# PROGRESS IN TECHNOLOGY DEVELOPMENT FOR CONVERSION OF $^{99}$Mo PRODUCTION--BATAN'S (INDONESIA) CONVERSION PROGRAM, PROGRESS IN THE CNEA (ARGENTINA) LEU FOIL/BASE-SIDE PROCESS, AND DEVELOPMENT OF INORGANIC SORBENTS FOR $^{99}$Mo PRODUCTION

Allen. J. Bakel, Dominique C. Stepinski, George F. Vandegrift,
Argentina Leyva, Artem V. Gelis, Andrew H. Bond, and Heather Mayes

Argonne National Laboratory
Chemical Engineering Division
Argonne, IL USA

## ABSTRACT

Currently, nearly all of the world's supply of $^{99}$Mo is produced from the fissioning of $^{235}$U in targets of high-enriched uranium (HEU). Conversion of these targets to low-enriched uranium (LEU) would ease worldwide concern over the use and transport of this weapons-grade material. This paper reviews three projects: 1) the ongoing conversion of BATAN's $^{99}$Mo production process from HEU oxide targets (Cintichem processing) to LEU foil targets (Cintichem processing), 2) demonstration of LEU foil targets and base-side processing in CNEA's facility, and 3) the evaluation of two inorganic Thermoxid sorbents for Mo recovery and purification in acidic U-bearing solutions.

## 1. Introduction

The overall goal of our program is to minimize, and ultimately eliminate the use of HEU in the production of $^{99}$Mo for $^{99m}$Tc medical isotope generators. The role of ANL in that goal is to provide technical support needed by the producers for conversion to LEU in $^{99}$Mo production. For current producers, this usually involves minimizing the negative effects of conversion on productivity and economic feasibility. For potential producers, it involves training, evaluating process options, and transferring technology.

## 2. Progress in the Conversion of the BATAN (Indonesia) Process

Several demonstrations of the LEU foil target Modified Cintichem process have been carried out in BATAN's Serpong $^{99}$Mo production facility since 1995 [1-6]. These demonstrations have been done using the same facility, and generally with the same equipment as BATAN's current HEU process. The aim of these demonstrations was to show that the LEU process produced $^{99}$Mo with sufficient yield and purity. The most recent full-scale demonstration was performed in May 2005, in which an LEU foil target was irradiated, disassembled and dissolved, and $^{99}$Mo was recovered and purified from the dissolved target.

BATAN and BATAN Technology will convert their $^{99}$Mo production from HEU oxide targets to LEU foil targets during the next year. This conversion must be accomplished with minimum effect on reliability, productivity, yield, and purity of product. Ideally, the existing equipment and procedures should be used in the LEU process. Current work is focused on demonstrating the entire LEU process in the BATAN production facility.

## A. Target

Because the $^{99}Mo$ is produced from fission of $^{235}U$, nearly five times as much LEU ( 20% $^{235}U$/total U) is needed as HEU (generally >90% $^{235}U$/total U) to contain the same amount of $^{235}U$, and to yield an equivalent amount of $^{99}Mo$ product. In order to minimize the negative impact of conversion, it is necessary to irradiate the LEU target in the same reactor position as the HEU target. A novel target design was required to fit this larger amount of uranium into the same irradiation position. Due to high uranium-density and excellent heat transfer properties of uranium metal, a uranium foil target was designed at ANL to fit on the same irradiation as the HEU oxide target [7, 8].

## B. Target disassembly/dissolution

The target currently in use at BATAN is a stainless steel tube with HEU oxide coated on the inside. The irradiated oxide is dissolved directly from the target. This dissolution of the oxide is a relatively slow step in the process, taking around two hours. In order to minimize the negative impact of conversion to LEU targets, the total dissolution time must be less than or equal to two hours. An irradiated LEU foil target must be disassembled to separate the LEU foil (and the attached Ni fission barrier) from the bulk of the target. The disassembly of the irradiated target is facilitated by the use of a cutting machine (Figure 1) designed and fabricated for the purpose. The disassembly takes 30-60 minutes, and will decrease with operational experience. After disassembly, the foil (Figure 1) is placed in a vessel and dissolved in nitric acid. The dissolution of the LEU foil (and the attached Ni fission barrier has been shown to be complete in less than 30 minutes [9]. The disassembly and dissolution of the LEU foil target can be done in less than the two hours needed to dissolve the HEU oxide target; and, therefore, imposes no time penalty during the dissolution step.

## C. $^{99}Mo$ recovery and purification

The compositions of the dissolver and product solutions from the May 2005 demonstration are shown in Table 1. The recovery measured during the May 2005 demonstration was 86%; similar to the recoveries seen in the HEU process, and those seen in earlier demonstrations. The purity of the product $^{99}Mo$ was well within established guidelines. These results show that the recovery and purity of the $^{99}Mo$ product from the LEU foil (modified Cintichem) process used during this demonstration are acceptable for production operations.

Table 1. Composition of the product solution from the May 2005 demonstration.

| Isotope | Product impurity, Ci/Ci $^{99}Mo$ |
|---|---|
| $^{99}Mo$ activity | 77.5 Ci (86% recovery) |
| $^{133}I$ | <8E-07 |
| $^{135}I$ | <2E-06 |
| $^{103}Ru$ | 8E-07 |
| $^{140}Ba(^{140}La)$ | 2E-06 |
| $^{132}Te$ | 9.E-08 |
| $^{239}Np$ | <5E-06 |

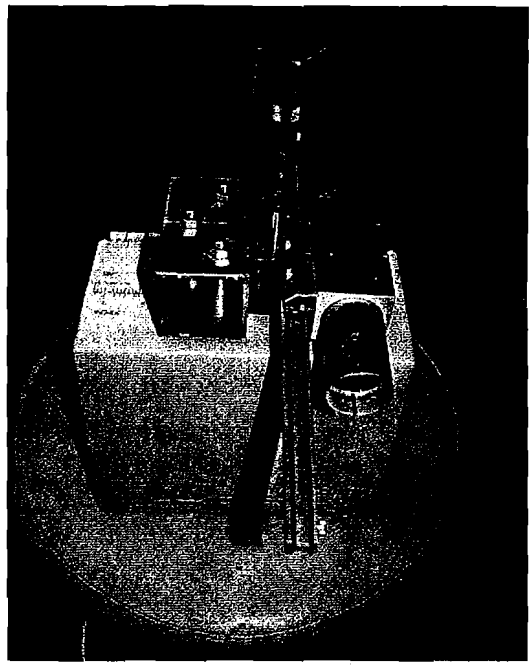

Figure 1. Photographs of a target cut with a custom-designed cutter (right) and of the target after being disassembled (above). Two foils (and the attached fission barriers) are shown in the foreground. Note that the left side of the inner tube was anodized and the right side was not anodized. The foils were easily removed from both sides, showing that anodization is not necessary.

**D. Summary of BATAN work**

The results of the May 2005 demonstration at BATAN's PUSPIPTEK facility shows that their conversion from HEU oxide targets to LEU foil targets can be accomplished with no negative impact on the processing time, recovery, or purity of the $^{99}$Mo product. Further work with BATAN will demonstrate the recovery and purity of the $^{99m}$Tc generator product derived from LEU-generated $^{99}$Mo.

**3. CNEA (Argentina) – Demonstration of LEU Foil Targets in a Base-Side Process**

CNEA is a commercial producer of $^{99}$Mo, and is the first producer to convert to LEU targets, using their LEU dispersion plate targets [10]. CNEA's interest in LEU foil targets is as a means for future increases in their production capacity. The demonstration of the LEU foil/base-side process by CNEA will give several major producers (IRE-Belgium, Mallinkrodt-Netherlands/NECSA-South Africa) important data and technology demonstrations to use in their planned conversions. A demonstration in the CNEA facility was planned for 2005, however, delays due to other commitments and regulatory approval prevented its completion. The delay has given us time to test and improve the equipment and procedures to be used. The issues leading to the previous delays have been cleared and the demonstration will be done in the first quarter of 2006.

**A. Target digestion**

The target and the target disassembly procedure are essentially the same as used in Indonesia, however, the digestion process is different. The uranium foil is digested in base (0.5 M NaOH) in the presence of $KMnO_4$ (oxidant) at 285°C and 90 bar (1400 psi) to convert U metal to $UO_3$. The details of the digestion have been published previously [11, 12].

**B. Mo recovery and purification**

The process equipment has been previously described, and consists of a sealed digester, and a processing module (Figure 2). This processing module contains means for filtering the digestion solution, tanks for storing solutions, a sorbent column for purification and recovery, and a flow meter for controlling flow through the column. Liquids are moved through the system by vacuum and are directed by a series of valves. The equipment and procedures for target disassembly, foil recovery, foil dissolution, recovery and purification of product have been extensively tested and documented in anticipation of a full-scale demonstration early in 2006.

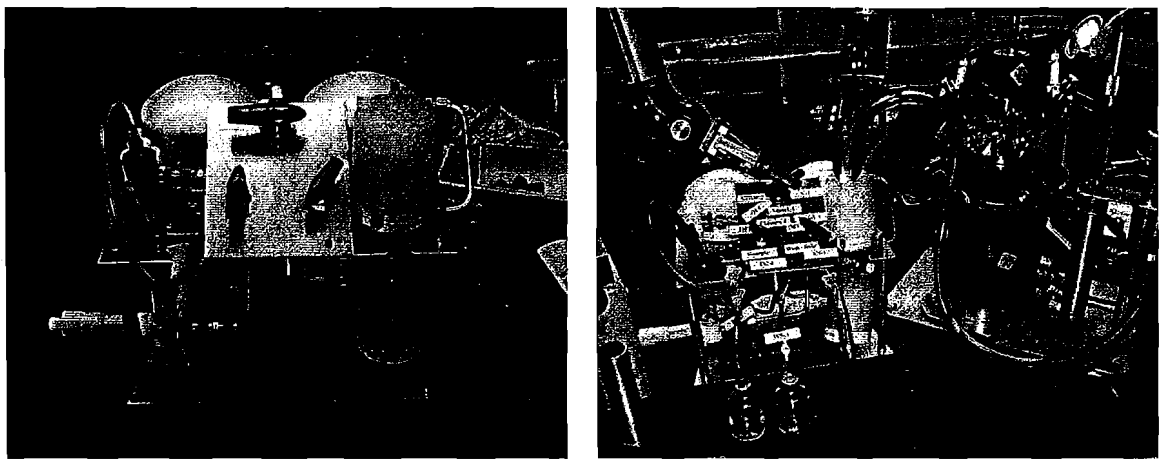

Figure 2. Photograph of processing equipment for use in the CNEA hot cell facility

**4. Sorbent Development**

The typical sorbent for recovering Mo from acidic solution is alumina. If alumina were used for LEU-target processing, then the total uranium needed, relative to an HEU target would require more sorbent in larger process columns, and would generate a larger volume of $^{99}$Mo product solution. These changes would negatively impact the $^{99}$Mo production by increasing the processing time and the amount of liquid waste generated. To minimize these negative effects, we are currently evaluating potential new sorbents, to recover Mo from high concentrations of uranium in acidic nitrate media. If the sorbents are found to recover molybdenum more efficiently than the commonly used alumina, then LEU could be substituted for HEU without the penalties of larger columns and larger solution volumes.

**A. Experimental**

**Materials.** $^{99}$Mo was obtained by stripping a $^{99m}$Tc generator (Bristol-Myers Squibb, North Billerica, MA) with 1.0 M $NH_4OH$, bringing the eluate to dryness and redissolving in 0.1 M $HNO_3$. $^{233}$U was obtained from Argonne National Laboratory stocks and was purified on an AG MP-1 column by eluting its daughters with 5 M HCl and subsequently stripping $^{233}$U with 0.1 M HCl. The $^{233}$U solution was brought to dryness and taken up in concentrated nitric acid (repeated twice) to convert the U(VI) into its nitrato form. Depleted $UO_2(NO_3)_2 \cdot 6H_2O$ was obtained from ANL's stocks and used without further purification. The Thermoxid sorbents, Radsorb and Isosorb, are available spherical solids of approximately 0.4-1.0 mm in diameter (20-40 mesh) and were used as received from TCI (Albuquerque, NM). The alumina was obtained as Acid

Alumina AG4, 100-200 mesh (Bio-Rad Laboratories) and was used as received. All other reagents were analytical grade and were used without further purification.

**Methods.** *Batch uptake measurements.* The sorption of metal ions by the inorganic ion-exchange sorbents from aqueous solutions was measured by equilibrating a 1 mL volume of a tracer-spiked aqueous solution of appropriate concentration with a known weight of sorbent following procedures described previously [13-15]. A one-hour mixing time was 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, Anotop 25 Inorganic Membrane Filter (Whatman Scientific). Blank experiments indicate that the filter does not uptake $^{99}$Mo. Duplicate experiments indicate that the reproducibility of the measurements was generally within 5%; however, the uncertainty interval may be higher for the highest and lowest $K_d$ values. Good mass balance was observed for all experiments.

Counting of aqueous samples was performed on a Minaxi Autogamma counter (gamma emitters) or a Packard model liquid scintillation counter. $^{99}$Mo was quantified by measurement of its 739 KeV and 778 KeV γ-rays. The activity of $^{99}$Mo in each sample was corrected for decay. $^{233}$U was quantified by measuring it's α emission by liquid scintillation counting.

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 weight 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, this amount of sorbent represents a large excess relative to the amount of radionuclide present.

*Uptake kinetics measurements.* The rate of radionuclide uptake on the sorbents was measured by equilibrating a series of equal weight (10 ± 1 mg) samples of sorbents with a tracer-spiked aqueous solution, as described previously [16]. Time zero was taken as the time at which a known volume of the tracer-spiked solution was introduced into the vials containing the sorbent and stirring commenced. At various time intervals, the aqueous phase was withdrawn from a test tube (thus establishing $t_{final}$) and filtered.

## B. Results and Discussion

*Kinetics of molybdenum uptake by the Thermoxid sorbents.* Figure 3 depicts the kinetics of uptake of trace levels of $^{99}$Mo by the Radsorb and Isosorb sorbents from 0.1 M $HNO_3$ solution. In both cases the equilibrium 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 only few hundred is required, therefore a satisfactory uptake in both cases is achieved in only 15 minutes. In considering these results, it must be noted that the uncertainty associated with very large values of $K_d$ can be considerable (unlike measurements at modest (~100) values for which a 5-10% uncertainty is typical) because, due to high uptake, distinguishing $A_s$ from the background count rate is difficult. For this reason it is

difficult to state indisputably that the $K_d$ values observed at t = 6 h are significantly greater or lower than those seen at 1 h.

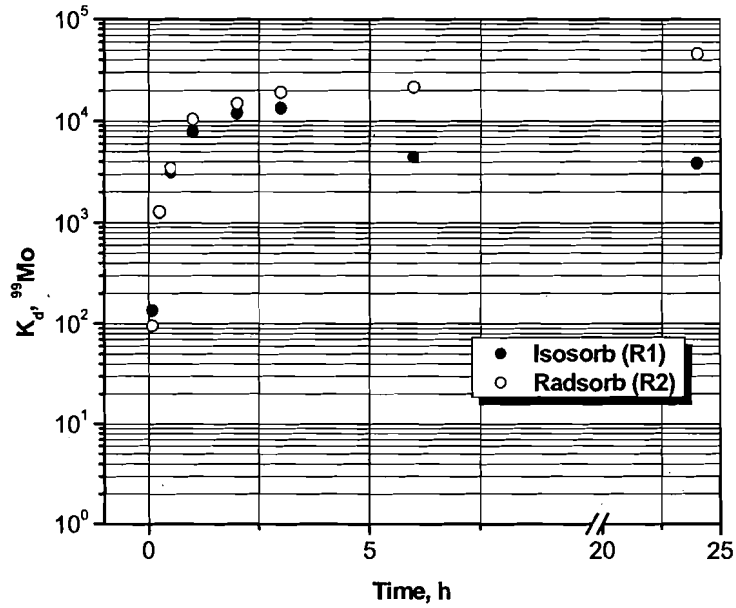


Figure 3. Kinetic of uptake of $^{99}$Mo from 0.1 M $HNO_3$ solutions by the Thermoxid sorbents.

*Evaluation of the Thermoxid sorbents for $^{99}$Mo/$^{233}$U separation.* Figure 4 depicts the uptake of trace levels of $^{99}$Mo and $^{233}$U by the Radsorb and Isosorb sorbents from nitric acid solutions. As shown in Figure 2, the retention of $^{99}$Mo by both sorbents is very high over the entire range of nitric acid concentrations examined. In contrast retention of $^{233}$U is comparatively low, the $K_d$ <20 over entire range of nitric acid concentrations examined generally implies very low retention in the column chromatographic mode. The resulting Mo/U separation factor of ≈ 1000 should give excellent Mo separation from U in a packed column. Based on the $^{99}$Mo $K_d$ measurements under these solution conditions, no breakthrough of Mo in a packed column is expected at the range over the aqueous phase nitric acid concentrations investigated.

*Evaluation of the Thermoxid sorbents for $^{99}$Mo separation from uranium solutions.* As discussed above, one of the major challenges of substituting LEU for HEU targets is the up-to fivefold increase in the amount of uranium needed to produce an equivalent amount of $^{99}$Mo, which poses a challenge of producing greater volumes of process solution and generating larger amounts of radioactive waste. In order to minimize the increases to volumes of process and waste solutions we are developing a process for the separation of Mo from concentrated uranium solutions. Figure 5 depicts the uptake of trace levels of $^{99}$Mo by the Radsorb and Isosorb materials and alumina from 1 M $HNO_3$ solutions of variable uranium content. As shown in Figure 5, both Thermoxid sorbents show a high retention of $^{99}$Mo up to uranium concentrations of 310 g/L. Based on these $K_d$ measurements, molybdenum should be efficiently separated on a packed column from solutions containing up to 310 g/L uranium in 1 M $HNO_3$. These results contrast the uptake values of $^{99}$Mo for alumina. Retention of $^{99}$Mo by alumina from uranium solutions is significantly lower than that observed for Thermoxid sorbents. The $K_d$ values of <50 over the entire range of uranium concentrations imply low uptake of $^{99}$Mo and may be inadequate for process operations. Therefore, the Thermoxid sorbents are preferable for the separation of Mo from nitric acid uranium solutions.

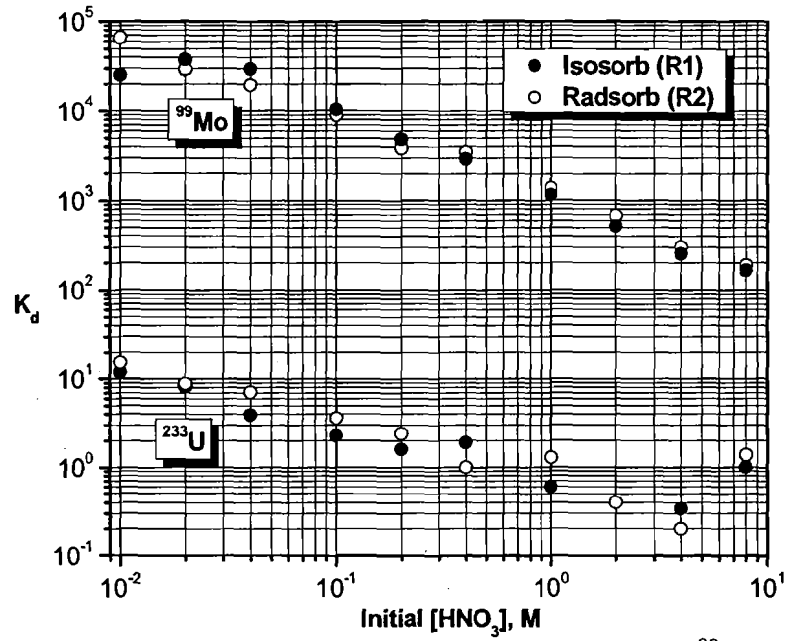


Figure 4. Effect of increasing nitric acid concentrations on the uptake of $^{99}Mo$ and $^{233}U$ by the Thermoxid sorbents.

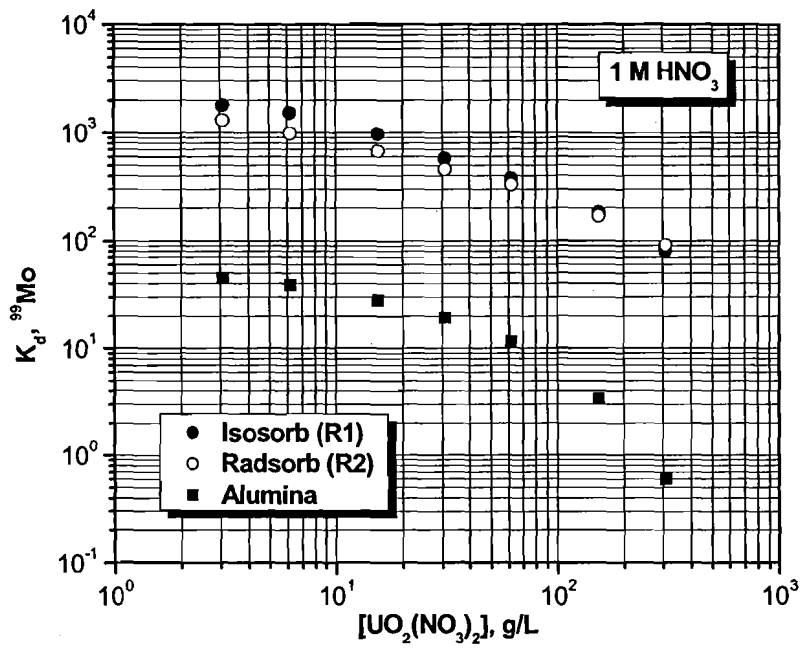


Figure 5. Effect of varying uranium concentrations on the uptake of trace levels of $^{99}Mo$ from 1 M $HNO_3$ by the Thermoxid sorbents and alumina.

*$^{99}Mo$ Column Breakthrough Study.* The uptake behavior of molybdenum on a column (12 mL bed volume) packed with the Radsorb sorbent from 1 M $HNO_3$ solutions containing high concentrations of uranium was investigated. The column breakthrough study is very encouraging, as the Mo is completely retained by the column. After passing 900 mL of 310 g/L of uranium solution, containing 150 ppm of stable Mo and tracer levels of $^{99}Mo$ at a flow rate of

1 mL/minute, no breakthrough of $^{99}Mo$ is observed as indicated by the absence of measurable activity above that expected for depleted uranium. These results are consistent with the values of $K_d$ reported above and suggest the superior performance of the Thermoxid sorbents for separation of Mo from nitric acid solutions containing macroquantities of uranium.

*Recovery of $^{99}Mo$.* Earlier distribution coefficients measurements indicate that $^{99}Mo$ is poorly sorbed from NaOH solutions (0.01M-2M) by the Thermoxid sorbents. In fact, the $K_d$ values observed in this study are not reported here due to large uncertainty associated with very low $K_d$ measurements and the difficulty of distinguishing between the high $A_s$ and $A_o$ values. We demonstrated here, as shown in Figure 6, that Mo is efficiently recovered from a Radsorb packed column (1 mL bed volume) with a 1 M sodium hydroxide solution, following the separation of Mo from 310 g/L uranium solution in 1 M $HNO_3$. Only seven bed volumes are required to strip the molybdenum from the column.

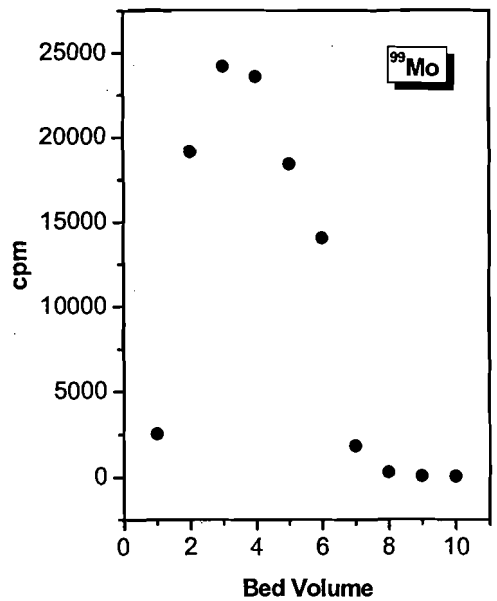


Figure 6. Elution of $^{99}Mo$ with 1 M NaOH from a column (1 mL bed volume) packed with Radsorb resin.

## C. Conclusions

The results presented here demonstrate that the Thermoxid sorbents, Radsorb and Isosorb, can provide efficient separation of molybdenum from concentrated uranium solutions. The observed $K_d$ values also suggest that these materials can separate Mo from concentrated U solutions more effectively than alumina. Purification of $^{99}Mo$ using these sorbents could permit shorter process times and smaller elution and waste volumes than conventional alumina columns used for HEU targets.

## 5. Acknowledgement

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA) Office of Defense Nuclear Nonproliferation, under Contract W-31-109-Eng-38.

## 6. References


1. Srinivasan, B.; Leonard, R. A.; Aase, S.; Vandegrift, G. F.; Moeridun, A. A.; Rauf, H.; Lubis, A.; Amini, S.; and Nampira, Y., Processing of LEU Targets for $^{99}$Mo Production—Dissolution of Metal Foils by Nitric Acid/Sulfuric Acid Mixtures. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, September, 1995, Paris, France.

2. Wu, D.; Landsberger, S.; and Vandegrift, G. F., Progress on Chemical Treatment of LEU Targets by the Modified Cintichem Process. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1996, Seoul, ROK.

3. Vandegrift, G. F.; Conner, C.; Sedlet, J.; Wygmans, D. G.; Wu, D.; Iskander, F., and Landsberger, S., Progress in Chemical Processing of LEU Targets for $^{99}$Mo Production—1997. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1997, Jackson Hole, Wyoming, USA.

4. Mutalib, A.; Purwati, B.; Adang, H. G. ; Hotman, L. ; Moeridoen; Kadarisman ; Sukmana, A.; Sriyono, Suripto, A.; Nasution, H.; Amin, D. L.; Basiran, A.; Gogo, A.; Sunaryadi, D.; Taryo, T.; Vandegrift, G. F.; Hofman, G.; Conner, C.; Sedlet, J.; Walker, D.; Leonard, R. A.; Wood, E. L.; Wiencek, T. C.; and Snelgrove, J. L, Full-scale Demonstration of the Cintichem Process for the production of 99Mo using a Low Enriched Target. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1998, Sao Paulo, Brazil.

5. Vandegrift, G. F.; Hofman, G. L.; Conner, C.; Snelgrove, J. L.; Mutalib, A.; Purwati, B.; Adang, H. G. ; Hotman, L. ; Kadarisman ; Sukmana, A.; Dicky, T. J.; Suripto, A.; Lutfi, D.; Amin, D. L.; Basiran, A.; Gogo, A.; Sarwani; and Taryo, T., Demonstration of $^{99}$Mo Production Using LEU Metal Foil Targets in the Cintichem Process. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1999, Budapest, Hungary.

6. Conner, C.; Sedlet, J.; Wiencek, T. C.; McGann, D. J.; Hofman, G. L.; Vandegrift, G. F.; Snelgrove, J. L.; Mutalib, A.; Gunawan, A. H.; Adang, H. G. ; Lubis, H.; Wisnukaton, K.; Kadarisman; Sukmana A.; Sriyono; Purwadi B; Jatmiko, D. T.; Suripto, A.; Amin, D. L.; Basiran, A.; Martoyo; Sarwani; and Taryo, T, Production of $^{99}$Mo from LEU Targets—Acid Side Processing. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 2000, Las Vegas, USA.

7. Wiencek, T. C. and Hofman, G. L, Development of Uranium metal Targets for $^{99}$Mo Production. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1993, Oarai, Japan.

8. Wiencek, T. C.; Hofman, G. L.; Wood, E. L.; Wu, C. T.; and Snelgrove, J. L, LEU 99Mo Target Fabrication and Testing: Overview, Status, and Plans. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1994, Williamsburg, USA.

9. Leonard, R. A.; Chen, L.; Mertz, C. J.; and Vandegrift, G. F, Progress in Dissolving Modified LEU Cintichem Targets. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1996, Seoul, ROK.

10. Pablo R. Cristini, Héctor J. Cols, Ricardo Bavaro, Marcelo Bronca, Roberto Centurión, Daniel Cestau, Production of Mo-99 from Low Enriched Uranium Targets. Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, September, 2002, Bariloche, Argentina.

11. A.V. Gelis, G. F. Vandegrift, , S. B. Aase, A. J. Bakel, J. R. Falkenberg, M. C. Regalbuto, and K. J. Quigley, "ANL Progress in Developing a Target and Process for Mo-99 Production: Cooperation with CNEA." Proceedings of the 2003 International Meeting on Reduced Enrichment for Research and Test Reactors, October, 2003, Chicago, IL, USA.

12. A. V. Gelis, K. J. Quigley, S. B. Aase, A. J. Bakel, A. Leyva, M. C. Regalbuto, and G. F. Vandegrift, ANL Progress On the Cooperation with CNEA for the Mo-99 Production: Base-Side Digestion Process. Proceedings of the 2003 International Meeting on Reduced Enrichment for Research and Test Reactors, November, 2004, Vienna, Austria.

13. Horwitz, E. P.; Chiarizia, R.; Dietz, M. L., A Novel Strontium-Selective Extraction Chromatographic Resin. *Solvent Extr. Ion Exch.* 1992, *10,* 313-336.

14. Horwitz, E. P.; Chiarizia, R.; Diamond, H.; Gatrone, R. C.; Alexandratos, S. D.; Trochimzuk, A. W.; Creek, D. W., Uptake of Metal-Ions by a New Chelating Ion-Exchange Resin. 1. Acid Dependencies of Actinide Ions. *Solvent Extr. Ion Exch.* 1993, *11,* 943-966.

15. Horwitz, E. P.; Dietz, M. L.; Chiarizia, R.; Diamond, H.; Maxwell S. L.; Nelson, M. R., Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion-Exchanger - Application to the Characterization of High-Level Nuclear Waste Solutions. *Anal. Chim. Acta* 1995, *310,* 63-78.

16. Chiarizia, R.; Horwitz, E. P.; Alexandratos, S. D., Uptake of Metal-Ions by a New Chelating Ion-Exchange Resin. 4. Kinetics. *Solvent Extr. Ion Exch.* 2004, *12,* 211-237.

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-Eng-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.