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## MO-99 RECOVERY FROM AQUEOUS-HOMOGENEOUS-REACTOR FUEL—BEHAVIOR OF TERMOXID SORBENTS

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### ABSTRACT

Argonne is currently performing R&D to develop <sup>99</sup>Mo-recovery from the fuel solution of an aqueous homogeneous reactor (AHR). For these studies, we assumed a uranyl nitrate fuel with a concentration of 150-235 g-U/L of low enriched uranium (LEU) at pH 1. To recover Mo-99 from a concentrated uranium solution, we are designing a separation system that utilizes either Termoxid T-52 or T-5M sorbents. Batch studies completed as a function of temperature (25, 55, & 85°C) indicate that both sorbents show enhanced uptake of Mo(VI) at higher temperatures. Results from uptake measurements and static and dynamic capacity studies are being performed to design a column with optimal properties for maximum recovery of <sup>99</sup>Mo in the shortest time.

### 1. Introduction

Technecium-99, <sup>99m</sup>Tc, the most widely used radioisotope in nuclear medicine, is produced from the decay of its parent <sup>99</sup>Mo, which is primarily produced from the fissioning of <sup>235</sup>U from targets containing enriched uranium.[1] Currently, about 95% of fission <sup>99</sup>Mo is produced using high enriched uranium (HEU) targets.[2] Converting from HEU to LEU requires about five times more uranium to produce the same amount of <sup>99</sup>Mo.[3] The use of Aqueous Homogeneous Reactors (AHRs), or solution reactors, presents an attractive alternative to the conventional target irradiation method of producing <sup>99</sup>Mo in that solutions eliminate the need for targets and can operate at much lower power than required for a reactor irradiating target reactor to produce the same amount of <sup>99</sup>Mo.[4,5] As the name implies, solution reactors consist of an enriched uranium salt (uranyl nitrate or sulfate) dissolved in a slightly acidic aqueous solution and contained in shielded tank or vessel.[4] Approximately 30 solution reactors have been built world-wide and operated over many years since the beginning of modern nuclear programs in

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the 1940s and 1950s.[4] Most of these reactors are no longer in service. However, in the 1990s a renewed interest in solution reactors for the production of medical isotopes has prompted interest in several countries (including the U.S., Russia, and China) to initiate programs to assess the feasibility of utilizing AHR technology for medical isotope production applications on commercial basis.[4] In the U.S., Babcock and Wilcox Technical Services Group is considering pursuing the Medical Isotope Production System (MIPS) as a means to produce Mo-99 commercially; Argonne researchers are assisting their analyses by (1) studying the aqueous chemistry of the MIPS under irradiation and Mo-recovery operations and (2) developing a process for recovering Mo-99 from the irradiated fuel solution.

Alumina is typically used to recover and purify  $^{99}\text{Mo}$  from acidic HEU solutions. However, LEU solutions have higher uranium concentrations (to keep solution volumes low), and figure 1 shows how alumina does not uptake Mo(VI) very well from solutions containing high concentrations of uranium.[6,7] Termoxid developed two sorbents T-52 (25 mole %  $\text{SnO}_2$  and 75 mole %  $\text{TiO}_2$ ) and T-5M (5 mole %  $\text{ZrO}_2$  and 95 mole %  $\text{TiO}_2$ ) that both show superior adsorption of  $^{99}\text{Mo}$  from concentrated  $\text{UO}_2(\text{NO}_3)_2$  solutions. The sorbents will make the transition to LEU not only feasible, but favorable, due to superior partitioning of molybdenum by these sorbents.[6]

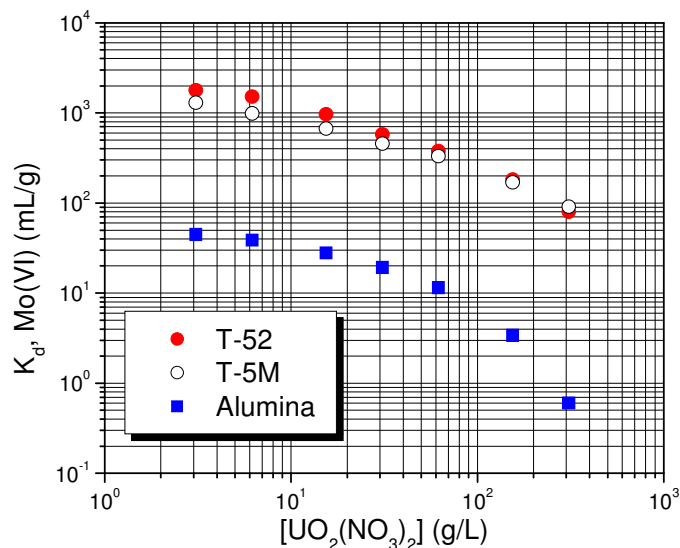


Figure 1. Effect of varying uranium concentrations on the uptake of trace levels of  $^{99}\text{Mo}$  from 1 M  $\text{HNO}_3$  by the Termoxid sorbents and alumina.

T-52 and T-5M were investigated to study their abilities to adsorb  $^{99}\text{Mo}$  from solutions containing increasing concentrations of uranium under static and dynamic conditions. Additionally, the sorbents' resistance to irradiation and contact with several different solutions has been examined. Four different batches of each sorbent were obtained to determine the disparities among the batches. T-52 and T-5M are manufactured by Termoxid Scientific and Production Company (Zarechnyi, Russia).

T-52 and T-5M will be used to design a column for the efficient recovery of  $^{99}\text{Mo}$  from an aqueous homogeneous reactor solution containing LEU. A uranyl nitrate solution containing 150-235 g-U/L at pH 1 will be used to recover Mo(VI). It is representative of the amount of uranium that will be in the MIPS LEU solution. Batch studies using T-52 and T-5M have been completed as a function of temperature, time, and uranium concentration. The static and dynamic capacity for molybdenum has been also determined. The ability of the sorbents to withstand chemical and radiation conditions without decomposition or significant changes in Mo(VI) adsorption behavior has been investigated. Results have provided insight for the design of a column with optimal features for the recovery and purification of  $^{99}\text{Mo}$ .

## 2. Experimental

Four different batches of Termoxid sorbents T-52 and T-5M were tested for the uptake of Mo(VI) to determine how much each batch varied in its ability to uptake Mo(VI). Kinetic studies were completed using batches of T-52 and T-5M obtained three to five years ago. Batch studies were done with solutions containing uranyl nitrate pH 1, 1-100 ppm stable Mo, and 0.25-0.3  $\mu\text{Ci/mL}$  of  $^{99}\text{Mo}$ . Batch studies were completed as a function of uranium and/or stable Mo concentration, temperature, and equilibration time. The uranium concentrations tested were 150, 185, 235, and 285 g-U/L as  $(\text{UO}_2(\text{NO}_3)_2)$  solution pH 1, and the temperatures were 25, 55, and 85°C. Results show that the adsorption behavior of the sorbents did not vary among batches to an extent greater than the variations obtained for each individual batch. As a result, one batch of each sorbent was used for the remaining studies.

### *Preparation of uranium solutions*

Uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2$ , solutions were prepared by dissolving a known amount of uranium metal plates in concentrated  $\text{HNO}_3$  to convert it to U(VI). The solution was evaporated to dryness, and the product was redissolved in distilled water (repeated 3 times). The pH was adjusted to 1 using NaOH, and 1-100 ppm of stable Mo was added to the uranyl nitrate solutions as  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . [7]

### *Preparation of $^{99}\text{Mo}$ spike solution.*

$^{99}\text{Mo}$  was obtained from a commercial  $^{99\text{m}}\text{Tc}$  generator (Lantheus Medical Imaging). The initial activity of  $^{99}\text{Mo}$  in the generator was 1 Ci. Generators were stripped using 5 mL of 1 M  $\text{NH}_4\text{OH}$ . The 1 M  $\text{NH}_4\text{OH}$  solution containing  $^{99}\text{Mo}$  was evaporated to dryness and redissolved in 0.1 M  $\text{HNO}_3$ . Approximately 0.3  $\mu\text{Ci}$  of  $^{99}\text{Mo}$  per 1 mL of uranyl nitrate solution was added to prepare the final spiked solution. [7]

### *Batch uptake measurements*

The uptake of Mo(VI) as a function of uranium and/or stable Mo concentration, temperature, and sorbent batch was determined by equilibrating 1 mL of a  $^{99}\text{Mo}$  spiked aqueous solution with a known amount ( $10 \pm 1$  mg) of sorbent for 24 hours at 25, 55, and 85°C using a thermostatted shaker bath. Aqueous solutions contained 150, 185, 235, and 285 gU/L and 1 ppm stable Mo. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a 0.22  $\mu\text{m}$  pore size PVDF membrane filters (Millipore). Blank experiments have shown that the filter does not uptake  $^{99}\text{Mo}$ .

### *Kinetic uptake measurements*

The sorption of Mo(VI) as a function of time was determined by equilibrating 1 mL of a  $^{99}\text{Mo}$  spiked 0.1 M  $\text{HNO}_3$  solution with a known amount ( $10 \pm 1$  mg) of sorbent for 5 min – 24 h at  $25^\circ\text{C}$ . Time zero was taken as the time at which a known volume of the  $^{99}\text{Mo}$  spiked solution contacts the sorbent and stirring is commenced. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a  $0.22\ \mu\text{m}$  pore size PVDF membrane filter (Millipore).

### *Counting of $^{99}\text{Mo}$*

The amount of activity remaining in the aqueous samples was determined using a germanium detector.  $^{99}\text{Mo}$  was quantified by measurement of its 739 keV  $\gamma$ -ray. The activity of  $^{99}\text{Mo}$  in each sample was corrected for decay. The extent of radionuclide uptake was expressed in terms of a distribution coefficient,  $K_d$ , defined as follows:

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

Here,  $A_o$  and  $A_s$  represent the aqueous phase activity ( $\mu\text{Ci}$ ) 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  $10 (\pm 1)$  mg in order to leave a measurable activity in the aqueous phase.[7] The error associated with the  $K_d$  measurements is directly related to the error obtained from counting  $^{99}\text{Mo}$ 's 739 keV  $\gamma$ -ray, which typically is 7-8%.

### *Available Capacity for Mo*

The available capacity of the sorbents for Mo was determined from a 150 and 235 g-U/L solution, pH 1 by batch studies at 25, 55 and  $85^\circ\text{C}$  with T-52 and T-5M. As the concentration (1-100 ppm Mo) and volume (1-10 mL) of solution was increased, while keeping the amount of sorbent constant, the maximum uptake of Mo from a 150 and 235 g-U/L (pH 1) solution was determined.

### *Effect of Wash Solutions on Sorbent Behavior*

One gram of each, T-52 and T-5M was contacted with 5 mL uranyl nitrate solution (235 g-U/L, 1 ppm stable Mo) for 6 hours at  $55^\circ\text{C}$  and then was contacted with 0.1 M  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ , and 4 mL of 1 M  $\text{NH}_4\text{OH}$  (10 minutes incubation) followed by washes with  $\text{H}_2\text{O}$  and 0.1 M  $\text{HNO}_3$ . After drying in the oven for 24 hours at  $105^\circ\text{C}$ , after each cycle a small portion of sorbent was collected for batch studies (done at  $55^\circ\text{C}$ ). The cycle of incubations and washes was repeated four times.

### *Column Studies*

Dynamic capacity measurements were done for T-52 and T-5M by passing a 235 g-U/L solution containing 1 ppm stable Mo and 0.25-0.3  $\mu\text{Ci}$   $^{99}\text{Mo}/\text{mL}$  through a column containing a known amount of sorbent. To determine the breakthrough of Mo(VI) in the column, the initial conditions utilized a  $1.5 \times 10$  cm column with a flow rate of 1.2 mL/min and a 15 mL bed volume of T-52. Subsequent conditions were readjusted by varying the bed volume to 3, 5, and 6 mL. For the 3, 6, and 15 mL columns, solution was heated using water bath set at  $60^\circ\text{C}$ . For the 5 mL column, solution was heated directly using a heating mantle at  $60^\circ\text{C}$  and a thermostatted column was used with the temperature held constant at  $60^\circ\text{C}$ .

### 3. Results

Figure 2 depicts the uptake of Mo(VI) from uranyl nitrate solutions (150, 185, 235, and 285 g-U/L) at pH 1 and 25°C. As expected,  $K_d$  values decrease with increasing uranyl nitrate concentrations. The sorbents T-52 and T-5M both adsorb Mo(VI) in a similar fashion at 25°C after 24 hours of equilibration as the concentration of uranium increases. No significant variation between different batches of the same sorbent was observed.

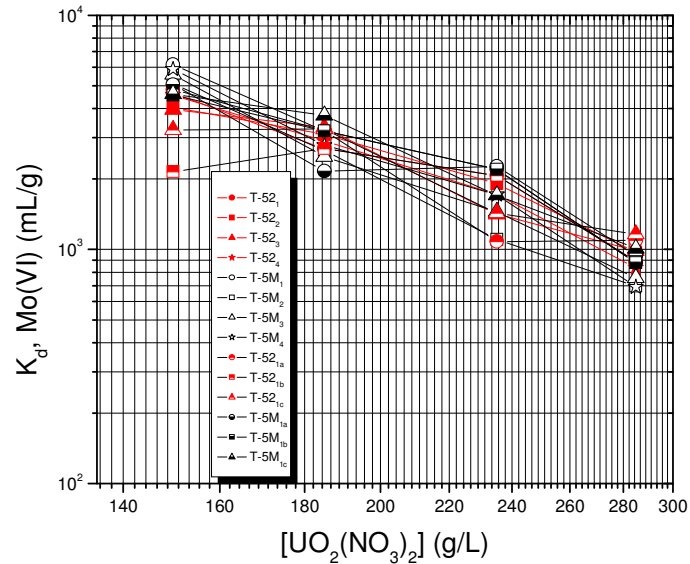


Figure 2. Uptake of Mo(VI) as a function of uranium concentration (pH 1) at 25°C for the batches of T-52 and T-5M (T-52<sub>1</sub>-T-52<sub>4</sub> & T-5M<sub>1</sub>-T-5M<sub>4</sub>) and the same batch of T-52 and T-5M (T-52<sub>1a</sub>-T-52<sub>1c</sub> & T-5M<sub>1a</sub>-T-5M<sub>1c</sub>).

Figure 3 shows the uptake of Mo(VI) as a function of uranyl nitrate concentration (150, 185, 235, and 285 g-U/L) at pH 1 and 55°C. At higher uranium concentrations (185-285 g-U/L), T-52 outperforms T-5M by nearly 30%. This suggests that T-52 would be a better choice for adsorbing <sup>99</sup>Mo from solutions kept at 55°C. Once again, the sorbents do not vary significantly from batch to batch.

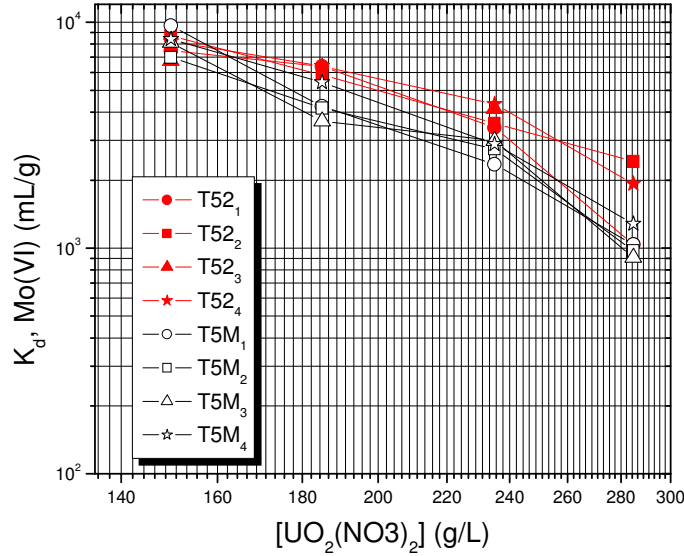


Figure 3. Uptake of Mo(VI) as a function of uranium concentration (pH 1) at 55°C for the batches of T-52 and T-5M (T-52<sub>1</sub>-T-52<sub>4</sub> & T-5M<sub>1</sub>-T-5M<sub>4</sub>).

Figure 4 shows the uptake of Mo(VI) a function of uranyl nitrate concentration at pH 1 and 85°C. Under these conditions, T-52 has significantly higher  $K_d$  values than T-5M for the uptake of Mo(VI). The uptake is 20% better for T-52 than for T-5M from solutions containing 150g-U/L but increases to nearly 50% from solutions containing (185-285 g-U/L). At higher temperatures, T-52 displays enhanced Mo(VI) uptake, and both sorbents adsorb Mo(VI) better at lower uranyl nitrate concentrations. Different batches of each sorbent continue to produce similar results.

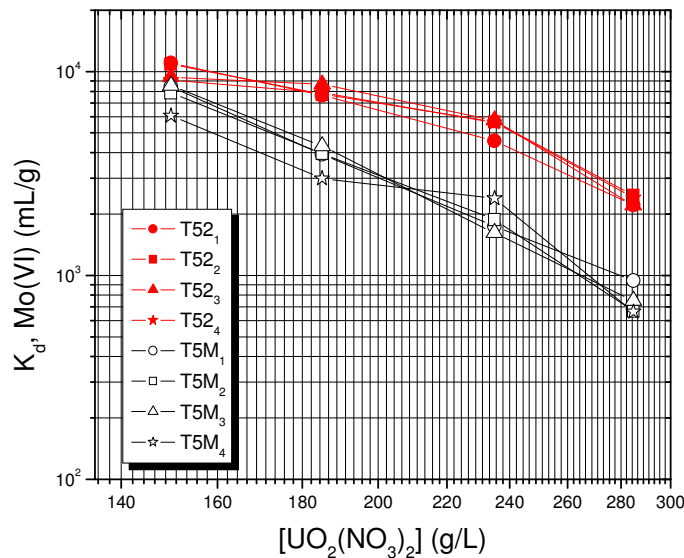


Figure 4. Uptake of Mo(VI) as a function of uranium concentration (pH 1) at 85°C for the batches of T-52 and T-5M (T-52<sub>1</sub>-T-52<sub>4</sub> & T-5M<sub>1</sub>-T-5M<sub>4</sub>).

Figure 5 depicts the kinetics of uptake of trace levels of  $^{99}\text{Mo}$  by older batches of T-52 and T-5M from a 0.1 M  $\text{HNO}_3$  at  $25^\circ\text{C}$ . For both sorbents, the  $^{99}\text{Mo}$  sorption achieved within 60 minutes is far greater than the minimum required for satisfactory performance in a packed column. To yield a suitable retention in a column mode, a  $K_d$  of at least several hundred is required; therefore, a satisfactory uptake in both cases is achieved in only 15 minutes. However, a  $K_d$  of several thousand would lead to an extremely efficient recovery process, and equilibrium has been reached for both sorbents in about 3 hours.

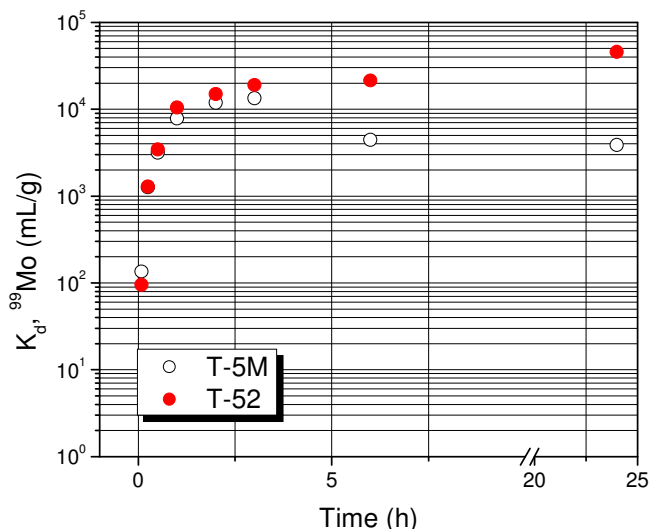


Figure 5. Uptake of  $^{99}\text{Mo}$  as a function of time from 0.1 M  $\text{HNO}_3$  at  $25^\circ\text{C}$  for and T-5M.

Figure 6 shows the amount of stable Mo that can be bound to the sorbents from solutions containing 150 and 235 g-U/L at pH 1 and 25, 55, and  $85^\circ\text{C}$ . As the concentration (1-100 ppm Mo) and volume (1-10 mL) of the solution was increased, while keeping the amount of sorbent constant, the maximum uptake of Mo at  $25^\circ\text{C}$  for T-52 and T-5M is  $\sim 0.25$  meq/g and at 55 –  $85^\circ\text{C}$  is  $\sim 0.55$  meq/g. Interestingly, T-52's capacity for Mo was slightly lower in the presence of a lower uranium concentration 150 versus 235 g-U/L. On the other hand, T-5M's capacity for Mo was slightly higher in the presence of a lower uranium concentration. This suggests that T-5M is less effective at adsorbing Mo than T-52 at higher uranium concentrations. Earlier studies showed that in a 1 M  $\text{HNO}_3$  solution, the loading capacities of both sorbents was  $\sim 3$  meq/g.[6]

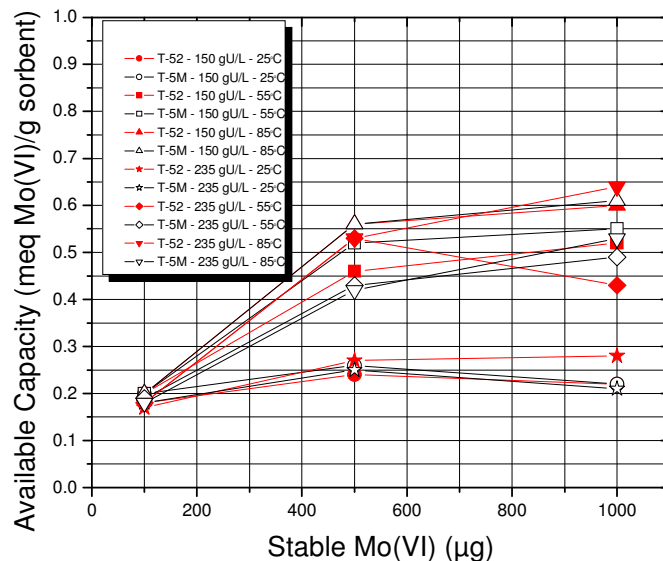


Figure 6. The available capacity of T-52 and T-5M for Mo(VI) from solutions containing 150 and 235 g-U/L (pH 1) at 25, 55, and 85 °C.

The ability of T-52 and T-5M to uptake Mo(VI) after incubation with a uranyl nitrate solution (235 gU/L) for 6 hours at 55°C followed by a contact with 0.1 M HNO<sub>3</sub>, H<sub>2</sub>O and 1 M NH<sub>4</sub>OH was determined. Results suggest that contact with the series of wash solutions does not affect the sorbents' ability to uptake Mo(VI). Figure 7 shows how the  $K_d$  values obtained for the uptake of Mo(VI) do not change significantly as the number of wash cycles increases. However, it has been shown that heating the sorbents in the oven for 24 hours at 105°C decreases their adsorption capacity for Mo(VI) by more than 50% for T-52 and ~ 40% for T-5M. In the future, the sorbents will not be dried prior to use in batch studies or column work.

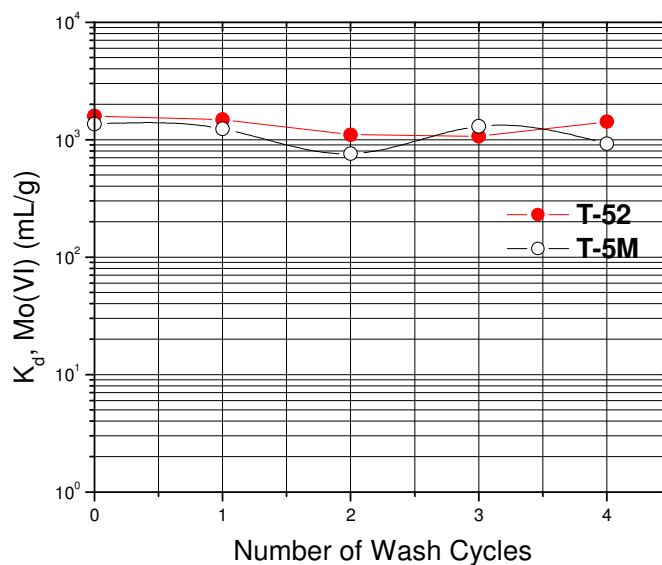


Figure 7. Uptake of Mo(VI) from a solution containing 235 g-U/L (pH 1) at 55°C and 24 hour equilibration time after a series of wash cycles.



Initial column studies using a 15 mL bed volume column (1.5 x 10 cm) of T-52 did not show any breakthrough of Mo(VI). 300 mL of a uranyl nitrate solution containing 1 ppm stable Mo and spiked  $^{99}\text{Mo}$  was passed through the column at a flow rate of 1.2 mL/min. 500  $\mu\text{L}$  of solution was collected for every 15 mL of solution that passed through the column, and a measurable amount of  $^{99}\text{Mo}$  was not observed in any of the samples. 15 samples were collected, and a breakthrough curve could not be generated.

Column studies using the same conditions mentioned above except 3 and 6 mL bed volumes showed minimal breakthrough of Mo(VI). Using the 3 mL column (1.5 x 2 cm), 165 mL of a uranyl nitrate solution containing 1 ppm stable Mo and spiked  $^{99}\text{Mo}$  was passed through the column. After 5 bed volumes passed through the column, 0.7% of Mo(VI) was collected, while 10.8% of Mo(VI) was collected after 55 bed volumes. Breakthrough was occurring too soon, so a 6 mL bed volume column (1.5 x 4 cm) was tested next. After passing 5 column volumes of solution through the column, breakthrough was 0.2% and after 55 bed volumes, 1.2% of Mo(VI) was collected. A total of 400 mL of 235 g-U/L spiked with  $^{99}\text{Mo}$  was loaded on the column. The 5 mL column used was slightly different (1 x 5 cm) and it was thermostatted at 60°C. 0.3%  $^{99}\text{Mo}$  was recovered after 250 bed volumes passed through the column (1500 mL). Figure 8 shows the % breakthrough of Mo(VI) for all of the columns tested. The breakthrough of Mo(VI) that was observed for the columns was most likely due to channeling. The likelihood of channeling increases significantly with increasing bead size and poor column packing.[8] The large, non-uniform sorbent particles (0.7-1.0 mm) aided in the initial bleeding of  $^{99}\text{Mo}$ . Additionally, no quality control measures were taken to ensure uniform packing. In order to generate a breakthrough curve for Mo(VI) using the same conditions, more solution needs to pass through the column. However, decreasing the bead size and increasing their uniformity, while ensuring proper packing, will help build a column that can generate a breakthrough curve for Mo(VI) using less volume.

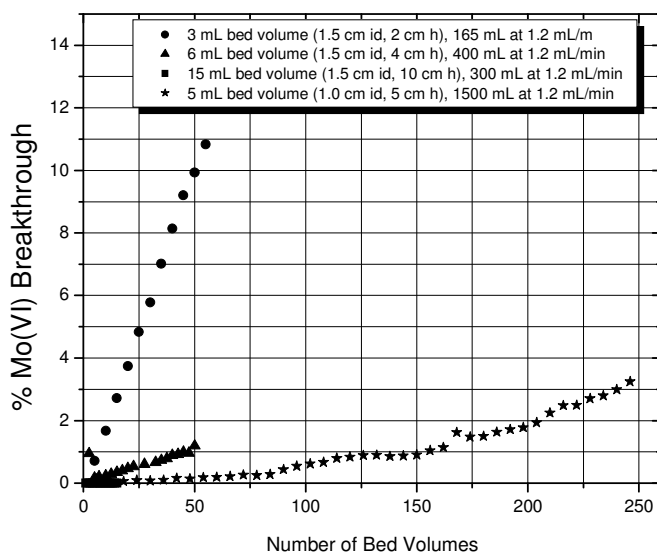


Figure 8. Breakthrough of Mo(VI) as a function of the number bed volumes from a 235 g-U/L solution at pH 1.

#### 4. Conclusions

Overall, T-52 shows superior uptake of Mo(VI) from an aqueous homogeneous reactor solution containing high concentrations of uranium - 185-285 gU/L. At higher temperatures (55 and 85°C), T-52 adsorbs Mo(VI) 30% (55°C) and 50% (85°C) better than T-5M. In addition, both sorbents have a higher capacity for Mo in the temperature range of 55-85°C - 0.55 meq/g then at 25°C - 0.25 meq/g. Both sorbents would be usable to recover <sup>99</sup>Mo from an AHR fuel solution. Future work will optimize the recovery operation and design the full-scale recovery column.

#### 5. Acknowledgements

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