RERTR PROGRESS IN MO-99 PRODUCTION FROM LEU

by


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

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ABSTRACT

The ANL RERTR program is performing R&D supporting conversion of $^{99}\text{Mo}$ production from HEU to LEU targets. Irradiation and processing of LEU targets were demonstrated at the Argentine Ezeiza Atomic Center. Target irradiation and disassembly were flawless, but the processing is not fully developed. In addition to preparing for, assisting in, and analyzing results of the demonstration, we performed other R&D related to LEU conversion: (1) designing a prototype production dissolver for digesting irradiated LEU foils in alkaline solutions and developing means to simplify digestion, (2) modifying ion-exchange columns used in the CNEA recovery and purification of $^{99}\text{Mo}$ to deal with the lower volumes generated from LEU-foil digestion, (3) measuring the performance of new inorganic sorbents that outperform alumina for recovering Mo(VI) from nitric acid solutions containing high concentrations of uranium nitrate, and (4) developing means to facilitate the concentration and calcination of waste nitric-acid/LEU-nitrate solutions from $^{99}\text{Mo}$ production.

1. 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% $^{235}\text{U}$. Technetium-99m, the daughter of $^{99}\text{Mo}$, is the most commonly used medical radioisotope in the world. Currently, most of the world’s supply of $^{99}\text{Mo}$ is produced by fissioning the $^{235}\text{U}$ in HEU targets, generally 93% $^{235}\text{U}$. Targets for the production of $^{99}\text{Mo}$ 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 UO$_2$ on the inside of a stainless steel tube. After irradiation, the $^{99}\text{Mo}$ is recovered from the irradiated uranium and purified.

To yield equivalent amounts of $^{99}\text{Mo}$, an LEU target must contain approximately five times the uranium as 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 $^{99}\text{Mo}$ product, and (3) limiting economic disadvantages.

2. Progress

Since reporting R&D results at the 2000 International RERTR Meeting [1,2], we have made progress in four R&D areas aimed at the conversion of $^{99}\text{Mo}$ production to LEU targets. Those areas are (1) developing and demonstrating the recovery and purification of $^{99}\text{Mo}$ from an LEU target in Argentina, (2) developing a production dissolver for digesting irradiated LEU foils by alkaline solution, (3) testing new inorganic sorbents for their ability to recover molybdenum from acidic uranium nitrate solutions, and (4) developing means to facilitate calcination of acidic uranium nitrate waste solutions.

Processing of Irradiated LEU Foils by CNEA A number of current producers dissolve/digest uranium-aluminide/aluminum-dispersion plates in alkaline solution as an initial step to recovering fission-produced $^{99}\text{Mo}$ from irradiated HEU. These producers include Argentine Comisión Nacional de Energía Atómica (CNEA), Institut National des Radioéléments (IRE), Mallinckrodt, and the South African Nuclear Energy Corporation Limited (NECSA). Argonne National Laboratory (ANL) is actively cooperating with one of these producers, CNEA, to convert its process to low-enriched
uranium (LEU). The CNEA process has been described in the literature [3] and has much in common with the Mallinckrodt process; both processes are based on that developed by A. Sameh [4]. In this process, the irradiated targets are heated in sodium hydroxide solution. The aluminum cladding and meat in the targets are dissolved to form soluble sodium aluminate, and the uranium is digested, forming a mixed precipitate of UO\textsubscript{2} and Na\textsubscript{2}U\textsubscript{2}O\textsubscript{7}. 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, the filtrate is fed to an anion-exchange column, which retains molybdenum and some other anionic species. After it is eluted from this column, the molybdenum is purified to meet pharmaceutical standards by a series of separation processes.

The LEU-modified process begins with a two-step digestion of irradiated LEU foils. Because the digestion of LEU 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. Early in 1999, ANL and CNEA began active cooperation with the goal of enabling CNEA to convert to LEU at the end of three years. It is a multifaceted program, and many steps are required to modify targets and the current process to allow the use of LEU targets. Progress during 2000 was described earlier [1]. Irradiations and process demonstrations were performed in December 2000 and May 2001.

Two targets containing four foils were irradiated May 3-8, 2001, for ~120 hours at a flux of 4-6x10\textsuperscript{13} n/cm\textsuperscript{2}/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 \textsuperscript{99}Mo Production Facility. After arrival at the \textsuperscript{99}Mo 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 \textsuperscript{99}Mo 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. 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 \textsuperscript{99}Mo was released to the sodium hydroxide solution, a second digestion step was performed by pressurizing the dissolver with 100-psig (0.7-MPa) oxygen and heating the dissolver again. This step converts the solid uranium dioxide into a solid sodium diuranate product; it 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 \textsuperscript{99}Mo 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 column. Following filtration, the \textsuperscript{99}Mo (as MoO\textsubscript{4}\textsuperscript{2-}) in the 175 mL of solution (dissolving solution plus dissolver rinses) was recovered on the AG MP-1 column, which was considerably smaller than that required for an equal amount of \textsuperscript{99}Mo from dissolving the current HEU targets. Any I\textsuperscript{-} 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 \textsuperscript{99}Mo escaped the column during loading and rinsing. The \textsuperscript{99}Mo was eluted from the column in 72 mL of solution, which was then prepared for the second \textsuperscript{99}Mo-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 2002. For this demonstration, a new prototype production dissolver has been designed and fabricated at ANL and is being tested. Studies are underway to size both the AG MP-1 and Chelex 100 columns and set maximum flow rates through the columns. We are also developing a one-step digestion process using potassium permanganate to oxidize uranium to U(VI) and iodine to iodate.

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 [5]. 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 was run with 100-psig (0.7-MPa) oxygen overpressure, corrosion was 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) O₂, 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 corrosion of the welded metal was similar to that of the rest of the coupon. Examination of 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 µm. Oxidation-layer thickness developed in the liquid phase varied from 10 to 20 µm, and that in the vapor phase varied from 20 to 50 µm.

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 <1µm. 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 µm/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 µm/hr. Therefore, 304 stainless steel is not an acceptable material of construction for the two-step digestion; however, both Hastelloy C-276 and Inconel 600 are acceptable.

The design of 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 will be accomplished using heat-tape tracing; cooling will be performed by blowing air. Figure 1 is 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) and has five lateral connections for accommodating pressure gauges, a pressure relief valve, a vacuum port and solution inlets. The bottom drain will be connected to a ball valve and filter. The top has a bayonet fitting for ease of closure. The unit is designed and has been tested to hold up to 1500 psig (10.3 MPa) pressure at 300°C.

The two-step process is effective but (1) having two warm-up, reaction, and cool-down periods doubles digestion time and (2) using pressurized oxygen leads to safety concerns. Therefore, we are
testing the addition of KMnO₄ to the digestion solution to perform the oxidation to U(VI) and I(V). Thus far, results have been very promising. Adding potassium permanganate dissolved in sodium or potassium 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. Further tests will be performed with low-burnup uranium foils and then with fully irradiated targets in Argentina.

CNEA-Process Column Sizing: R&D is being undertaken to size the AG MP-1 and Chelex 100 columns and to set optimum conditions for their use in the LEU process. The molybdate-sorption kinetics of AG MP-1 are extremely fast. Equilibrium in static tests is reached in 15-30 minutes. The partitioning coefficient for Mo(VI) is inversely dependent on the hydroxide concentration and will be in the 100-200 mL/g range for hydroxide concentrations contemplated for the process; AG MP-1 has a 2.3 meq/g loading capacity for molybdate. Distribution ratios for MoO(SCN)₅²⁻ on Chelex 100 under process conditions are extremely high (≥10⁷ mL/g) once the Mo(VI) has been reduced and complexed. The conversion is relatively slow at 22°C, taking 80 minutes to reach completion. Future work will measure the effects of temperature on this reaction. All of these activities will be completed for implementation during the CNEA demonstration in spring 2002.

Mo-Specific Sorbents for Solutions with High Concentrations of HNO₃ and UO₂(NO₃)₂: Two inorganic sorbents were tested for their ability to recover molybdenum from nitric acid solutions with significant concentrations of uranyl nitrate. These patented sorbents were produced in Russia for Technology Commercialization International Inc. (TCInternational). They are 0.4-1.0 mm spherical particles with high mechanical strength. Reported below are the results of our initial screening of these two materials. In the first series of tests, the effects of contact time, nitric acid concentration, and uranyl nitrate on the partitioning coefficient of ⁹⁹Mo (Kₐ, mL/g) were studied for these two sorbents (designated as R-1 and R-2) and compared with alumina (Aldrich aluminum oxide, activated, acidic, Brockmann 1, ~150 mesh). From data presented in Table 1, several observations can be made:

- Both R-1 and R-2 have higher affinity for Mo(VI) than does alumina at all solution compositions and contact times.
- Their affinity is especially higher from solutions of concentrated uranium.
- When the concentration of uranium is high, the R-2 sorbent has ~100 times higher affinity for Mo(VI) than does alumina.
- Sorbent R-1 appears to have better kinetic properties than do R-2 and alumina, and thus will allow faster feed flow rates through the column.

In separate column tests, we found that molybdenum is easily stripped from these sorbents in the same manner used for alumina. The loading capacity for both sorbents is ~3 meq/g. Based on these preliminary results, we feel that use of either of these materials should (1) allow a more efficient
recovery of molybdenum than the current alumina column and (2) generate a waste-solution volume for LEU processing equal to, or perhaps less than, that for current HEU target processing.

Table 1. Partitioning coefficient (Kd) for sorption of tracer $^{99}$Mo for three sorbents vs. contact time and concentrations of nitric acid and uranyl nitrate. All contacts were performed at 22-25°C while test tubes containing 2 mL of solution and 0.1 g of sorbent were slowly rotated to provide mixing.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Sorbent R-2</th>
<th>Sorbent R-1</th>
<th>Al₂O₃</th>
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<tr>
<td></td>
<td>Kd(Mo) mL/g</td>
<td>Kd(Mo) mL/g</td>
<td>Kd(Mo) mL/g</td>
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<tr>
<td>[HNO₃], M</td>
<td>4 hr</td>
<td>24 hr</td>
<td>48 hr</td>
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Chemically Facilitated Calcination of Uranium-Nitrate/Nitric-Acid Waste Solutions: Argonne is cooperating with MDS Nordion, Atomic Energy of Canada Ltd. (AECL), and SGN to develop technical means for converting $^{99}$Mo production at Chalk River, Ontario, Canada to LEU [6]. When LEU targets are dissolved in nitric acid, the dissolver solution will contain approximately five times more uranium than HEU targets for the same $^{99}$Mo yield. Consequently, the waste solution from initial molybdenum recovery will have far higher concentrations of uranium and perhaps a greater volume than that generated from the current process. For disposal, the waste solution must be stabilized as a solid. Direct calcination to a uranium/fission-product oxide product has been accepted as a suitable long-term storage form [6,7]. The technical challenge being addressed is developing means to use the same equipment and facilities to deal with LEU waste as were designed to treat HEU waste. The barrier(s) in concentrating and calcining these solutions are:

- Higher evaporation rates may be required (if LEU conversion increases waste-solution volume).
- Following evaporation of liquids, formation of approximately five times more UNH (uranyl nitrate hexahydrate) will test the capacity of the equipment and storage containers.
- Dehydration and denitration of molten UNH can be messy. Pairing this with its larger volume in the case of LEU targets makes contamination of equipment a great concern.

The path Argonne chose to address these potential problems is to (1) study the limits of direct evaporation/calcination of the nitric-acid/UNH solution and (2) use chemical means (precipitation of uranyl oxalate) to eliminate the formation of UNH. Assisted calcination with oxalic acid has been attempted by two means.

In the first method, the uranium-nitrate/nitric-acid solution and a saturated oxalic-acid solution (at a 1.1 oxalate/uranyl mole ratio) are simultaneously fed to the calciner at the same rate as liquid evaporates. Experiments begin with an initial charge of 100 mL of the uranium solution.

In the second method, the calciner cup is initially filled with solid oxalic acid and 100 mL of the nitric-acid/UNH solution. The uranium solution is fed to the calciner at the same rate that condensate is collected until 1 mole of uranium is added per 1.1 mole of oxalate already in the cup. Both methods produce the same product, a mixture of UO₂ and U₃O₇. The material is easily removed from the cup in the form of powder.

Addition of the aqueous 1 M oxalic acid solutions requires significantly more evaporation than adding solid oxalic acid; thus, adding solid H₂C₂O₄•2H₂O to the cup before startup is the preferred option. Argonne is developing a chemical and engineering understanding of both direct and oxalate-assisted
calcination using a simplified calciner system, glassware studies, and solid, liquid, and off-gas analyses. This information will allow SGN to develop a testing program to pilot these processes in a duplicate of the calcining unit in place at the New Processing Facility at Chalk River.

3. CONCLUSIONS AND FUTURE WORK

Argonne continues to partner with $^{99}\text{Mo}$ producers to convert targets from HEU to LEU. The cooperation with CNEA is on schedule, and we are planning additional demonstrations in spring 2002 for all aspects of production—from target fabrication to the final $^{99}\text{Mo}$ product. Our work on the Russian sorbents for molybdenum recovery will continue; we are looking for a partner to test them under production conditions. Our R&D on facilitated calcination has not yet demonstrated an assured winner or loser; pilot testing by SGN will be required to make that decision. The next phase of development work is being discussed with our MDS Nordion partners; Argonne research will support the pilot demonstrations by SGN. The extremely successful cooperation with Indonesia, which is nearing completion, was inactive in 2001. As soon as the world political situation improves, we will visit our colleagues in Indonesia to observe them (1) demonstrate that LEU-produced $^{99}\text{Mo}$ will achieve the same $^{99m}\text{Tc}$ yield and purity from a generator as HEU-produced $^{99}\text{Mo}$ and (2) fabricate LEU-foil targets for irradiation. We will continue to pursue the building of active programs with other $^{99}\text{Mo}$ producers.

4. REFERENCES


