Development of Recovery and Purification Processes for Mo-99 from an Accelerator-Driven Subcritical Target Solution: Determination of Distribution Coefficients for Competing Components and Micro-SHINE Tracer Column Results

Chemical Sciences and Engineering Division

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Development of Recovery and Purification Processes for Mo-99 from an Accelerator-Driven Subcritical Target Solution: Determination of Distribution Coefficients for Competing Components and Micro-SHINE Tracer Column Results

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ABSTRACT

Both batch and column studies were performed related to the processes developed for recovery and concentration of Mo from a SHINE uranyl-sulfate target solution. The batch studies indicate that most components of the target solution will not strongly compete with Mo for adsorption sites and, therefore, will not affect the column design. The batch studies for Te(IV) indicate that it strongly adsorbs on titania, and its concentration in target solution is sufficient to potentially affect adsorption of Mo. The tracer column experiments indicate that Mo(VI) is not reduced under micro-SHINE irradiation conditions because all Mo was recovered in the product fractions. The experiments also indicated that Mo-product will contain 10-15 column volumes (CVs) and not 20-30 CVs as previously observed. Contrary to the results of batch studies, the results of the tracer column experiments indicate that Te did not adsorb on the column.

1 INTRODUCTION

Argonne National Laboratory is assisting SHINE Medical Technologies in developing recovery and purification processes for molybdenum-99 (Mo-99) from an accelerator-driven, subcritical target consisting of an aqueous uranyl-sulfate solution. 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 <1 L prior to entry into the low-enriched uranium (LEU)-modified Cintichem purification process. Argonne has developed plant-scale column designs for the initial Mo recovery column and the concentration column. Although the Sachtopore sorbent used with this column is specific for Mo(VI), other fuel components adsorb on the column during Mo recovery. Their behavior will affect (1) Mo recovery/column capacity and, therefore, the size of the column; (2) waste stream composition and, therefore, treatment and disposal options; and (3) requirements for the Mo purification process.

We have studied the behavior of the fission-product components in the Mo recovery process using both batch and column methods. Individual tracers and irradiated "micro-SHINE" solutions were used. Batch equilibrium tests were performed for two components of the target solution, Tc and Te, which are present in significant concentrations when compared to Mo and could compete with Mo for adsorption sites. Batch adsorption equilibrium tests using Pu-242, Np-237, and Zr-95 in $NaHSO_4$ solutions at pH 1 were also performed to estimate the linear adsorption parameters of these target-solution components. Other fission products that form oxoanions in acidic solution and might adsorb on titania are Se, Nb, Rh, Sn, and Sb; however, their fission yield is ~ 50-100 times lower than the Mo yield. As a result, they will not strongly compete with Mo for sorption sites. Ruthenium has a fission yield in the same order of magnitude as Mo; however, tracer Ru is not available, and adsorption parameters cannot be determined at this time.

2 EXPERIMENTAL

S110 sorbent (TiO$_2$, 110 μm, 60 Å) was purchased from ZirChrom Separations, Inc. (Anoka, Minnesota). Uranyl sulfate, UO$_2$SO$_4$, solutions were prepared by oxidizing U$_3$O$_8$ with 30% H$_2$O$_2$ and adding stoichiometric amounts of concentrated sulfuric acid and water (if needed) and heating to 100° C. Technecium-99m was obtained from a commercial Tc-99m generator by stripping with saline solution. Technetium-99 was obtained from Argonne stocks. Tellurium-123m was obtained from Eckert & Ziegler Isotope Products Laboratories.

Isotherm data for Tc and Te were obtained by equilibrating 10 ± 1 mg of sorbent with 1 mL of 130 g-U/L uranyl sulfate solution at pH 1 containing an appropriate amount of stable Te(IV) or Tc-99 and the corresponding tracer for 24 h at 80° C. Tracer amounts of Pu-242, Np-237, and Zr-95 in sulfate solutions at pH 1 were also used to estimate the linear adsorption parameters. These results were obtained by equilibrating 10 ± 1 mg of sorbent with 1 mL of 1 M NaHSO$_4$ solution at pH 1 for 24 h at 80° C.

3 RESULTS AND DISCUSSION

3.1 BATCH STUDIES

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 the pore-phase concentrations by an equilibrium isotherm. We used the Langmuir model to calculate the sorption of Mo in this study:

$$q = \frac{a\,C}{1 + b\,C}$$

where q is the amount of species sorbed on the column packing and equilibrated with the concentration of species in the mobile phase, C, and a and b are Langmuir isotherm parameters. In this study, both q (meq/L) and C (mol/L) of the species of interest are described on a volume basis, where the dry packing density of S110 sorbent is 1.3 g/mL. Tellurium-IV is the predominant species present in irradiated aqueous solutions.[1] Langmuir isotherm parameters for Te were estimated from batch data measured for varying Te-IV concentrations in solutions of 130 g-U/L uranyl sulfate at pH 1 and 80° C. Figure 1 shows the batch data along with the Langmuir fit to those data. The Langmuir isotherm parameters fitted using the Origin 9 software are a = 8040 and b = 153 mM^{-1} (R^2 = 0.99). The results indicate that Te(IV) strongly adsorbs on titania sorbent. It was determined that Te(VI) is not soluble in sulfate solutions at 1 mM.

Batch studies were also performed to estimate the Langmuir isotherm parameters of Tc in the concentration range of 10^{-2}–10^{-9} M. However, the Langmuir isotherm values for Tc were not measurable due to very low uptake of Tc on titania. Technetium does not adsorb on titania sorbent.

Tracer amounts of Pu-242(IV), Np-237(V), and Zr-95 in sulfate solutions at pH 1 were used to estimate the linear adsorption parameters. The results are presented in Table 1. The K_d values for Np-237 were not measurable due to very low uptake. The K_d value for Pu-242 at pH 1 is ~50, which can be converted to the linear adsorption parameter, a = 0.065. The K_d value for Zr-95 at pH 1 is ~850, which can be converted to the linear adsorption parameter, a = 1.1. In comparison, the linear adsorption parameter for Mo in 130 g-U/L UO_2SO_4 solution at pH 1 is a = 1881.

3.2 MICRO-SHINE TRACER COLUMN STUDIES

For the column studies, a micro-SHINE uranyl-sulfate solution containing 1 ppm $FeSO_4$ (irradiated on September 3, 2013) was used as a spike for a depleted uranyl-sulfate solution containing 0.003 mM stable Mo, added as Na_2MoO_4. A 0.66-cm I.D. x 3-cm long column was packed with a pure titania sorbent made up of 110 µm particles with 60 Å pores. Approximately 260 mL of the uranyl-sulfate solution containing the irradiated micro-SHINE solution (2 mL) and 0.003 mM stable Mo was passed through the column in 2 hours. After the feed solution was
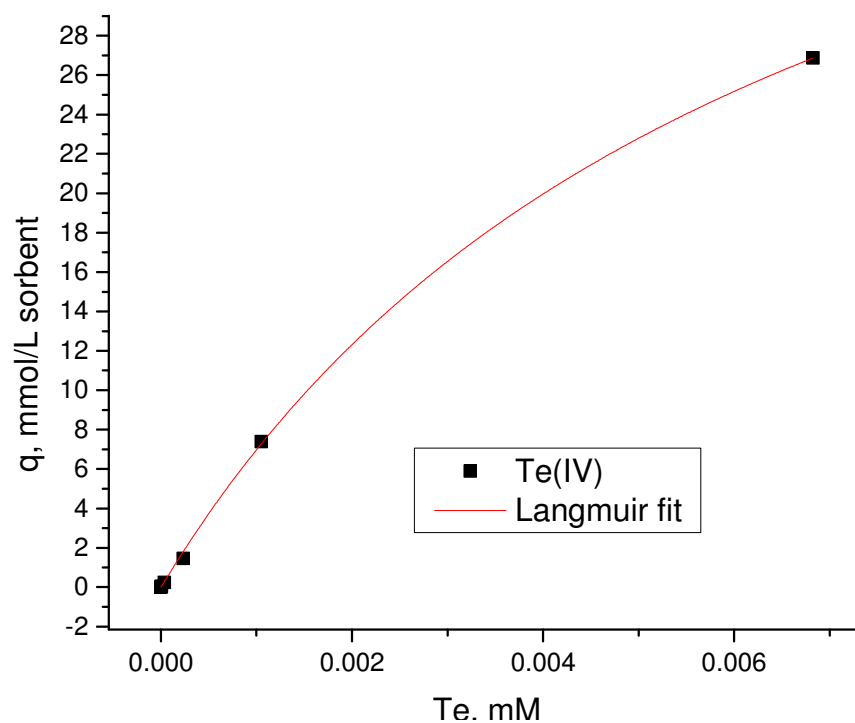
FIGURE 1 Te(IV) Isotherm Data from Batch Tests and Langmuir Isotherm Model Fit

TABLE 1 Distribution Coefficients (K_d) of Pu-242, Np-237, and Zr-95 from 1 M NaHSO$_4$ on S110 Sorbent

NaHSO$_4$ Solution	pH	K_d Pu-242 (mL/g)	K_d Np-237 (mL/g)	K_d Zr-95 (mL/g)
#1 - 0.38 M	0.98	60	-	860
#2 - 0.46 M	1.01	50	-	940
#3 - 0.55 M	1.02	60	-	830
#4 - 0.63 M	1.02	40	-	810
#5 - 1.26 M	1.04	40	-	800
#6 - 0.38 M	0.3	2	-	960
#7 - 0.46 M	0.31	6	-	740
#8 - 0.55 M	0.295	1	-	950
#9 - 0.63 M	0.297	8	-	830
#10 - 12.6 M	0.302	9	-	1060

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loaded onto the column at a flow rate of 2.2 mL/min, the column was washed with 10 column volumes (CV) of 0.1 M H_2SO_4 and 10 CVs of H_2O in the up-flow direction. The column and all solutions were heated to 80° C. Molybdenum was recovered by passing 30 CVs of 0.1 M NaOH at 1 mL/min through the column in the down-flow direction; the Mo product was collected in portions of 6, 8, 6, and 10 CV.

Table 2 shows the gamma-counting results for the fission products that had clean peaks and showed accurate decay patterns over a period of 3 days for the various streams. Gamma-counting results are ±5%, and the majority of Mo-99 was recovered in strip portions #2 and #3. These results indicate that less than 30 CVs of 0.1 M NaOH is required to achieve a high Mo-recovery yield. The Mo recovery is highly dependent on pH, and once the column reaches a pH >10, Mo elutes fairly quickly (~100% in 13 CVs). These data show that less volume will be required to strip Mo from the recovery column and, therefore, achieve a more concentrated feed to the concentration column operation. These factors will lead to less time in the concentration step for entry into the LEU-modified Cintichem purification process. Previous experiments[2] showed that the Mo-product volume would contain 20-30 CVs for entry into the concentration column, but it now appears that 10-15 CVs is sufficient. Less feed volume requires a smaller column, which decreases processing time and allows for quicker entry into the purification process.

These data also indicate that Mo(VI) has not been reduced to Mo(IV) or Mo(V) under the micro-SHINE irradiation conditions because all Mo adsorbed on the titania column and was easily recovered with 0.1 M NaOH. A significant amount of Zr (~65%) remains adsorbed on the column with about half of the iodine, which is consistent with previous tracer tests performed with the same titania sorbent. One surprising result is that Te-132 did not adsorb on the titania column, and this contradicts the above tracer test results showing that Te adsorbs as well as Mo on the titania sorbent. The irradiation environment may have changed the Te chemistry, removing its ability to adsorb on titania.

The column effluent was then treated with a mixture of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ to convert the uranyl sulfate solution to a uranyl nitrate solution. These results are discussed in the report entitled *FY-13 Progress Report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions.*[3]

TABLE 2 Partitioning of Irradiated Uranyl Sulfate Solution Components on the Micro-SHINE Column

Stream	Sr-91	Zr-97	Mo-99	Ru-103	Rh-105	I-131	Te-132	I-133	Ba-140	Ce-141	Ce-143
Effluent	91	33	0	100	100	29	100	3	100	100	100
Acid Wash	-	2	-	-	-	-	-	-	-	-	-
H_2O Wash #1	-	-	-	-	-	-	-	-	-	-	-
Strip #1 (1-6 CVs)	-	-	-	-	-	-	-	-	-	-	-
Strip #2 (7-14 CVs)	-	0.2	83	-	-	4	-	17	-	-	-
Strip #3 (15-20 CVs)	-	-	18	-	-	8	-	16	-	-	-
Strip #4 (21-30 CVs)	-	-	2	-	-	-	-	11	-	-	-
H_2O Wash #2	-	-	-	-	-	-	-	-	-	-	-
Amount left on column	9	64.8	0	0	0	59	0	53	0	0	0

4 FUTURE WORK

Five liters of sodium bisulfate spiked with 100 mCi of Mo-99 and I-131 will be irradiated next. The solution will be passed through an initial Mo-recovery column, and samples will be collected during irradiation. These steps will be done remotely, but sample retrieval will be done manually. The Mo-product solution will be acidified and passed through a concentration column, and the final product from the concentration column will be purified by the LEU-modified Cintichem process. The concentration column and purification processes will be performed in a hot cell in a Linac facility using manipulators.

After the 5-L sodium bisulfate experiments, 5 L of uranyl sulfate (low enriched uranium; 19.8% U-235; 140 g-U/L) will be irradiated several times for short periods to gain an understanding of gas generation rates, pH changes in solution, and solution volume loss. After several short irradiations, the 5-L solution containing 0.003 mM stable Mo, added as Na_2MoO_4, will be irradiated for 14 hours, which will produce ~2 Ci Mo-99. The solution will be passed through the initial Mo recovery column (2 cm ID X 10 cm length) at a flow rate of 40 mL/min. The solution and column will be heated to 80° C. The column will be washed with 10 CVs of 0.1 M H_2SO_4 and 10 CVs of H_2O. The Mo will be recovered by using 10-15 CVs of 0.1 M NaOH. Samples will be collected remotely during the column process and retrieved manually at least 24 hr post-irradiation. The Mo product solution will be acidified by nitric acid addition and passed through a titania concentration column. The Mo will be recovered using 1 M NH_4OH heated to 70° C. The Mo-product solution will be purified using the LEU-modified Cintichem process. The final purified product will be shipped to a Tc-99m generator manufacturer. The concentration column and purification processes will be performed in a hot cell in the Linac facility using manipulators. The 14-hour irradiation of 5-L uranyl sulfate and subsequent Mo-recovery and purification process will be performed at least four times.

5 CONCLUSIONS

The results of batch studies indicate that most components of the target solution will not strongly compete with Mo for adsorption sites and, therefore, will not affect the column design. The batch studies for Te(IV) indicate that it strongly adsorbs on titania and its concentration in target solution is on the same order as that of Mo. Therefore, the potential effects of Te on Mo loading will be explored using the VERSE (Versatile Reaction Separation, Purdue University, IN). On the other hand, the results of the tracer column experiments indicated that Te did not adsorb on the column. The potential explanations for these conflicting results may be the redox chemistry and tracer level concentrations of Te in the column experiment.

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