VERSE Simulations and Experiments of Competing Components in Molybdenum Adsorption and Recovery Process

Chemical Sciences and Engineering Division
About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY
Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's SciTech Connect (http://wwwosti.gov/scitech/)

Reports not in digital format may be purchased by the public from the
National Technical Information Service (NTIS):
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 805-6000
Fax: (703) 605-6800
Email: orders@ntis.gov

Reports not in digital format are available to DOE and DOE contractors from the
Office of Scientific and Technical Information (OSTI):
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: reports@osti.gov

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.
VERSE Simulations and Experiments of Competing Components in Molybdenum Adsorption and Recovery Process

by
A.J. Youker, D.C. Stepinski, and G.F. Vandegrift
Chemical Sciences and Engineering Division, Argonne National Laboratory

L. Ling and N.-H. L. Wang
Chemical Engineering, Purdue University

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

July 2014
This page intentionally left blank
VERSE SIMULATIONS AND EXPERIMENTS OF COMPETING COMPONENTS IN MOLYBDENUM ADSORPTION AND RECOVERY PROCESS


1 INTRODUCTION

Argonne National Laboratory is assisting SHINE Medical Technologies in their efforts to become a domestic Mo-99 producer. In collaboration with Purdue University, Argonne has designed two columns for the separation, recovery, and concentration of Mo-99 from an irradiated uranyl-sulfate solution. The initial Mo-recovery column utilizes a titania sorbent with 110 µm particles and 60 Å pores, while the much smaller concentration column uses the same titania sorbent with 40 µm particles. Purdue University’s VERSE (VErsatile Reaction SEparation) model has been employed to aid in the design of the plant-scale columns for SHINE Medical Technologies.

Although the titania sorbents used here are extremely specific for Mo(VI), other fuel components do adsorb on the column during Mo recovery. Their behavior may affect (1) Mo recovery/column capacity and, therefore, the size of the column; (2) waste stream compositions and, therefore, treatment and disposal options; and (3) requirements for the Mo-purification process.

Data are collected in a batch mode and small-scale column setting and input into VERSE. Physical properties of the mobile phase, such as viscosity and density, and of the stationary phase, such as void fraction, are also 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. The effect of potential competing components had not been input into VERSE until now.

The main species expected to compete with Mo for adsorption sites on titania are Te and Zr. This assumption is based on batch and column data obtained in a uranyl sulfate or sodium bisulfate solution that will be discussed in this report. Neither Tc nor Np adsorb on titania, and Pu adsorbs to a very small extent on titania at pH 1. This report examines calculations by the VERSE code of Te and Zr adsorption on Mo adsorption and recovery.

For this report, experiments were performed to examine the behavior of fission-product components in the recovery process using both batch and column tests with individual radiotracers and irradiated micro-SHINE solutions. Batch equilibrium tests were conducted for two components of 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 NaHSO₄ 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
selenium, niobium, rhodium, tin, and antimony; however, their fission yield is ~ 50-100 times lower than Mo’s yield. As a result, they will not strongly compete with Mo for sorption sites. Ruthenium has a fission yield similar to Mo; however, tracer Ru is not available, and adsorption parameters could not be determined at this time from the column experiment performed using a micro-SHINE solution.

We used VERSE to simulate the Mo capture and stripping processes in the presence of Te and Zr. The Bi-Langmuir model was used to describe the adsorption of different components [1]. Site 1 is the sum of the Lewis acid sites and the Brønsted base sites, and Site 2 is the Brønsted acid site. Since Mo and Te are mainly present as o xoanions in solution, they are likely to compete with each other to adsorb on Site 1. Zirconium is present as a cation, so it adsorbs on Site 2. When NaOH was used to strip the Mo, the OH\(^-\), which is the strongest Lewis base, can displace the adsorbed Mo and Te from Site 1. However, at a high pH, the Na\(^+\) has a lower affinity than Zr with Site 2, so that a large portion of Zr remains adsorbed on the column. Some Zr shows up in the effluent during loading because Site 2 has a lower capacity and affinity for Zr at pH = 1.

The isotherm parameters for Mo and Te were obtained from batch equilibrium tests. The isotherm parameters for Zr and NaOH were fine-tuned to satisfy the following conditions: (1) OH\(^-\) has the highest affinity with Site 1; (2) Na\(^+\) has much lower affinity with Site 2 than Zr; (3) the capacity of Zr is estimated from the data for the loss of Zr in the capture step; and (4) the capacities of NaOH on Site 1 and Site 2 are consistent with the values obtained previously [1]. The diffusivities of Te and Zr are assumed to be the same as that of Mo, which has been published previously [2]. The diffusivity of NaOH was obtained previously as well [3].
2 EXPERIMENTAL

S110 sorbent (TiO$_2$, 110 µm, 60 Å) was purchased 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.

Technetium-99m was obtained from a commercial Tc-99m generator by stripping with saline solution; Tc-99 was obtained from Argonne stocks; and Te-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. The results were obtained by equilibrating 10 ± 1 mg of sorbent with 1 mL of various NaHSO$_4$ solutions for 24 h at 80°C.

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$_2$MoO$_4$. A 0.66-cm inner diameter (I.D.) x 3 cm length (L) column was packed with a pure titania sorbent made up of 110 micron particles with 60 Å pores. Approximately 260 mL of uranyl-sulfate solution spiked with an 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 loaded onto the column at a flow rate of 2.2 mL/min, the column was washed with 10 column volumes (CVs) of 0.1 M H$_2$SO$_4$ and 10 CVs of H$_2$O 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 four portions of 6, 8, 6, and 10 CVs.

VERSE simulations were done using batch and micro-SHINE tracer column data to examine the effects of competition from Te and Zr on Mo adsorption on titania.
### RESULTS

Langmuir isotherm parameters for Te(IV) were estimated from batch data measured for varying ion concentrations in solutions of 130 g-U/L uranyl sulfate at pH 1 and 80°C. Langmuir isotherm parameters fitted using Origin 9 were $a = 8040$ and $b = 153$ mM$^{-1}$ (Figure 1). The results indicate that Te(IV) adsorbs strongly on titania. These isotherm parameters were input into VERSE to examine how Te affects Mo adsorption and/or recovery on a titania sorbent.

Batch studies were also performed to estimate Langmuir isotherm parameters for Tc in the concentration range of $10^{-2}–10^{-9}$ M. The Langmuir isotherm values for Tc were not measurable due to very low uptake of Tc on titania. Technetium does not adsorb on titania, and as a result, it will not affect Mo adsorption or recovery. Thus, it was not included in the VERSE model simulations.

Tracer amounts of Pu-242(IV), Np-237(V), and Zr-95 in sodium bisulfate solutions at pH 1 were used to estimate the linear adsorption parameters. The results are presented in Table 1. The distribution ratio ($K_d$) for Np-237 was not measureable 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 a 130 g-U/L $\text{UO}_2\text{SO}_4$ solution at pH 1 is $a = 1892$. We did not include Pu and Np in the VERSE competition model because Pu has low $K_d$ values compared to Mo, and $K_d$ values for Np could not be
measured. However, Zr competition was investigated with VERSE because it adsorbs fairly well on titania.

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 by using 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 using the same titania sorbent. One surprising result is that Te-132 did not adsorb on the titania column. This finding contradicts previous tracer test results that showed Te adsorbs as well as Mo on the titania sorbent. Because the Te concentration was extremely low (no stable Te was added to the feed solution) in the column experiment, Te’s ability to adsorb on titania for the purpose of VERSE modeling will be based on results obtained from the batch studies.

Table 3 shows the various parameters input into VERSE to model the effects of competition from Te and Zr on Mo adsorption and recovery. Data from the micro-SHINE column experiment were used to estimate Langmuir parameters for Zr, which is suspected to adsorb on the Brønsted acid site. The simulation results showed that 37% of the Zr was eluted, whereas 63% remained adsorbed on the column, which is representative of what was observed in the micro-SHINE tracer column experiment. In the simulations, Site 1 = Lewis acid site + Brønsted base site and Site 2 = Brønsted acid site. Zirconium exists as a cation and cannot adsorb on Site 1, so the isotherm parameters a₁ and b₁ values for Zr are zero.
### TABLE 2 Gamma Counting Results for the Micro-SHINE Tracer Column Experiment

<table>
<thead>
<tr>
<th>Stream</th>
<th>Sr-91</th>
<th>Zr-97</th>
<th>Mo-99</th>
<th>Ru-103</th>
<th>Rh-105</th>
<th>I-131</th>
<th>Te-132</th>
<th>I-133</th>
<th>Ba-140</th>
<th>Ce-141</th>
<th>Ce-143</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effluent</td>
<td>91</td>
<td>33</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>29</td>
<td>100</td>
<td>3</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Acid Wash</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O Wash #1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Strip #1 (1-6 CVs)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Strip #2 (7-14 CVs)</td>
<td>-</td>
<td>0.2</td>
<td>83</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>17</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Strip #3 (15-20 CVs)</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Strip #4 (21-30 CVs)</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O Wash #2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amount left on column</td>
<td>9</td>
<td>64.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>59</td>
<td>0</td>
<td>53</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### TABLE 3 Parameters Input into VERSE to Model Competition from Te and Zr [4,5]

<table>
<thead>
<tr>
<th>System Parameters</th>
<th>L (cm)</th>
<th>ID (cm)</th>
<th>R (µm)</th>
<th>ε_b</th>
<th>ε_p</th>
<th>CSTR (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>0.66</td>
<td>55</td>
<td>0.35</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td>Isotherm Parameters</td>
<td>a_1</td>
<td>b_1 (1/mM)</td>
<td>a_2</td>
<td>b_2 (1/mM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1.892</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>8.040</td>
<td>153</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0</td>
<td>0</td>
<td>10,000</td>
<td>6,666</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>10,000</td>
<td>10</td>
<td>1</td>
<td>0.0023</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Transfer Parameters</td>
<td>D_b x 10^7 (cm^2/min)</td>
<td>D_p x 10^5 (cm^2/min)</td>
<td>k_f (cm/min)</td>
<td>E_b (cm^2/min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo, Te, Zr</td>
<td>141</td>
<td>4</td>
<td>From Wilson and Geankoplis (1966)</td>
<td>From Chung and Wen -1968</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>680</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Numerical Parameters</td>
<td>Axial Elements</td>
<td>Collocation Points</td>
<td>Tolerance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Step Size (L/ε_b)</td>
<td></td>
<td>Axial</td>
<td>Particle</td>
<td>Absolute (mM)</td>
<td>Relative</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.1</td>
<td>4</td>
<td>2</td>
<td>10^-7 (Mo)</td>
<td>10^-7 (NaOH)</td>
</tr>
</tbody>
</table>

Figure 2 shows the VERSE simulation for the adsorption of Mo, Te, and Zr on the 0.66 cm I.D. x 3 cm L titania column (same column size used for the micro-SHINE tracer test). According to experimental and simulation results, Zr does not adsorb as strongly on titania as Te or Mo. It adsorbs on the Brønsted-base site, which is not occupied by Te or Mo. Technetium adsorbs better on the titania sorbent than Mo, and it occupies the same sites as Mo. Because Te has a bC (i.e., nonlinear isotherm parameter multiplied by the concentration of the species of interest) value of 0.46, it will affect Mo adsorption to a certain extent. The sorbent can be considered to have significantly more adsorption sites than needed to fully adsorb the Mo, so the competition from Te is unlikely to change the adsorption or recovery of Mo. Figure 3 shows the column profiles generated by VERSE at the end of loading and the effect of varying Te concentrations on Mo adsorption. These data will be validated during the mini-SHINE 5-L experiments, where comparable concentrations of stable Te will be added to the target solution.

Figure 4 shows the effects of Zr and Te on Mo recovery simulated using VERSE. Neither element appears to affect the Mo recovery, but a significant amount of Te will be present in the Mo product. This result will not create a big concern because the LEU-Modified Cintichem purification process will remove the Te. Very little if any Zr will contaminate the Mo product because the sodium from the NaOH is not capable of removing the Zr from the Brønsted-base sites on titania. The simulated Mo-stripping curve is consistent with the experimental data because most of the Mo can be collected in 7-14 CVs, with a small portion found in the last 15 to 20 CVs.

**FIGURE 2** VERSE Simulation of Mo, Te, and Zr Loading on Titania
FIGURE 3 VERSE Simulation of Column Profiles for Mo Loading with Varying Te Concentrations

FIGURE 4 VERSE Simulation of Mo, Te, and Zr Stripping on Titania
4 CONCLUSIONS

Based on Langmuir batch data and VERSE simulations, Te is expected to be the biggest source of competition for Mo-adsorption sites. The bC value for Te is 0.46, indicating that Te will compete with Mo for adsorption sites. As a result, the minimum column volume ($CV_{\text{min}}$) for Mo capture will increase. However, for a sufficiently large column (much larger than $CV_{\text{min}}$), the capture yield of Mo will not be affected. Current designs do not utilize $CV_{\text{min}}$, and the lengths of the columns are at least 10% larger than is necessary to capture all the Mo.

Another issue will be contamination in the Mo product, but again the concentration column and LEU-Modified Cintichem process will remove any contaminants such as Te. Mini-SHINE experiments will add a stable concentration of Te to mimic plant-scale conditions, where the concentrations of Mo and Te are comparable.
5 REFERENCES


