ANL/CSE-13/20

Mo Recovery Updates and Physical Properties of Uranyl Sulfate Solutions

Chemical Science and Engineering Division

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prepared for
U.S. Department of Energy, National Nuclear Security Administration,
Office of Defense Nuclear Nonproliferation

September 14, 2012

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Mo RECOVERY UPDATES AND PHYSICAL PROPERTIES OF URANYL SULFATE SOLUTIONS

1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting Morgridge Institute for Research (MIR) in their efforts to develop SHINE, which is an accelerator-driven process that will use a uranyl sulfate solution for the production of molybdenum-99 (Mo-99). An integral part of the process is the development of a plant-scale column for the separation and recovery of Mo-99. 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 several different target solution configurations with uranium concentrations varying from 90 to 150 g-U/L; Mo concentrations ranging from 1.73×10^{-3} to 3.55×10^{-3} mM; and solution volumes varying between 142 and 395 L. Direct downscale column results confirm the validity of most of the plant-scale designs because typically less than 1% Mo is found in the effluent and 90–100 ± 5% Mo can be recovered under the appropriate stripping conditions.

To design a Mo-recovery system for the SHINE project, batch, breakthrough, and pulse tests were conducted to determine isotherm, mass transfer, and system parameters. The VERSE program was used to calculate the mass-transfer zone under various loading times and velocities to design Mo separation and recovery columns using a pure titania sorbent with 110-µm particles and 60-Å pores. The plant-scale column designs assume a temperature of 60°C for most configurations and 80°C for feed solutions containing 130 g-U/L uranyl sulfate. VERSE-designed recovery systems have been tested and verified in laboratory-scale experiments, and this approach has been shown to be very successful.

In addition to the development of a plant-scale column design for the separation and recovery of Mo-99, Argonne measured several physical properties of uranyl sulfate solutions as a function of temperature and uranium concentration. SHINE needs data to model various target solution configurations in order to see how properties such as density, pH, viscosity, thermal conductivity, and specific heat change with temperature and vary for solutions with different uranium concentrations.

2 EXPERIMENTAL

2.1 BATCH STUDIES

The uptake of Mo(VI) was determined by equilibrating 1 mL of a Mo-99 spiked aqueous solution with a known amount (10 ± 1 mg) of sorbent for 24 hours at 60°C or 80°C using a thermostated shaker bath. Aqueous solutions contained tracer Mo-99 and 10^{-10} to 10^{-4} M Mo was added as $Na_2MoO_4 \cdot 2\ H_2O$ in the presence of uranyl sulfate (90–150 g-U/L). After equilibration, the solution was withdrawn and filtered using a syringe fitted with a 0.22-µm pore size PVDF (polyvinylidene fluoride) 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), which we receive on a weekly basis. The initial activity of Mo-99 in a generator is typically between 1 and 10 Ci. However, we receive a Tc-99m generator when the activity remaining in the generator is insufficient for patient administration. Typically, a spent Tc-99m generator contains 0.1–0.3 Ci of Mo-99, which is more than enough for our tracer batch and column work.

Mo-99 was removed from the generator by placing a serum vial containing 1-M NH_4OH on the needle labeled “Saline Charge.” After that, 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 hot plate, and re-dissolving it in 0.1-M H_2SO_4.

2.3 COUNTING OF Mo-99

The amount of activity in the aqueous samples was determined using a germanium 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. The extent of radionuclide uptake in batch studies was expressed in terms of a distribution coefficient, K_d, shown in equation (1):

$$K_d = \left(\frac{A_o - A_s}{W}\right) \Big/ \frac{A_s}{V} \quad . \tag{1}$$

Here, A_0 and A_s represent the aqueous phase activity (µCi) before and after equilibration, respectively; W is the dry weight of the sorbent (g); and V is the volume of the aqueous phase (mL).

2.4 INDUCTIVELY COUPLED OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

Inductively coupled optical emission spectroscopy was used to determine the concentration of uranium, and the error associated with these measurements is ±5%.

2.5 COLUMN DESIGN PARAMETERS

The parameters and physical properties of uranyl sulfate given below were input into VERSE to design the plant-scale columns for the five different target solution configurations being considered by SHINE. Table 1 shows the calculated density and viscosity values for the different uranyl sulfate solutions.

1. The sorbent utilized for the Mo-recovery column is S110, a pure titania sorbent with 110-µm particles and 60-Å pores.

2. Langmuir isotherm parameters were estimated from Mo batch data measured for solutions with varying Mo concentrations in solutions containing 90 and 150 g-U/L uranyl sulfate at 60°C and 130 g-U/L uranyl sulfate at 80°C.

3. 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).

4. The density of a 130 g-U/L uranyl-sulfate solution at pH 1 was determined experimentally to be 1.16 g/mL at 80°C. The densities of the remaining solutions were calculated by fitting data found in the literature (see Table 1) (Orban et al. 1956; McDuffie 1960).

5. Viscosities for the target solutions were estimated by fitting published data obtained at 20.0, 30.0, 44.8, 59.8 75.0, and 90.0°C (see Table 1) (Rhodes and Barbour 1923).

6. *Eb*, axial dispersion estimated using Chung and Wen (1968) correlation.

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

8. Sorbent intra-particle voidage was obtained from the manufacturer, $\varepsilon p = 0.40$. Total void fraction, εt, was determined experimentally to be 0.608 and inter-particle voidage, $\varepsilon b = 0.35$, value was calculated [$\varepsilon t = \varepsilon b + \varepsilon p \times (1 - \varepsilon b)$].

2.6 DENSITY MEASUREMENTS

The densities of uranyl sulfate solutions containing approximately 90–140 g-U/L were determined using a Mettler-Toledo density meter. Measurements were made from 20 to 80°C.

TABLE 1 Calculated Values for the Density and Viscosity of Uranyl Sulfate Solutions at 60°C and 80°C

g-U/L	ρ (g/mL)	μ (Cp)	Temperature (°C)
90	1.1	0.59	60
104.2	1.12	0.61	60
130	1.16[a]	0.47	80
124.8	1.15	0.64	60
146.8	1.18	0.68	60

[a] Value was determined experimentally using a Mettler-Toledo density meter.

The errors associated with these measurements are ±0.02 g/mL at 20°C and ±0.05 g/mL for the remaining temperatures.

2.7 pH MEASUREMENTS

The pH values of several uranyl sulfate solutions containing approximately 90–140 g-U/L were determined using an Orion-Ultra pH electrode and meter. The electrode was calibrated with pH 1 and pH 3 buffers. In addition, prior to each uranyl sulfate measurement, the pH of the pH 1 buffer was measured as a function of temperature from approximately 22–80°C, and adjustments to the pH measurements for the uranyl sulfate solutions over the temperature range of approximately 22–80°C were made accordingly.

2.8 VISCOSITY MEASUREMENTS

The viscosities of uranyl sulfate solutions containing approximately 90–140 g-U/L were determined from approximately 22 to 80°C using a Cambridge viscometer. The errors associated with these measurements are ±0.3% for temperatures between 22 and 60°C and ±2% for temperatures between 70 and 80°C.

2.9 THERMAL CONDUCTIVITY AND SPECIFIC HEAT MEASUREMENTS

A Thermtest thermal conductivity meter that also measures specific heat (when the density of the solution is known) was purchased. Unfortunately, the materials used to construct the sensor were not corrosion resistant to pH 1 uranyl sulfate solutions. The manufacturer stated silicone caulk could be used to prevent further corrosion. However, generating a new calibration curve for the sensor with the silicone caulk was not easy or reliable. Thermtest is manufacturing a custom sensor that will be corrosion resistant. As a result, the thermal conductivity and specific heat measurements will not be available until Argonne receives the new sensor.

3 LANGMUIR RESULTS

The uptake of Mo was determined in a batch mode as a function of increasing Mo concentration. It has been shown previously that Mo adsorption on titania sorbents follows Langmuir behavior (Knopf 2003). There are four basic assumptions associated with the Langmuir model:

1. All adsorption sites are equal.

2. Adsorbing species do not interact with each other.

3. The adsorption mechanism does not vary for the same species.

4. The adsorbing species will form a single monolayer and only occupy free adsorption sites (Knopf 2003).

The model for Langmuir-type adsorption is shown by equation (2), where q_i represents the amount of species *i* adsorbed on the sorbent, a_i is the linear isotherm parameter, b_i is the non-linear isotherm parameter, and C_i represents the aqueous-phase concentration of *i* in equilibrium with q_i (Langmuir 1916).

$$q_i = \frac{a_i * C_i}{(1 + b_i C_i)} \tag{2}$$

Langmuir-type data were obtained in solutions containing 90 and 150 g-U/L uranyl sulfate at 60°C and 130 g-U/L at 80°C. Figures 1, 2, and 3 show the Langmuir data obtained in uranyl sulfate solutions containing 150 g-U/L at 60°C, 90 g-U/L at 60°C, and 130 g-U/L at 80°C. The data were fit to the Langmuir model using Origin 8.5.1. Table 2 shows the *a* linear and *b* nonlinear parameters input into VERSE to design the plant-scale columns for the five different target solution configurations. The same *a* and *b* values obtained in a 90 g-U/L uranyl sulfate solution were used to generate column designs for a 104.2 g-U/L uranyl sulfate solution. In addition, the same *a* and *b* values obtained in a 150 g-U/L uranyl sulfate solution were used to generate column designs for a 124.8 and a 146.8 g-U/L uranyl sulfate solution.

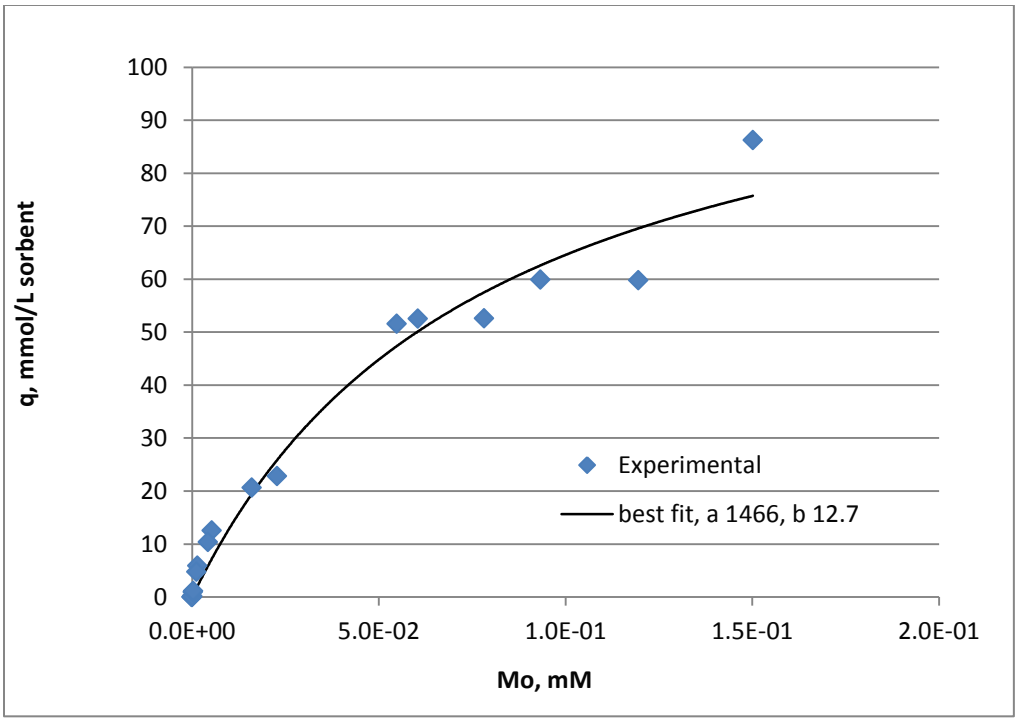

FIGURE 1 Plot of Langmuir-Type Adsorption on a Titania Sorbent in the Presence of a 150 g-U/L Uranyl Sulfate Solution with Origin Fitting at 60°C

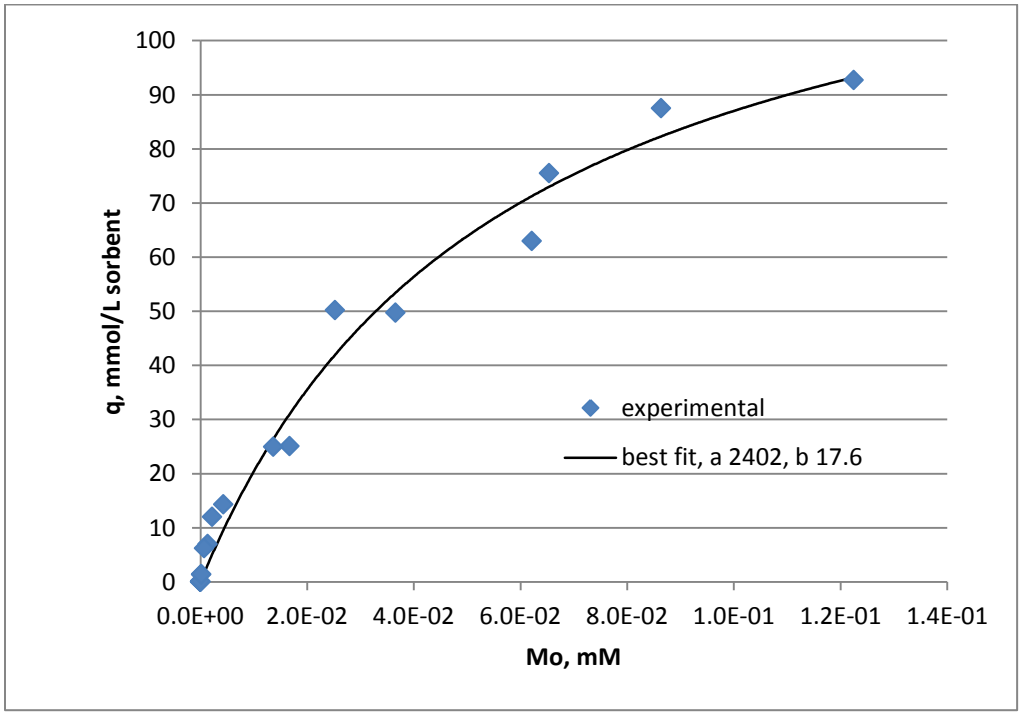

FIGURE 2 Plot of Langmuir-Type Adsorption on a Titania Sorbent in the Presence of a 90 g-U/L Uranyl Sulfate Solution with Origin Fitting at 60°C

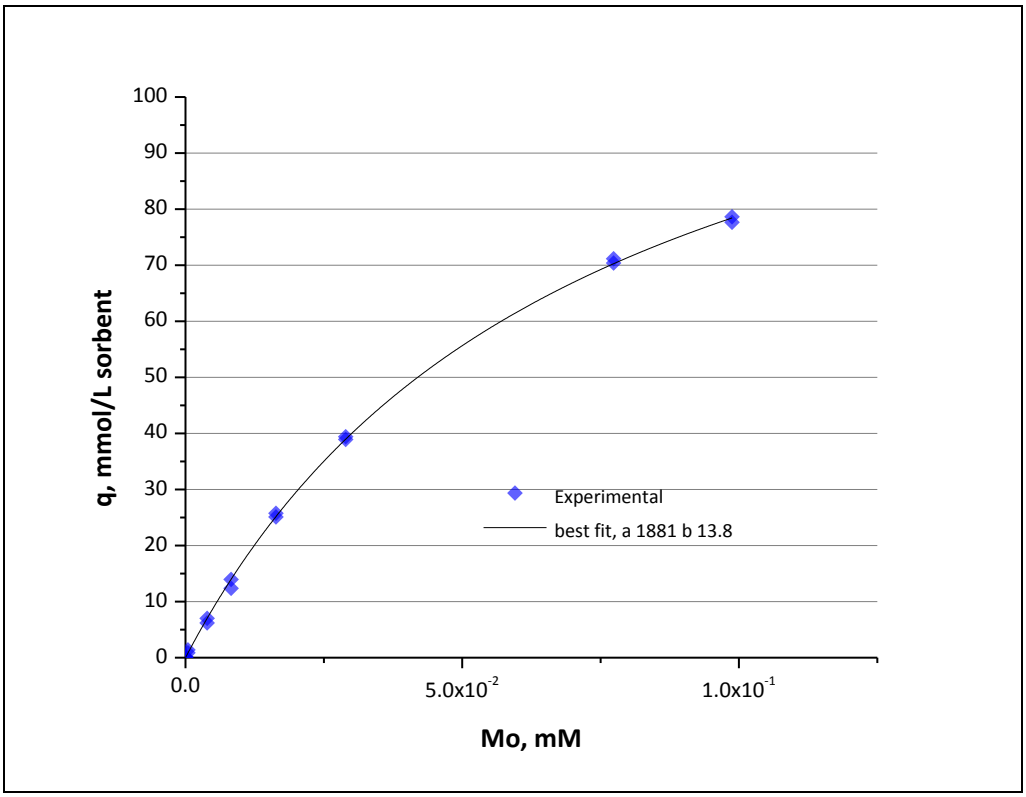

FIGURE 3 Plot of Langmuir-Type Adsorption on a Titania Sorbent in the Presence of a 130 g-U/L Uranyl Sulfate Solution with Origin Fitting at 80°C

TABLE 2 The *a* and *b* Parameters for the Five Different Target Solution Configurations

U Concentration (g-U/L)	Temperature (°C)	Langmuir *a* value	Langmuir *b* value (mM^{-1})
90	60	2402	17.6
104.2	60	2402	17.6
124.8	60	1466	12.7
130	80	1881	13.8
146.8	60	1466	12.7

4 RESULTS

4.1 PLANT-SCALE COLUMN DESIGNS

Table 3 shows the five different target solution configurations being considered by SHINE Medical Technologies for the production of Mo-99. Potential column designs were developed for loading the target solution onto the column over periods of 2, 4, and 6 hours. Plant-scale column designs for the different configurations with loading times of 4 and 6 hours are shown in Appendix I. In the tables shown below, the mass-transfer zone (MTZ) was calculated for each column diameter based on the linear velocity required to complete loading the column in the specified time period. The column length was increased by 10% above the MTZ and rounded up to the nearest centimeter to account for system parameter uncertainties. The column volume, mass of sorbent, pressure drop, and sorbent loading were calculated from the column geometry. Tables 4–8 show the potential column designs for the different configurations with a loading time of 2 hours.

TABLE 3 Target Solution Configurations Being Considered by SHINE

Uranyl Sulfate, (g-U/L)	Vol. (L)	Fission Power (kW)	Mo (mmol)	Mo (mM)	Mo-99 (Ci)
90	395	112.7	7.03×10^{-1}	1.78×10^{-3}	5000
104.2	257.7	97.2	6.06×10^{-1}	2.35×10^{-3}	4313
130	262	87.5	5.50×10^{-1}	2.10×10^{-3}	3882
124.8	178.3	85.1	5.31×10^{-1}	2.98×10^{-3}	3776
146.8	142.3	80.9	5.05×10^{-1}	3.55×10^{-3}	3589

TABLE 4 Preliminary Designs for Recovery of Mo from 395 L of 90 g-U/L, 1.78×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 2-hour loading time, 3.3 L/min)

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)
12	29.1	18.25	20	2262	2941	0.87	1.70
15	18.63	11.77	13	2297	2986	0.36	1.67
20	10.48	6.73	8	2513	3267	0.13	1.53
25	6.71	4.39	5	2454	3191	0.05	1.57
30	4.66	3.13	4	2827	3676	0.03	1.36

TABLE 5 Preliminary Designs for Recovery of Mo from 257.7 L of 104.2 g-U/L, 2.35×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 2-hour loading time, 2.1 L/min)

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)
12	18.99	12.28	13	1470	1911	0.38	2.26
15	12.15	7.93	9	1590	2068	0.17	2.09
20	6.84	4.53	5	1571	2042	0.05	2.11
30	3.04	2.13	3	2121	2757	0.01	1.56

TABLE 6 Preliminary Designs for Recovery of Mo from 262 L of 130 g-U/L, 2.10×10^{-3} mM Mo, at 80°C (S110, 99.9% recovery, 2-hour loading time, 2.2 L/min)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (L)	Sorbent Weight (kg)	ΔP (atm)	Mo-99/Sorbent Mass (Ci/g)
10	27.82	17.36	20	1.6	2.04	0.63	1.90
12	19.32	12.04	14	1.6	2.06	0.30	1.89
15	12.37	7.80	9	1.6	2.07	0.13	1.88
20	6.96	4.43	5	1.6	2.04	0.04	1.90

TABLE 7 Preliminary Designs for Recovery of Mo from 178.3 L of 124.8 g-U/L, 2.98×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 2-hour loading time, 1.5 L/min)

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)
10	18.92	15.66	17	1335	1736	0.53	2.18
15	8.41	7.07	8	1414	1838	0.11	2.05
20	4.73	4.06	5	1571	2042	0.04	1.85
25	3.03	2.67	3.5	1718	2233	0.02	1.69

TABLE 8 Preliminary Designs for Recovery of Mo from 142.3 L of 146.8 g-U/L, 3.55×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 2-hour loading time, 1.2 L/min)

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)
10	15.1	12.97	14	1100	1429	0.37	2.51
12	10.49	9.07	10	1131	1470	0.18	2.44
15	6.71	5.87	7	1237	1608	0.08	2.23
20	3.77	3.39	4	1257	1634	0.03	2.20

Despite the fact the sorbent utilization for the different configurations can be increased by 28–32% by increasing the loading time from 2 to 4 hours, and by 42–44% by increasing the loading time from 2 to 6 hours, it was decided saving time was more important than using less sorbent. The optimal column designs being considered and tested on a laboratory scale focus on a loading time of 2 hours. Another way to increase sorbent utilization is to decrease Mo recovery from 99.9% to 99% in VERSE, but that option is not being pursued. From a separation and recovery standpoint, the optimal configuration should have the highest Mo concentration and lowest feed volume. The target solution configuration that looks most promising is the 146.8 g-U/L design because it has the best sorbent utilization and smallest column sizes. Lowering the column volume has at least two benefits: (1) decreasing the volume and mass of the spent column material in the waste, and (2) lowering the volumes of the column wash streams and the Mo-product stream.

Under the conditions modeled in this study, the calculated mass transfer area is nearly proportional to the inverse of the linear velocity. Therefore, as long as the volume is kept constant, the geometry of the column is not a key factor. The column geometry should be sized for easy, reliable packing, to maintain the relatively low pressure drop in the column, and to accommodate other economic and operational factors.

Based on having the column pressure drop below 0.5 atm and having a column geometry that can be easily and reliably packed, the following column dimensions are suggested:

- For recovery of Mo in 2 hours, the recommended column is 10 × 14 cm (ID × L) utilizing approximately 1.4 kg of sorbent with a ΔP 0.37 atm. The projected acid wash volume for this design is 5.5 L, projected water wash is 5.5 L, and projected Mo-product volume is 22–33 L.

4.2 DOWNSCALE COLUMN EXPERIMENTS

Several laboratory-scale column experiments were performed in an effort to test the VERSE plant-scale column designs. The column sizes that were tested were chosen based on the availability of the columns and the amount of feed volume. Results from 1–4 downscale

experiments are shown for each of the different target solution configurations being considered by SHINE in Table 9. All column experiments were done using a depleted uranium solution as uranyl sulfate (pH 1), with stable Mo at the specified concentration added as sodium molybdate and tracer Mo-99.

The feed solution was heated to 60 or 80°C prior to being loaded onto the column. The column was kept at 60 or 80°C using heat tape, and stainless steel coils wrapped in heat tape were placed immediately before and after the column inlet and outlet to ensure the temperature of the solution entering the column was maintained at 60 or 80°C. The strip solution was heated to 70°C to achieve optimal Mo recovery because lower Mo recoveries were observed when the strip solution was kept at room temperature or heated to temperatures $\geq$80°C. Each column experiment was performed as follows:

1. Column was equilibrated with 10 column volumes (CVs) of 0.1-M H_2SO_4.

2. Feed solution (heated to the appropriate temperature) was loaded onto the column at a specific linear velocity in the upflow direction (to concentrate Mo on the bottom of the column and prevent entrapment of fission gases for future column runs with irradiated solutions).

3. Column was washed with 5 CVs of 1-M H_2SO_4 in the upflow direction (to ensure any adsorbed Pu is removed from the column for future runs with irradiated solutions).

TABLE 9 Results for the Downscale Column Experiments for the Five Different Target Solution Configurations

U Concentration (g-U/L)	Mo Concentration (mM)	Feed Volume (mL)	Column ID (cm)	Column L (cm)	% Mo Effluent	% Mo Recovered	Loading Velocity (cm/min)	Stripping Velocity (cm/min)	Feed Temperature (°C)
90	1.73×10^{-3}	441	1	8	0.3	82[a]	5	5	60
90	1.73×10^{-3}	288	1	5	1.0	90	3	3	60
90	1.73×10^{-3}	372	1	5	0.7	100	4	4	60
90	1.73×10^{-3}	468	1	5	1.1	94	5	5	60
104	2.35×10^{-3}	504	1	3	0.2	96	3.1	1.6	60
125	2.98×10^{-3}	196	0.66	5	0.1	100	4.7	2.3	60
130	2.10×10^{-3}	665	1	5	0.08	100	7	3.5	80
130	2.10×10^{-3}	665	1	5	0.11	86	7	7	80
130	2.10×10^{-3}	665	1	5	0.33	81[b]	7	3.5	80
146	3.55×10^{-3}	364	1	4	0.66	92	3.8	1.9	60
146	3.55×10^{-3}	364	1	4	0.1	66	3.8	3.8	60

[a] 1-M NH_4OH used to elute Mo was not heated.

[b] 1-M NH_4OH used to elute Mo was heated to 80°C, which created a lot of bubbles.

4. Column was washed with 5 CVs of H_2O in the upflow direction (to remove any acid).

5. Mo was eluted by passing 30 CVs of 1-M NH_4OH heated to 70°C through the column in the downflow direction.

6. Column was washed with 5 CVs of H_2O in the upflow direction. A freshly packed titania column was used for each experiment.

The plant-scale column designs generated using VERSE assume 99.9% Mo will be adsorbed and recovered. Direct downscale column experiments show that 0.1–1.1 ± 5% (of the 0.1–1.1%) Mo is found in the effluent. Due to the error associated with the gamma counting results, 1% or less Mo in the effluent shows good Mo adsorption and effective column design.

Mo recoveries ranged from 66 to 100 ± 5% for the downscale column experiments. Results from the downscale column experiments suggest that the stripping velocity should be half of the loading velocity to achieve 90–100 ± 5% recovery of Mo. For example, only 66% Mo was recovered when the loading and strip velocities were the same for the 146 g-U/L experiment; however, 92% Mo was recovered when the linear velocity for the strip solution was decreased from 3.8 to 1.9 cm/min. In addition, the temperature of the strip solution should be maintained at 70°C to ensure diffusion into the sorbent pores and release of Mo. For example, 82% Mo was recovered for the 90 g-U/L experiment when the strip solution was not heated, and 81% Mo was recovered for the 130 g-U/L experiment when the strip solution was heated to 80°C (100% Mo was recovered under the same conditions for the 130 g-U/L experiment when the strip solution was heated to 70°C). When the temperature of the strip solution exceeds approximately 70°C, a significant number of bubbles form and are subsequently passed through the column, decreasing the amount of Mo recovered.

For the plant-scale operation, recovering approximately 80–85% of the Mo actually formed after purification will be viewed as a success. Since the expected Mo yield for the LEU-Modified Cintichem purification process is between 85 and 90%, the recovery operation must recover 95% of the Mo. The column experiments completed thus far have not studied the effects of other fission and activation products on Mo adsorption and recovery or the effects of a high radiation field on Mo redox chemistry. The mini-SHINE experiments will examine the effects of potential competing components on Mo adsorption and recovery because approximately 2 Ci Mo-99 and all other fission products will be produced by irradiating 5 L of a uranyl sulfate solution at the linac. In addition, the effect of a high radiation field on Mo redox chemistry will be studied in the mini-SHINE experiments, because if less Mo is adsorbed or recovered on the titania column than what is expected, a portion of Mo(VI) may have been reduced to Mo(IV) or Mo(V). If this is the case, an oxidizing agent such as potassium permanganate will be used to ensure Mo is present as Mo(VI).

4.3 DENSITY RESULTS

A Mettler-Toledo density meter was used for all density measurements. It is equipped with a hollow glass tube that vibrates at a certain frequency, and when a solution enters the tube, the frequency changes. As the mass increases, the frequency decreases, and the new frequency can be used to determine the density of the solution at the specified temperature. The densities of uranyl sulfate solutions with concentrations ranging from approximately 90 to 140 g-U/L and temperatures from 20 to 80°C were determined. The values are shown in Table 10. The results are reasonable because for all samples the density decreases as the temperature increases. Errors of ±0.02 to 0.05 g/mL mean that using density as a means to measure uranium concentration is not accurate enough for SHINE.

Density values for uranyl sulfate solutions at 60°C were required for VERSE simulations to design a column for the SHINE process. Literature data were used to generate a line to calculate the densities of different uranyl sulfate solutions being considered by SHINE at 60°C (current target solution temperature is now 80°C). Table 11 shows a comparison between measured and calculated densities for uranyl sulfate solutions at 60°C, with pH 1. The differences between the calculated and measured density values are lower than the errors associated with the measurements alone, which confirms that the calculated values initially used in the VERSE simulations were reliable.

4.4 PH MEASUREMENTS

The pH measurements were completed using an Orion Ultra pH electrode and meter. The effect of temperature on the pH of the pH 1 buffer was more significant than anticipated. As a result, adjustments to the pH values of the uranyl sulfate solutions were made. The typical pH changes observed for a pH 1 buffer as a function of temperature are shown in Table 12.

TABLE 10 Density Values Measured for Uranyl Sulfate Solutions

Sample (g-U/L)	Density (g/mL)						
	20°C	30°C	40°C	50°C	60°C	70°C	80°C
88	1.128	1.123	1.119	1.112	1.104	1.094	1.092
103	1.154	1.150	1.145	1.140	1.134	1.128	1.122
117	1.172	1.168	1.163	1.158	1.152	1.146	1.139
128	1.182	1.178	1.173	1.168	1.161	1.155	1.149
130	1.193	1.189	1.184	1.178	1.171	1.164	1.160
138	1.199	1.195	1.191	1.185	1.179	1.173	1.166

TABLE 11 Calculated and Measured Density Values

Uranium Concentration (g-U/L)	Calculated ρ (g/mL)	Measured ρ (g/mL)
88	1.10	1.10
103	1.12	1.13
128	1.15	1.16
138	1.17	1.18

TABLE 12 pH Values Measured for pH 1 Buffer as a Function of Temperature

Temperature (°C)	pH
25.2	1.01
30.1	0.99
40.2	1.03
50.0	1.05
59.9	1.08
70.2	1.11
80.1	1.17

The overall trend showed that the pH of the uranyl sulfate solutions increased as the temperature increased. This contradicts previous literature data that showed that the pH of a uranyl sulfate solution decreases as the temperature increases (Orban et al. 1956). However, the dissociation of HSO_4^- decreases with increasing temperature, which lessens the amount of free H^+ in solution (Knopf 2003). All solutions contain an excess of sulfuric acid to keep the pH at 1, and the excess HSO_4^- most likely accounts for the decreased pH values observed at higher temperatures. Figure 4 shows a plot of pH versus temperature for uranyl sulfate solutions containing approximately 80–140 g-U/L, room temperature pH between 1 and 1.3, and temperatures from approximately 22 to 80°C. A more detailed table of the pH results is given in Appendix B.

4.5 VISCOSITY MEASUREMENTS

Viscosity measurements were completed using a Cambridge viscometer. Approximately 2 mL of a solution is placed in a thermostated sample holder, and a small magnetic piston is inserted into the holder. The piston is surrounded by liquid sample, and it moves up and down a

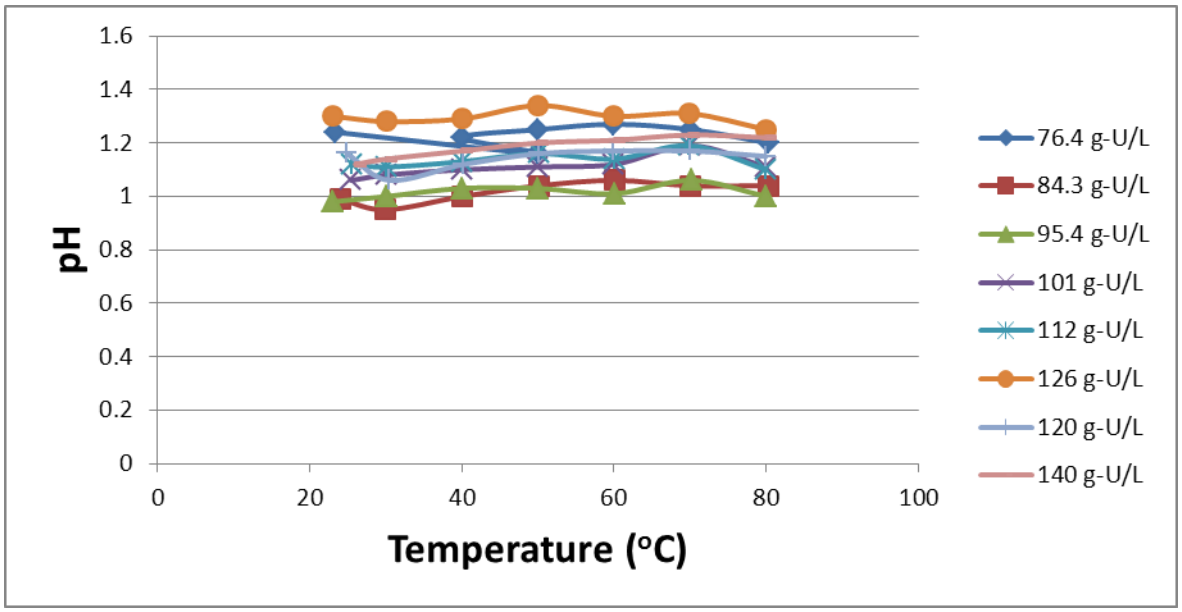

FIGURE 4 A Plot of pH Versus Temperature for Uranyl Sulfate Solutions

distance of 0.2 in. inside the sample cell through the use of magnetic coils. The time required to make the two-way cycle can be used to determine the viscosity of the solution at a specific temperature.

Results are shown in Figure 5, but it is worth noting that the values obtained at higher temperatures (70–80°C) are not as accurate as the values obtained at lower temperatures. This is because the system is closed, but does not have a condenser. As a result, condensation formed on top of the sample holder. The value obtained for the viscosity was heavily dependent on the amount of time required to complete the measurement. For the measurements between 70 and 80°C, an average of three separate measurements were taken, but the error associated with these measurements is still about 2%. A detailed table of the viscosity results is shown in Appendix C.

Viscosity values for uranyl sulfate solutions at 60°C were required for VERSE simulations to design a column for the SHINE process. Literature data were used to generate a line to calculate the viscosities of different uranyl sulfate solutions being considered by SHINE at 60°C (current target solution temperature is now 80°C). Table 13 shows a comparison between measured and calculated viscosities for uranyl sulfate solutions at 60°C, with pH 1. The differences between the calculated and measured viscosity values are within 0.04 Cp, which confirms that the calculated values initially used in the VERSE simulations were reliable.

4.6 THERMAL CONDUCTIVITY AND SPECIFIC HEAT MEASUREMENTS

The Thermtest thermal conductivity meter measures thermal conductivity, thermal diffusivity, and specific heat if the density of the solution is known. A thin platinum wire

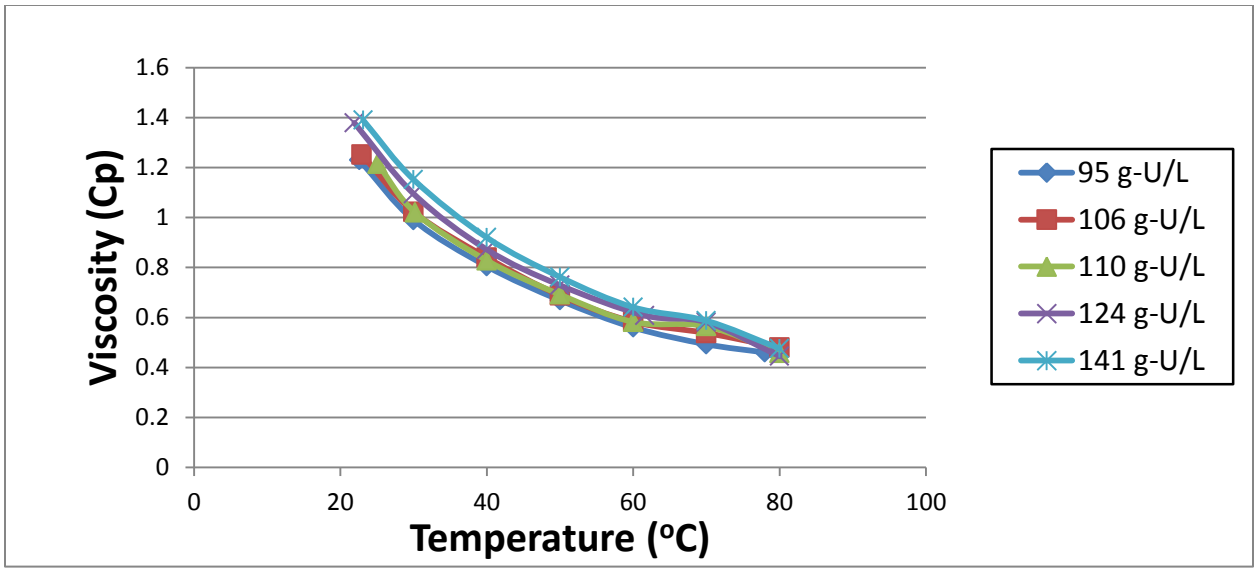

FIGURE 5 A Plot of Viscosity Versus Temperature for Uranyl Sulfate Solutions

TABLE 13 Calculated and Measured Viscosity Values

Uranium Concentration (g-U/L)	Calculated μ (Cp)	Measured μ (Cp)
95	0.59	0.56
106	0.61	0.58
110	0.62	0.58
124	0.64	0.61
141	0.67	0.64

attached to a sensor and thermocouple is inserted in a cylinder containing about 50 mL of solution. A current is sent through the wire to heat the solution, and the resistance of the wire is measured with respect to time. A temperature-time profile is generated that can be used to determine the thermal properties of the solution. Unfortunately, the thermal conductivity sensor corroded in the presence of pH 1 sulfuric acid. The manufacturer suggested coating the soldering joints with silicone caulk to prevent corrosion in the future. After doing this, a reliable calibration curve could not be generated. As a result, the manufacturer is making a custom sensor for us that is resistant to corrosion in acidic media. The sensor will not be available for at least 2–4 weeks. As soon as the new sensor has been received, the measurements will be made for thermal conductivity and specific heat of uranyl sulfate solutions containing 90–140 g-U/L with temperatures ranging from 20 to 80°C.

5 CONCLUSIONS AND FUTURE WORK

Several column designs have been generated for the SHINE target solution configurations, and downscale column designs have been tested using non-irradiated uranyl sulfate solutions with stable Mo and tracer Mo-99. Overall, the direct downscale experiments show that any of the five potential target solution configurations can be used to design a column with the parameters needed for good Mo adsorption and recovery. Two important factors were identified during the downscale column experiments to increase Mo recovery: (1) decreasing the stripping velocity by 50% compared to the loading velocity and (2) heating the strip solution to 70°C. Both factors will be implemented for the plant-scale operation.

Three parameters have been discussed that affect column efficiency: Mo concentration, uranium concentration, and feed flow rate. From a Mo-recovery perspective, target-solution designs with the highest power density (and thus the highest Mo concentrations), even with higher uranium concentrations, will require columns with the lowest volumes. For example, the plant-scale column designs for the 146.8 g-U/L uranyl sulfate target solution configuration with a Mo concentration of 3.55×10^{-3} mM are the most efficient. For the recovery of Mo in 2 hours, the recommended column is 10 cm × 14 cm (ID × L) using approximately 1.4 kg of sorbent with a pressure drop of 0.37 atm. The projected acid wash volume for this design is 5.5 L, projected water wash is 5.5 L, and projected Mo-product volume is between 22 and 33 L. For any of the other potential target solution configurations, the plant-scale column designs (2-hour loading) with internal diameters of 10–12 cm are the best options because they are the smallest columns and will minimize wash and waste volumes. Increasing the loading time was also discussed to increase overall column efficiency, but it is not being implemented at this point.

Modifications to the current plant-scale column designs will most likely occur after results from the mini-SHINE experiments have been obtained. The effect of potential competing components on Mo adsorption and recovery may increase the column sizes slightly; however, the length of the mass-transfer zone has already been increased by 10% to account for system problems. As a result, increasing the column size may not be necessary. In addition, an oxidizing agent may need to be added to one or more steps during the plant-scale operation to ensure Mo is present as Mo(VI).

Once the final SHINE target solution configuration has been determined, Langmuir data will be obtained using the proper uranium concentration and temperature. In addition, if modifications are needed based on results from the mini-SHINE experiments, those will be implemented as well.

Density, pH, and viscosity measurements have been made for potential SHINE target solutions containing between 90 and 140 g-U/L uranyl sulfate at temperatures between 20 and 80°C. The density and viscosity results follow what was expected where both parameters decrease with increasing temperature. Density and/or viscosity values can be used to generate an estimate of uranium concentration (±5–10%) but cannot be used as a means to determine the concentration within 1% or less. The pH actually increased as temperature increased, which contradicts a previous literature report (Orban et al. 1956). A feasible explanation is the fact that

there is an excess of sulfate in solution, and bisulfate dissociation decreases with increasing concentration, resulting in less free H^+ in solution (Knopf 2003). The thermal conductivity and specific heat measurements will be completed once the new sensor that is compatible with acidic solutions arrives at Argonne.

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APPENDIX A:

PLANT-SCALE COLUMN DESIGNS FOR THE POTENTIAL SHINE TARGET SOLUTION CONFIGURATIONS WITH LOADING TIMES OF 4 AND 6 HOURS

TABLE A-1 Preliminary Designs for Recovery of Mo from 395 L of 90 g-U/L, 1.78×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 4-hour loading time, 1.7 L/min)

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)
10	20.96	18.07	19	1492	1940	0.6	2.58
12	14.55	12.64	14	1583	2058	0.31	2.43
15	9.31	8.19	9	1590	2068	0.13	2.42
20	5.24	4.73	6	1885	2450	0.05	2.04
25	3.35	3.13	4	1963	2553	0.02	1.96

TABLE A-2 Preliminary Designs for Recovery of Mo from 395 L of 90 g-U/L, 1.78×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 6-hour loading time, 1.1 L/min)

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)
10	13.97	14.88	16	1257	1634	0.34	3.06
12	9.7	10.42	12	1357	1764	0.17	2.83
15	6.21	6.77	8	1414	1838	0.07	2.72
20	3.49	3.93	5	1571	2042	0.03	2.45

TABLE A-3 Preliminary Designs for Recovery of Mo from 257.7 L of 104.2 g-U/L, 2.35×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 4-hour loading time, 1.1 L/min)

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)
8	21.36	20	21	1056	1372	0.7	3.14
10	13.67	12.7	14	1100	1429	0.3	3.02
15	6.08	5.53	6.5	1149	1493	0.06	2.89
20	3.42	3.19	4	1257	1634	0.02	2.64

TABLE A-4 Preliminary Designs for Recovery of Mo from 257.7 L of 104.2 g-U/L, 2.35 × 10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 6-hour loading time, 0.7 L/min)

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)
8	14.24	15.6	17	855	1111	0.38	3.88
10	9.11	10	11	864	1123	0.16	3.84
15	4.05	4.6	5.5	972	1264	0.03	3.41
20	2.28	2.67	3.5	1100	1429	0.01	3.02

TABLE A-5 Preliminary Designs for Recovery of Mo from 178.3 L of 124.8 g-U/L, 2.98 × 10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 4-hour loading time, 0.7 L/min)

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)
8	14.78	17.27	18	905	1176	0.44	3.21
10	9.46	11.17	12	942	1225	0.19	3.08
12	6.57	7.8	9	1018	1323	0.1	2.85
15	4.2	5.13	6	1060	1378	0.04	2.74

TABLE A-6 Preliminary Designs for Recovery of Mo from 178.3 L of 124.8 g-U/L, 2.98 × 10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 6-hour loading time, 0.5 L/min)

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)
6	17.52	25.34	26	735	956	0.75	3.95
8	9.85	14.37	15	754	980	0.24	3.85
10	6.31	9.27	10	785	1021	0.1	3.70
15	2.8	4.27	5	884	1149	0.02	3.29

TABLE A-7 Preliminary Designs for Recovery of Mo from 262 L of 130 g-U/L, 2.10 × 10^{-3} mM Mo, at 80°C (S110, 99.9% recovery, 4-hour loading time, 1.1 L/min)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (L)	Sorbent Weight (g)	ΔP (atm)	Mo-99/Sorbent mass (Ci/g)
8	21.74	19.16	22	1.1	1440	0.55	2.70
10	13.91	12.4	14	1.1	1430	0.23	2.71
12	9.66	8.8	10	1.1	1470	0.12	2.64
15	6.18	5.8	7	1.1	1490	0.05	2.61

TABLE A-8 Preliminary Designs for Recovery of Mo from 262 L of 130 g-U/L, 2.10×10^{-3} mM Mo, at 80°C (S110, 99.9% recovery, 6-hour loading time, 0.7 L/min)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (L)	Sorbent Weight (g)	ΔP (atm)	Mo-99/Sorbent Mass (Ci/g)
6	25.76	28.32	31	0.9	1180	0.96	3.29
8	14.49	16	18	0.9	1180	0.31	3.29
10	9.27	10.4	12	0.9	1170	0.13	3.32
12	6.44	7.2	8	0.9	1180	0.06	3.29
15	4.12	4.71	6	0.97	1260	0.03	3.08

TABLE A-9 Preliminary Designs for Recovery of Mo from 142.3 L of 146.8 g-U/L, 3.55×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 4-hour loading time, 0.6 L/min)

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)
6	20.97	25.21	26	735	956	0.95	3.75
8	11.8	14.27	15	754	980	0.31	3.66
10	7.55	9.19	10	785	1021	0.13	3.52
15	3.36	4.2	5	884	1149	0.03	3.12

TABLE A-10 Preliminary Designs for Recovery of Mo from 142.3 L of 146.8 g-U/L, 3.55×10^{-3} mM Mo, at 60°C (S110, 99.9% recovery, 6-hour loading time, 0.4 L/min)

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)
5	20.13	30.1	31	609	791	1.09	4.54
6	13.98	20.96	22	622	809	0.54	4.44
8	7.86	11.87	13	653	849	0.18	4.23
10	5.03	7.67	9	707	919	0.08	3.91

APPENDIX B:

pH MEASUREMENTS FOR URANYL SULFATE SOLUTIONS WITH DIFFERENT INITIAL PH VALUES AND DIFFERENT SULFATE CONCENTRATIONS

TABLE B-1 pH Measurements for Uranyl Sulfate Solutions as a Function of Temperature and Uranium Concentration

U (0.32 M) Temp. (°C)	SO_4^{2-} (0.60 M) pH	U (0.35 M) Temp. (°C)	SO_4^{2-} (0.58 M) pH	U (0.40 M) Temp. (°C)	SO_4^{2-} (0.67 M) pH	U (0.42 M) Temp. (°C)	SO_4^{2-} (0.72 M) pH
23.4	1.24	24.0	0.99	23.1	0.98	25.4	1.06
50.0	1.16	30.0	0.95	30.1	1.00	30.1	1.08
40.0	1.22	40.1	1.00	40.1	1.03	40.1	1.10
50.0	1.25	50.1	1.04	50.0	1.03	50.0	1.11
60.0	1.27	60.1	1.06	60.1	1.01	60.0	1.12
70.1	1.25	70.1	1.04	70.2	1.06	70.1	1.19
80.4	1.20	80.3	1.04	80.0	1.00	80.0	1.11

U (0.47 M) Temp. (°C)	SO_4^{2-} (0.73 M) pH	U (0.53 M) Temp. (°C)	SO_4^{2-} (0.82 M) pH	U (0.53 M) Temp. (°C)	SO_4^{2-} (0.67 M) pH	U (0.61 M) Temp. (°C)	SO_4^{2-} (0.95 M) pH
25.5	1.12	23.1	1.30	24.9	1.16	26.0	1.12
30.2	1.11	30.1	1.28	30.5	1.06	30.2	1.14
40.0	1.13	40.0	1.29	40.3	1.12	40.0	1.17
50.1	1.16	50.1	1.34	50.1	1.16	50.1	1.20
60.1	1.14	60.0	1.30	60.0	1.17	60.1	1.21
70.0	1.19	70.0	1.31	70.1	1.17	69.9	1.23
80.0	1.10	80.0	1.25	80.0	1.15	80.1	1.22

U (0.40 M) Temp. (°C)	SO_4^{2-} (0.49 M) pH	U (0.40 M) Temp. (°C)	SO_4^{2-} (0.52 M) pH	U (0.43 M) Temp. (°C)	SO_4^{2-} (0.54 M) pH	U (0.45 M) Temp. (°C)	SO_4^{2-} (0.55 M) pH
27.0	1.79	27.0	1.01	25.4	1.02	25.4	1.62
30.1	1.67	30.4	0.90	30.8	1.07	30.8	1.63
40.4	1.66	40.2	0.94	40.0	1.06	40.0	1.65
50.2	1.69	50.1	0.96	50.2	1.05	50.2	1.65
60.2	1.70	60.3	0.98	60.5	0.99	60.5	1.68
70.1	1.70	70.2	0.99	70.0	1.06	70.0	1.64
80.0	1.71	80.2	1.12	80.1	1.09	80.1	1.63

U (0.46M) Temp. (°C)	SO_4^{2-} (0.57 M) pH	U (0.52 M) Temp. (°C)	SO_4^{2-} (0.66 M) pH	U (0.57 M) Temp. (°C)	SO_4^{2-} (0.68 M) pH	U (0.59 M) Temp. (°C)	SO_4^{2-} (0.78 M) pH
25.0	1.22	26.0	1.12	27.0	1.24	27.1	1.07
30.9	1.14	30.1	1.11	30.3	1.28	30.6	1.10
40.0	1.23	40.1	1.13	39.9	1.26	40.0	1.23
50.1	1.27	49.9	1.13	50.1	1.28	50.0	1.27
60.2	1.23	60.1	1.14	60.3	1.30	60.0	1.28
70.1	1.18	69.9	1.12	70.0	1.34	70.1	1.29
80.1	1.18	80.1	1.13	80.0	1.39	80.1	1.30

APPENDIX C:

VISCOSITY MEASUREMENTS FOR URANYL SULFATE SOLUTIONS

TABLE C-1 Viscosity Measurements for Uranyl Sulfate Solutions as a Function of Temperature and Uranium Concentration

95 g-U/L Uranyl Sulfate		106 g-U/L Uranyl Sulfate		110 g-U/L Uranyl Sulfate		124 g-U/L Uranyl Sulfate		141 g-U/L Uranyl Sulfate	
Temperature (°C)	Viscosity (Cp)	Temperature (°C)	Viscosity (Cp)	Temperature (°C)	Viscosity (Cp)	Temperature (°C)	Viscosity (Cp)	Temperature (°C)	Viscosity (Cp)
22.6	1.23	22.9	1.25	25.1	1.22	21.9	1.38	23.1	1.39
30	0.99	30	1.02	30.2	1.02	30	1.10	30	1.15
40.0	0.81	40.0	0.84	40.0	0.83	40.0	0.87	40.0	0.92
50.0	0.67	50.0	0.69	50.0	0.69	50.0	0.73	50.0	0.76
60.0	0.56	60.0	0.58	60.0	0.58	61.6	0.61	60.0	0.64
70.0	0.49	70.0	0.54	70.0	0.57	70.0	0.58	70.0	0.59
78.0	0.46	80.0	0.48	80.0	0.46	80.0	0.45	80.0	0.48

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