ANL/CSE-13/24

Plant-Scale Concentration Column Designs for SHINE Target Solution

Chemical Science and Engineering Division

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by
Dominique C. Stepinski, Amanda J. Youker, and George F. Vandegrift
Chemical Science and Engineering Division, Argonne National Laboratory

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PLANT-SCALE CONCENTRATION COLUMN DESIGNS FOR SHINE TARGET SOLUTION

1 INTRODUCTION

Argonne is assisting Morgridge Institute for Research (MIR) in their efforts to develop SHINE, an accelerator-driven process that will utilize a uranyl-sulfate solution for the production of fission product Mo-99. An integral part of the process is the development of a column for the separation and recovery of Mo-99 followed by a concentration column to reduce the product volume from 15–25 L to less than 1 L. Argonne has collected data from batch studies and breakthrough column experiments to utilize the VERSE (Versatile Reaction Separation) simulation program (Purdue University) to design plant-scale product concentration processes.

Plant-scale columns for 2, 4, and 6 hr loading times were designed for separation of Mo-99 from 130 g-U/L uranyl-sulfate solution. The Mo-99 product solution volumes from the recovery of Mo-99 from 260 L of uranyl sulfate are 23.5, 17.6, and 14.5 L for the 2, 4, and 6 hr loadings, respectively; the resulting Mo concentration in 0.1-M NaOH is 2.34×10^{-2}, 3.13×10^{-2}, and 3.81×10^{-2} mM, respectively. The resulting product can be acidified to pH 2 using nitric acid and passed through a concentration column to reduce volume to less than 1 L. Concentration column designs have been generated for each of the three process scenarios (2, 4, and 6 hr). The plant-scale concentration column designs assume loading temperature of 80°C.

Three sorbents were evaluated for design of the concentration column: (1) pure titania sorbent with 40 µm particle size and 60 Å pore size (Zirchrom Separations, Anoka, MN); (2) acidic alumina with a 32- to 63-µm particle size and 50- to 60-Å pore size (Dynamic Adsorbents, Norcross, GA); and (3) neutral alumina with a 32- to 63-µm particle size and 50- to 60-Å pore size (Dynamic Adsorbents, Norcross, GA). To design a Mo-concentration process for the SHINE project, batch, breakthrough, and pulse tests were conducted to determine isotherm, mass transfer, and system parameters. VERSE-designed recovery systems have been tested and verified in laboratory-scale experiments, and this approach has been shown to be very successful.

Smaller particle size sorbents offer greater sorbent utilization and better overall process efficiency (due to lower interparticle void fraction). Therefore, sorbents with ~40-µm particle size were chosen for concentration column designs. The optimal loading time for these Mo process conditions and a 40 µm sorbent is ~1 hr. A shorter loading time would increase pressure drop (ΔP) to unacceptable levels. Decreasing the loading time cannot be attempted by increasing column inner diameter (ID) and increasing flow rate because such designs would produce very thin pancake columns that cannot be reliably and reproducibly packed. One solution to decreasing loading time would be to use a larger particle size sorbent such as titania, which has a 110-µm particle size. However, increasing particle size and increasing flow rates would increase column sizes and decrease the overall concentration process efficiency.

2 EXPERIMENTAL

2.1 BATCH STUDIES

The uptake of Mo(VI) from 0.1-M $NaNO_3$ solutions, with a pH of 2 or 5, was determined by equilibrating 1 mL of a Mo aqueous solution with a known amount (10 ± 1 mg) of sorbent for 24 hr at 80°C using a thermostated shaker bath. Aqueous solutions contained tracer Mo-99 and 0.001- to 1-mM Mo added as $Na_2MoO_4 \cdot 2\ H_2O$ in the presence of $NaNO_3$. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a 0.22-µm pore size polyvinylidene difluoride (PVDF) membrane filter.

2.2 PREPARATION OF Mo-99 SPIKE SOLUTION

Mo-99 was obtained from a spent Tc-99m generator (provided by Hot Shots Nuclear Medicine). The initial activity of Mo-99 in a generator is typically between 1 and 10 Ci. Typically, we use a spent Tc-99m generator that contains 0.1–0.3 Ci of Mo-99.

Mo-99 was removed from the generator by placing a serum vial containing 1-M NH_4OH on the needle labeled "Saline Charge." Then, an evacuated serum vial was placed on the needle labeled "Receiver." When no more bubbles appeared in the "Receiver" vial, the "Receiver" bottle was removed from the generator. The Mo-99 spiked solution was prepared by bringing the solution to dryness on a hotplate, and re-dissolving it in 0.01-M HNO_3.

2.3 BREAKTHROUGH EXPERIMENTS

A 0.074-mM Mo solution spiked with Mo-99 in 0.1-M NaNO3 (with pH 2) was used for breakthrough experiments. An ÄKTA Purifier Liquid Chromatography System (GE Healthcare) unit was used to pass the solution through the column in the upflow direction. ID Omnifit columns (0.66 cm) filled with sorbent to approximately 0.5 cm were used. The columns/sorbents were pre-equilibrated with 0.01-M HNO_3. All the solution inlets were primed and filled up to the injection valve to minimize dead volume. Samples (5 or 5.5 mL) were collected using a fraction collector, and the Mo concentration was determined using gamma counting.

2.4 COUNTING OF Mo-99

The amount of activity in the aqueous samples was determined using a NaI(Tl) well detector. Mo-99 was quantified by measurement of its 739-keV γ-ray. The activity of Mo-99 in each sample was corrected for decay.

3 RESULTS AND DISCUSSION

3.1 ESTIMATION OF THE EFFECTIVE ISOTHERM PARAMETERS OF Mo 0.1-M $NaNO_3$ SOLUTION, pH 2 AND 5

When sorption rates are higher than the controlling mass transfer rate, local equilibrium can be achieved between the solid and pore phases. Under such conditions, the solid-phase concentrations are related to pore-phase concentrations by an equilibrium isotherm. The Langmuir model was tested for the sorption of Mo in this study:

$$q_i = \frac{a_i C_i}{1 + b_i C_i} \tag{1}$$

where q_i is the amount of species i sorbed on the column packing and equilibrated with the concentration in mobile phase, C_i. In this study, both q_i (meq/L) and C_i (mmol/L) of the Mo isotherm are described on volume basis assuming 1.3-g/mL dry packing density of TiO_2 sorbent and 0.98 g/mL of alumina sorbents.

TiO_2 (40 µm) and acidic and neutral Al_2O_3 (32–63 µm) were evaluated for recovery of Mo from 0.1-M $NaNO_3$ solution at pH values of 2 and 5 (Figures 1–6). The data from batch equilibrium experiments were used to estimate the effective Mo isotherm parameters for TiO_2 and Al_2O_3 sorbents. Solutions and sorbents for all batch equilibrium data were equilibrated for 24 hr at 80°C. Langmuir isotherm parameters were fitted using Origin 8.5.1. The Langmuir isotherm model parameters at pH 5 for TiO_2 are a = 4588, b = 6.27 mM^{-1}; acidic Al_2O_3 a = 1711, b = 2.97 mM^{-1}; and neutral Al_2O_3 a = 425, b = 0.001 mM^{-1}. The Langmuir isotherm model parameters at pH 2 for TiO_2 are a = 223000, b = 1530 mM^{-1}; acidic Al_2O_3 a = 16800, b = 162 mM^{-1}; neutral Al_2O_3 a = 7210, b = 34 mM^{-1}. Langmuir adsorption constants at pH 2 are two orders of magnitude higher than at pH 5. Therefore, loading conditions at pH 2 were chosen for the concentration column designs.

3.2 COLUMN DESIGN PARAMETERS

The intrinsic, mass transfer parameters and physical properties of 0.1-M $NaNO_3$ given below were input into VERSE to design the plant-scale concentration.

1. The Brownian diffusivity (D_∞) value of $HMoO_4^-$ in water at 25°C (viscosity = 0.8851 cp) was reported to be 8.3×10^{-4} cm^2/min (Xu and Pruess 2001; Marcus 1997).

2. The density of a 0.1-M $NaNO_3$ solution of pH 2 at 80°C was assumed to be the same as that of water: 0.97 g/mL.

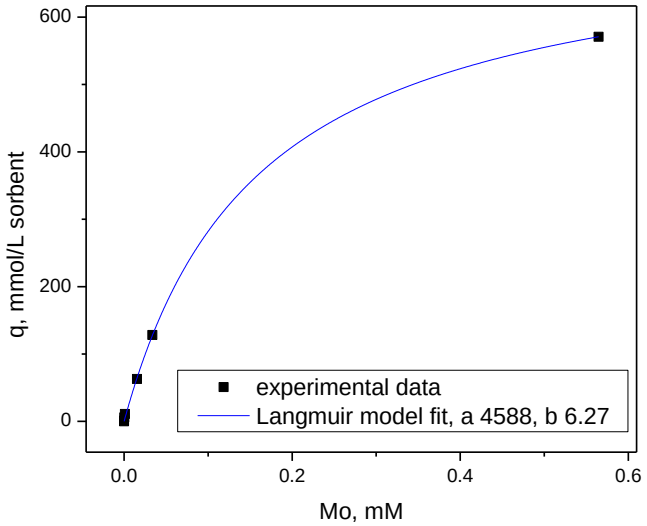

FIGURE 1 Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Adsorption of Mo on 40 µm Titania Sorbent Form 0.1-M $NaNO_3$, pH 5 Solutions at 80°C

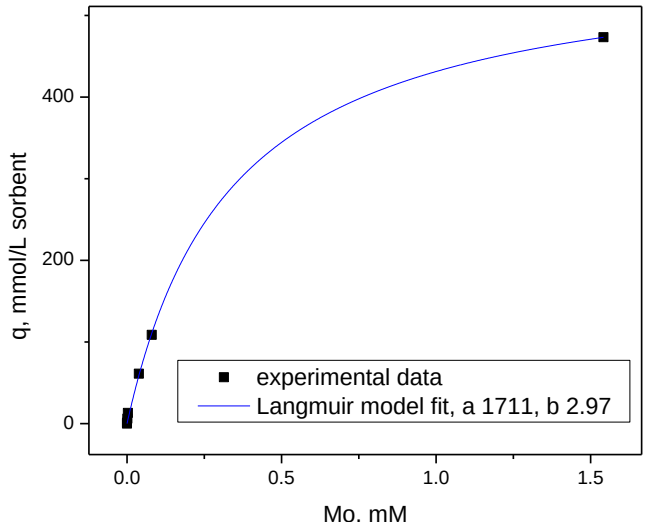

FIGURE 2 Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Adsorption of Mo on 32- to 63-µm Acidic Alumina Sorbent Form 0.1-M $NaNO_3$, pH 5 Solutions at 80°C

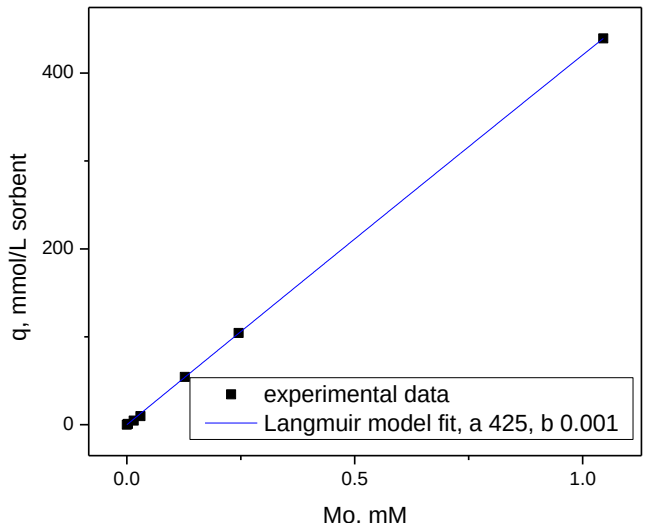

FIGURE 3 Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Adsorption of Mo on 32- to 63-µm Neutral Alumina Sorbent Form 0.1-M $NaNO_3$, pH 5 Solutions at 80°C

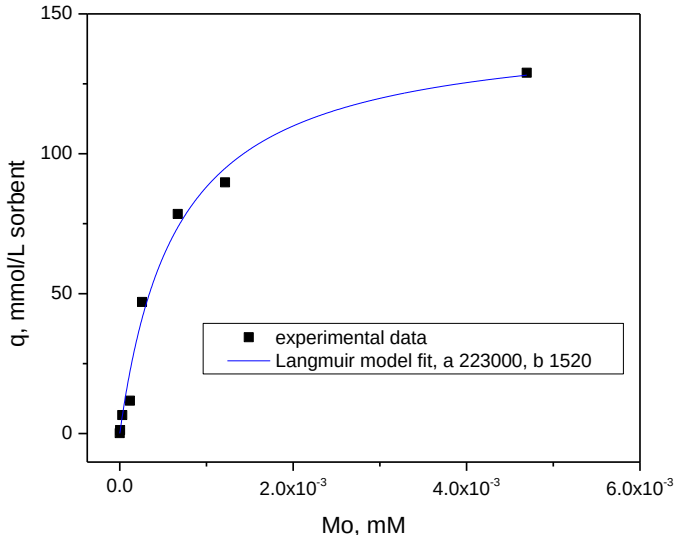

FIGURE 4 Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Adsorption of Mo on 40-µm Titania Sorbent Form 0.1-M $NaNO_3$, pH 2 Solutions at 80°C

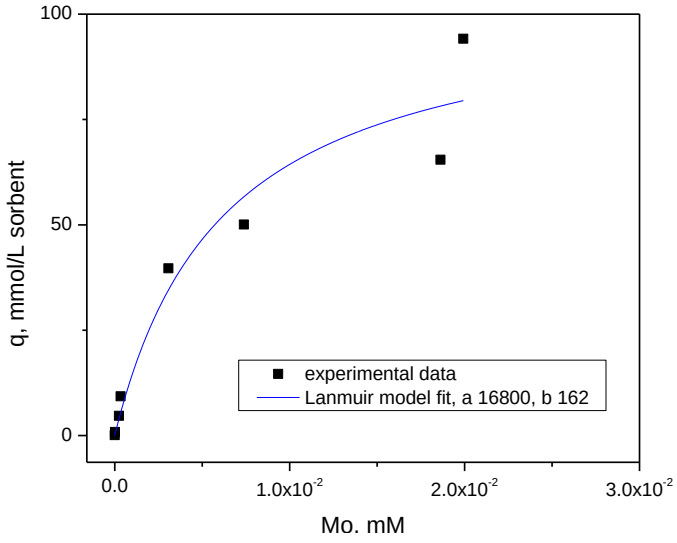

FIGURE 5 Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Adsorption of Mo on 32- to 63-µm Acidic Alumina Sorbent Form 0.1-M $NaNO_3$, pH 2 Solutions at 80°C

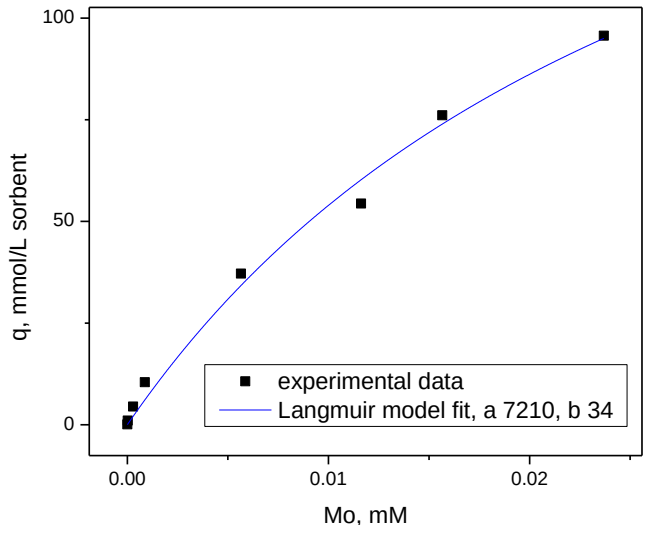

FIGURE 6 Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit for Adsorption of Mo on 32- to 63-µm Neutral Alumina Sorbent Form 0.1-M $NaNO_3$, pH 2 Solutions at 80°C

3. Viscosity of a 0.1-M $NaNO_3$ solution of pH 2 at 80°C was also assumed to be the same as that of water: 0.355 cp.

4. The Stokes-Einstein equation was used to correct D_∞ for viscosity and temperature effects. At 80°C, $D_{\infty,Mo}$ in 0.1-M $NaNO_3$ solution of pH 2 was calculated to be 2.34×10^{-3} cm^2/min.

5. *Eb*, axial dispersion estimated using the Chung and Wen correlation (1968) (Rhodes and Barbour 1923).

6. *kf*, mass transfer coefficient estimated using Wilson and Geankoplis (1966).

7. For titania, 40-µm sorbent intra-particle voidage was obtained from the manufacturer, εp = 0.40. Total void fraction, εt = 0.599, was determined experimentally using acetone tracer and inter-particle voidage, εb = 0.33, value was calculated [εt = εb + εp × (1 – εb)]. For alumina 32- to 63-µm total void fraction, εt = 0.608, was determined experimentally using acetone tracer; inter-particle voidage, εb = 0.36 was determined experimentally using albumin tracer and εp = 0.39 was the calculated value.

3.3 PRESSURE DROP CALCULATIONS

Pressure drop, ΔP, within sorbent bed is calculated using Ergun equation, where ε_b is inter-particle void fraction, μ is solution viscosity, ρ is solution density, d_p is diameter of sorbent particle, u_s is superficial velocity, and L is length of the column.

$$\Delta P = L \times \left[150 \frac{(1-\varepsilon_b)^2}{\varepsilon_b{}^3} \frac{\mu u_s}{d_p{}^2} + 1.75 \frac{(1-\varepsilon_b)}{\varepsilon_b{}^3} \frac{\rho u_s{}^2}{d_p}\right] \quad (2)$$

Column designs are chosen based on maximum ΔP = 0.5 atm.

3.3.1 Estimation of the Mo Intraparticle Diffusivity Values (D_p) for Titania and Acidic Alumina from Breakthrough Curves

For determination of intraparticle diffusivity, D_p, for acidic alumina, a breakthrough experiment using 0.1-M $NaNO_3$, 0.074-mM Mo, and pH 2 was conducted (Figure 7). The breakthrough curve was obtained by loading 470 mL of feed solution onto a 6.6 × 4.6 mm acidic alumina, 32- to 63-µm column at 5 cm/min at 80°C. The intraparticle diffusivity was estimated by comparing the experimental Mo breakthrough curves with VERSE simulations. In 0.1-M $NaNO_3$, pH 2 solution, the intraparticle diffusivity of Mo on alumina, is estimated to be $D_p = 4.25 \times 10^{-5}$ cm^2/min, $D_\infty/D_p = 55$. The agreement between experimental Mo breakthrough curves and model prediction indicates that (a) the adsorption of Mo in 0.1-M $NaNO_3$ can be described by the effective Langmuir isotherm, and (b) the numerical parameters and the intrinsic

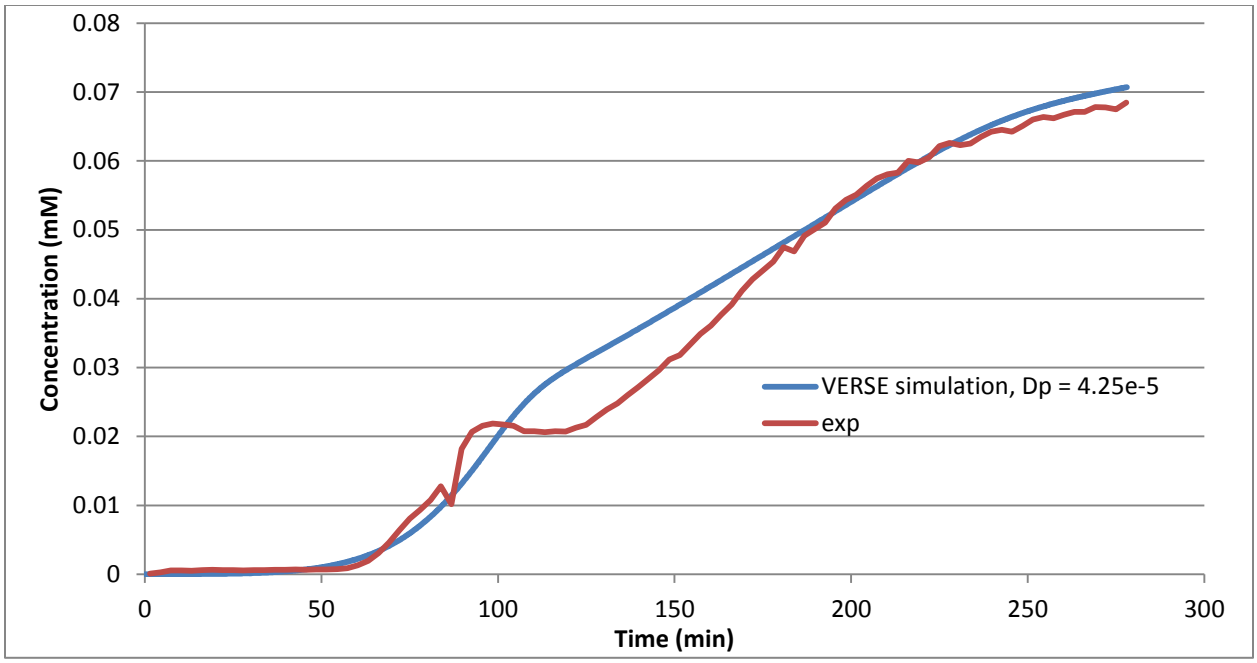

FIGURE 7 Estimation of D_p for 32- to 63-µm Acidic Alumina Sorbent from Breakthrough Experiment

model parameters (including void fractions, isotherm, and mass transfer parameters) are sufficiently accurate to predict the Mo breakthrough for alumina sorbent.

For determination of intraparticle diffusivity, D_p, for titania 40 µm, 505 mL of solution prepared in the same batch as that used for the alumina breakthrough experiment was passed through a 6.6 × 4.5 mm column at 5 cm/min at 80°C. No breakthrough was detected for a whole run, even though VERSE simulations, assuming $D_p = 7.79 \times 10^{-5}$ cm^2/min, $D_\infty/D_p = 30$, predicted a breakthrough midpoint at 282 mL. This indicates that the Langmuir Isotherm parameters are underestimated, due to a large error associated with large adsorption constant values. The D_p value is also likely to be higher than estimated based on previous Mo separation work.

3.3.2 Estimation of Effective Acidic Alumina Mo Capacity Value (*q*) from Breakthrough Curve

The plateau of acidic alumina was incomplete and did not reach $C_{f,Mo} = 0.074$ mM (Figure 7). To calculate the capacity for alumina from the breakthrough experiment, the breakthrough curve was assumed to be symmetric, and the breakthrough volume was the elution volume at half of the $C_{f,Mo}$ (= 0.037 mM).

Since the *q* values estimated from the breakthrough experiment were expected to be more reliable than the batch data in the nonlinear range, they were used to improve the estimates of the nonlinear Langmuir *b* parameters. The linear isotherm parameter (*a*) was assumed to be the same

as that estimated from batch tests, while the nonlinear isotherm parameters was recalculated [$b = (aC_f/q - 1)/C_f$] such that the q values matched the q values obtained from the breakthrough experiment at the feed concentration $C_{f,Mo}$. The new isotherm parameter b for adsorption of Mo on acidic alumina was determined to be 120 mM^{-1} and was used in VERSE simulations.

3.4 PLANT-SCALE COLUMN DESIGNS

Column designs were developed for concentrating Mo product separated from 130 g-U/L uranyl sulfate solutions and stripped with 0.1-M NaOH. Since three loading times (2, 4, and 6 hr) were considered for recovery of Mo from uranyl sulfate, three different scenarios were considered for design of the concentration column, as shown in Tables 1, 6, and 11. For each scenario, a 99% and 99.9% Mo loading column was designed for titania and alumina sorbents (Tables 2–5, 7–10, and 12–15). For each concentration column, a loading time of 1 hr was chosen to enable utilization of sorbent particle size of approximately 40 µm and remain within the ΔP 0.5 atm. Column lengths were calculated by adding 10% to the Mass Transfer Zone (MTZ) length and rounding up to the nearest 0.5 or whole number. It is difficult and unreliable to pack a column with a greater accuracy than 0.5 cm. The recommended column designs are highlighted.

As indicated by the breakthrough experiment, under these process conditions isotherm and mass transfer parameters for titania are higher than those utilized in VERSE simulations. Therefore, the length of MTZ is overestimated. Upon determination of isotherm and mass transfer parameters through a breakthrough experiment, some of the titania column designs might change from 1.5 to 1 cm in length. Column designs less than 1 cm in length are not recommended because it would be difficult and unreliable to pack a very thin pancake column.

Based on having the column pressure drop below 0.5 atm and having a column geometry that can be easily and reliably packed, recommended column designs are highlighted. Strip volumes are calculated based on our previous experiments that indicate that Mo can be stripped from a titania column with 16 BV of 1-M NH_4OH at 70°C.

TABLE 1 Process Conditions Following a 2-hr loading Mo Recovery Process from 130 gU/L

Parameter	Value
Solution	0.1-M $NaNO_3$, pH 2
Mo concentration	2.34×10^{-2} mM
Volume	23.52 L
Loading time	60 min
Flow rate	392 mL/min
Loading temperature	80°C

TABLE 2 40-µm Titania Sorbent, 99% Recovery Concentration Column Designs Following a 2-hr Loading Mo Recovery from 130 gU/L[a]

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	40.75	1.16	1.5	14	18	0.56	213.49	230.9
4	31.20	0.89	1.0	13	16	0.21	245.17	201.1
5	19.97	0.57	1.0	20	25	0.14	156.91	314.2
6	13.87	0.41	0.5	14	18	0.05	217.93	226.2

[a] The recommended column design is highlighted.

TABLE 3 40-µm Titania Sorbent, 99.9% Recovery Concentration Column Designs Following a 2-hr Loading Mo Recovery from 130 gU/L[a]

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
5	19.97	0.72	1.0	20	25	0.14	156.91	314.2
6	13.87	0.52	1.0	28	36	0.09	108.97	452.4
8	7.80	0.31	0.5	25	32	0.03	122.59	402.1

[a] The recommended column design is highlighted.

TABLE 4 32- to 63-µm Acidic Alumina Sorbent, 99% Recovery Concentration Column Designs Following a 2-hr Loading Mo Recovery from 130 gU/L[a]

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	40.75	2.98	3.5	34	33	0.48	117.63	538.8
4	31.20	2.30	3.0	38	37	0.31	105.07	603.2
5	19.97	1.49	2.0	39	38	0.13	100.87	628.3
6	13.87	1.07	1.5	42	42	0.07	93.40	678.6
8	7.80	0.63	1.0	50	49	0.03	78.81	804.2

[a] The recommended column design is highlighted.

TABLE 5 32- to 63-µm Acidic Alumina Sorbent, 99.9% Recovery Concentration Column Designs Following a 2-hr Loading Mo Recovery from 130 gU/L[a]

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	3.07	3.5	44	43	0.36	90.06	703.7
5	19.97	1.99	2.5	49	48	0.17	80.70	785.4
6	13.87	1.40	2.0	57	55	0.09	70.05	904.8
8	7.80	0.82	1.0	50	49	0.03	78.81	804.2

[a] The recommended column design is highlighted.

TABLE 6 Process Conditions Following a 4-hr Loading Mo Recovery Process from 130 gU/L

Parameter	Value
Solution	0.1-M $NaNO_3$, pH 2
Mo concentration	3.13×10^{-2} mM
Volume	17.59 L
Loading time	60 min
Flow rate	293 mL/min
Loading temperature	80°C

TABLE 7 40-µm Titania Sorbent, 99% Recovery Concentration Column Designs Following a 4-hr Loading Mo Recovery from 130 gU/L[a]

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	30.48	0.99	1.5	14	18	0.31	213.49	230.9
4	23.33	0.76	1.0	13	16	0.16	245.17	201.1
5	14.93	0.49	1.0	20	25	0.10	156.91	314.2
6	10.37	0.35	0.5	14	18	0.04	217.93	226.2

[a] The recommended column design is highlighted.

TABLE 8 40-µm Titania Sorbent, 99.9% Recovery Concentration Column Designs Following a 4-hr Loading Mo Recovery from 130 gU/L[a]

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)
3.5	30.48	1.19	1.5	14	18	0.31	213.49	230.9
4	23.33	0.92	1.0	13	16	0.16	245.17	201.1
5	14.93	0.60	1.0	20	25	0.10	156.91	314.2
6	10.37	0.43	0.6	16	20	0.04	198.12	248.8

[a] The recommended column design is highlighted.

TABLE 9 32- to 63-µm Acidic Alumina Sorbent, 99% Recovery Concentration Column Designs Following a 4-hr Loading Mo Recovery from 130 gU/L[a]

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	30.48	2.33	3.0	29	28	0.30	137.24	461.8
4	23.33	1.80	2.5	31	31	0.19	126.09	502.7
5	14.93	1.17	1.5	29	29	0.07	134.50	471.2
6	10.37	0.83	1.0	28	28	0.03	140.10	452.4
8	5.83	0.49	1.0	50	49	0.02	78.81	804.2

[a] The recommended column design is highlighted.

TABLE 10 32- to 63-µm Acidic Alumina Sorbent, 99.9% Recovery Concentration Column Designs Following a 4-hr Loading Mo Recovery from 130 gU/L[a]

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)
3.5	30.48	3.07	3.5	34	33	0.36	117.63	538.8
4	23.33	2.37	3	38	37	0.23	105.07	603.2
5	14.93	1.57	2.0	39	38	0.10	100.87	628.3
6	10.37	1.09	1.5	42	42	0.05	93.40	678.6
8	5.83	0.66	1.0	50	49	0.02	78.81	804.2

[a] The recommended column design is highlighted.

TABLE 11 Process Conditions Following a 6-hr Loading Mo Recovery Process from 130 gU/L

Parameter	Value
Solution	0.1-M $NaNO_3$, pH 2
Mo concentration	3.81×10^{-2} mM
Volume	14.45 L
Loading time	60 min
Flow rate	241 mL/min
Loading temperature	80°C

TABLE 12 40-µm Titania Sorbent, 99% Recovery Concentration Column Designs Following a 6-hr Loading Mo Recovery from 130 gU/L[a]

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
2.5	49.07	1.73	2.0	10	12	0.67	313.82	157.1
3.5	25.03	0.89	1.0	10	12	0.17	320.23	153.9
5	12.27	0.45	0.5	10	12	0.04	313.82	157.1
6	8.52	0.32	0.5	14	18	0.03	217.93	226.2
8	4.79	0.19	0.5	25	32	0.02	122.59	402.1

[a] The recommended column design is highlighted.

TABLE 13 40-µm Titania Sorbent, 99.9% Recovery Concentration Column Designs Following a 6-hr Loading Mo Recovery from 130 gU/L[a]

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)
3.5	25.03	1.07	1.5	14	18	0.26	213.49	230.9
5	12.27	0.55	1.0	20	25	0.08	156.91	314.2
6	8.52	0.39	0.5	14	18	0.03	217.93	226.2
8	4.79	0.24	0.5	25	32	0.02	122.59	402.1

[a] The recommended column design is highlighted.

TABLE 14 32- to 63-µm Acidic Alumina Sorbent, 99% Recovery Concentration Column Designs Following a 6-hr Loading Mo Recovery from 130 gU/L[a]

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
2.5	49.07	3.91	4.5	22	22	0.74	179.33	353.4
3.5	25.03	2.01	2.5	24	24	0.13	164.69	384.8
5	12.27	1.00	1.5	29	29	0.06	134.50	471.2
6	8.52	0.71	1.0	28	28	0.03	140.10	452.4
8	4.79	0.41	1.0	50	49	0.02	78.81	804.2

[a] The recommended column design is highlighted.

TABLE 15 32- to 63-µm Acidic Alumina Sorbent, 99.9% Recovery Concentration Column Designs Following a 6-hr Loading Mo Recovery from 130 gU/L[a]

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)
3.5	25.03	2.61	3.0	29	28	0.25	137.24	461.8
5	12.27	1.31	1.5	29	29	0.06	134.50	471.2
6	8.52	0.93	1.5	42	42	0.04	93.40	678.6
8	4.79	0.55	1.0	50	49	0.02	78.81	804.2

[a] The recommended column design is highlighted.

4 CONCLUSIONS

Based on discussion with the SHINE team, the most likely process scenarios are utilization of a 99% or 99.9% recovery titania concentration column following a 2 hr recovery from a uranyl sulfate, as described in Tables 2 and 3. For the 99% recovery, a 4 × 1 cm (ID × L) using 16 g of titania sorbent with a ΔP of 0.21 atm is recommended. The projected acid wash volume for this design is 63 mL, water wash is 63 mL, and the Mo-product volume in 1-M NH_4OH is projected to be 201 mL.

For the 99.9% recovery, a 4 × 1.5 cm (ID × L) titania column with 24 g of sorbent and a ΔP of 0.32 atm is recommended. The projected acid wash volume for this design is 94 mL, water wash is 94 mL, and the Mo-product volume in 1-M NH_4OH is projected to be 302 mL.

Several alumina and titania column designs will be verified with downscale column designs using 0.1-M $NaNO_3$, pH 2 solutions with stable Mo and tracer Mo-99.

5 REFERENCES

Chung, S.F., and C.Y. Wen, 1968, "Longitudinal Dispersion of Liquid Flowing through Fixed and Fluidized Beds," *American Institute of Chemical Engineers Journal* 14: 857–866.

Marcus, Y., 1997, *Ion Properties*, Marcel Dekker, Inc., New York, NY.

Rhodes, F.H., and C.B. Barbour, 1923, "The Viscosities of Mixtures of Sulfuric Acid and Water," *Ind. Eng. Chem*. 15: 850.

Wilson, E.J., and C. Geankoplis, 1966, "Liquid Mass Transfer at Very Low Reynolds Numbers in Packed Beds," *Industrial & Engineering Chemistry Fundamentals* 5(1): 9–14.

Xu, T., and K. Pruess, 2001, "On Fluid Flow and Mineral Alteration in Fractured Caprock of Magmatic Hydrothermal Systems," *Journal of Geophysical Research* 106(B2): 0148–0227. DOI: 10.1029/2000JB900356.

Chemical Science and Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 205
Argonne, IL 60439-4837

www.anl.gov

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