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Separation, Purification, and Clean-Up Developments for MIPS and SHINE

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ABSTRACT

Argonne has demonstrated that Mo-99 can be separated from LEU (low-enriched uranium) solutions containing 90 – 300 g-U/L as uranyl nitrate or uranyl sulfate. Batch and column data have been collected and input into the VERSE (Versatile Reaction Separation) code to design plant-scale columns for Mo adsorption and recovery for the MIPS and SHINE processes. Additionally, the radiolytic stability of alpha-benzoin oxime (ABO), an important reagent used to precipitate Mo in the LEU-Modified Cintichem process, has been investigated and can withstand radiation doses representative of several kilocuries of Mo-99. Finally, four different methods have been examined as potential clean-up options for the recycled irradiated uranyl-nitrate and -sulfate solutions, but UREX processing (preceded by conversion to nitrate for uranyl-sulfate target solutions) appears to be the best route.

Introduction

Argonne is supporting Babcock and Wilcox Technical Services Group (BWTSG) and Morgridge Institute of Research (MIR) in their efforts to produce a domestic supply of Mo-99. BWTSG plans to build an aqueous homogeneous reactor (AHR) that will utilize a uranyl nitrate solution to produce Mo-99. MIR is developing an accelerator-driven process that will most likely use a uranyl sulfate solution for Mo-99 production. The Medical Isotope Production System (MIPS) proposed by BWTSG and the Subcritical Hybrid Intense Neutron Emitter (SHINE) planned by MIR will both use a pure titania sorbent to separate Mo-99. Batch and column data have been collected and input into VERSE to design plant-scale column conditions for complete Mo adsorption from uranyl nitrate and uranyl sulfate solutions and full Mo recovery using 1 M NH₄OH. Recovered Mo will then be purified using the LEU-Modified Cintichem process, and

experiments have been done that examine the radiolytic stability of alpha-benzoin oxime, which is used to precipitate Mo in the process. Results indicate that ABO is much more stable than anticipated when exposed to high levels of radiation. Lastly, Argonne has investigated four different methods to clean up the uranyl sulfate solution, but conversion to uranyl nitrate followed by UREX processing appears to be the best option if clean-up is required.

Progress in the Mo-99 separation and recovery processes will be discussed separately for the MIPS and SHINE projects because each project is at a different stage in the development process. Plant-scale column designs have been generated for MIPS, but data are still being collected to design a plant-scale column for SHINE. Both MIPS and SHINE are considering the use of the LEU-Modified Cintichem process for Mo purification, so the Van de Graaff (VDG) irradiation tests that have been performed using ABO will benefit both companies. Lastly, the fuel clean-up options are being examined for MIR, but developments in this area are beneficial for BWTSG as well.

Experimental

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 or 1 – 48 hours for kinetic tests at 60°C using a thermostated shaker bath. Aqueous solutions contained tracer Mo-99 and 1 ppm stable Mo added as $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ in the presence of sodium sulfate, sodium nitrate, uranyl sulfate, or uranyl nitrate. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a $0.22 \mu\text{m}$ pore size PVDF membrane filter.

Preparation of Mo-99 Spike Solution.

Mo-99 is removed from a Tc-99m generator by placing a serum vial containing 1 M NH_4OH on the needle labeled “Saline Charge”. Then an evacuated serum vial is placed on the needle labeled “Receiver”. The Mo-99 spiked solution is prepared by bringing the solution to dryness on a hot plate, and re-dissolving it in 0.05 M H_2SO_4 or 0.1 M HNO_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 was expressed in terms of a distribution coefficient, K_d , shown in equation (1).

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

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

Column Tests

An AKTA liquid chromatography system is used to pass solution through titania columns of variable size. The feed solution containing stable Mo and tracer Mo-99 is loaded onto the column in the upflow direction. After loading is complete, the column is washed with pH 1 acid (nitric or sulfuric) and water in the upflow direction. Mo is eluted from the column using 1 M NH_4OH in the downflow direction, and a final water wash is performed in the upflow direction.

Van de Graaff Tests

The radiation stability studies of alpha-benzoin oxime (ABO), which is a key reagent used in the LEU Modified Cintichem process, were performed using a 3 MeV Van de Graaff generator (VDG) at Argonne. These experiments are important because Cintichem never processed more than 1000 Ci of Mo-99 per batch, and there is a concern that larger batches would cause radiolytic decomposition of ABO and lead to significant Mo losses. The formation of a Mo-ABO precipitate was based on the LEU Modified Cintichem process procedure, but it was scaled down to about 9 mg of ABO per single experiment (actual Cintichem process uses ~400 mg of ABO). After forming the precipitate, the solution was removed and samples of Mo-ABO were irradiated in the presence and absence of 0.1 M HNO₃. Prior to the irradiation of ABO, the dose rate from the VDG electron beam was determined using an oxalic acid dosimeter.[1] The samples of Mo-ABO precipitate were irradiated for 20-160 minutes at 1-10 μA current, and doses up to 24.4 GRad were delivered. After the irradiation, the Mo-ABO precipitate was washed with 0.1 M HNO₃, filtered, and then dissolved in a solution of hot 0.4 M NaOH/1% H₂O₂ and 0.2 M NaOH/1% H₂O₂. The distribution of Mo-99 activity on a filter and in the HNO₃ and NaOH fractions was determined from gamma counting.

Results and Discussion

Mo-99 Separation Developments for MIR

Argonne became involved with Morgridge in May 2011, and as a result, the design of a plant-scale column is still underway. Initially, the feed solutions being considered for MIR contained 90 and 150 g-U/L as uranyl sulfate. Additionally, ZirChrom Separations, Inc discontinued their Sachtopore (pure titania) sorbent with 80 micron particles and 60 angstrom pores, which has been used previously in all Mo separation and recovery work. As a result, several different sachtopore sorbents with different particle and pore sizes were tested in an effort to find a replacement for S80. Mo uptake from a variety of different titania sorbents was studied in a batch mode as a function of time to determine the effects of particle and/or pore size on the kinetics of Mo adsorption. Results are also shown for Mo uptake from a 150 g-U/L uranyl nitrate solution because MIR has not completely ruled out the use of uranyl nitrate. The pure titania sorbent with 110 micron particles and 60 angstrom pores S110(60) performed the best. Mo uptake was fairly consistent using both 90 g-U/L uranyl sulfate and 150 g-U/L uranyl nitrate solutions after 1 – 40 hours of contact time using S110(60) sorbent. It appears that equilibrium has been reached after 40 hours using a 90 g-U/L uranyl sulfate solution; whereas, it may take 48 hours or more for equilibrium to be reached using a 150 g-U/L uranyl nitrate solution. S80(60) performed the next best; however, the uptake of Mo was much better from a solution containing 150 g-U/L uranyl nitrate compared to a solution containing 90 g-U/L uranyl sulfate. S40(60) performed similarly to S80(60) in the presence of 90 g-U/L uranyl sulfate. Sorbents with larger pore sizes behaved much worse. S80(300), S40(300), and S80 (500) adsorbed the least amount of Mo, and the kinetics were slower. These results suggest that using a titania sorbent with larger pore sizes is not be a good choice for the design of a Mo separation and recovery column. K_d values using titania sorbents with larger pore sizes are about 1000 times less after 20 – 48 hours of contact time. The results are shown in Figure 1.

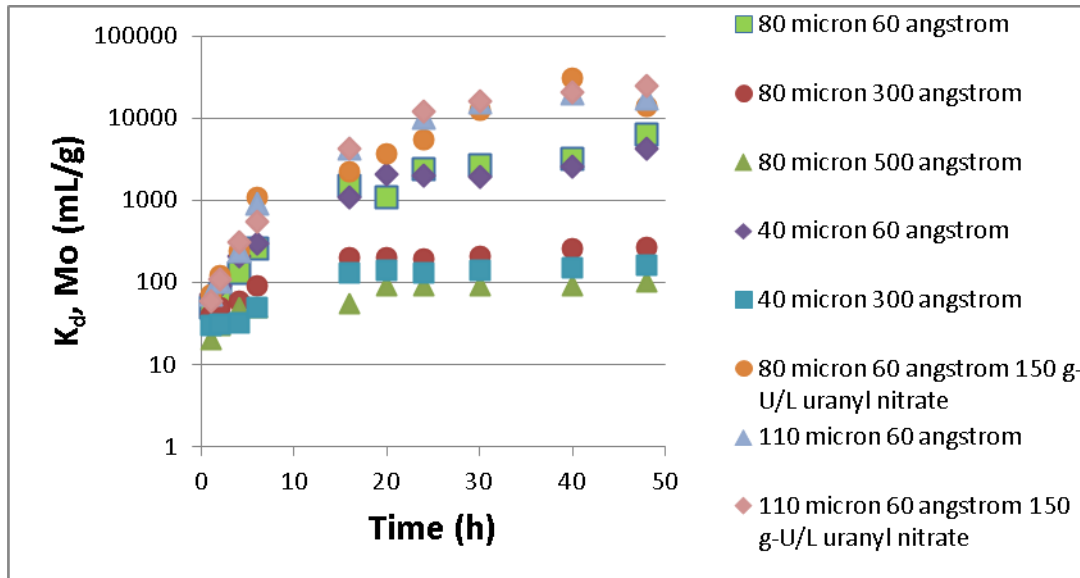


Figure 1. Kinetic data for the uptake of Mo from solutions containing 90 g-U/L uranyl sulfate or 150 g-U/L uranyl nitrate using pure titania sorbent with different particle and pore sizes.

Langmuir Results for MIR

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.[2]

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.[3]

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 with 0.63 M Na₂SO₄, 1.26 M Na₂SO₄, 1.26 M NaNO₃, 90, 150, and 300 g-U/L UO₂SO₄, and 150 g-U/L UO₂(NO₃)₂ solutions (Figure 2). The large range of conditions investigated was due to the fact that a final fuel composition for MIR has not been chosen yet. Titania sorbents with 60 angstrom pores and particle sizes of 40, 80, and 110 microns were tested. A significant amount of data was collected using a titania sorbent with 80 micron particles and 60 angstrom pores; however, the manufacturer will no longer be producing S80 as of August 15, 2011. As a result, titania sorbents with 40 and 110 micron particles and 60

angstrom pores are being considered for the design of the plant-scale Mo separation and recovery column. Figure 2 shows that S80 adsorbs the most Mo in the presence of 1.26 M NaNO_3 , which is representative of the nitrate concentration in a 150 g-U/L uranyl nitrate solution. S80 adsorbs slightly less Mo in the presence of Na_2SO_4 solutions (0.63 and 1.26 M), which is not surprising because sulfate competes more strongly with Mo than nitrate for titania adsorption sites. In the presence of uranium, Mo uptake by S80 is the best in the presence of a 150 g-U/L uranyl nitrate solution followed by 90 g-U/L, 150 g-U/L, and 300 g-U/L uranyl sulfate solutions.

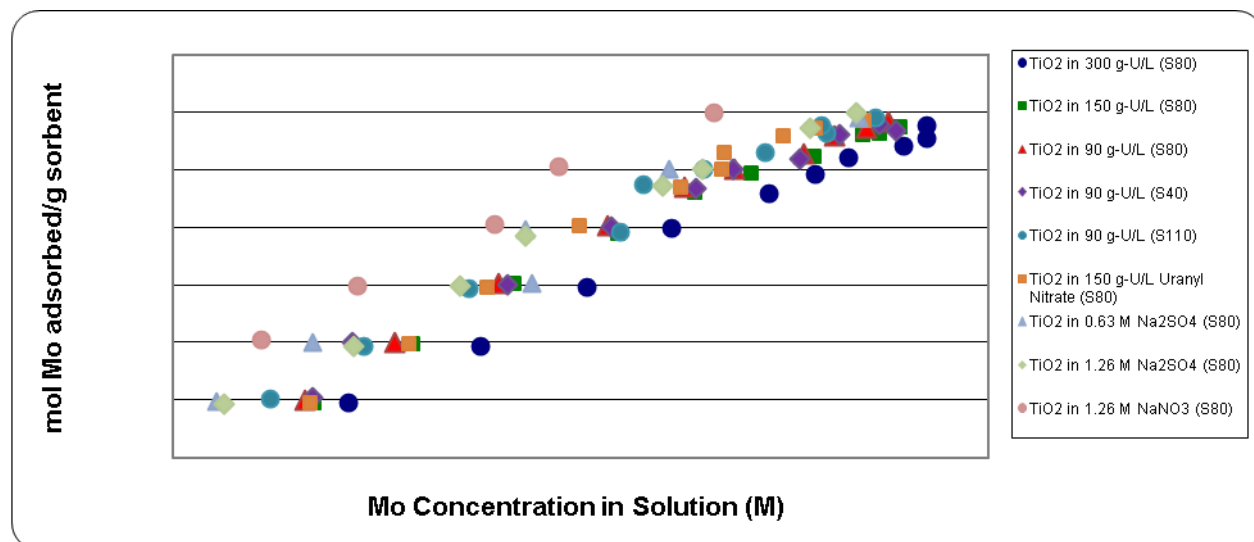


Figure 2. Plot of Langmuir type adsorption on titania sorbents in the presence of uranyl sulfate, uranyl nitrate, sodium sulfate, and sodium nitrate.

When these data were obtained, a 90 g-U/L uranyl sulfate solution was the top candidate for the SHINE fuel solution; however, a range of 110 – 140 g-U/L is now being considered. As a result, Langmuir-type data were obtained using a 90 g-U/L uranyl sulfate solution with a pure titania sorbent containing 40, 80, and 110 micron particle sizes and 60 angstrom pore sizes. (Figure 3) Langmuir data show that S110 performs the best and would be the top candidate for the design of the Mo separation and recovery column from a solution containing 90 g-U/L uranyl sulfate. The S110 sorbent performs better than S40 and S80 with pore sizes of 60 angstrom and much better than sorbents with pore sizes of 300 and 500 angstroms as was seen with the kinetic results. The same results would be expected for a solution containing 110 – 140 g-U/L as uranyl sulfate. The saturation point for Mo adsorption on titania is not reached because Mo precipitates in uranium solutions past ~ 0.6 mM. Additionally, Mo precipitates on the surface of titania at a concentration ≥ 10 mM Mo in sodium nitrate solutions.

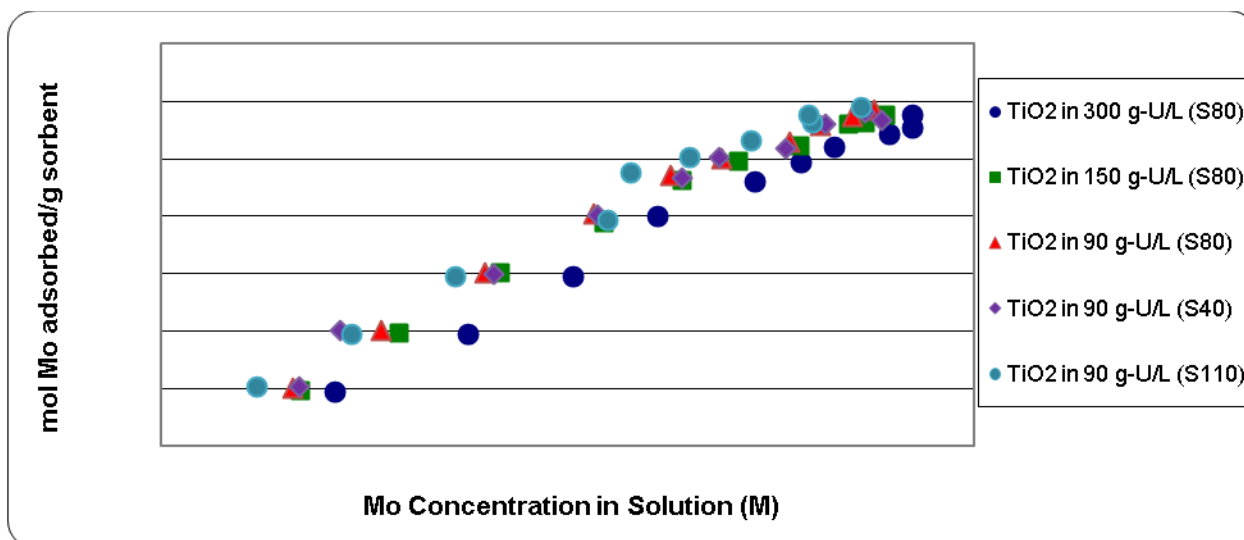


Figure 3. Plot of Langmuir type adsorption in the presence of 90, 150, and 300 g-U/L uranyl sulfate using titania sorbents with particle sizes of 40, 80, and 110 microns.

Mo adsorption on titania sorbents in the presence of uranyl nitrate or sulfate solutions follows Langmuir-type behavior. Langmuir data can be used to estimate conditions for column experiments, where the sorbent's capacity for Mo can be determined in a column setting. Batch data are better at estimating the linear isotherm parameter associated with the Langmuir model, while column tests can be used to estimate the non-linear parameter associated with the Langmuir model. Batch data and small-scale column data are then input into the VERSE (VERsatile REaction SEparation) simulator to design a plant-scale column for Mo separation and recovery. VERSE was developed by Dr. Linda Wang at Purdue University, and it is used to generate column sizes and parameters for large scale separation processes by using experimental data collected in a batch mode and small-scale column setting. Two different types of column experiments are typically performed, which are Mo breakthrough experiments and 2-hour Mo loading experiments. Batch data were input into VERSE and a and b values were estimated for solutions containing 150 g-U/L uranyl sulfate ($a = 1155$ and $b = 23 \text{ mM}^{-1}$) and 90 g-U/L uranyl sulfate ($a = 1421$ and $b = 18 \text{ mM}^{-1}$). Figure 4 shows the data collected using 150 g-U/L and 90 g-U/L uranyl sulfate solutions fit to the Langmuir model with R^2 values of 0.99 and 0.98.

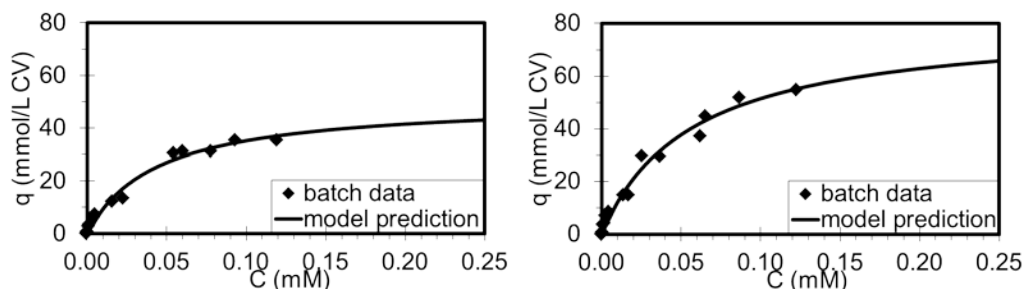


Figure 4. Batch data using 150 g-U/L uranyl sulfate (left) and 90 g-U/L uranyl sulfate (right) fit to the Langmuir model.

Mo Breakthrough Column Experiments

Mo breakthrough column experiments have been initiated using a 90 g-U/L uranyl sulfate solution containing 0.045 mM Mo and tracer Mo-99. Table I shows the column dimensions and parameters that VERSE predicted for obtaining full Mo breakthrough from a 90 g-U/L (0.045 mM Mo) uranyl sulfate solution using a S110 column.

Table I. Preliminary breakthrough experimental designs for 0.045 mM Mo in 90 g-U/L UO_2SO_4 at 60°C.

Sorbent	ID (cm)	L (cm)	CV (mL)	u_s/L (min^{-1})	u_s (cm/min)	Mo amount *(meq/CV)	ΔP (atm)	Flowrate (mL/min)	To achieve a complete breakthrough curve	
									Time (hr)	Volume* (mL)
S110	0.66	1	0.34	3	3	0.0032	0.01	1.0	> 10	> 616
S110	0.66	1	0.34	4	4	0.0032	0.01	1.4	10	821
S110	0.66	1	0.34	5	5	0.0032	0.01	1.7	10	1026
S110	1.0	1	0.8	3	3	0.0074	0.01	2.4	> 10	> 1414
S110	1.0	1	0.8	4	4	0.0074	0.01	3.1	10	1885
S110	1.0	1	0.8	5	5	0.0074	0.01	3.9	10	2356
S110	1.0	1.5	1.2	3	4.5	0.0111	0.01	3.5	> 10	> 2121
S110	1.0	1.5	1.2	4	6.0	0.0111	0.02	4.7	10	2827
S110	1.0	1.5	1.2	5	7.5	0.0111	0.02	5.9	10	3534
S110	1.0	2.0	1.6	3	6	0.0148	0.02	4.7	> 10	> 2827
S110	1.0	2.0	1.6	4	8	0.0148	0.03	6.3	10	3770
S110	1.0	2.0	1.6	5	10	0.0148	0.04	7.9	10	4712

Mo breakthrough column experiments have been completed using a 0.66 cm ID by 1 cm L S110 column and a 1 cm ID by 1 cm L S110 with a 90 g-U/L uranyl sulfate solution containing 0.045 mM Mo and tracer Mo-99. Linear velocities ranged from 3 – 5 cm/min, and results are shown in Figures 5 and 6. VERSE predicted that full Mo breakthrough would be achieved after >616, 821, and 1026 mL of a 90 g-U/L uranyl sulfate solution containing 0.045 mM Mo and tracer Mo-99 passes through a 0.66 cm ID by 1 cm at 3, 4, and 5 cm/min. Experimental results show that S110 performs better than expected based on VERSE predictions. Figure 5 shows that full Mo breakthrough is not achieved after 980 mL at 3 cm/min and 1330 mL at 4 cm/min are passed through the column. Full Mo breakthrough is still not achieved until 1750 mL of solution are passed through the column at 5 cm/min. The same type of behavior is observed using a 1 cm ID by 1 cm L S110 column where VERSE predicted full Mo breakthrough would occur after >1414, 1885, 2356 mL are passed through the column at 3, 4, and 5 cm/min. Figure 6 shows that after 2100 mL at 3 cm/min and 2247 mL at 4 cm/min are loaded onto the column, full Mo breakthrough still has not been reached. Surprisingly, it appears that Mo begins to breakthrough more rapidly at 3 cm/min rather than at 4 cm/min.

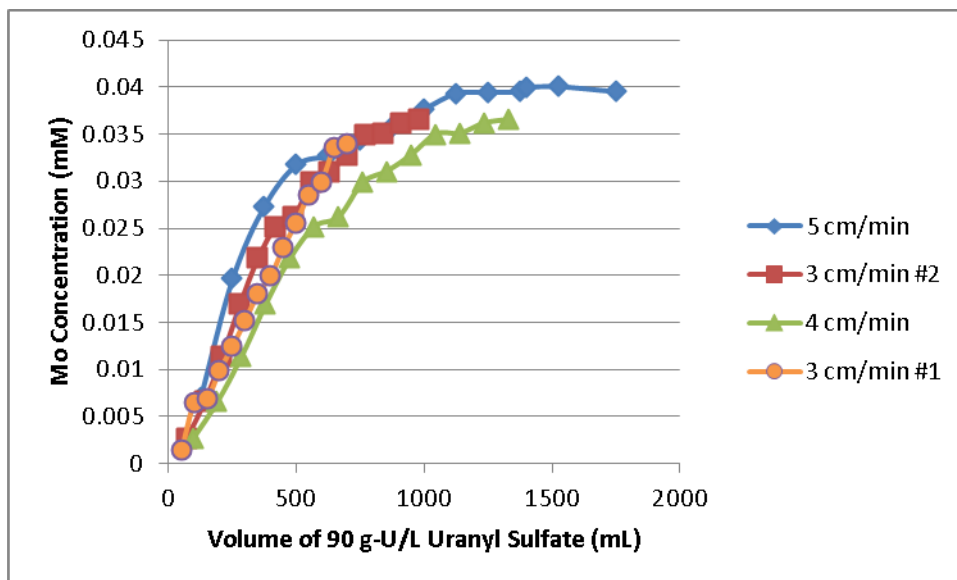


Figure 5. Mo breakthrough column results for 0.66 cm ID by 1 cm L S110 column.

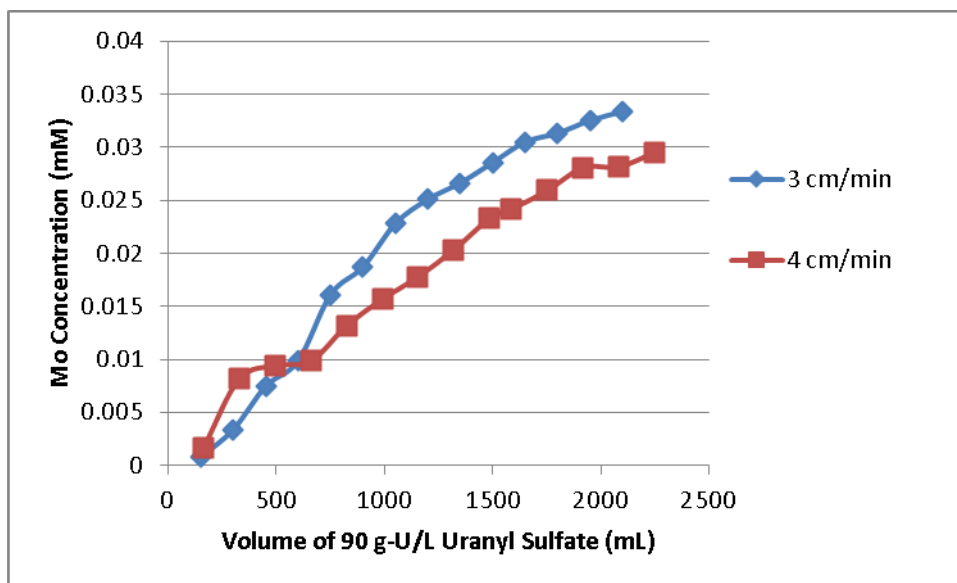


Figure 6. Mo breakthrough column results for 1 cm ID by 1 cm L S110 column.

Argonne will continue to gather Mo breakthrough data under various conditions. Mo breakthrough curve results will be input into VERSE to design the plant-scale column for the separation and recovery of Mo. Once, the plant-scale column has been designed, small-scale column experiments that are a direct downscale of the plant operation will be performed.

Mo-99 Separation Developments for MIPS

Eight column runs were performed using S40 and S110 pure titania sorbents with 60 angstrom pore sizes. Results are shown in Table II, and S110 outperforms S40. A significant amount of Mo is observed in the effluent for S40 sorbent. Mo recoveries varied from 73-89% and were not greatly affected by the stripping velocities. The lowest Mo recovery was obtained at 7.5 cm/min (77% recovered). Potassium permanganate (0.5 wt.%) was added to the first water wash to

potentially improve Mo recovery by promoting the oxidation of any reduced Mo to Mo(VI). With recoveries of 73% and 89%, the results obtained with permanganate are within the range obtained without permanganate. For these runs, a smaller amount of permanganate was used due to pressure problems with the AKTA system, and it was not added to the strip solution due to precipitation in 1 M NH₄OH. Mo breakthrough curves are also being done for MIPS to ensure that plant-scale column designs for S80 can be used with S110.

Table II. Column run results for S40 and S110 sorbents.

Date of Run	Column Size (ID x L)	Velocity (cm/min)	Sorbent	%Mo in Effluent	%Mo in Washes	%Mo Recovered	Stripping Agent
09/15/11	1.5 x 3.1	9	S40	16.0	0.6	86.0	1 M NH ₄ OH
09/21/11	1.5 x 6.2	3	S110	1.0	0.6	88.0	1 M NH ₄ OH
09/23/11	1.5 x 6.3	5	S110	1.0	1.0	85.0	1 M NH ₄ OH
09/26/11	1.5 x 2.6	5	S40	32.0	0.3	80.0	1 M NH ₄ OH
09/28/11	1.5 x 6.3	10	S110	1.0	0.1	77.0	1 M NH ₄ OH
09/30/11	1.5 x 6.3	7.5	S110	2.0	0.1	85.0	1 M NH ₄ OH
10/06/11	1.5 x 6.2	7.5	S110	7.3	0.8	73.0*	1 M NH ₄ OH
10/12/11	1.5 x 6.2	3	S110	7.0	1.0	89.0*	1 M NH ₄ OH

*0.5 wt. % KMnO₄ was added to the first water wash.

Radiolytic Stability of ABO

Two scenarios of the Mo-ABO complex were simulated with MCNPX in order to determine the absorbed dose in ABO during a 20 minute Cintichem processing step from 1 kCi of Mo-99. Mo-99 recovery is being studied as a function of absorbed dose to ABO with a 3 MeV Van de Graaff accelerator. This simulation provides a link between Mo-99 activity and dose in ABO, which correlates Mo-99 recovery with activity. Both simulated geometries assumed a total of 400 mg of ABO, which corresponds to a realistic mass during the precipitation process. The first scenario was modeled as two layers of glass beads (4 mm diameter) with a thin (~46 μm) layer of Mo-ABO precipitate around each bead. The second geometry was much simpler – a single layer (~204 μm thick) of Mo-ABO precipitate on top of a frit. The simulations gave 76.2 Mrad and 148.3 Mrad doses for the glass bead and the mono layer geometries, respectively. These two models represent two extremes of a realistic situation, when some of the precipitate would be deposited on the glass beads and some on the frit as a single layer. Therefore, a realistic 20 minute dose in ABO from a 1 kCi Mo-99 source should be in the range of doses provided by this simulation study.

For each irradiation Mo-ABO sample, one control sample, which was not irradiated at the VDG was processed. The average Mo-99 recovery in the NaOH fraction for the control sample in the absence and the presence of 0.1 M HNO₃ was 96.4%±4% and 93.7%±4.5%, respectively. Most of the residual Mo-99 activity was found on the filter and almost none in HNO₃ fraction as expected. Washing the precipitate from the irradiated samples with 0.1 M HNO₃ lead to the formation of a yellowish-orange solution, which suggests partial dissolution of ABO, or its radiolytic degradation products. However, the data from gamma analysis show no significant presence of Mo in this solution. The yellow-orange color of the nitric acid wash slowly disappears at higher doses (~1GRad); however, at this point some Mo-99 was detected.

In general, it was observed that the stability of the Mo-ABO precipitate is much higher when the irradiations were performed in the absence of nitric acid. For these experiments, no significant decrease in Mo-99 recovery was observed for doses up to ~6.1 GRad, which is equivalent to processing ~41 kCi of Mo-99. However, the results for the irradiations of Mo-ABO in the presence of 0.1 M HNO₃ suggest that ~10 kCi of Mo-99 can be processed without significant loss of Mo-99 during the HNO₃ wash. During the Cintichem processing steps, several portions of fresh 0.1 M nitric acid are used to wash the ABO precipitate; therefore, the data obtained from the irradiations in the presence of nitric acid more realistically represent the maximum activity of Mo-99 that could be processed by a single Cintichem run.

Potential Methods for Cleanup of Irradiated Uranyl Sulfate Target Solutions

Several methods are being considered by Argonne for periodic cleanup of the irradiated uranyl sulfate solutions if deemed necessary. These methods include conversion to nitrate media followed by UREX processing, solvent extraction of uranyl sulfate, precipitation of uranyl ion as uranyl peroxide, and anion exchange of uranyl sulfate complexes. Currently, the conversion of uranyl sulfate to uranyl nitrate followed by UREX is best option for cleanup. Argonne is not involved in the fuel clean-up work for BWTS, but UREX processing would be recommended for a uranyl nitrate solution as well, and MIR has not completely ruled out the use of uranyl nitrate.

Conversion to Nitrate Media Followed by UREX Processing

This multistep process begins with the conversion of the sulfate solution to a nitrate solution by the addition of calcium nitrate, which will precipitate much of the sulfate as the calcium salt. If enough Ca(NO₃)₂ is added (sufficient relative to the uranyl sulfate) to completely precipitate almost all of the sulfate as CaSO₄, there will be a solution of uranyl nitrate and almost all of the accompanying fission and activation products plus ~2 g/L of soluble CaSO₄. The CaSO₄ precipitate should be quite low in radioactivity. The Ba-140 sulfate will definitely precipitate, but the fate of radioactive Sr is not known because strontium sulfate has a solubility of ~0.1 g/L; however, it may be co-precipitated with BaSO₄. The lanthanide sulfates will be in solution (e.g., lanthanum sulfate has a solubility of ~30 g/L). There may be a few minor fission products that will precipitate. The precipitation process would likely be a batch type operation with a removable reservoir/filter apparatus.

Once most of the sulfate is replaced by nitrate, the uranium solution would be purified using the UREX process. The resulting uranyl nitrate product in 0.01 M HNO₃ would be ideally suited for uranium precipitation using ammonium hydroxide (or ammonia) to produce ammonium

diuranate. This technique is well understood and, with pH control, produces a quantitative and filterable precipitate. The ammonium-diuranate solid would subsequently be placed in a furnace and heated to $\sim 400^\circ\text{C}$ to form UO_3 . [4] This process typically produces U_3O_8 , but UO_3 is better because it can be used directly to prepare uranyl sulfate. The liquid waste from the uranium precipitation would be very low in radioactivity and could either be evaporated or solidified using Acid Bond or another acceptable solidification process. The UO_3 is then dissolved in H_2SO_4 for reuse; this step may need some development. The uranium will dissolve without much difficulty, but we need to have a solution of pH 1, so there cannot be any excess H_2SO_4 . Unlike the uranyl nitrate system, where heat can be used to drive off HNO_3 , excess H_2SO_4 is more problematic and would most likely require an additional precipitation step.

Direct Solvent-Extraction Process for Uranyl Sulfate

This process is based on the extraction of uranyl-disulfate anion by a solvent composed of two-parts trioctyl ammonium sulfate (TOA) and one-part trioctyl phosphate (TOPO) diluted with either an alkane or tetrachloroethylene. In this process, uranium is extracted into the organic phase as $\text{UO}_2(\text{SO}_4)_2^{2-}$ anion with two trioctyl ammonium cations and one trioctyl phosphate. If the proper aqueous stripping solution is chosen, uranyl sulfate will be stripped and the trioctyl ammonium salt will remain in the sulfate form to be recycled directly to the extraction section. Oxalic acid or other hydrophilic complexants are being examined as possible stripping agents. The complexant must have three important properties—forms strong complexes with uranyl ion, will not displace sulfate in the organic-phase trioctyl ammonium sulfate salt, and can be destroyed in the aqueous uranyl-sulfate product solution without leaving residue in the solution.

Concerns being addressed are (1) getting the concentrations of TOA and TOPO as high as possible in the organic phase to allow a workable, robust solvent extraction system, (2) measuring decontamination factors from other components in the irradiated solution that can be achieved by this process, and (3) finding stripping conditions that will allow facile conversion of the product solution to the composition of the target solution; however, experimental work on this system has shown that the solvent extraction process holds little promise for success. This option will not be pursued further.

Precipitation of Uranyl Ion as Uranyl Peroxide

In principal, the precipitation should be straight forward; the solubility product ($K_{\text{sp}} = [\text{UO}_2^{2+}] \times [\text{O}_2^{2-}]$) for uranyl peroxide is 1.3×10^{-36} . [5] However, there are many factors that influence the concentrations of free UO_2^{2+} ion and free O_2^{2-} ions, and therefore the completeness of the precipitation. For uranyl ion, there are pH-dependent hydrolysis reactions that form the species $\text{UO}_2\text{OH}^{1+}$, $\text{UO}_2(\text{OH})_2$, and $\text{UO}_2(\text{OH})_3^{1-}$ and sulfate complexes UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, and $\text{UO}_2(\text{SO}_4)_3^{4-}$. The free peroxide-ion concentration is also affected by the pH, due to formation of the weak acids H_2O_2 and HO_2^- . The relative concentrations of uranyl-sulfate complexes are also related to pH through the equilibria of sulfate ion with HSO_4^- and H_2SO_4 . Further complications involving the precipitation are that peroxide ion can also form complexes with uranyl ion $\text{UO}_2(\text{O}_2)_2^{2-}$ and $\text{UO}_2(\text{O}_2)_3^{4-}$.

Low pH will increase uranyl-ion solubility by keeping the concentration of peroxide ion very low. As the pH is increased, the free uranyl ion concentration will drop due to an increase in the

importance of hydrolysis reactions, complexation with sulfate, and eventually complexation with peroxide ion.

Development activities for this step are (1) to find optimized conditions for performing this precipitation and (2) to measure decontamination factors from other irradiated-solution components. As well as the pH dependence, conditions of stirring and peroxide addition must be developed that allow formation of a highly crystalline, filterable precipitate. Under the wrong conditions, the precipitate will resemble a “buttery” precipitate that can only be collected by centrifugation. Thoroughly washing the precipitate is vital to getting high decontamination factors for the uranium.

Once the precipitate is filtered and washed, it must be thermally treated to form UO_3 . This thermal process must be carefully performed to minimize reduction to U_3O_8 , which would be more difficult to dissolve directly in sulfuric acid.[6] The last step is the dissolution of UO_3 in sulfuric acid to prepare a solution for recycle. It was suggested that direct dissolution of uranyl peroxide in sulfuric acid be examined. This would require finding a method to destroy peroxide in the solid during the dissolution process. This will be tested by using a combination of heat and solid catalysts. Experimental work has shown that the uranyl peroxide precipitate could not be filtered. It was even difficult to centrifuge. This method does not look promising.

Anion Exchange of Uranyl Sulfate Complexes

Because of the high concentrations of uranyl sulfate in these solutions and low capacity of resins, this approach was abandoned in favor of a solvent extraction anion exchange process.

Conclusions

Pure titania sorbent with 110 micron particles and 60 angstrom pores has proven to be top performer for the separation of Mo-99 from a uranyl nitrate or uranyl sulfate solution. Optimization of the Mo-99 recovery process is still underway. Results from the VDG irradiation tests show that up to 10 kCi of Mo-99 can be processed using the LEU-Modified Cintichem process without losses due to ABO degradation. Finally, UREX processing preceded by conversion of uranyl sulfate to uranyl nitrate is the best method to clean-up the fuel if it is required.

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