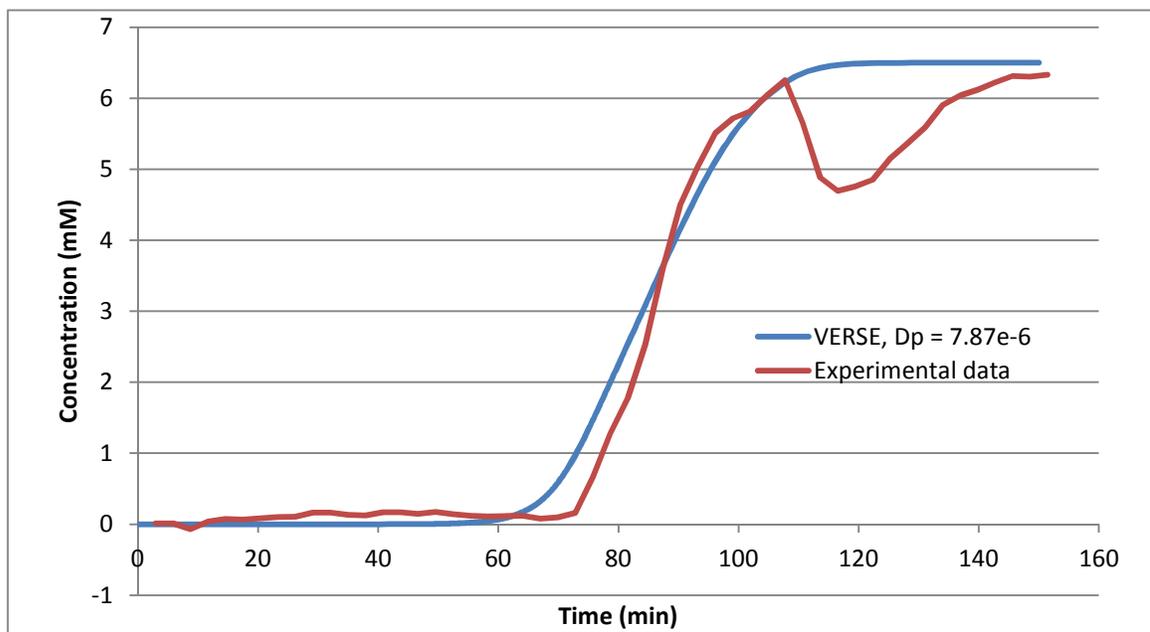


FIGURE 2 Estimation of Mo D_p for S40 Sorbent from Breakthrough Experiment

To enable processing of a target solution obtained from dissolving 225 g uranium when the volume of solution varies between 0.5 L and 1 L, we calculated alternative process conditions for loading Mo on a 3.5 x 5 cm column. Table 2 gives the solution properties, mass transfer parameters, and intraparticle diffusivity (D_p) values determined with VERSE simulations for various uranium solutions. The viscosities of the uranyl nitrate solution at pH 0 were calculated with the correlation listed in HW-57386 (Krigens, 1968). The Stokes-Einstein equation was then used to correct the D_{∞} for solution viscosity and temperature effects. The Mo intraparticle diffusivities for S40 sorbent were calculated assuming $D_{\infty}/D_p = 70$. VERSE was then used to calculate the mass transfer zone (MTZ). The results, shown in Table 2, indicate that larger solution volumes can be loaded at the same flow rate of 25 mL/min, since the combined effects of increased solution volume and higher intraparticle diffusivity have minimal effect on the MTZ.

2.2 COLUMN DESIGN VERIFICATION WITH TRACER IRRADIATED TARGET SOLUTION

The feed was prepared by dissolving irradiated LEU foil along with 250 g uranium in ambient pressure dissolver (Jerden et al., 2014). Stable Mo, Na₂MoO₄, was added to the feed to increase the concentration of Mo to 5.4 mM, which is reflective of the amount of Mo in a fully irradiated target. The ~650 mL (899 g, ~350 g-U/L) of irradiated target solution was loaded on a

3.5 x 5 cm column containing 63 g of S40 sorbent at 25 mL/min and 60 °C. The loading was followed by a ~ 260 mL 1 M HNO₃ wash and 75 mL H₂O wash. The Mo was stripped from the column with 0.1 M NaOH at 5 cm/min and 25 °C. The strip was divided into four fractions containing 224, 292, 293, and 120 mL of solution, respectively.

Tables 3 and 4 show partitioning of uranium and fission products between process streams. All activities were decay corrected to the start of Mo recovery process (on 5/1/2014 at 8 am). Table 3 shows the activities (μCi) of the irradiated solution components in process streams, and Table 4 indicates percent partitioning normalized to 100%. The counting results indicate that 99.3% Mo was loaded on the column. Subsequently, 28.3% of Mo was in strip fraction #2, and 70.1% Mo in strip fraction #3 (98.4% Mo recovery). Strip fraction #1 and #4 contained 1% Mo. The Mo activities in the nitric acid wash and water wash fraction #1 were below detection limits.

Furthermore, Tables 3 and 4 indicate that the majority of radionuclides, including uranium, iodine, alkaline metals (Ba and Sr), transition metals (Cd, Rh, and Ru), and lanthanides (Ce and Nd) partition into the eluent and nitric acid wash streams. Only Sb was found in the Mo

TABLE 2 Design of Column Process Conditions for Alternative Target Solution Volumes

U conc. (gU/L)	Volume (mL)	Mo (mM)	T (°C)	viscosity (cp)	density (g/mL)	D _{Mo} (cm ² /min)	D _p (cm ² /min)	ID (cm)	flowrate (mL/min)	time (min)	MTZ (cm)	U (M)	NO ₃ (M)	L (cm)
450	500	7	60	1.49	1.6204	5.51E-04	7.87E-06	3.5	25	20	1.90	1.89	4.78	5
409	550	6.4	60	1.34	1.5650	6.13E-04	8.75E-06	3.5	25	22	1.88	1.72	4.44	5
375	600	5.8	60	1.22	1.5189	6.73E-04	9.61E-06	3.5	25	24	1.87	1.58	4.15	5
346	650	5.4	60	1.13	1.4798	7.26E-04	1.04E-05	3.5	25	26	1.87	1.45	3.91	5
321	700	5.0	60	1.06	1.4464	7.74E-04	1.11E-05	3.5	25	28	1.85	1.35	3.70	5
300	750	4.7	60	1	1.4174	8.21E-04	1.17E-05	3.5	25	30	1.87	1.26	3.52	5
281	800	4.4	60	0.95	1.3920	8.64E-04	1.23E-05	3.5	25	32	1.88	1.18	3.36	5
265	850	4.1	60	0.92	1.3696	8.92E-04	1.27E-05	3.5	25	34	1.90	1.11	3.22	5
250	900	3.9	60	0.88	1.3497	9.33E-04	1.33E-05	3.5	25	36	1.92	1.05	3.10	5
237	950	3.7	60	0.85	1.3319	9.66E-04	1.38E-05	3.5	25	38	1.93	1.00	2.99	5
225	1000	3.5	60	0.83	1.3158	9.89E-04	1.41E-05	3.5	25	40	1.95	0.95	2.89	5

TABLE 3 Partitioning of Irradiated Target Solution Components between Process Streams

Isotope	Half-life (days)	Feed (μCi)	Eluent (μCi)	1 M HNO_3 Wash (μCi)	H_2O Wash (μCi)	Strip fraction 1 (μCi)	Strip fraction 2 (μCi)	Strip fraction 3 (μCi)	Strip fraction 4 (μCi)	Sorbent (μCi)	Mass Balance (%)
Ba-140	12.79	1.1E+01	8.3E+00	1.1E+00	-	-	-	-	-	-	8.5E+01
Ce-141	32.28	3.3E+00	2.7E+00	3.7E-01	-	-	-	-	-	-	9.1E+01
Ce-143	1.40	3.3E+01	2.5E+01	3.2E+00	-	-	-	-	-	-	8.7E+01
I-133	0.87	3.3E+01	2.5E+01	2.9E+00	2.8E-03	1.1E-02	1.0E-01	1.5E-01	-	-	8.7E+01
I-135	0.27	7.7E+00	8.3E+00	7.0E-01	-	-	-	-	-	-	1.2E+02
Mo-99	2.74	2.4E+01	1.4E-01	-	-	4.3E-02	6.2E+00	1.5E+01	1.7E-01	-	9.1E+01
Nd-147	11.06	5.1E+00	4.5E+00	9.5E-01	-	-	9.2E-03	-	-	-	1.1E+02
Pm-151	1.18	2.2E+00	1.8E+00	2.4E-01	-	-	-	-	-	-	9.1E+01
Rh-105	1.47	7.5E+00	6.4E+00	7.0E-01	-	-	-	-	-	-	9.5E+01
Ru-103	39.35	1.6E+00	1.2E+00	1.6E-01	1.5E-04	-	4.0E-03	3.5E-03	7.4E-04	-	8.4E+01
Sb-127	3.85	6.8E-01	8.8E-02	1.2E-01	-	3.2E-01	-	-	-	8.8E-03	8.0E+01
Sm-153	1.93	1.0E+01	8.6E+00	1.0E+00	2.4E-03	3.4E-03	-	-	-	-	9.4E+01
Sr-91	0.40	1.4E+01	1.3E+01	1.6E+00	5.7E-04	-	-	-	-	-	1.0E+02
Te-132	3.25	1.8E+01	1.8E+00	2.7E-01	5.7E-04	9.7E-03	5.9E-03	5.8E-03	1.0E-02	1.6E-01	1.3E+01
U-237	6.75	1.5E+01	8.7E+00	1.4E+00	-	-	-	-	-	-	6.9E+01
Y-93	0.46	2.6E+01	2.8E+01	0.0E+00	-	-	-	-	-	-	1.1E+02
Zr-95	64.40	2.1E+00	1.9E+00	-	-	4.8E-03	3.6E-03	1.6E-03	-	2.7E-02	9.2E+01

product stream (~ 60% in strip fraction #1). Other irradiated target components such as Ru, I, Te, and Zr partitioned <1% into the Mo strip fractions #1-3. Fractions of Sb (1.6%), Te (7.1%), and Zr (1.4%) remained on the sorbent.

Table 5 shows the activities of I-131 and La-140, which are growing in from their respective parents, Te-131m and Ba-140; therefore, their activities are not decay-corrected. The activities of these isotopes were determined ~ 24 h after the column experiment. As with other irradiated solution components, Te and Ba and their daughter isotopes mainly partition in the eluent and acid-wash process streams.

TABLE 4 Percent Partitioning of Irradiated Target Solution Components Normalized to 100%

Isotope	Half-life (days)	Eluent (%)	1 M HNO ₃ Wash (%)	H ₂ O Wash (%)	Strip fraction 1 (%)	Strip fraction 2 (%)	Strip fraction 3 (%)	Strip fraction 4 (%)	Sorbent (%)	Mass Balance (%)
Ba-140	12.79	88.2	11.8	-	-	-	-	-	-	85.1
Ce-141	32.28	87.9	12.1	-	-	-	-	-	-	91.4
Ce-143	1.404	88.8	11.2	-	-	-	-	-	-	86.9
I-133	0.867083	89.0	10.1	0.0	0.0	0.4	0.5	-	-	87.3
I-135	0.274167	92.2	7.8	-	-	-	-	-	-	116.0
Mo-99	2.743056	0.7	-	-	0.2	28.3	70.1	0.8	-	91.3
Nd-147	11.06	82.4	17.5	-	-	0.2	-	-	-	106.3
Pm-151	1.18	88.2	11.8	-	-	-	-	-	-	91.3
Rh-105	1.473333	90.2	9.8	-	-	-	-	-	-	95.1
Ru-103	39.35	88.0	11.4	0.0	-	0.3	0.3	0.1	-	84.1
Sb-127	3.85	16.3	22.5	-	59.5	-	-	-	1.6	79.7
Sm-153	1.9285	89.2	10.7	0.0	0.0	-	-	-	-	94.4
Sr-91	0.400417	89.2	10.8	0.0	-	-	-	-	-	103.0
Te-132	3.246	79.5	11.9	0.0	0.4	0.3	0.3	0.5	7.1	12.8
U-237	6.75	86.2	13.8	-	-	-	-	-	-	69.4
Y-93	0.455417	100.0	0.0	-	-	-	-	-	-	110.0
Zr-95	64.4	98.1	-	-	0.3	0.2	0.1	-	1.4	91.8

TABLE 5 Partitioning of Decay Products between Process Streams

Isotope	Half-life (days)	Parent	Half-life (days)	Total Activity, (μCi)									Mass Balance (%)	Analysis date
				Feed	Eluent	1 M HNO ₃ Wash	H ₂ O Wash	Strip fraction 1	Strip fraction 2	Strip fraction 3	Strip fraction 4	Sorbent		
I-131	8.02	Te-131m	1.25	4.2E+00	2.9E+00	3.3E-01	ND	2.2E-03	BD	BD	BD	6.3E-03	78.3	5/2/2014
La-140	1.68	Ba-140	12.79	5.9E+00	4.5E+00	5.4E-01	ND	BD	BD	BD	ND	ND	85.8	5/2/2014

3 CONCLUSIONS

Langmuir isotherm parameters for uptake of Mo from 450 gU/L solution, 1 M H⁺ solution on S40 sorbent were determined $a = 347$, $b = 0.5 \text{ mM}^{-1}$. Mo intraparticle diffusivity in 450 g-U/L solution, 1 M H⁺ solution for S40 sorbent was estimated $D_p = 7.87 \times 10^{-6} \text{ cm}^2/\text{min}$. To enable processing of a target solution obtained from dissolving 225 g uranium when the volume of solution varies between 0.5 L and 1 L, alternative process conditions for loading Mo on a 3.5 x 5 cm column were evaluated. It was determined that larger volumes of solution can be loaded under the same process conditions as the combined effects of increased solution volume and higher intraparticle diffusivity have minimal effect on the MTZ.

Irradiated tracer containing uranyl nitrate solution (899 g, ~350 g-U/L) was loaded onto 3.5 x 5 cm column with S40 sorbent at 25 mL/min and 60 °C. The majority of Mo, 98.4%, was recovered in strip fractions #2 and #3 (product). The partitioning of actinides, lanthanides, and fission products between different process streams was determined. The majority of activity from other radionuclides, including iodine, actinides, lanthanides, alkaline metal, and transition metal ions, reported to the eluent and acid-wash fractions (waste). Fission products found in the Mo product stream are < 1% of I-133, Ru-103, Te-132, and Zr-95; 60% Sb was found in the Mo strip #1 fraction.

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