

**THERMOXID SORBENTS FOR THE SEPARATION
AND PURIFICATION OF ⁹⁹MO**

by

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THERMOXID SORBENTS FOR THE SEPARATION AND PURIFICATION OF ⁹⁹MO

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ABSTRACT

The Argonne National Laboratory Reduced Enrichment for Research and Test Reactors Program is performing R & D supporting conversion of ⁹⁹Mo production from high-enriched to low-enriched uranium targets. One of the major obstacles to conversion is the fivefold increase of the amount of uranium needed to produce an equivalent amount of ⁹⁹Mo. The additional uranium could lead to an increase in the volume of liquid processed and the volume of liquid waste. The use of an efficient, high capacity sorbent would allow for small purification columns and minimum liquid volumes throughout the process. Thermoxid has developed an inorganic sorbent that meets these requirements. Our batch tests show that Thermoxid sorbents have much higher Kd(Mo) values than the commonly used alumina under a wide variety of conditions (20 – 100 g U / L, 0.5 – 1.5 M HNO₃, 4, 24, and 48 hours) relevant to acid-side ⁹⁹Mo production and recovery processes. The Kd(Mo) values for the Thermoxid and alumina sorbents are inversely proportional to both uranium concentration and acidity. Overall, these new sorbents appear to have superior performance and would allow for smaller separation/purification columns than are possible using alumina as the sorbent.

INTRODUCTION

To reduce nuclear proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) Program is working to reduce the use of high-enriched uranium (HEU) in research and test reactors by substituting low-enriched uranium (LEU) fuel and targets. Radioactive decay of ⁹⁹Mo produces ^{99m}Tc (half-life of 2.75 days), which is used in large quantities in nuclear medicine. Neutron fission of ²³⁵U generates ⁹⁹Mo; the ²³⁵U is generally in the form of HEU (93% enriched ²³⁵U) targets. Because LEU contains <20% ²³⁵U, a five fold increase in the total amount of uranium is needed to produce an equivalent amount of ⁹⁹Mo. Such an increase in total uranium would lead to an increase in the amount of radioactive waste, and possibly, a reduction in facility throughput. ANL's role is to help each producer minimize the negative impact of LEU conversion on their process [1]. Previous studies have addressed the amount of solid waste [2] and the off gas generated during waste processes [3]. The current study will evaluate the potential of a new sorbent (Thermoxid). If Thermoxid is found to have higher Kd values than the commonly-used alumina [4, 5], then the process columns could be made smaller. These smaller columns could result in smaller liquid volumes downstream, and therefore, a reduced volume of liquid waste.

Thermoxid type sorbents are manufactured by Thermoxid Scientific and Production Company (Zarechnyi, Russia) for Technology Commercialization International Inc. (TCInternational). The sorbents are manufactured as 0.4-1.0 mm spherical particles with high mechanical stress [1]. The sorbents evaluated here are specifically designed to for Mo recovery.

The purpose of this work was to evaluate the effectiveness of Thermaxid sorbents in acidic ^{99}Mo recovery and purification processes. In particular, the K_d values were compared to those for alumina sorbent under identical conditions.

EXPERIMENTAL

Aim of Experiments

These experiments were designed measure the K_d values for two Thermaxid sorbents for the recovery and purification of ^{99}Mo . In particular, the K_d 's will be compared to those for alumina. This will be done by conducting simple batch tests and measuring the extent of retention of ^{99}Mo . Variables will include acidity, uranium concentration and time. These experimental conditions were chosen to be relevant to the recovery of ^{99}Mo from acidic solutions obtained from uranium foil target dissolution.

Batch Tests

A series of batch tests was done to determine K_d (^{99}Mo) values under a wide variety of conditions. Each batch test was done with three different sorbents [Thermaxid R-1, Thermaxid R-2, and alumina (Aldrich aluminum oxide, activated, acidic, Brockmann 1,150 mesh)]. About 100 mg of the dry sorbent was placed into a 10 mL culture tube, along with 2 mL of the appropriate solution, and the tube was tumbled for the duration of the experiment. Fifteen different solutions were prepared: 0.5, 1.0, and 1.5 M HNO_3 and uranium concentrations of 20, 40, 60, 80, and 100 g U / L of solution. The uranium was added as the soluble uranyl nitrate hexahydrate salt. A stock solution of stable Mo (0.1064 g Mo / mL of solution) was prepared with $\text{Na}_2[\text{MoO}_4]\cdot 2\text{H}_2\text{O}$. This stable Mo stock solution was added to each of the fifteen experimental solutions to yield a final concentration of 1.064×10^{-5} g Mo / mL of solution.

Generators for $^{99\text{m}}\text{Tc}$ are commercially available as ^{99}Mo sorbed onto a shielded alumina column. We elute $^{99\text{m}}\text{Tc}$ by passing dilute sodium nitrate through the column. To recover the ^{99}Mo , concentrated ammonium hydroxide was passed through the column, and evaporated to dryness. The salt was then redissolved in dilute nitric acid, and filtered before use as radiotracer in this study. The tracer was added so that the 20 minute gamma count of the stock U-Mo acid solutions had an uncertainty less than 2%.

Gamma counting was performed with a high purity germanium well-geometry detector. Efficiency varied from ~5% to ~60% depending on the energy. Previous work has shown that uncertainty in these measurements was typically 5-10%, accounting for pipetting and statistical variance in peak area. The K_d values were calculated by comparing the gamma (181.4 keV) count rate for the collected test solutions to the count rate of stock solutions. The decay of ^{99}Mo with time was taken into account.

A K_d , or partitioning coefficient is a measure of the effectiveness of a solid phase to sorb a species from solution. It is defined as the amount of the species of interest (per gram of sorbent) divided by the amount of species in the solution in contact with the sorbent (per mL). K_d values are reported in mL/g. In general, if K_d values are $>10,000$, then the sorbent effectively acts as a filter for the species of interest; if K_d values are between 10,000 and 1000, then the separation is excellent; if K_d values are between 1000 and 100, then the separation is good; and if the K_d values are between 100 and 10, then the separation is poor.

RESULTS AND DISCUSSION

Kd (Mo) as a function of acidity

The Kd values from these experiments were examined as a function of nitric acid concentration. Experiments were conducted at 0.5, 1.0, and 1.5 M HNO₃. Figure 1 shows selected data that illustrate the general trend of Kd values as a function of acidity. All of the data collected in this study is presented in Table 1. The Kd values decrease as acidity increases (at a constant uranium concentration); this is true of both Thermoxid sorbents and alumina. Similar behavior has previously been observed for alumina in the acidity range of 0.1 to 1.0 M HNO₃ [4].

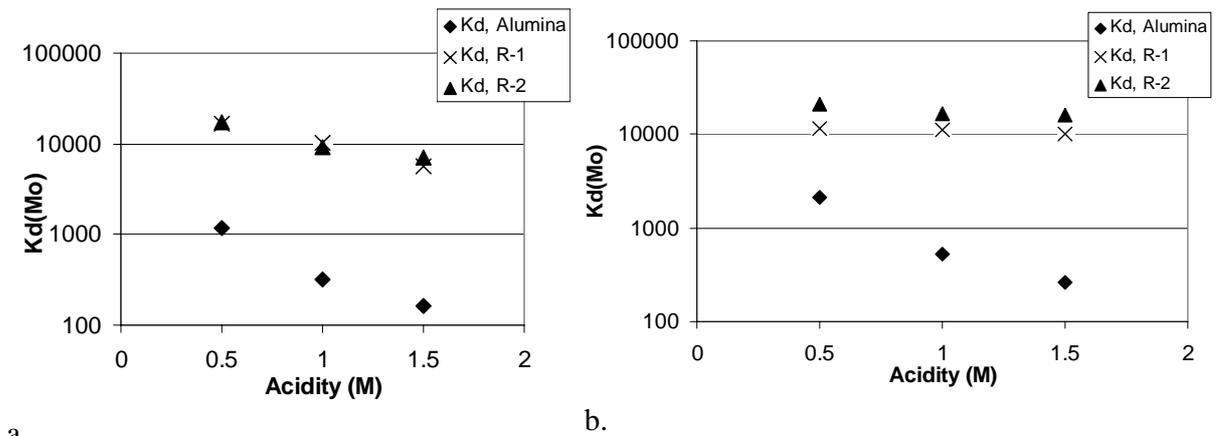


Figure 1. Kd values as a function of nitric acid concentration. These data are presented to illustrate the general trends; all of the data are presented in Table 1. Data in chart a. was collected after 25 hours of contact time, and 40 g U / L; data in chart b. was collected after 48 hours of contact time, and 40 g U / L.

Kd as a function of uranium concentration

The Kd values from these experiments were examined as a function of uranium concentration. Experiments were conducted at 20, 40, 60, 80, and 100 g U/L of solution. Figure 2 shows selected data that illustrate the general trend of Kd values as a function of uranium concentration. All of the data collected in this study is presented in the Table 1. The Kd values decrease as uranium concentration increases (at a constant acidity); this is true of both thermoxid sorbents as well as alumina. Similar behavior has previously been observed for alumina in the range of 0 to 320 g U / L of solution [4]. Data in Figure 3 shows that the trend of decreasing Kd with increasing U concentration extends to 320 g U / L. Further, at the higher U concentrations the Thermoxid sorbents have much higher kd values than alumina, and R-2 has significantly higher Kd values than R-1.

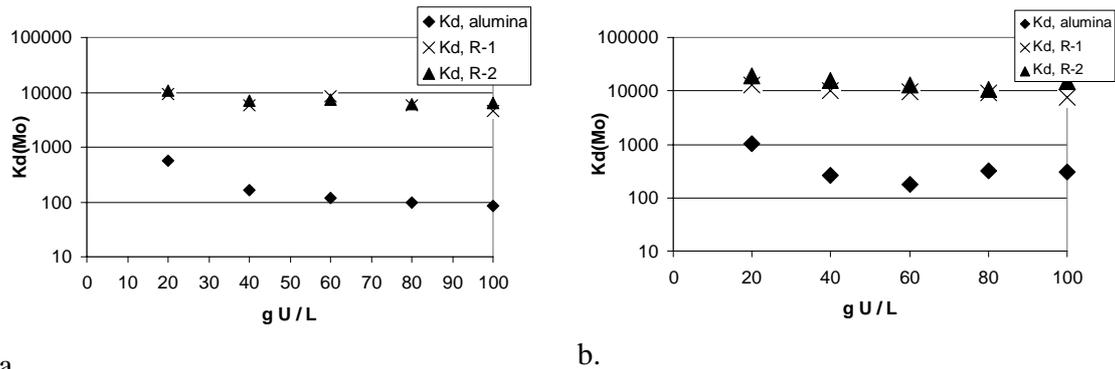


Figure 2. K_d values as a function of uranium concentration. These data are presented to illustrate the general trends; all of the data are presented in Table 1. Data in chart a. was collected after 25 hours of contact time, and 1.5 M acid; data in chart b was collected after 48 hours of contact time, and 1.5 M acid.

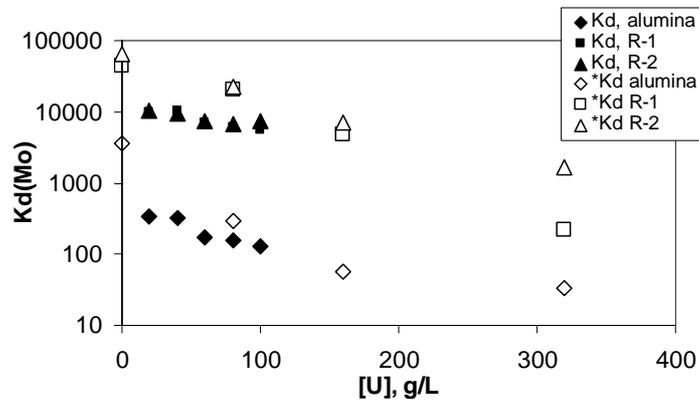
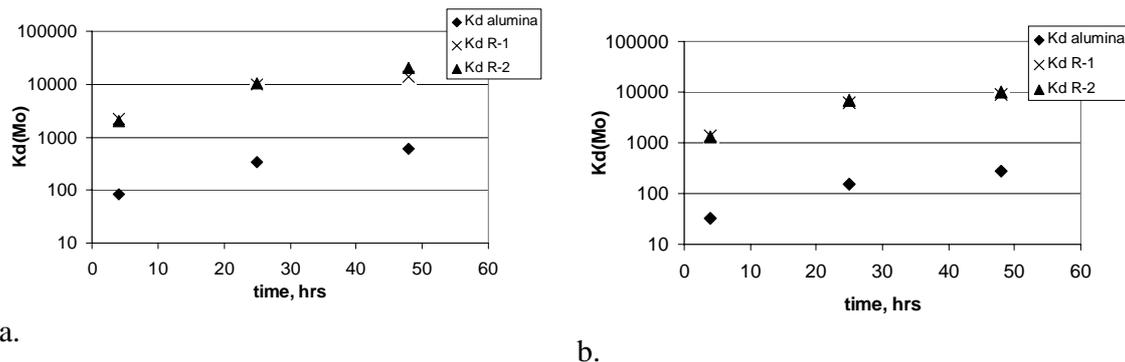


Figure 3. K_d values as a function of uranium concentration. Data from this study are compared to data from reference [1] (*). These data were collected from 24-hour tests with 1.0 M acid. Note that the data from reference [1] were from tests using a different batch of the Thermoxid sorbents.

Kd as a function of time

The K_d values from these experiments were examined as a function of time. Tests were terminated after 4, 25, and 48 hours of contact time; the tests were tumbled during the entire contact time. Figure 3 shows selected data that illustrate the general trend of K_d values as a function of time. All of the data collected in this study is presented in the Table 1. The data in Figure 4 suggest that none of the sorbents have reached equilibrium with Mo by 25 hours contact time under the conditions of this study. Therefore, the flow rates required for columns using Thermoxid sorbents will be comparable to those for columns using alumina.



a. b.
 Figure 4. K_d values as a function of contact time. These data are presented to illustrate the general trends; all of the data are presented in Table 1. Data in chart a. was collected from tests with 1.0 M acid and 20 g U / L; data in chart b. was collected from tests with 1.0 M acid and 80 g U / L.

Thermoxid sorbents were evaluated as an alternative to alumina in the recovery and purification of ^{99}Mo from irradiated uranium foils. A primary purpose of this study was to compare the effectiveness of Thermoxid sorbents to the commonly-used alumina for the separation of Mo from acidic uranium-rich solutions. The K_d values for thermoxid tests are in all cases (Figures 1-4; Table 1) are at least 10 times the K_d values for the identical alumina tests.

In nearly all of our tests, the K_d values observed in 48-hour tests were larger than the K_d values obtained at 25 hours. Data presented here and previously [1], show that R-1 has more favorable kinetics than R-2, and will thus allow faster feed flow through a column. The loading capacities for the two Thermoxid sorbents have been measured as about 3 meq/g, which is similar as that for alumina. Further column tests are underway. Based on these results, we feel that the use of either of the Thermoxid sorbents should (1) allow a more efficient recovery of ^{99}Mo than current alumina columns, and (2) generate a waste solution volume for LEU processing equal to, or less than for current HEU target processing.

Table 1. Kd values for each test conducted in this study

[U]	[H+]	time (hrs.)	Kd alumina	Kd R-1	Kd R-2	[U]	[H+]	time (hrs.)	Kd alumina	Kd R-1	Kd R-2
20	2	4	130			40	2	4	39		
20	2	25	546			40	2	25	163		
20	2	48	1011			40	2	48	266		
20	2	4		3139		40	2	4		1740	
20	2	25		9343		40	2	25		5665	
20	2	48		13129		40	2	48		10194	
20	2	4			3033	40	2	4			1666
20	2	25			10962	40	2	25			7115
20	2	48			19367	40	2	48			16009
20	1	4	85			40	1	4	70		
20	1	25	334			40	1	25	320		
20	1	48	590			40	1	48	528		
20	1	4		2211		40	1	4		2232	
20	1	25		9803		40	1	25		10309	
20	1	48		13874		40	1	48		11341	
20	1	4			2050	40	1	4			1827
20	1	25			10202	40	1	25			9326
20	1	48			20333	40	1	48			13550
20	0.5	4	428			40	0.5	4	274		
20	0.5	25	1856			40	0.5	25	1856		
20	0.5	48	2949			40	0.5	48	2100		
20	0.5	4		4420		40	0.5	4		3240	
20	0.5	25		21552		40	0.5	25		16640	
20	0.5	48		31313		40	0.5	48		11371	
20	0.5	4			3262	40	0.5	4			2804
20	0.5	25			20287	40	0.5	25			17420
20	0.5	48			22106	40	0.5	48			21285

Table 1 continued

[U]	[H+]	time (hrs.)	Kd alumina	Kd R-1	Kd R-2	[U]	[H+]	time (hrs.)	Kd alumina	Kd R-1	Kd R-2
60	2	4	33			80	2	4	34		
60	2	25	117			80	2	25	96		
60	2	48	177			80	2	48	323		
60	2	4		1668		80	2	4		1336	
60	2	25		8628		80	2	25		5891	
60	2	48		9830		80	2	48		9218	
60	2	4			2329	80	2	4			1461
60	2	25			7438	80	2	25			6173
60	2	48			13138	80	2	48			10590
60	1	4	53			80	1	4	33		
60	1	25	168			80	1	25	157		
60	1	48	395			80	1	48	272		
60	1	4		2047		80	1	4		1385	
60	1	25		6988		80	1	25		6117	
60	1	48		13842		80	1	48		8813	
60	1	4			1795	80	1	4			1325
60	1	25			7372	80	1	25			6849
60	1	48			14817	80	1	48			10175
60	0.5	4	163			80	0.5	4	94		
60	0.5	25	774			80	0.5	25	430		
60	0.5	48	1269			80	0.5	48	778		
60	0.5	4		1861		80	0.5	4		2172	
60	0.5	25		11229		80	0.5	25		7989	
60	0.5	48		13788		80	0.5	48		10204	
60	0.5	4			2157	80	0.5	4			1950
60	0.5	25			12950	80	0.5	25			11474
60	0.5	48			3403	80	0.5	48			11132

Table 1 continued

[U]	[H+]	time (hrs.)	Kd alumina	Kd R-1	Kd R-2
100	2	4	36		
100	2	25	86		
100	2	48	296		
100	2	4		1769	
100	2	25		4677	
100	2	48		7495	
100	2	4			1415
100	2	25			6305
100	2	48			14589
100	1	4	54		
100	1	25	129		
100	1	48	442		
100	1	4		2203	
100	1	25		5608	
100	1	48		7915	
100	1	4			1912
100	1	25			7224
100	1	48			5714
100	0.5	4	187		
100	0.5	25	284		
100	0.5	48	1546		
100	0.5	4		3215	
100	0.5	25		7752	
100	0.5	48		17805	
100	0.5	4			2802
100	0.5	25			8584
100	0.5	48			18874

CONCLUSIONS

The Thermoxid sorbents evaluated here showed high Kd values for ⁹⁹Mo from acidic, uranium-rich solutions. The Kd values observed with the Thermoxid sorbents were much higher (at least 10 times) than those with alumina under all conditions. Therefore, Thermoxid sorbents are potentially much better sorbents than alumina as part of an acidic ⁹⁹Mo recovery and purification process.

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