

**Mo-99 2014 TOPICAL MEETING ON
MOLYBDENUM-99 TECHNOLOGICAL DEVELOPMENT**

**June 24-27, 2014
Hamilton Crowne Plaza
Washington D. C.**

Column Optimization for Mo Separation and Recovery

A.J. Youker¹, D.C. Stepinski¹, L. Ling², N-H.L. Wang² and G.F. Vandegrift¹

¹Chemical Sciences and Engineering
Argonne National Laboratory, 9700 South Cass Avenue, 60439 Argonne, IL – United States

²Chemical Engineering
Purdue University, 1154 Forney Hall, 47906 West Lafayette, IN – United States

ABSTRACT

Argonne National Laboratory has collaborated with Purdue University to design Mo-separation and recovery columns using a titania sorbent. Purdue University's VERSE (VErsatile Reaction SEparation) simulator has been utilized to design plant-scale columns for the separation and recovery of Mo-99 from irradiated uranyl-nitrate and uranyl-sulfate solutions. Data are collected in a batch mode and small-scale column setting and input into VERSE. Column dimensions and flow rates are determined by VERSE and can continuously be optimized as more data are collected. Tracer experiments using direct downscale columns have validated the plant-scale designs. Data from the mini-SHINE experiments will be input into VERSE for further optimization, as the effects of a high radiation field may change redox chemistry, speciation, and adsorption of Mo and other fission products on titania. Molybdenum-separation and recovery from a low-enriched uranium solution as nitrate or sulfate has been successfully demonstrated using a titania sorbent.

Introduction

There are currently no Mo-99 producers in the US, and most of the current international producers utilize highly enriched uranium (HEU) targets to produce Mo-99 [1]. The use of a low enriched uranium (LEU) target requires about five times more uranium overall to produce the same amount of Mo-99 compared to using an HEU target [2]. As a result, a new separation process is needed because alumina, which is used to separate Mo-99 from HEU, does not adsorb Mo very well in the presence of larger quantities of uranium [3]. Argonne has demonstrated that Mo-99 can be separated, recovered, and purified from a low enriched uranium (LEU) solution as uranyl-nitrate or uranyl-sulfate using a titania sorbent.

Mo-99 adsorption and breakthrough data were collected in the presence of uranyl-nitrate and uranyl-sulfate solutions in a batch mode and small-scale column setting. These types of data were input into VERSE to generate plant-scale columns for both processes. Direct down-scale column experiments using DU tracer solutions spiked with Mo-99 show good Mo adsorption and recovery. As more data are collected during the mini-SHINE experiments, the effects of redox chemistry and fission product competition will be present, and the plant-scale column designs can continuously be optimized with the new data using VERSE.

Experimental

Preparation of Mo-99 Spike Solution

Mo-99 was obtained from a commercial Tc-99m generator (Lantheus Medical Imaging). The initial activity of Mo-99 in the generator was 1 Ci. Generators were stripped using 10 mL of 1 M NH₄OH. The 1 M NH₄OH solution containing Mo-99 was evaporated to dryness and re-dissolved in pH 1 H₂SO₄ or HNO₃. Approximately 1 μCi of Mo-99 per 1 mL of uranyl-sulfate or uranyl-nitrate solution was added to prepare the final spiked solution.

Batch Studies

The uptake of Mo as a function of Mo concentration was determined by contacting 1 mL of a Mo-99 spiked aqueous solution with a known amount (10 ± 1 mg) of sorbent for 24 hours at 60–80°C using a thermostated shaker bath. Aqueous solutions contained 90 - 150 g-U/L uranyl-sulfate or uranyl-nitrate and 1 × 10⁻¹⁰ – 1 × 10⁻⁴ M Mo as Na₂MoO₄. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a 0.22 μm pore size PVDF membrane filter (Millipore). Blank experiments have shown that the filter does not uptake Mo-99.

Counting of Mo-99

The amount of activity remaining 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 was expressed in terms of a distribution coefficient, K_d, (equation 1) defined as follows:

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

Here, A_o 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). The amount of sorbent used was kept at 10 (± 1) mg in order to leave a measurable activity in the aqueous phase. The error associated with the K_d measurements is directly related to the error obtained from counting Mo-99's 739 keV γ-ray, which typically is 7-8%.

Frontal Curves

Frontal curve experiments were completed using an AKTA liquid chromatography system (GE Healthcare) and columns containing a titania sorbent with 80-110 micron particles and 60 angstrom pores. A freshly packed titania column was used for each experiment, and column sizes of 0.66 cm internal diameter (ID) by 1 cm length (L) and 1 cm ID by 1 cm L were used. Linear velocities of 3, 4, and 5 cm/min were tested. The feed solution contained 90 - 150 g-U/L

uranyl-sulfate or uranyl-nitrate, pH 1 with 1-10 μM Mo as Na_2MoO_4 and tracer Mo-99. The column was equilibrated with 10 column volumes (CV) of pH 1 H_2SO_4 or HNO_3 , and the feed solution was loaded onto the column in the upflow direction. Several fractions of the effluent were collected and gamma counted using a germanium detector. When the activity of Mo-99 in the effluent was equal to the original Mo-99 activity in the feed solution, taking into account decay, it was determined that full Mo breakthrough had been achieved.

Direct Down-scale Column Experiments

Small-scale column tests were also performed using an AKTA Liquid Chromatography system to validate the plant-scale column designs. Titania columns were equilibrated with pH 1 H_2SO_4 or HNO_3 at 60-80°C, and uranium solutions containing stable Mo and tracer Mo-99 were loaded onto the column in the upflow direction. Columns were washed with 10 CVs of pH 1 acid followed by water both in the upflow direction. Mo was eluted using 20-30 CVs of 0.1 M NaOH or 1 M NH_4OH in the downflow direction.

Results and Discussion

Batch Study and Mo Breakthrough Results

Figure 1 shows a plot of moles of Mo adsorbed per gram of sorbent versus Mo concentration in a 150 g-U/L uranyl-nitrate and uranyl-sulfate solution. The data follow the Langmuir model of adsorption. Mo adsorption on a titania sorbent is slightly better in uranyl nitrate compared to uranyl sulfate, and this is due to the fact that sulfate competes more strongly with Mo for adsorption sites than nitrate. Table 1 shows results from Mo batch study experiments in the presence of a 0.63 M Na_2SO_4 and a 1.26 M NaNO_3 solution. The sulfate and nitrate concentrations are equivalent to what is present in a 150 g-U/L solution of each, and in the Mo concentration range ($1 \times 10^{-6} - 1 \times 10^{-5}$ M) expected for both uranyl-nitrate and uranyl-sulfate solutions, the K_d values are $\sim 0.3 - 3.2$ times higher for nitrate compared to sulfate. Figure 2 shows results from a Mo breakthrough curve experiment using a small titania column in the presence of a 150 g-U/L uranyl-nitrate solution. Titania's capacity for Mo in a column setting and batch mode are needed for VERSE simulations.

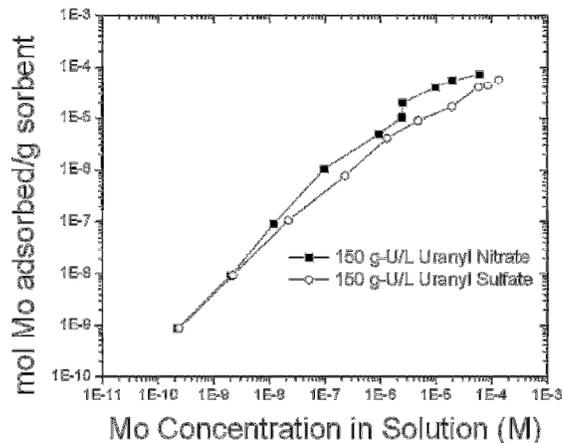


Figure 1. Langmuir data obtained in a batch mode.

Table 1. K_d results for Mo adsorption in Na_2SO_4 and NaNO_3 .

Initial Mo (M)	$\text{TiO}_2, K_d, \text{Mo}$ 0.63 M SO_4^{2-}	$\text{TiO}_2, K_d, \text{Mo}$ 1.26 M NO_3^-
1.00E-08	3900	4000
1.00E-07	4200	4600
1.00E-06	4900	7600
1.00E-05	3400	11000
5.00E-05	3100	5200
1.00E-04	1900	4200
2.00E-04	900	7900
4.00E-04	700	4000
6.00E-04	500	2800
8.00E-04	400	1200

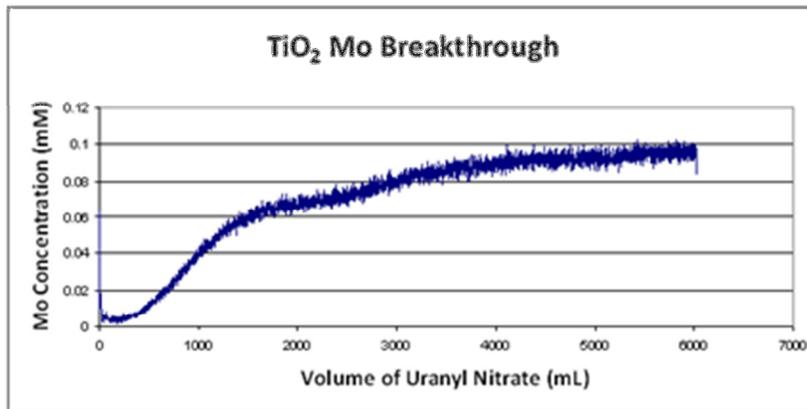


Figure 2. Mo-breakthrough data obtained using a 150 g-U/L uranyl nitrate solution.

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 [4]. 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 [4].

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 .

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

Langmuir-type data were obtained in solutions containing 150 g-U/L uranyl-sulfate. Figure 3 shows the Langmuir data obtained in the presence of a uranyl-sulfate solution containing 150 g-U/L, and the Origin 8.5.1 fitting of the data. The linear and non-linear parameters best modeled by Origin are $a = 1421$ and $b = 18 \text{ mM}^{-1}$. Similar data were collected and reported for solutions containing 150 g-U/L uranyl-nitrate, and the Origin-modeled parameters are $a = 5479$ and $b = 34 \text{ mM}^{-1}$ [5].

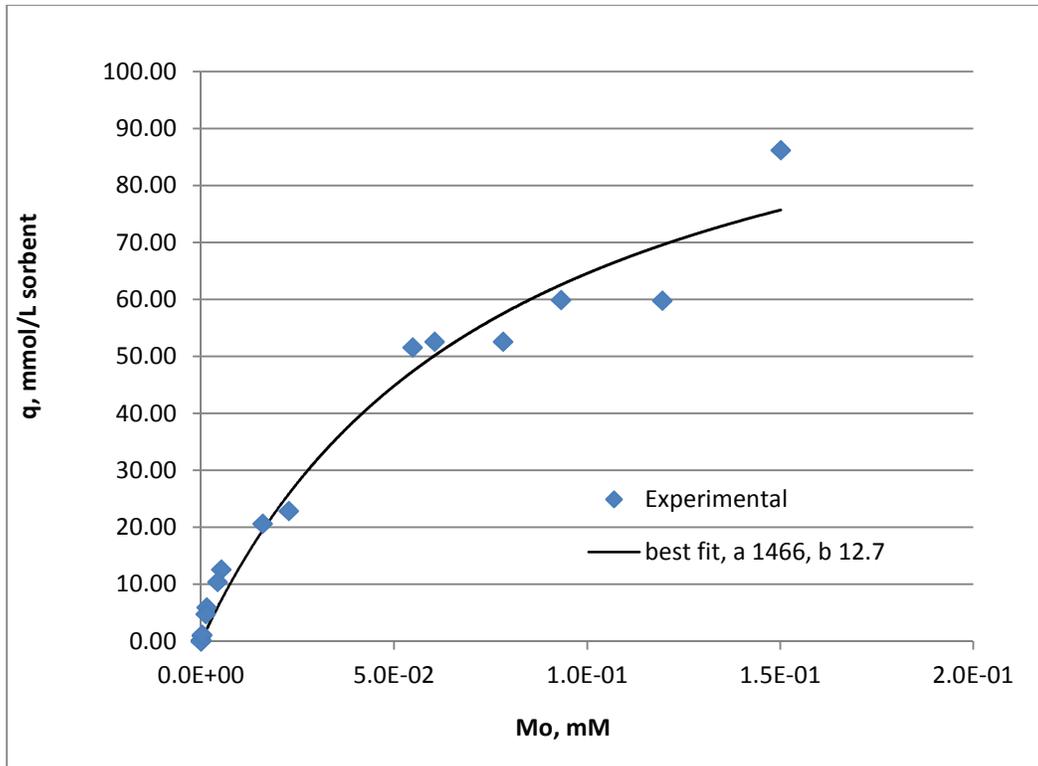


Figure 3. Plot of Langmuir type adsorption on a titania sorbent in the presence of a 150 g-U/L uranyl sulfate with Origin fitting.

Other important parameters required for VERSE modeling, such as density, viscosity, interparticle diffusivity, and intraparticle diffusivity, have been described previously [5,6,7].

Direct Down-Scale Column Results

Results for down-scale column experiments for S110 (pure titania sorbent with 110 μm particles, supplied by ZirChrom Separations), are shown in Table 2. The feed solution contained 0.0045 mM stable Mo and tracer Mo-99 and 150 g-U/L uranyl-nitrate. Linear velocities ranged from 3-10 cm/min for both loading and stripping, and results show an effect of linear velocity on Mo recovery. As the linear velocity increases, the %Mo recovery decreases from 88% to 77%. Additionally, temperature control especially during the strip was not controlled very well in these column experiments. Modifications have been made for the direct down-scale column experiments using uranyl-sulfate solutions, where the stripping velocity is half of the loading velocity, and temperature is controlled better to maintain a temperature of 60-80°C during Mo recovery.

Table 2. Results for direct down-scale column experiments using a uranyl-nitrate solution.

Column Size (ID x L)	Velocity (cm/min)	Sorbent	%Mo in Effluent	%Mo in Washes	%Mo Recovered	Stripping Agent
1.5 x 6.2	3	S110	1.0	0.6	88.0	1 M NH_4OH
1.5 x 6.3	5	S110	1.0	1.0	85.0	1 M NH_4OH
1.5 x 6.3	7.5	S110	2.0	0.1	85.0	1 M NH_4OH
1.5 x 6.3	10	S110	1.0	0.1	77.0	1 M NH_4OH

Results for down-scale column experiments for S110 in the presence of a uranyl-sulfate solution are shown in Table 3. The feed solution contained 0.002-0.004 mM stable Mo and tracer Mo-99 and 90-146 g-U/L uranyl-sulfate. Linear velocities ranged from 3-7 cm/min for loading and 1.6-7 cm/min for stripping, and again results show an effect of linear velocity on Mo recovery. As the linear velocity increases, the %Mo recovery decreases from 100% to 86%. Temperature during stripping was much more controlled during the experiments with uranyl-sulfate solutions, and results indicate that heating the strip solution improved Mo recoveries significantly. Since the latest set of direct down-scale column experiments, it has been determined that pH is the main factor for decreasing the number of column volumes of strip solution generated. Subsequent mini-SHINE sodium bisulfate column experiments have added a 3 column volume wash using 1 M NaOH before stripping with 0.1 M NaOH. Future experiments may utilize 1 M NaOH as the sole strip solution without a base wash prior to stripping.

Table 3. Results for direct down-scale column experiments using a uranyl-sulfate solution.

U (g-U/L)	Column Size (ID x L)	%Mo in Effluent	%Mo Recovered	Loading Velocity (cm/min)	Stripping Velocity (cm/min)
90	1 x 5	1.0	90	3	3
90	1 x 5	0.7	100	4	4
90	1 x 5	1.1	94	5	5
104	1 x 3	0.2	96	3.1	1.6
125	0.66 x 5	0.1	100	4.7	2.3
130	1 x 5	0.08	100	7	3.5
130	1 x 5	0.11	86	7	7
146	1 x 4	0.66	92	3.8	1.9
146	1 x 4	0.1	66	3.8	3.8

Plant-Scale Column Designs

Using batch data, Mo-breakthrough data, and small-scale column data, VERSE was utilized to generate plant-scale column designs for both a uranyl-nitrate and uranyl-sulfate solution. Table 4 shows the results obtained for plant-scale column designs for uranyl-nitrate and uranyl-sulfate solutions assuming uranium concentrations between 90 and 150 g-U/L and Mo concentrations in the range of 0.002 – 0.005 mM. The designs include a 10% increase in column length to account for potential adsorption of any other fission products. Column designs have been generated for phase 1 and phase 2 mini-SHINE experiments where the effects of fission product competition will be present. Once these data are collected, they will be input into VERSE to determine if changes in column designs are needed.

Table 4. Plant-scale column designs for uranyl nitrate and uranyl sulfate solutions.

Solution	ID (cm)	L (cm)	CV (L)
Uranyl Nitrate	12	9.7	1.1
Uranyl Sulfate	12	13	1.5

Conclusions

VERSE is a useful tool for the efficient design of large-scale separation without requiring a significant amount of data. Batch data, Mo-breakthrough data, and small-scale column data along with some other physical characteristics of the feed solution and sorbent material are all that is required to generate a plant-scale column design. Optimization of the separation process is continuously made as more data are collected. As clearly shown by the data, VERSE can be utilized to generate column designs for many different media and processes.

References

- [1] Vandegrift, G.F. “Facts and Myths Concerning ⁹⁹Mo Production with HEU and LEU Targets,” Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, November 6-10, 2005, Boston, MA.
- [2] Snelgrove, J.L., Hofman, G.L., Wiencek, T.C., Wu, C.T., Vandegrift, G.F., Aase, S., Buchholz, B. A., Dong, D. J., Leonard, R.A., and Srinivasan, B. “Development and Processing of LEU Targets for Mo-99 Production—Overview of the ANL Program,” Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, September 18-22, 1995, Paris, France.
- [3] Ziegler, A.J., Stepinski, D.C., Krebs, J.F., Bakel, A.J., and Vandegrift, G.F. “Mo-99 Recovery from Aqueous-Homogeneous-Reactor Fuel—Behavior of Termoxid Sorbents,” Proceedings of the RERTR 2008 International Meeting, October 5-9, 2008 Washington D.C.
- [4] Langmuir, I. “The Constitution and Fundamental Properties of Solids and Liquids. Part I Solids.” *Journal of the American Chemical Society*. (1916). **38**, 2221-2295.
- [5] Chung, P.-L. Wang, N.-H. L., Stepinski, D.C., Youker, A.J., Krahn, E.O., and Vandegrift, G.F. “Design, Scale Up, and Optimization of Column Processes for the Recovery of a Medical Isotope, Purdue University Progress Report, May 31, 2011.
- [6] Youker, A.J., Stepinski, D.C., Ling, L., and Vandegrift, G.F. “Mo Recovery Updates and Physical Properties of Uranyl Sulfate Solutions,” Argonne National Laboratory, ANL/CSE-13/20, September 2012.
- [8] Youker, A.J., Stepinski, D.C., Ling, L., Chung, P-L., and Vandegrift, G.F. “Plant-Scale Concentration Column Designs for SHINE Target Solutions,” Argonne National Laboratory, ANL/CSE-13/24, September 2012.

Funding Source

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.