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SORBENT SELECTION FOR ^{99}Mo RECOVERY FROM IRRADIATED AQUEOUS HOMOGENEOUS REACTOR FUEL SOLUTIONS

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ABSTRACT

Argonne National Laboratory is currently assisting Babcock and Wilcox Technical Services Group in development of a ^{99}Mo recovery process from the low enriched uranium (LEU) fuel solution of an aqueous homogeneous reactor (AHR). Six sorbents have been evaluated for their ability to recover Mo from a uranyl-nitrate solution; T52 and T5M - manufactured by Termoxid Scientific and Production Company (Zarechnyi, Russia), alumina, a pure TiO_2 sorbent and an organically-bonded TiO_2 sorbents. Sorbent physical properties have been determined and correlated with each sorbent's chemical and radiolytic stabilities and ability to recover Mo effectively and efficiently from all other irradiated fuel components. The results of these studies reveal that only T52, T5M and pure TiO_2 sorbent are possible candidates for Mo-recovery from the fuel solution. Organically-bonded TiO_2 sorbents degraded under chemical conditions relevant to AHRs. Alumina's high solubility under conditions relevant to AHRs and low Mo uptake make alumina a highly unlikely candidate. T52 and TiO_2 sorbents have better chemical stability than T5M, and both T5M and TiO_2 sorbents retain significant amounts of uranium and require scrubbing with high volumes of nitric acid. Given what is known at this time, Argonne would down select to two sorbents; T52 and pure TiO_2, as the preferred candidates for Mo recovery for irradiated AHR fuel solutions.

1. Introduction

Technetium-99m is the most commonly used medical isotope in the world with the estimated usage of 25 million procedures annually. ^{99m}Tc is a daughter of ^{99}Mo, which is currently produced mainly by fissioning ^{235}U from high enriched uranium (HEU). Currently, the United States has no domestic production of ^{99}Mo and is experiencing a shortage of this medical isotope due to repairs and maintenance of NRU reactor in Canada and HFR reactor in Netherlands. Babcock and Wilcox Technical Services Group (B&W) is developing a domestic production of ^{99}Mo - Medical Isotope Production System (MIPS), which will produce ^{99}Mo in an aqueous homogeneous reactor (AHR) solution of low enriched uranium (LEU). After irradiation, molybdenum will be separated from the fuel solution, which will be returned to the reactor for next irradiation. Production of ^{99}Mo in AHR is advantageous compared to producing ^{99}Mo by

irradiating a target because the steps of target production and dissolution are eliminated. The process also results in minimal uranium waste, and, in principle, the fuel solution can be recycled for up to 20 years. Aqueous homogeneous reactors are also attractive due to their geometry-inherent nuclear safety, efficient neutron utilization, and potentially lower capital and operating costs. Argonne National Laboratory is assisting B&W in development of MIPS by developing a separation process of ^{99}Mo from a 10-300 g/L uranyl nitrate solution. Argonne National Laboratory has evaluated six sorbents for their ^{99}Mo capacity, physical characteristics, radiolytic and chemical stability, effect of solution composition on Mo sorption, uranium uptake, sorbent-washing conditions, Mo recovery from the sorbent, and uptake of other fuel solution components by the sorbent. We have found that alumina has low uptake of Mo from uranyl nitrate solution and has poor chemical stability. Sorbents T52, T5M, and TiO_2 are highly selective for Mo(VI) over other fission products and uranium. However, the pure TiO_2 sorbents and T5M uptake significant amounts of uranium during loading and require large volumes of wash solution. Therefore, the pure TiO_2 sorbent and T52 were down selected for further studies given their superior chemical and radiolytic stability and highest Mo capacity under conditions relevant to AHR. The process goals of MIPS separation system are to process the fuel solution through the column as quickly as possible, with high Mo yield, minimum pressure drop in the column, and a high concentration factor for the Mo product. The productivity of a Mo-recovery system highly depends on sorbent selectivity, capacity, and intraparticle diffusivity. Column productivity can be maximized by optimizing column length and diameter, linear velocity of the feed solution, and sorbent particle size. Through our collaboration with Purdue University, we are providing data required for their utilizing VERSE software for modeling column designs to develop a most efficient separation system.

2. Experimental

2.1 Batch uptake measurements

The partitioning of species between the sorbents and aqueous solutions was measured by equilibrating a 1-mL volume of aqueous solution of appropriate composition (concentrations of Mo(VI), $UO_2(NO_3)_2$ or $NaNO_3$, and HNO_3) with a known mass of sorbent. A 24 h mixing time was typically used for the uptake equilibrium measurements. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a 0.2 μm pore size, PVDF Membrane Filter. Blank experiments indicate that the filter does not uptake ^{99}Mo. The amount of ^{99}Mo activity in the aqueous samples in the absence of uranium was quantified by counting the activity in the 650-800 keV window using a 1480 Wizard 3" NaI gamma detector or in the presence of U by measuring the 739 keV γ-ray on a Ortec HPGe detector. The activity of ^{99}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:

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

Here, A_o and A_s represent the aqueous phase activity (cpm) before and after equilibration, respectively; W is the dry mass of the sorbent (g), and V is the volume of the aqueous phase (mL). The amount of sorbent used was generally kept at 10 (± 1) mg in order to leave a measurable activity in the aqueous phase.

Activity of ^{233}U was determined using a Model 3100 Liquid Scintillation Counter and Optima gold Liquid Scintillation cocktail.

2.2 Mo recovery column studies

Columns were packed with 2 mL of T5M, T52, TiO_2 and alumina sorbents, pre-equilibrated with 0.1 M HNO_3, and loaded with 50 µL of 10 ppm Mo in 0.1 M HNO_3 solution spiked with ^{99}Mo. The columns were then washed with five 1-mL portions of 0.1 M HNO_3 followed by seven 1-mL portions of 1 M NaOH. Recovery of Mo was calculated from counting the starting Mo solution and the individually collected fractions on a NaI gamma counter.

2.3 U stripping column studies

Recovery of uranyl nitrate was determined by loading 50 µL of a 150 g-U/L solution spiked containing tracer amounts of U-233 onto a 2-ml bed volume column of sorbent. Sorbents were loaded into the columns as slurry in 0.1 M HNO_3. Uranyl nitrate was eluted from the column using 0.1 M HNO_3. Uranyl nitrate from S80 was eluted with an additional 10 bed volumes of 1 M HNO_3.

3. Results and Discussion

Sorbents have been evaluated for recovery of Mo from 60 °C solutions containing 0.5 ppm Mo and 90-150 g-U/L at pH 1. Results presented in **Figure 1** indicate that T52, T5M, pure TiO_2 sorbent, and the organically-bonded TiO_2 sorbents can be used to design an efficient column, where Mo can be separated from the feed at high flow rates. A K_d values of 272 mL/g for alumina and 500 mL/g for titania powder from a 145 g/L uranium solution indicate that it would be difficult to design a separation system based on alumina or titania powder. These low K_d values indicate that at least ten-times greater amount of sorbent would be required to design a column using alumina or titania powder than using T52, T5M or TiO_2 sorbents. Column size and sorbent mass should be minimized for any production-scale process because larger columns result in less concentrated product, higher backpressure, longer process times, and larger waste volumes.

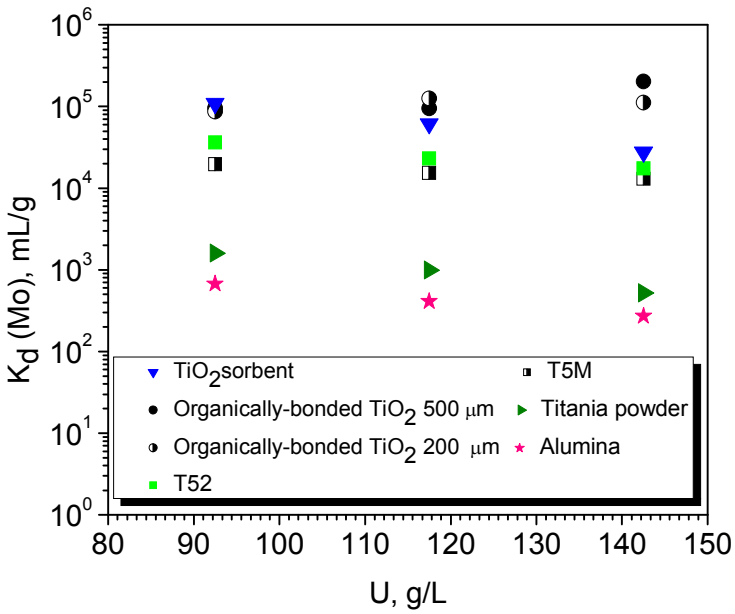

Figure 1. Uptake of 0.5 ppm of Mo from a uranyl nitrate solutions, pH 1, at 60 °C, 24 h, by sorbents under consideration for MIPs.

3.2 Langmuir Isotherm – sorbent capacity

A Langmuir Isotherm was obtained from 145 g/L U solution, pH 1 at 60 °C. The concentration of uranium in the AHR could vary over a range of 10-300 g/L. Average value of 145 g/L was chosen for this study. The results indicate that the capacity of the sorbent, q_{max} at Mo concentration of 0.35×10^{-6} M is ~2×10^{-5} mol Mo/g sorbent for alumina, ~ 8×10^{-5} for T5M and ~1×10^{-4} mol Mo/g sorbent for T52 and pure TiO_2 sorbent. A Langmuir isotherm is also used to calculate adsorption constant a, which defines q_{max}. These data, along with solution viscosity, Mo diffusivity, and mass transfer zone length are used for modeling column designs.

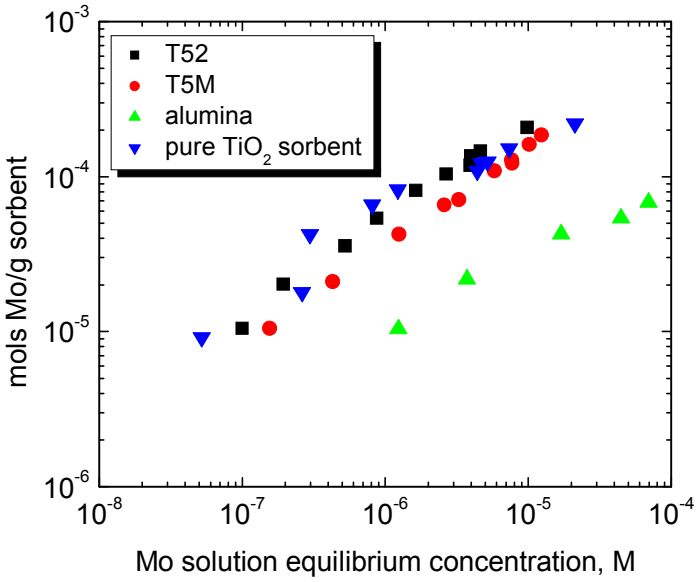

Figure 2. Langmuir Isotherm data for determination of sorbent capacity (q_{max}) and Langmuir sorption constant.

3.3 Chemical stability

3.3.1 Sorbent stability to pH 1 and 14 washing cycles

The chemical stabilities of T5M, T52, pure TiO_2 sorbent and organically-bonded TiO_2 sorbents were determined by exposing the sorbents to cycles of contacts with 0.1 M HNO_3 (stirring for 3 h at 60 °C) and 1 M NaOH (stirring for 1 h at 60 °C). Sorbents were exposed to 0, 3, 5, and 10 cycles of washes. The effect of chemical treatments was defined by measuring the Mo K_d values (Figure 3). The results indicate that uptake of Mo by T5M. T52 and pure TiO_2 sorbent is not significantly affected by the chemical treatment. However, organically-bonded TiO_2 sorbents degraded and formed a white powder after the first cycle of washes. The initial drop in K_d values observed in Figure 3 is most likely due to the fact that the sorbents not subjected to any washing cycles were not pre-equilibrated with HNO_3. The unequilibrated sorbents adsorb HNO_3, which causes an increase in pH of the Mo solution and, therefore, an increase in the sorption of Mo. The K_d values do not decrease further upon exposure to HNO_3 and NaOH and indicate that the sorbents are stable under the conditions investigated here.

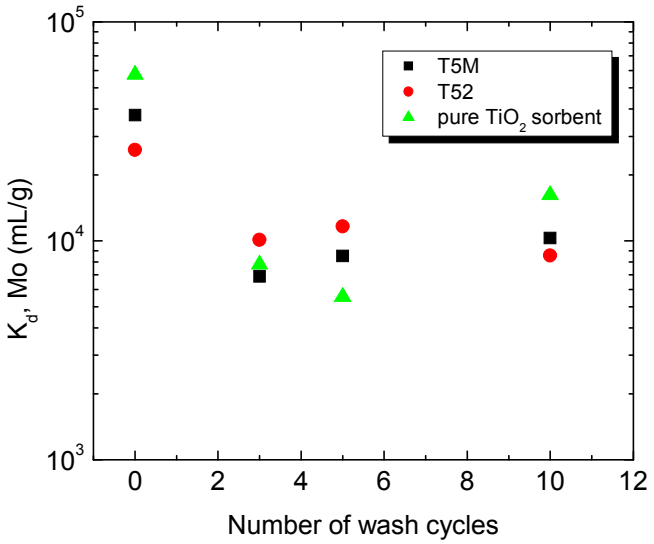

Figure 3. Sorbent stability after exposure to pH 1 and pH 14 washing cycles.

3.3.2 Dissolution of sorbents

The solubility of T5M, T52, and pure TiO_2 sorbent in nitric acid was determined by contacting untreated sorbents with 0.1 M HNO_3 solution for several days at room temperature (Table 1). Solubility of sorbents was also determined by contacting pretreated sorbents with 1ppm Mo solution in 0.1 M HNO_3 for 24 h at 60 °C (Table 1). Sorbents were pretreated by exposing to 5 and 10 cycles of 0.1 M HNO_3 and 1 M NaOH washes. It was found that the solubility of titania-based sorbents is very low, 200-400 ppb range, and is lowest for T52 and pure TiO_2 sorbents.

Table 1. ICP-MS results for solubility (ppb) of TiO_2 based sorbents in 0.1 M HNO_3 and Mo containing solutions.

Sample ID	Ti (ppb)	Zr (ppb)	Sn (ppb)
T5M*	363	8.02	<0.68
T5M-5	345	28.9	<0.68
T5M-10	307	32.2	<0.68
T52*	185	8.51	1
T52-5	211	9.72	0.81
T52-10	222	8.02	<0.68
TiO_2 sorbent*	268	7.29	<0.68
TiO_2 sorbent-10	176	9.44	<0.68

* Contacted with 0.1 M HNO3, several day at room temperature

Sorbent-5 and -10 indicates number of cycles washing with 0.1 M HNO3 (3h, 60 °C) and 1 M NaOH (1h, 60 °C).

The solubility of alumina sorbents is three orders of magnitude higher than the solubility of titania-based sorbents (Table 2). The differences in leachability of alumina samples from different suppliers reflect the uniformity of particle size. For example, alumina from Sigma-

Aldrich is not of sorbent quality and contains a large amount of fines, where as the AG4 sample from BioRad, has a narrow particle size distribution which is reflected in its lower leachability under these conditions.

Table 2. ICP-MS results of alumina solubility (ppm) in 0.1 M HNO_3 determined at RT (6 days) and 60 °C (24 h).

	Solubility of Alumina (ppm)						
	Sorbent Technologies		Dynamic Adsorbents			BioRad	Sigma Aldrich
Conditions	Act. I (50-200 μm)	Super Act. I (50-200 μm)	Alumina R (50-200 μm)	Act. I (50-200 μm)	Super Act. I (50-200 μm)	AG4 (150 mesh)	Act. I (150 mesh)
RT, 6 days, 0.1 M HNO_3	200	213	157	109	142	93.2	436
60°C, 24 h, 0.1 M HNO_3	278	334	245	222	195	181	415

High solubility of alumina is a concern as the high concentrations of Al^{3+} leads to possibility of having an aluminum-supersaturated reactor solution and aluminum-hydroxide precipitation and independent particle growth. The effect of aluminum ions on speciation and solubility of other components of the reactor solution should be also fully investigated if alumina is used as sorbent for Mo separation from AHR solution.

The composition of aqueous phases after contact with T5M (anatase) and T52 (rutile) and alumina are consistent with solubility diagrams modeled using the thermo-chemical modeling code OLI-ESP, Figure 4. The results indicate that alumina might be meta-stable in dilute nitric acid, and based on equilibrium thermodynamics it is predicted to be soluble at pH = 1. Based on the model predictions for anatase and rutile, it is possible to get measurable dissolved concentrations of titanium by leaching with a 0.1 M nitric acid solution. As indicated by the solubility diagrams and data reported by Sugamoto et al. the solubility of hydrous TiO_2 is nearly proportional to the second power of the acid concentration below pH 2.[1] Therefore, treatment of titania with acid solutions below pH 1 is not recommended. The ICP-MS results suggest that the TiO_2 sorbent (anatase) is as stable as T52 (rutile). This is most likely due to a uniform particle size of TiO_2 sorbent.

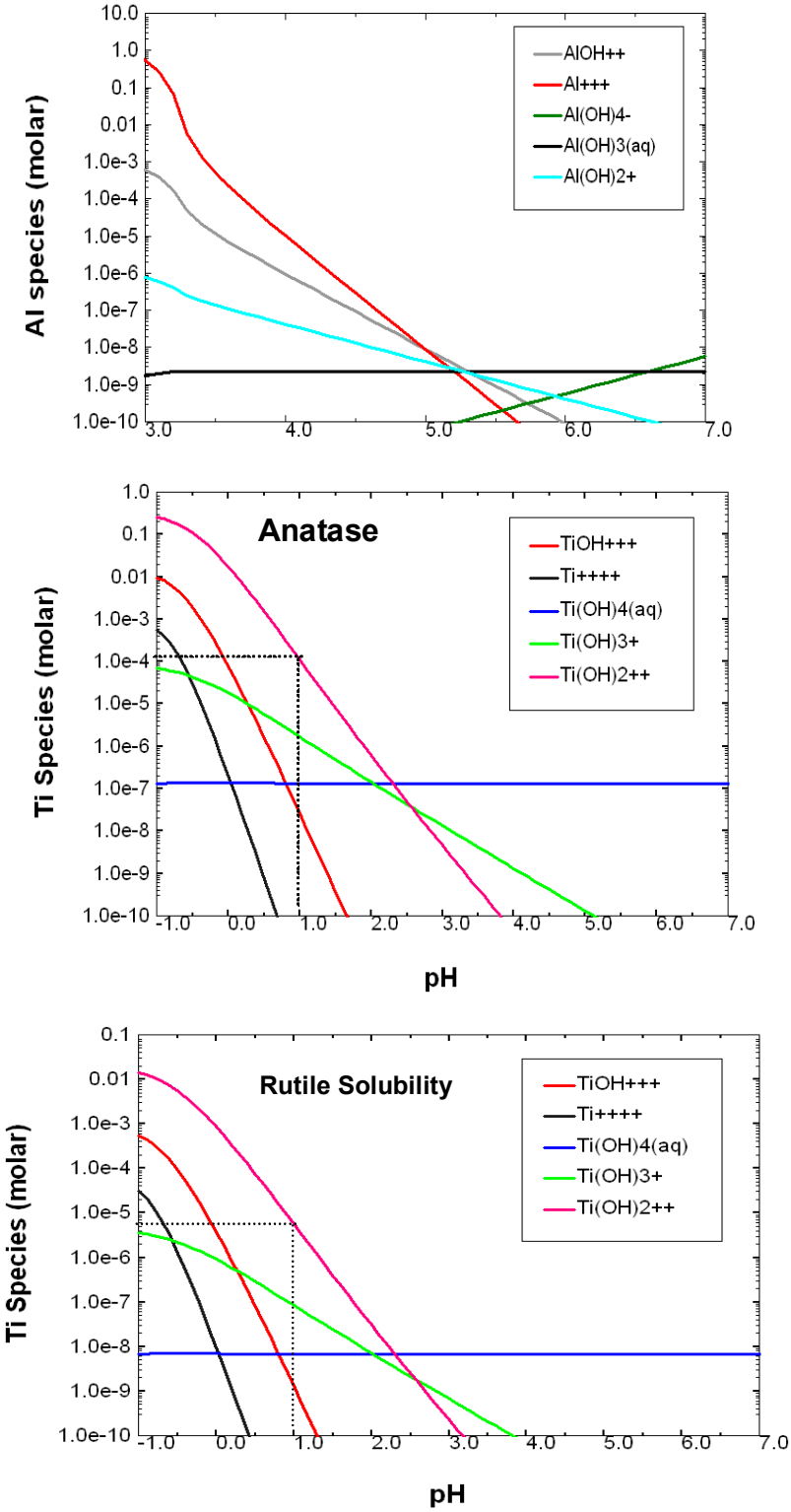

Figure 4. Solubility diagrams for alumina (top), anatase (middle) and rutile (bottom) modeled using the thermo-chemical modeling code OLI-ESP

3.4 Radiolytic stability

The radiolytic stability of T5M, T52, pure-TiO_2 sorbent and alumina was determined by contacting the sorbents, ~10 mg, with 150 g-U/L uranyl nitrate solution and irradiating using the Van de Graff generator. The irradiation doses were 311 kGy and 1.15 MGy. After irradiation, the uranium solution was removed and a new solution, containing 150 ,g-U/L, 0.7 ppm Mo and Mo-99 tracer at pH 1, was contacted with the sorbents. The sorbents were equilibrated for 24 h at 60 °C, and K_d values were obtained. The results in Figure 5 indicate that within the irradiation doses investigated, the sorbents do not lose their Mo-sorption properties, as indicated by constant (within experimental error) K_d values.

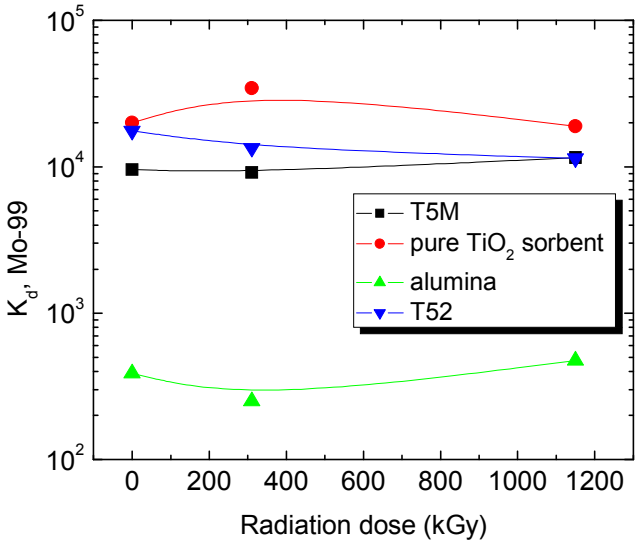

Figure 5. Effect of radiation dose on uptake of Mo.

3.4 Uranium Recovery

3.4.1 Batch studies

The uptake of uranium was determined as a function of HNO_3 concentration. The results in Figure 6 indicate that uranyl nitrate sorbs on T5M and TiO_2 sorbents. At 0.1 M HNO_3, the pure TiO_2 sorbent and T5M have ^{233}U K_d values of 24 and 28, respectively, whereas T52 and alumina display K_d values ~ 2. These results indicate that uranium can be efficiently washed from T52 and alumina using 0.1 M HNO_3, whereas pure TiO_2 sorbent and T5M might need to be washed with 1 M HNO_3 to efficiently remove uranyl nitrate from the column.

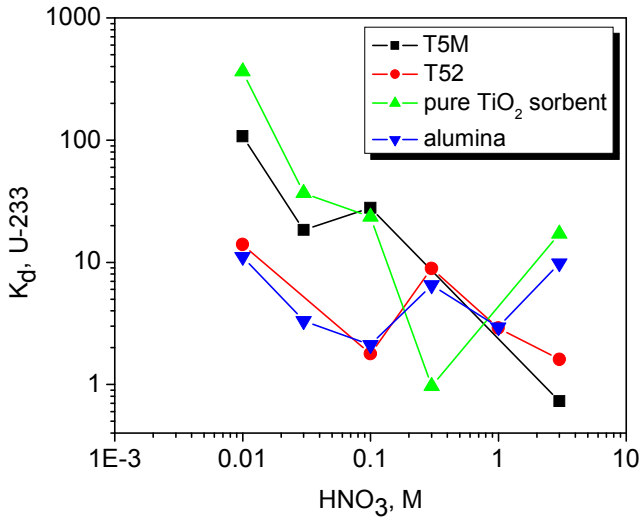

Figure 6. Uptake of tracer levels of ^{233}U (60 °C, 24 h) from HNO_3 solutions.

3.4.2 Column studies

The results of batch studies on uptake of uranyl nitrate by the sorbents were confirmed by small-column experiments as shown in Figure 7. As expected, uranyl nitrate is eluted faster from a T52 column than from a T5M column. Unexpectedly, a urany-nitrate peak emerges earlier from a T5M column than from an alumina column, even though T5M has K_d values that are one order of magnitude higher than those obtained for alumina. This can be explained by channeling of uranium through the larger sorbent particles of T5M (0.2-0.4 mm). In fact, the long uranium tail on a T5M packed column and the higher amount of 0.1 M HNO_3 needed to elute uranium from T5M as compared to alumina confirms the results of batch studies. High uranium K_d values for the pure-TiO_2 sorbent are also confirmed by the column tests. Elution of uranyl nitrate from the pure-TiO_2 sorbent was not complete after ten bed volumes of 0.1 M HNO_3 and only 76 ± 5 % of uranium was recovered. The elution was completed by passing an additional ten bed volumes of 1 M HNO_3.

The need to use 1 M HNO_3 to remove uranium from a TiO_2 column does not automatically disqualify its use in the MIPS, as the recovered uranyl nitrate in 1 M HNO_3 solution can be used to adjust the pH of reactor fuel solution. However, the solubility of TiO_2 under those conditions might be a concern, as discussed above in the chemical stability section, and will be investigated further. Additionally, scrubbing TiO_2 sorbent with 1 M HNO_3 may lead to a loss of Mo. When the TiO_2 sorbent is loaded with Mo to ~5 x 10^{-7}mol Mo/g sorbent (conditions relevant to MIPS) and is contacted with 1 M HNO_3 (24 h, 60 °C), 1.5% of Mo is desorbed.

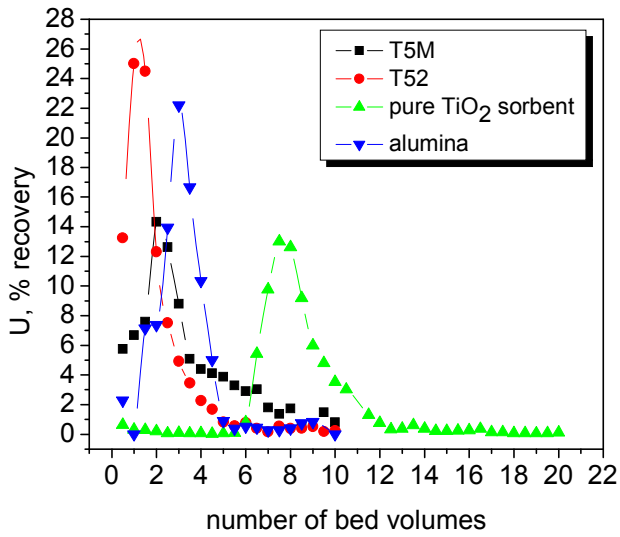

Figure 7. Elution of uranium from T5M, T52, pure-TiO_2 sorbent, and alumina.

3.5 Mo Recovery

Small columns were prepared to investigate stripping of Mo from T5M-, T52-, pure-TiO_2 sorbent-, and alumina-packed columns using 1 M NaOH to elute Mo. The results in Table 3 indicate that Mo can be recovered with greater that 95 percent recovery for T5M, T52, and the pure-TiO_2 sorbents. Product recovery from alumina was ~90%. These results will be repeated in the future to achieve a more accurate product recovery. Figure 8 shows the elution of Mo from T5M-, T52-, the pure-TiO_2-sorbent-, and alumina-packed columns and indicates that Mo can be eluted within 4 bed volumes for all sorbents.

Table 3. Percent recovery of Mo-99 from T5M, T52, TiO_2 sorbent, and alumina.

Mo Recovery	T5M	T52	TiO_2 sorbent	Alumina
Total % recovery*	97 ± 5 %	93 ± 5 %	100 ± 5 %	88 ± 5 %

*Includes 5 mL of 0.1 M HNO_3 washes.

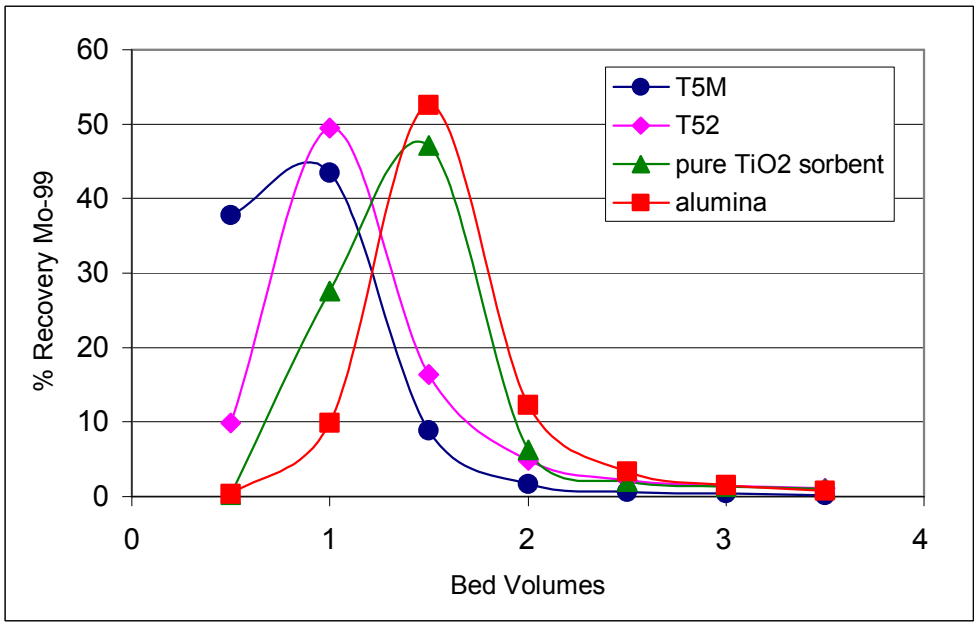

Figure 8. The percent recovery of Mo-99 as a function of the number of bed volumes.

3.6 Uptake of competing components

Uptake of competing components was measured by contacting T5M and T52 (1 g) with 10 mL of a simulated fuel solution, pH 1, without uranium, for 24 h at 55 ^{o}C (Table 4). The composition of the fuel solution was based on ORIGEN calculations for 90 days burn up for an AHR fuel solution.[2] The components of the fuel solution were analyzed by ICP-MS (Fe, Se, Rb, Sr, Y, Mo, Ru, Rh, Ag, Cd, Sn, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd) and ion-chromatography (I^-). The components that exhibit K_d values above 10 for T52 are Fe (42), Ru (88), Se (≥49) and Rh (14). For T5M, K_d (Se) was ≥49 and K_d (Ru) was 44. K_d (I^-) was 1 and 6 for T52 and T5M, respectively.

Uptake of competing components was also measured for the pure-TiO_2 sorbent and alumina under similar conditions (Table 4). The following components of the fuel solution were analyzed by ICP-MS; Fe, Se, Rb, Sr, Y, Zr, Mo, Ru, Ag, Cd, Sn, Te, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd. The components that exhibit K_d values above 10 for the pure-TiO_2 sorbent are Se (≥349), Zr (60), Ag, (147), Sn (18), and Te (≥4373). For alumina, K_d Se is ≥349, Ag is 24, Sn is 48, and Te is ≥4373. Rh, which was present as perrhenate anion at pH 1, was not analyzed for uptake by TiO_2 sorbent and alumina, but is likely to exhibit K_d values above 10.

Table 4. Uptake of ions from a simulated fuel solution in the absence of uranium

	Sorbent K_d values			
Element	**T52**	**T5M**	**TiO_2 sorbent**	**alumina**
Fe	42	9	5	0
Se	≥49	≥49	≥ 349	≥ 349
Rb	0.1	0.0	0	0
Sr	0.0	0.0	0	0
Y	0.7	0.1	0	0
Mo	≥2599	137	≥3110	≥3110
Ru	88	44	3	1
Rh	14	3	-	-
Ag	0.0	0.0	147	24
Cd	2	0.5	0	0
Sn	0.0	4.8	18	49
Cs	0.2	0.0	0	0
Ba	0.1	0.0	0	0
La	0.1	0.0	0	0
Ce	0.2	0.0	0	0
Nd	0.2	0.0	0	0
Sm	0.9	0.2	0	0
Eu	0.9	0.2	0	0
Gd	1	0.3	0	0
I	1	6	-	-
Zr	-	-	60	9
Te	-	-	≥4373	≥4373

4. Conclusions

To recover ^{99}Mo from an aqueous homogeneous reactor (AHR) fuel solution, Argonne has evaluated seven potential sorbents - T52 (25 mole % of SnO_2 and 75 mole % TiO_2) and T5M (5 mole % of ZrO_2 and 95 mole % TiO_2), alumina, pure TiO_2 sorbent, organically-bonded TiO_2 sorbents (200 and 500 μm) and titania powder (80 μm). These sorbents were evaluated in terms of their uptake of Mo from uranyl nitrate solution and their chemical and radiolytic stability. In our studies, we have found that alumina has low uptake of Mo from uranyl nitrate solution and has poor chemical stability. Organically-bonded TiO_2 sorbents decompose under relevant chemical conditions. Sorbents T52, T5M, and TiO_2 are highly selective for Mo(VI) over other fission products and uranium. However, TiO_2 sorbents and T5M uptake uranium and require large volumes of wash solution. The pure-TiO_2 sorbent and T52 are down selected for further studies given their superior chemical and radiolytic stability and highest Mo uptake.

5. Acknowledgements

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6. References

[1] Sugimoto, T.; Zhou, X.; Muramatsu, A. *J. Colloid Interface Sci.,* **2002**, *252*, 339.
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