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by

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ABSTRACT

Argonne National Laboratory (ANL) is cooperating with the Argentine Comisión Nacional de Energía Atómica (CNEA) to convert their ⁹⁹Mo production process, which uses high enriched uranium (HEU), to low-enriched uranium (LEU). Progress discussed in this year's paper includes optimization of (1) the digestion of LEU foil by sodium hydroxide solution and (2) the primary recovery of molybdenum by anion exchange. Also discussed are ANL/CNEA plans for demonstrating the irradiation and digestion of LEU-foil targets and recovering Mo in Argentina later this year. Our results show that, up to this point in our study, conversion of the CNEA process to LEU appears viable.

INTRODUCTION

Technetium-99m, the daughter of ⁹⁹Mo, is the most commonly used medical radioisotope in the world. A number of current producers dissolve/digest uranium-aluminide/aluminum-dispersion plates in alkaline solution as an initial step to recovering fission-product ⁹⁹Mo from irradiated high-enriched uranium (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) has begun a cooperation with one of these producers, CNEA, to convert their process to low-enriched uranium (LEU).

The 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 UO₂ and Na₂U₂O₇. 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. As is common to all HEU processes we have studied, only the dissolution/digestion and primary molybdenum-recovery steps should be affected by conversion to LEU.

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Early in 1999, ANL and CNEA began active cooperation with a goal to allow CNEA to convert to LEU at the end of three 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

LEU-Foil Target

To yield equivalent amounts of ^{99}Mo , an LEU target must contain five times as much uranium as an HEU target. To keep the geometry the same as the HEU target, the LEU target requires a denser form of uranium. To that end, targets containing LEU in the form of a metal foil are being developed. A new annular-style target for irradiating LEU foils has been tested. The annular target is fabricated by sandwiching a piece of LEU foil between an inner and outer tube and then expanding the inner tube into the outer tube [3]. The results of the latest irradiations of this type of target are reported elsewhere in this conference [4].

Currently, CNEA irradiates aluminum-clad uranium-alloy miniplates containing HEU for the production of ^{99}Mo . Since the new annular targets are cylindrical, they will not fit into CNEA's existing irradiation fixture. The CNEA staff has designed, fabricated, and hydrotested a new irradiation fixture that will accommodate four annular targets. The irradiation fixture maintains proper coolant velocities across the targets and balances the flow between the inside and outside of the targets.

Each of CNEA's miniplates contains ~ 1.1 g HEU (1.0 g ^{235}U), and CNEA can irradiate up to 12 plates in their current rig. The annular replacement target will be 36-mm OD and have a length of 145 mm (to fit into their existing transfer cask). A target with these dimensions can contain ~ 35 g LEU (7 g ^{235}U), assuming a $140\text{-}\mu\text{m}$ thick foil. Thus, the new annular target will allow CNEA to increase their production capacity for ^{99}Mo . We have been working with CNEA on the targets to ensure that the irradiation fixture and targets will be compatible. Four targets (each containing two foils) are being fabricated for irradiation in the Ezeiza Atomic Center's RA-3 reactor in Argentina during November 2000. The test matrix (Table 1) will verify earlier success in Indonesia and will test the use of three fission-recoil-barrier materials (Al, Zn, and Ni) and the effects of their thickness on uranium-foil integrity following irradiation. The rationale for the test matrix is:

- Foils 00-10, 00-11, 00-15, and 00-17 will allow evaluation of the effects of varying the thickness of an aluminum fission-recoil barrier.
- Irradiation of foil 00-15 will allow a comparison to the June 2000 irradiation of a similar target in the Indonesian RSG-GAS reactor.
- Foils 00-10 and 00-17 will provide information on the reproducibility of fabrication and irradiation behavior.
- Foils 00-12, 00-13, and 00-16 will allow comparison of the performance of Ni-foil and Ni-plated barriers. Nickel fission-recoil barriers have produced the best results to date. Tests in 1999 showed that although nickel does not dissolve in alkaline solution, uranium could be digested if the electroplated uranium foil were cut to expose uranium. These three foils will also allow

evaluation of the viability of Ni-foil and/or Ni-plated uranium foils for base-side processing.

- Foil 00-14 will allow further evaluation of electroplated zinc as a fission-recoil barrier.

Following visual inspection, some of the foils will be digested. The resultant product will be filtered, and the filtrate will be run through an anion exchange column for recovery of molybdenum. Conditions will be based on the studies summarized below.

Table 1. Test Matrix for LEU-Target to be Irradiated in the CNEA RA-3 Reactor in November 2000.

Target ^a	Foil ^b	Barrier	Barrier Thickness, mm	Anodized Tubes?
1	00-10	Al Foil	0.040	Yes
	00-11	Al Foil	0.060	Yes
2	00-12	Ni Foil	0.015	Yes
	00-13	Ni Foil	0.015	No
3	00-14	Zn Plated	0.030	Yes
	00-15	Al Foil	0.025	Yes
4	00-16	Ni Plated	0.015	Yes
	00-17	Al Foil	0.040	Yes

^a Dimensions of the targets are ID = 31.72 (+0.13/-0.08) mm, OD = 36 (+0.13/-0.08) mm, and length = 145 (+2/-5) mm. Each target will contain two foils.

^b All foils will have nominal dimensions of 9.7 cm x 3 cm x 130 μ m.

Optimization of LEU-Foil Digestion for ⁹⁹Mo Recovery

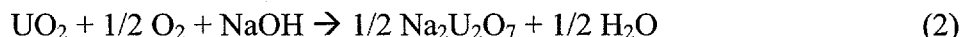
Because uranium metal digests very slowly in boiling concentrated sodium-hydroxide solutions at ambient pressure, we have developed means to digest the irradiated foil at elevated temperature and, therefore, pressure using a closed dissolver/digester. Results of this study were provided during last year's RERTR meeting [5]. In this work, we are using the dissolver developed for acid-side dissolution of uranium foil in a closed system. This closed dissolver can be operated at pressures up to 720 psig (5.1 MPa). The dissolver is described elsewhere [6,7]. The key results of last year's work were:

- At a temperature of ~220°C, 130- μ m-thick foil can be completely converted to UO₂ in about 30 minutes.

- The reaction is insensitive to the concentration of hydroxide and appears to follow the rate and path expected for uranium corrosion by steam:



- Addition of oxygen to the digester does not affect the above reaction or its rate but does change the product to $\text{Na}_2\text{U}_2\text{O}_7$:



Because generating hydrogen gas in a 100-psig (789-kPa) oxygen atmosphere was deemed a safety concern, this option was not pursued.

- Foils with zinc fission-recoil barriers dissolved at the same rate as did those with no zinc barrier.

All experiments in 1999 were performed using unirradiated depleted-uranium (DU) foils. Although we understood the means and rate of the reaction, we needed to know the effects of this digestion on the fate of fission and neutron adsorption products. Specific concerns were the fate of Mo, I, Pu, and Np--all of which have multiple oxidation states. To learn the fate of these irradiation products, small pieces (~100 mg) of LEU foil were irradiated in the ANL Intense Pulsed Neutron Source (IPNS) [8]. To prepare for irradiation, the foils were double encapsulated in aluminum cans. Irradiations were approximately 24 hours long in an average total neutron flux of $\sim 2 \times 10^{11}$ neutrons/cm²·sec. In the hole used for our irradiations, the neutron flux is thermalized to some extent but is still considerably harder than in a research reactor where the fast/thermal neutron flux ratio is ~3. After irradiation and at least 24 hours of cooling, the irradiated foil was removed from the aluminum cans and cut into three pieces. One piece was dissolved in nitric acid to measure yields of fission products and ²³⁹Np; the other two pieces were digested in aqueous sodium hydroxide in two separate experiments. In most cases, DU foil was added to the dissolver to increase uranium mass to a more prototypic value. Carrier amounts of molybdate and iodide ion were added to the hydroxide solution to provide typical amounts of these fission products from fully irradiated foils. Following digestion, the precipitated uranium oxide was filtered and washed. A material balance was calculated for irradiation products based on (1) their irradiation yield determined from the nitric acid solution, (2) their activity in the filtrate, and (3), in some cases, gamma counting of the dissolved precipitate.

The results of studies when the dissolver contained sodium hydroxide solution under a helium atmosphere were:

- The digestion occurred as predicted by 1999 results.
- The product of the uranium digestion was UO_2 .
- The precipitate quantitatively removed the ²³⁹Np.
- Because molybdate retention by the anion-exchange column is inversely proportional to the hydroxide concentration, the ability to use lower concentrations of hydroxide ion should be beneficial to the initial ⁹⁹Mo-recovery step.

- About half of the alkaline-soluble fission products (e.g., Mo, I, Cs) were lost to the precipitate. This was true for ^{99}Mo and radioiodine isotopes whether or not carriers were present in sodium-hydroxide solution prior to digestion.
- Dissolving the precipitated uranium dioxide in hydrochloric acid produced only minor amounts of hydrogen gas (showing that $<1\%$ of the uranium was not converted to UO_2).

The loss of molybdenum to the precipitate is intolerable; therefore, means were developed to release the ^{99}Mo from the UO_2 . As was stated earlier, digestion in the presence of oxygen leads to sodium diuranate rather than UO_2 . Because this is the form of uranium currently produced during digestion of CNEA's HEU targets, where loss of molybdenum to the precipitate is minor, we hypothesized that oxygen addition is vital to release of molybdenum.

To avoid producing a potentially explosive mixture, the digestion process was converted to a two-step process. In the first step, the foil was converted to UO_2 , generating hydrogen gas. After completion of this reaction, the hydrogen gas was purged from the vessel, then 100-psig (789-kPa) oxygen was added to the vessel, thus converting the UO_2 to $\text{Na}_2\text{U}_2\text{O}_7$. By this action, $>99\%$ of the molybdenum was released from the precipitate. Conditions for this process have not yet been optimized, but it is likely the entire digestion operation can be completed in less than one hour.

Oxidation of the uranium-oxide precipitate appears to have a second benefit. Following the filtration, the filtrate is fed to an anion exchange column, where molybdenum is recovered and purified from other fission products. Radioiodine (in the form of iodide) in the filtrate is held on the resin also, and the radiation due to its presence degrades the column and can hinder stripping of molybdenum. Results of anion exchange runs following oxygen conversion indicate that a significant portion of the iodide is being transformed to higher oxidation states (e.g., iodate) that are not as strongly retained by the ion exchange column. This could lead to enhanced stability of the ion-exchange media and, therefore, to consistently higher ^{99}Mo yields.

Primary Recovery of Molybdenum by Anion Exchange

In the current CNEA process for HEU targets, anion exchange is employed for the primary separation of molybdenum [1]. In this step, molybdenum is adsorbed onto the anion-exchange resin, AG 1 X8, as molybdate ion from a 1.6–2 M NaOH solution. The AG 1-X8 resin in chloride form is available from Bio-Rad Laboratories and is converted to the hydroxide form before use.

Last year's studies focused on the effects of hydroxide and zincate concentrations on the recovery of molybdenum using AG 1 anion exchange. The results of that study were:

- The addition of zinc fission barriers to the targets would not degrade the recovery of ^{99}Mo from the digestion filtrate.
- Retention of molybdenum is enhanced by lowering the hydroxide concentration in the feed to the anion exchange column. The hydroxide concentration in the HEU feed is set by the requirement of retaining aluminate ion in solution; this requirement will not be important in the LEU foil targets.

During 2000, we have increased our understanding of the important system parameters in the primary molybdenum-recovery step and looked at the potential use of two macroporous resins, AG-MP (Bio-Rad Laboratories) and Reillex HPQ (Reilly Industries, Inc.). Macroporous resins show faster exchange kinetics and, therefore, allow higher flow rates. Reillex HPQ also has superior stability to radiation damage [9,10]. Developing these options can lead to an improved process and act to alleviate any penalties associated with conversion to LEU targets.

The objective of our studies this year was to optimize conditions for the initial recovery of molybdenum in the anion-exchange separation for the demonstration to be run in Argentina in November 2000. Based on these studies, the optimum conditions to be used for recovery of Mo are:

Feed: Filtrate plus precipitate-wash solution--hydroxide concentration, $\sim 0.75 \text{ M NaOH}$.
A small quantity of NaOCl is added to the feed to keep molybdenum in the (VI) oxidation state.

Wash: 0.75 M NaOH

Strip: $0.5 \text{ M NH}_3 - 1 \text{ M Na}_2\text{SO}_4$

Except for the lower concentration of sodium hydroxide in the feed, the conditions are the same as those currently used by CNEA.

CONCLUSIONS AND FUTURE WORK

The cooperation between ANL and CNEA is focused on allowing CNEA to convert ^{99}Mo production to LEU at the end of 2002. Both sides have active R&D underway in various aspects of the conversion. This paper has primarily discussed efforts at ANL. Thus far, we have shown that:

- LEU metal-foil targets can replace the current HEU targets in the reactor and allow the same or more ^{235}U to be irradiated. Targets are scheduled to be tested in the RA-3 reactor during November 2000.
- Molybdenum can be recovered from irradiated metal targets by removing the uranium foil from the target and digesting the foil in a two-step operation. The uranium is first converted to UO_2 using alkaline solution with the release of hydrogen gas. Following digestion, the hydrogen is purged, oxygen is added to the dissolver, and the mixture is reheated to convert the uranium dioxide to sodium diuranate.
- This two-step digestion appears to have the additional benefit of converting iodide to species with less affinity for the anion-exchange resin, alleviating the severe radiolytic damage undergone by the resin during ^{99}Mo recovery operation. This should provide reliably higher yields.
- Using the macroporous version of AG-1 (AG MP-1) is a viable option. Its faster exchange kinetics will allow higher flow rates through the column and/or smaller columns.

- Although partitioning of molybdenum is not as high for the Reillex HPQ resin, it also is a viable option, especially at the reduced hydroxide concentration allowable by the elimination of aluminum from the dissolver filtrate. Its higher stability to radiation damage could be an important factor.
- Initial experiments suggest that the zinc fission-recoil barrier required on the LEU foil should not present a problem to the current processing scheme.

Future activities will move the process chemistry to full LEU process demonstrations in the CNEA hot cells. Provided the November demonstrations are successful, conversion of the Argentine process is on schedule. Thus far, ANL and CNEA progress has been substantial, and we see no roadblocks to successful conversion.

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REFERENCES

- [1] R. O. Marques, P. R. Cristini, H. Fernandez, and D. Marziale, "Operation and Installation for Fission ^{99}Mo Production in Argentina," Fission Molybdenum for Medical Use, Proc. of Technical Committee Mtg. Organized by the International Atomic Energy Agency, Karlsruhe, October 13-16, 1987, IAEA-TECDOC-515 (1989) 23-33.
- [2] A. A. Sameh and H. J. Ache, "Production Techniques of Fission Molybdenum-99," *Radiochimica Acta* 41 (1987) 65-72.
- [3] C. Conner, E. F. Lewandowski, T. C. Wiencek, G. L. Hofman, M. W. Liberatore, D. Walker, D. McGann, G. F. Vandegrift, and J. L. Snelgrove, "Development, Fabrication, and Testing of LEU Metal Foil Targets for ^{99}Mo Production," Proceedings of the 1999 International Meeting on Reduced Enrichment for Research and Test Reactors, held in Budapest, Hungary, October 3-8, 1999, in press.
- [4] C. Conner, G. F. Vandegrift, J. Sedlet, T. C. Wiencek, D. J. McGann, G. L. Hofman, J. L. Snelgrove, A. Mutalib, A. H. Gunawan, H. G. Adang, H. Lubis, K. Wisnukaton, Kadarisman, A. Sukmana, Sriyono, B. Purwadi, D. T. Jatmiko, A. Suropto, D. L. Amin, A. Basiran, Martoyo, Sarwani, and T. Taryo, "Production of Mo-99 from LEU Targets--Acid-Side Processing," this proceedings.
- [5] G. F. Vandegrift, R. A. Leonard, S. B. Aase, J. Sedlet, Y. Koma, C. Conner, C. R. Clark, and M. K. Meyer, "Modification of Base-Side ^{99}Mo Production Processes for LEU Metal-Foil Target," International Meeting on Reduced Enrichment for Research and Test Reactors, Budapest, Hungary, October 3-8, 1999, in press.

- [6] B. Srinivasan, R. A. Leonard, S. Aase, G. F. Vandegrift, Moeridun, A. A. Rauf, H. Lubis, A. Hardi, S. Amini, and Y. Nampira, "Processing of LEU Targets for ^{99}Mo Production--Dissolution of Metal Foils by Nitric-Acid/Sulfuric-Acid Mixtures," Proceedings of the XVIII International Meeting on Reduced Enrichment for Research and Test Reactors, Paris, France, September 17-21, 1995, Paper no. 3-2 (1996).
- [7] A. Mutalib, B. Purwadi, Adang H. G., Hotman L., Moeridoen, Kadarisman, A. Sukmana, Sriyono, A. Suropto, H. Nasution, D. L. Amin, A. Basiran, A. Gogo, D. Sunaryadi, T. Taryo, G. F. Vandegrift, G. Hofman, C. Conner, J. Sedlet, D. Walker, R. A. Leonard, T. C. Wiencek, E. L. Wood, and J. L. Snelgrove, "Full-Scale Demonstration of the Cintichem Process for the Production of Mo-99 Using a Low-Enriched Target," Proceedings of the XXIth International Meeting on Reduced Enrichment for Research and Test Reactors, held in São Paulo Brazil, October 18-23, 1998, in press.
- [8] A description of the IPNS and research being performed at the facility can be found at the following web site: <http://www.pns.anl.gov/accsys.htm>.
- [9] S. F. Marsh, "ReillexTM HPQ: A New, Macroporous Polyvinylpyridine Resin for Separating Plutonium Using Nitrate Anion Exchange," Solvent Extr. Ion Exch., 7 (1989) 889-908.
- [10] K. R. Ashley, J. R. Ball, A. B. Pinkerton, K. D. Abney, N. C. Schroeder, "Sorption Behavior of Pertechnetate on Reillex-HPQ Anion Exchange Resin from Nitric Acid Solution," Solvent Extr. Ion Exch., 12 (1994) 239-259.