ANL PROGRESS IN DEVELOPING A TARGET AND PROCESS FOR CONVERTING CNEA Mo-99 PRODUCTION TO LEU

by

G. F. Vandegrift, A. Gelis, S. Aase, A. Bakel, E. Freiberg, Y. Koma, and C. Conner

Argonne National Laboratory 9700 S. Cass Avenue Argonne, IL 60439-4841, U.S.A.

RERTR-2002

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National ("Argonne") Laboratory 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.

* Work supported by the U.S. Department of Energy, Office of Nonproliferation and National Security, under Contract No. W-31-109-ENG-38.

ANL PROGRESS IN DEVELOPING A TARGET AND PROCESS FOR CONVERTING CNEA Mo-99 PRODUCTION TO LEU

G. F. Vandegrift, A. Gelis, S. Aase, A. Bakel, E. Freiberg, and C. Conner

Argonne National Laboratory 9700 S. Cass Avenue., Argonne, IL--USA

ABSTRACT

The primary mission of the Reduced Enrichment in Research and Test Reactors (RERTR) Program is to facilitate the conversion of research and test reactor fuel and targets from high-enriched uranium (HEU) to low-enriched uranium (LEU). One of the current goals at Argonne National Laboratory (ANL) is to convert ⁹⁹Mo production at Argentine Comisión Nacional de Energía Atómica (CNEA) from HEU to LEU targets. Specifically addressed in this paper is ANL R&D related to this conversion: (1) designing a prototype production vessel for digesting irradiated LEU foils in alkaline solutions, (2) developing means to improve digestion efficiency, and (3) modifying ion-exchange processes used in the CNEA recovery and purification of ⁹⁹Mo to deal with the lower volumes generated from LEU-foil digestion

INTRODUCTION

To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) program is working to limit the use of high-enriched uranium (HEU) by substituting low-enriched uranium (LEU) fuel and targets. Low-enriched uranium contains <20%²³⁵U. Technetium-99m, the daughter of ⁹⁹Mo, is the most commonly used medical radioisotope in the world. Currently, most of the world's supply of ⁹⁹Mo is produced by fissioning the ²³⁵U intargets containing HEU, generally 93% ²³⁵U. Targets for the production of ⁹⁹Mo are generally either (1) miniature Al-clad fuel plates or pins containing U-Al alloy or UAl_X dispersion fuel or (2) a thin film of UO₂ on the inside of a stainless steel tube. After irradiation, the ⁹⁹Mo is recovered from the irradiated uranium and purified.

To yield equivalent amounts of ⁹⁹Mo, an LEU target must contain approximately five times the uranium as does an HEU target. Consequently, substituting LEU for HEU requires changes in both target design and chemical processing. Three major challenges have been identified when substituting LEU for HEU: (1) modifying the targets and purification processes as little as possible, (2) assuring continued high yield and purity of the ⁹⁹Mo product, and (3) limiting economic disadvantages.

The Argentine Comisión Nacional de Energía Atómica (CNEA) process has been described in the literature [1] and has much in common with the Mallinckrodt process; both processes are based on that developed by A. Sameh [2]. In this process, the irradiated targets are heated in sodium hydroxide solution. The aluminum cladding and meat in the targets are dissolved to form sodium aluminate, and the uranium is digested, forming a mixture of UO_2 and $Na_2U_2O_7$. The digestion should be done in about 2 L of 1.8-2.0 M NaOH solution to provide enough sodium hydroxide and the volume to keep aluminum in solution. If either smaller volume or less hydroxide is used, aluminum hydroxide will precipitate, which clogs the filter, preventing removal of the solution from the digester. Molybdenum is soluble in alkaline

solutions as the molybdate ion, but the actinides and many of the metallic fission-products precipitate as hydroxide salts. Following filtration of the dissolver solution, the filtrate is fed into an anion-exchange column, which retains molybdenum and some other anionic species. A series of separation processes purifies the molybdenum to meet pharmaceutical standards.

It is practically impossible to design the Al-clad fuel plates with the LEU instead of the HEU due to 5-fold increase in the total weight of uranium. Therefore, we have developed targets of LEU metal foil, which is wrapped in a thin aluminum-foil fission-recoil barrier. The foil is held between two aluminum tubes that have been swaged for good thermal contact and welded closed at each end [3, 4]. The fission-recoil barrier is present to avoid interaction between the uranium foil and the material of the target to allow the foil to be removed from the target before digestion. Aluminum mass is significantly lower than for the HEU targets. So, the LEU target can be digested in 200 mL of 1.8 M NaOH, that results in substantial (about 10-fold) decrease in the amount of the liquid radioactive waste.

Early in 1999, ANL and CNEA began active cooperation with a goal to allow CNEA to convert to LEU within a few years. It is a multifaceted program with many steps required to modify targets and the current process to allow the use of LEU targets.

PROGRESS

Since reporting R&D results at the 2000 International RERTR Meeting [5,6], we have made progress aimed at the conversion of ⁹⁹Mo production to LEU targets. Those areas are (1) developing and demonstrating the recovery and purification of ⁹⁹Mo from an LEU target in Argentina, (2) developing a production dissolver (3) modifying the process for digesting irradiated LEU foils by alkaline solution, (4) modifying anion exchange columns used in the recovery and purification of ⁹⁹Mo to deal with lower volumes generated from LEU-foil digestion. Each of these items is discussed below.

Processing of Irradiated LEU Foils by CNEA

The LEU-modified process began with a two-step digestion of irradiated LEU foils. Because the digestion of LEU metal foils generates less than 10% of the solution volume of that from dissolving HEU targets, the size of the primary Bio-Rad AG MP-1 (hydroxide form) and Bio-Rad Chelex 100 anion-exchange columns are significantly smaller than for the current HEU process. This advantage creates far less liquid waste and cuts processing time considerably; however, development is required to downsize equipment and specify process conditions.

Two targets containing four foils were irradiated May 3-8, 2001, for ~120 hours at a flux of $4-6x10^{13}$ n/cm²/s. Following irradiation, the targets were allowed to cool in the reactor pool for 10 hours and then transported to a processing hot cell in the ⁹⁹Mo Production Facility. After arrival at the ⁹⁹Mo production facility, the targets were disassembled and inspected. An irradiated 9-g LEU foil with a 40-µm aluminum fission recoil barrier was processed to recover ⁹⁹Mo using the two-step alkaline digestion and a slightly modified anion exchange process. The foil was loaded into the dissolver. The atmosphere inside the dissolver was evacuated, and 50 mL of sodium hydroxide solution was injected. The dissolver was then heated to dissolve the

aluminum barrier and to convert the uranium foil into a solid uranium oxide product according to the reactions (1) and (2):

$$Al + 3 H_2O \rightarrow Al(OH)_3 + 3/2 H_2 \tag{1}$$

$$U + 2 H_2 O \rightarrow UO_2 + 2 H_2 \tag{2}$$

During this initial digestion step, the temperature of the dissolver was controlled to limit the pressure in the dissolver to 700 psig (4.8 MPa). After 45 minutes, the dissolver was cooled, and hydrogen gas and the released fission gasses were vented to a vacuum tank, where they were stored until the fission gases decayed. To ensure that all of the ⁹⁹Mo was released to the sodium hydroxide solution, a second digestion step was performed by pressurizing the dissolver with 85-psig (0.59-MPa) oxygen and heating the dissolver again. This step converts the solid uranium dioxide into a solid sodium diuranate product according to the reaction (3):

$$UO_2 + 1/2 O_2 + NaOH \rightarrow 1/2 Na_2U_2O_7 + 1/2 H_2O$$
 (3)

Oxygen also converts iodide to iodate, which sorbs far less strongly on the AG MP-1 column. Again, the temperature was controlled to limit the pressure in the dissolver to 700 psig (4.8 MPa). Following digestion, the suspension in the dissolver was filtered to separate the solid sodium diuranate product and alkaline-insoluble activation and fission products from the solution containing ⁹⁹Mo and other alkaline-soluble fission products.

The initial digestion of the foil and the oxygen conversion of the oxide proceeded smoothly. We used a sintered metal filter that CNEA provided to filter the suspension from the digester. The solution passed easily through the filter; however, some solids appeared in the filtrate. We are not sure what the composition of the solids was (i.e., precipitated uranium that passed through the filter or corrosion products from the sintered metal filter) or what impact they may have had on the subsequent ion exchange process. However, the solids appeared to collect in the glass-wool packing at the top of the anion exchange column. Following filtration, the 99 Mo (as MoO₄²⁻) in the 175 mL of solution (dissolving solution plus dissolver rinses) was recovered on the AG MP-1 anion exchange column, which was considerably smaller than that required for an equal amount of ⁹⁹Mo from dissolving the current HEU targets. Any I in the feed solution would also be sorbed. Wash solution was then passed through the column to remove impurities. Less than 0.03% of the ⁹⁹Mo escaped the column during loading and rinsing. The ⁹⁹Mo was eluted from the column in 72 mL of solution, which was then prepared for the second ⁹⁹Mo-purification step using Chelex 100. Because of the considerably lower volume of the strip solution from the anion-exchange step, this column was also considerably smaller than that used in HEU-target processing. The strip solution volume for removing molybdenum from the Chelex 100 column was 50 mL. The yield and purity of the molybdenum effluents in both columns were measured by gamma spectroscopy. Results were qualitatively as expected, but problems associated with sample dilution preclude a quantitative description of results. The next CNEA demonstration is planned for spring 2003. For this demonstration, a new prototype production dissolver has been designed and fabricated at ANL and is being tested.

Prototype Dissolver for CNEA Production

To allow for early testing of the alkaline digestion of irradiated LEU foil at CNEA, we

used the ANL dissolver designed for nitric acid dissolution of foil in the modified Cintichem process demonstrations performed in Indonesia [7]. Although the design was awkward to use in the CNEA hot cells, it did allow us to test the digestion and processing of LEU foils. Early work showed that the material of construction, 304 stainless steel, undergoes minimal corrosion when contacted with sodium hydroxide solution alone; however, when the reaction is run with 100-psig (0.7-MPa) oxygen overpressure, corrosion is severe. A series of corrosion tests was conducted to compare the corrosion rates of 304 stainless steel, Hastelloy C-276, and Inconel 600 during the second digestion step of the LEU target dissolution (i.e., in the presence of oxygen). These tests were conducted in a vessel, containing one of the coupons, sodium hydroxide solution, and 100-psig (0.7 MPa) O_2 , that was heated to ~250°C (470 psig total pressure) for about 100 hours. After the test, the coupon was removed, rinsed, and dried.

Visual examination of the corroded coupons showed that the 304 stainless steel coupon was much more affected by these conditions than either the Hastelloy C-276 or the Inconel 600 coupon. The corroded 304 stainless steel coupon had developed a thin red/brown layer in the liquid phase, a somewhat thicker layer in the vapor phase, and a much thicker layer at the vapor-liquid interface. In addition, significant pitting was observable in the interface region. The corroded 304 stainless-steel coupon with scanning electron microscopy (SEM) showed that the maximum thickness of the oxidation layer (at the vapor-liquid interface) varied from 50 to 100 μ m. Oxidation-layer thickness developed in the liquid phase varied from 10 to 20 μ m, and that in the vapor phase varied from 20 to 50 μ m.

The corroded Hastelloy coupon had developed a very thin green-brown layer in the vapor phase, a thin gray layer at the vapor-liquid interface, and no observable layer in the liquid phase. The corroded Inconel 600 had developed a very thin yellow/brown layer in the vapor phase, a thin gray layer at the vapor-liquid interface, and no observable layer on the section exposed to the liquid phase. The oxidation layers on the corroded Hastelloy C-276 and Inconel 600 coupons were not observable with SEM and, therefore, were <1 μ m. Welded metal showed the same corrosion as the rest of the coupon.

Based on our observations, the corrosion rate of the 304 stainless steel would be as much as 1 μ m/hr during the second step of foil digestion. On the other hand, the corrosion rates for the Hastelloy C-276 and Inconel 600 under the same conditions would be <0.01 μ m/hr. Therefore, 304 stainless steel is not an acceptable material of construction for the two-step digestion using oxygen; however, either Hastelloy C-276 or Inconel 600 is acceptable.

The production dissolver is being developed. To allow testing of various operations in a hot-cell environment, a prototype was fabricated from 304 stainless steel. Heating is accomplished using heat-tape or ceramic-bead heater tracing; cooling will be performed by blowing air through a stainless steel sleeve that contains the digester body. Figure I shows a photograph of the prototype body and a schematic of the entire unit. This unit will be able to accommodate ~70 g of LEU foil (~14 g of ²³⁵U). The digester has a stainless-steel valve at the bottom for draining material five connectors on the body for thermocouple insertion and quick connect for feeding liquids or gases and for venting gases from the digester. When the digester is closed, the bayonet-style cap is lowered onto the digester with a screw and twisted to lock the

cap. A Viton O-ring is used as a gasket to contain the pressure generated during target digestion, and is replaced with each use of the digester.

The valves currently on the stainless steel digester have seat materials made from PEEK (the bottom valve is shown on the Figure II). The valves are rated to 230°C and 1100 psig. Over time, the seat material has degraded and the valve leaks during cool down; up to 10 mL of solution has been observed as leakage. We are looking at replacing these valves with ones with stainless-steel seats. These valves can be welded to Hastelloy, and are rated to 290°C and 1100 psig and should be more acceptable for long term use under hot cell conditions. They will be installed on the stainless steel digester at ANL. If these valves prove to be superior to the previous ones, then they will be installed on the Hastelloy digester being fabricated.



Fig. I. Prototype and Conceptual Design of the ANL-Designed LEU-Foil Digester



Fig II. The Bottom Valve of the ANL-Designed LEU-Foil Digester

Process Modification

The two-step process is effective but (a) having two warm-up, reaction, and cool-down periods doubles digestion time and (b) using pressurized oxygen leads to safety concerns. Therefore, we are testing the addition of potassium permanganate to the digestion solution to perform the oxidation to U(VI). Thus far, results have been promising. Adding potassium permanganate dissolved in sodium hydroxide solution converts all the uranium to an alkali diuranate, iodide is oxidized, and molybdate is not sorbed on the MnO₂ precipitate that is generated. However, hydrogen gas generated in the digester due to the interactions of Al and U with water (equations (2) and (3)) can react with permanganate ions by the following reaction:

$$2MnO_4^- + H_2 + 2OH^- \rightarrow 2MnO_4^{-2-} + 2H_2O$$
(4)

The product of reaction 4, $MnO_4^{2^-}$, is reduced by hydrogen gas, resulting in a formation of MnO_2 [8]. So, the amount of potassium permanganate added to the digester has to be high enough to react with both uranium foil and hydrogen gas. Otherwise, uranium oxidation to sodium diuranate and molybdenum release into the solution phase will not be complete.

If appropriate amount of potassium permanganate is used, the oxidation to U(VI) can be performed at one step, without the use of oxygen gas. This process is shorter and potentially less hazardous than two-step one with O_2 gas. A second benefit of using KMnO₄ is that the digestion can be done at lower sodium hydroxide concentration. As was discussed above, 1.8-2.0 M NaOH should be used to form sodium aluminate to avoid the precipitation of aluminum hydroxide, which clogs the filter. According to the literature data, manganese dioxide, a product of potassium permanganate's reduction, makes a solid solution with aluminum hydroxide [9]. Experiments performed at ANL demonstrate that mixed Mn and Al oxide phase does not clog the filter, and the digestion solution containing ⁹⁹Mo as a molybdate ion can be completely removed from the vessel without any technical complications. Therefore, there is no need to have a high concentration of NaOH, and 0.5 <u>M</u> NaOH solution can be efficiently used for digestion. This results in much higher uptake of molybdate ion on the AG MP-1 anion exchanger, utilized as the first purification step of ⁹⁹Mo from the other fission products.

The dependence of MoO_4^{2-} distribution ratios, K_d , on hydroxide concentration is shown on Figure III (for these experiments, AG 1-X8 anion exchanger was used, which possesses the same properties as AG MP-1, but has slightly slower kinetics). The data in the Fig III show that the sorption of MoO_4^{2-} is less favorable at hydroxide concentrations >0.1 <u>M</u>. At lower hydroxide concentrations, 0.01 - 0.1 M, sorption of various fission products are likely to occur as well as Mo(VI). Therefore, sodium hydroxide concentration should in the 0.1 – 1 M range.

Potassium permanganate has a limited solubility at room temperature: ~0.4 M in H₂O and ~0.35 M in 0.5 M NaOH. The solubility goes up as the temperature increases. If a one 35-g LEU target (~6.9 g ²³⁵U) is digested, hot KMnO₄/NaOH solution must be added to the digester to provide enough permanganate. The digestion of two 35-gram LEU targets using KMnO₄ in one step does not appear feasible without significant increase in the digester capacity.



Figure III. Distribution ratios of ⁹⁹Mo between AG 1-X8 anion exchange resin and NaOH solution at 25°C.

For the above reasons, we are investigating various options for the digestion procedure. They will be tested at ANL with low-burnup $(10^{-5}\%)$ uranium foils prior to the tests with fully irradiated targets in Argentina. Four different processes are being investigated (Table 1). Process A is a one-step digestion using KMnO₄ to oxidize uranium metal to U(VI), Processes B and C are two-step digestions with KMnO₄/0.5 M NaOH solution utilized for the first digestion step. No more than 100-300 mL of solution would be required for digestion. The use of permanganate eliminates the problem with Al(OH)₃ precipitation and consequent clogging the filter. As the second step, the digester will be vented to release H₂ and fission gases, and either solid KMnO₄ (B) or O₂ gas (C) will be added for the second step. Thus, large amount of U, up to 70 g LEU (~14 g ²³⁵U) could be digested with the total volume of feed to the first ion-exchange column being less than 400 mL including the volume of the rinse solutions. Process D is the two-step process used in the first CNEA demonstration.

To release ⁹⁹Mo into the solution, uranium metal has to be converted to sodium diuranate. The oxidation goes through an intermediate step--formation of uranium dioxide:

$$U_{metal} \rightarrow UO_2 \rightarrow Na_2U_2O_7$$
 (6)

Therefore, completeness of the oxidation to U(VI) can be used as a characteristic parameter for Mo release from irradiated uranium. A series of "cold" experiments has been conducted to study conversion of depleted uranium to sodium diuranate. A piece of depleted uranium foil was digested and the resultant precipitate was filtered, dried, and analyzed by X-ray diffractometry (XRD). Some results are shown in Table 2 and on Figure IV, which demonstrate that using 100 psig O₂ (Table 2) or solid potassium permanganate for the second step (Fig. IV, spectrum #3) achieve nearly 100% conversion of U metal to sodium diuranate. Based on results of these "cold" experiments and the tests with irradiated, low-burn-up foils, the most successful procedure will be recommended for use in the next CNEA demonstration.

Process	Α	В	С	D
Description	1-step Step 1: dissolved MnO ₄ ⁻	2-step MnO ₄ ⁻ Step 1: dissolved MnO ₄ ⁻ Step 2: solid KMnO ₄	2-step MnO ₄ ⁻ /O ₂ Step 1: dissolved MnO ₄ ⁻ Step 2: O ₂	2-step OH ⁻ -alone/O ₂ Step 1: OH ⁻ only Step 2: O ₂
Advantages	 No O₂ gas addition required Digester can be fabricated from stainless steel Digestion takes less than half as long as 2-step digestions KMnO₄ addition allows use of lower [OH⁻], therefore more efficient Mo recovery in ion exchange 	 No O₂ gas addition required Digester can be fabricated from stainless steel Feed volume is not set by KMnO₄ addition, therefore, lower than process A KMnO₄ addition allows use of lower [OH⁻], therefore more efficient Mo recovery in ion exchange 	 Feed volume is not set by KMnO₄ addition, therefore lower than process A KMnO₄ addition allows use of lower [OH⁻], therefore, more efficient Mo recovery in ion exchange 	 No KMnO₄ addition allows feed volume to be set by geometry and Al solubility; therefore, lower feed volumes than other processes. Absence of MnO₂ generates less solid-waste volume
Disadvantages	 Generates greater volume of solid uranium waste due to presence of MnO₂ Greater volume of digester feed required to meet KMnO4 needs 	 Generates greater volume of solid uranium waste due to presence of MnO₂ Digestion takes more than twice as long as 1-step digestions 	 Generates greater volume of solid uranium waste due to presence of MnO₂ Digestion takes more than twice as long as 1-step digestions Digester must be Hastelloy 	 Downstream processing made less efficient due to higher [OH⁻] Digestion takes more than twice as long as 1-step digestions Digester must be Hastelloy

Table 1. Optional procedures for digestion of irradiated targets

	Volume of	[KMnO ₄],	U, g	Initial	% U(VI)			
	sol'n, mL	М		P _{O2} , psi*				
	400	0.1	9.37	27	65 - 80			
	400	0.1	9.36	45	65 - 80			
	400	0.1	9.7	100	90 - 95			
	200	0.2	10.4	100	90 - 95			
*	* $1 \text{ noi} \sim 7 \text{ ls} \text{ De}$							

Table 2. Two-step digestion with $KMnO_4/0.5 M$ NaOH and O_2 gas (process C). Conditions for the 2nd step: 35 min at 285 °C.

* 1psi \approx 7 kPa



Figure IV. XRD spectra of the precipitates following the digestion. Conditions of the second step vary: spectrum 1- 27 psi O₂; spectrum 2- 100 psi O₂; spectrum 3- solid KMnO₄ (no O₂)

CNEA-Process Column Sizing

The objective of the AG MP-1 effort was to determine the optimal column size and flow rate for the CNEA LEU process. A series of static batch tests were done to determine the batch capacity of the AG MP-1 resin. AG MP-1 has a 2.3 meq/g loading capacity for molybdate. The molybdate-sorption kinetics of AG MP-1 are extremely fast. Equilibrium in static tests was reached in 15-30 minutes. Another series of Mo(VI) sorption tests in the dynamic regime has been carried out using 1-g columns. One of the sorption curves is shown on Figure V.



Figure V. Breakthrough curve for molybdate sorption onto AG MP-1 (1 g) column from 0.5 <u>M</u> NaOH. Flow rate was 4.7 mL/min. $[MoO_4^{2-}] = 1.122 \cdot 10^{-3} M$.

The conditions used in the experiments were similar to the conditions for Mo sorption from the filtrate solutions following the digestion of the irradiated foil except there were no other fission products/impurities in the solution. A column with 1 g of AG MP-1 was tested for processing an low-burn-up depleted uranium foil. All of the sodium molybdate (250 mL of solution) was absorbed onto 1 g of AG MP-1 in the OH⁻ form at flow rates between 5 and 8 mL/min. The recovery of Mo from the AG MP-1 resin was >99%. In another test, 480 mL of the filtrate solution containing ⁹⁹Mo and other fission products was generated following the digestion of irradiated depleted uranium foil. The solution was passed through 1-g AG MP-1 column (Figure VI). The 15% breakthrough of ⁹⁹Mo observed in the test is due to the sorption of other fission products/impurities onto AGMP-1. We performed IPC-MS analysis of the filtrate and found rather high concentrations of U, Cr, and Fe. The species of U and Cr may sorb onto anion exchanger resulting in a decrease of the dynamic capacity of the column, causing the Mo breakthrough.

In order to allow for an increase in the flow rate during loading and to avoid ⁹⁹Mo breakthrough, it is recommended that 2 g of AG MP-1 be used. A larger column will be tested during the processing of a low-burnup target later this year.



Figure VI. Breakthrough curve of sodium molybdate sorption from the filtrate solution onto AGMP-1 column (1g), flow rate was 6 mL/min.

Distribution ratios for $MoO(SCN)_5^{2-}$ on Chelex 100 under process conditions are rather high $(\geq 10^3 \text{ mL/g})$ once the Mo(VI) has been reduced and complexed. The conversion takes 25-30 minutes to reach completion. Visible spectrometry was applied to observe the kinetics of the complex formation (Figure VII). Under LEU process conditions conversion in complete in less than 30 minutes.



Figure VII. Determination of optimal conditioning time for formation of MoO(SCN)₅²⁻

A series of static batch tests were done to estimate the capacity of the Chelex-100 resin. Based on these data, a column was sized for processing an irradiated depleted uranium target. This processing run was done with 6 g of 200-400 mesh CHELEX-100 resin. No breakthrough occurred after 95 mL of the AG MP-1 eluent was passed through the Chelex-100 column at 2 mL/min. Comparison of the strip solutions and the feed solution show that 94% of the Mo was

recovered from the CHELEX column. Stripping with small amounts of hydrogen peroxide improves recovery to 100% in the laboratory. A 6-g column at 2 mL/min is recommended as adequate for CNEA's process.

It should be noted that the total volume of feed, wash and strip solutions used for all ⁹⁹Mo purification steps obtained from LEU is about 1/10 that in the current HEU-based process.

CONCLUSIONS AND FUTURE WORK

Although we have encountered challenges to the digestion process, significant progress has been made:

- The digester designed and fabricated at ANL is appropriate for dissolution of 70 g of irradiated U. Some minor modification might be needed, depending on the digestion/oxidation method used.
- Four digestion/oxidation methods are currently being investigated. Each of the four methods will be used on irradiated targets at ANL during this calendar year. A recommendation will be made based on the ease of operation and on the yield of ⁹⁹Mo.
- Column sizing is near completion; 2 g of AG MP-1 and 6 g Chelex-100 columns are recommended for processing. Adequate flow rates are 6-8 mL/min and 2 mL/min for AG MP-1 and CHELEX, respectively.

We are planning the next processing demonstrations for spring 2003. Targets are fabricated and will be shipped to Argentina soon. The use of LEU-foil targets and either one- or two-step process to digest the irradiated foils will allow for a significant decrease in ⁹⁹Mo production time and volume of liquid radioactive waste.

REFERENCES

- R. O. Marques, P. R. Cristini, H. Fernandez, and D. Marziale, "Operation and Installation for Fission ⁹⁹Mo Production in Argentina," Fission Molybdenum for Medical Use Proceedings of Technical Committee Meeting Organized by the International Atomic Energy Agency, Karlsruhe, October 13-16, 1987, IAEA-TECDOC-515 (1989) pp. 23-33.
- 2. A. A. Sameh and H. J. Ache, "Production Techniques of Fission Molybdenum-99," Radiochimica Acta 41 (1987), pp 65-72.
- T. C. Wiencek, D. J. McGann, and G. L. Hofman, "Development of Annular Targets for ⁹⁹Mo Production," Proc. of the XXIInd International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1999, Budapest, Hungary, in press.
- 4. G. L. Hofman, T. C. Wiencek, E. L. Wood, J. L. Snelgrove, A. Suripto, H. Nasution, D. Lufti-Amin, and A. Gogo, "Irradiation Tests of ⁹⁹Mo Isotope Production Targets Employing Uranium Metal Foils," Proc. of the XIXth International Meeting on Reduced Enrichment for Research and Test Reactors, October 7-10, 1996.

- G. F. Vandegrift, Y. Koma, H. Cols, C. Conner, S. Aase, M. Peter, D. Walker, R. A. Leonard, and J. L. Snelgrove, "Production of Mo-99 from LEU Targets--Base Side Processing," Proceedings of the 2000 International Meeting on Reduced Enrichment for Research and Test Reactors, ANL/TD/TM01-12, Argonne National Laboratory, July 2001, p. 115
- C. Conner, J. Sedlet, T. C. Wiencek, D. J. McGann, G. L. Hofman, G. F. Vandegrift, and J. L. Snelgrove (ANL, USA), A. Mutalib, A. H. Gunawan, H. G. Adang, H. Lubis, K. Wisnukaton, Kardarisman, A. Sukmana, Sriyono, B. Purwadi, D. T. Jatmiko, A. Suripto, D. L. Amin, A. Basiran, Martoyo, Sarwani, and T. Taryo (BATAN, Indonesia), "Production of Mo-99 from LEU Targets--Acid-Side Processing," Proceedings of the 2000 International Meeting on Reduced Enrichment for Research and Test Reactors, ANL/TD/TM01-12, Argonne National Laboratory, July 2001, p. 101.
- 7. G. F. Vandegrift, C. Conner, G. L. Hofman, J. L. Snelgrove, A. Mutalib, B. Purwadi, H. G.Adang, H. Lubis, Kadarisman, A. Sukmana, Sriyono, D. T. Jatmiko, A. Suripto, D. L. Amin, A. Basiran, A. Gogo, Sarwani, and T. Taryo, "Development of Annular Targets for ⁹⁹Mo Production," Proceedings of the XXIInd International Meeting on Reduced Enrichment for Research and Test Reactors, October, 1999, Budapest, Hungary, in press.
- 8. A. H. Webster and J. Halpern, "Kinetics of the reduction of permanganate in aqueous solution by molecular hydrogen", *Trans. Faraday Soc.*, **53**, 1957, p. 51.
- 9. A. Navrotsky, "Issues in the energetics of metastable oxides and oxyhydroxides" in "Aqueous chemistry and geochemistry of oxides, oxyhydroxides, and related materials : symposium held April 8-12, 1996, San Francisco, California, U.S.A.", (ed J. A. Voigt) p.8