

DEVELOPMENT AND PROCESSING OF LEU TARGETS
FOR MO-99 PRODUCTION--OVERVIEW OF THE ANL PROGRAM*

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ABSTRACT

Most of the world's supply of $^{99\text{m}}\text{Tc}$ for medical purposes is currently produced from the decay of ^{99}Mo derived from the fissioning of high-enriched uranium (HEU). Substitution of low-enriched uranium (LEU) silicide fuel for the HEU alloy and aluminide fuels used in most current target designs will allow equivalent ^{99}Mo yields with little change in target geometries. Substitution of uranium metal for uranium oxide films in other target designs will also allow the substitution of LEU for HEU.

During 1995, we have continued to study the modification of current targets and processes to allow the conversion from HEU to LEU. A uranium-metal-foil target was fabricated at ANL and irradiated to prototypic burnup in the Indonesian RSG-GAS reactor. Postirradiation examination indicated that minor design modifications will be required to allow the irradiated foil to be removed for chemical processing. Means to dissolve and process LEU foil have been developed, and a mock LEU foil target was processed in Indonesia. We have also developed means to dissolve the LEU foil in alkaline peroxide, where it can be used to replace HEU targets that are currently dissolved in base before recovering and purifying the ^{99}Mo . We have also continued work on the dissolution of U_3Si_2 and have a firm foundation on dissolving these targets in alkaline peroxide. The technology-exchange agreement with Indonesia is well underway, and we hope to expand our international cooperations in 1996.

INTRODUCTION

Technetium-99m, the daughter of ^{99}Mo , is the most commonly used medical radioisotope in the world. It is relied upon for over nine million medical procedures each year in the U.S. alone, comprising 70% of all nuclear medicine procedures. Most ^{99}Mo is produced in research and test reactors by the irradiation of targets containing high-enriched uranium (HEU). Because the worldwide effort to fuel research and test reactors with low enriched uranium (LEU) instead of with HEU has been so successful, HEU is now used only for ^{99}Mo production in some countries. In addition, while there are only a few major producers of ^{99}Mo , many nations with developing nuclear programs are seeking to become producers of ^{99}Mo , both for domestic and foreign consumption. Therefore, an important component of the U.S. RERTR program's goal of reducing world commerce in HEU is the development of means to produce ^{99}Mo using LEU. Initial development work was carried out from 1986 to 1989, when the effort was halted by lack of funding. DOE authorized resumption of this work in 1993. The two principal aspects of the work are target development and testing and chemical process development.

As we did for fuel development and testing, the RERTR program is developing international partnerships for the ^{99}Mo development work. These partnerships are especially important because, at the present time the U.S. does not have irradiation facilities suitable for ^{99}Mo targets. An agreement was signed with the Indonesian National Atomic Energy Agency (BATAN) in November 1994, and, as will be reported at this meeting, our joint work is well underway. We are also pursuing cooperation with other potential users of LEU for ^{99}Mo production. Last year we discussed cooperation with the Argentine National Atomic Energy Commission (CNEA) and wrote the first draft of a cooperation agreement. However, we had insufficient resources to pursue that agreement during a time of intense work with BATAN, but we intend to pursue that agreement during this next year. In addition, we are discussing cooperation with the Korea Atomic Energy Research Institute (KAERI). We have also submitted a proposal to DOE to fund cooperation with the South Africa Atomic Energy Corporation, Ltd.

Targets for the production of ^{99}Mo are generally either (1) miniature Al-clad fuel plates [1-9] or pins [10,11] containing U-Al alloy or UAl_x dispersion fuel similar to that used, at least in the past, to fuel the reactor or (2) a thin film of UO_2 coated on the inside of a stainless steel tube [12,13]. The ^{99}Mo is extracted first by dissolving either the entire Al-clad fuel plate or pin or by dissolving the UO_2 and then performing a series of extraction and purification steps. Both acid and basic dissolutions are used, and each producer has its own special process. The highly competitive nature of the business and the stringent regulations governing the production of drugs make each producer reluctant to change its process. Therefore, the RERTR program's strategy is to develop, in parallel, minimum modifications to the most widely used and potentially most useful processes.

In order to yield equivalent amounts of ^{99}Mo , the LEU targets must contain about five times as much uranium as the HEU targets they replace. We have concentrated on U_3Si_2 dispersion fuels and uranium foils to replace the two general target types mentioned above. Brief summaries of

our progress during the past year are given below. Full discussions are given in other papers at this meeting.

U₃Si₂ DISPERSION FUEL TARGETS AND PROCESSING

The U₃Si₂-Al dispersion fuel developed for reactor conversion offers, from the fabrication and irradiation performance points of view, a suitable alternative for the reactor fuel-type targets mentioned above. Since the fabricability and irradiation behavior of this fuel are well known, no target development work is needed. The presence of silicon presents a challenge in the chemical processing, however, so our work on dispersion targets is focused on chemical processing. We have previously presented reports on target processing using basic [14-18] and acidic [15-17] dissolution. Progress during this past year will be discussed by Buchholz [19] at this meeting.

Several series of uranium silicide particle dissolution experiments were conducted at 40, 50 and 60°C using 5M H₂O₂ and base concentrations ranging from 0.05 to 5M NaOH. Uranium dissolution and peroxide destruction rates increased with temperature and achieved maxima at 1.0 to 1.5M NaOH. These experiments showed that the dissolution rates behaved similarly for uranium foil and silicide particles over a wide range of base concentrations. Lower base concentrations are attractive for dissolution since less acid is required to neutralize solutions during processing, resulting in a lower amount of active waste.

Last year we reported that a 42%-burnup sample from an old RERTR miniplate dissolved much-less-rapidly than unirradiated samples [18]. In an attempt to understand why, samples of an unirradiated LEU silicide miniplate were annealed at 450°C for 0, 3, 6, and 12 h in order to simulate progressively irradiation-enhanced reaction of the U₃Si₂ and aluminum. The aluminum alloy cladding dissolved easily for all samples but heat treatment retarded the dissolution of the meat, doubling the time required to disperse the U₃Si₂ particles. Metallographic inspection of a partially dissolved annealed sample indicated that the matrix aluminum sintered, blocking channels and pores in the meat that provided pathways for the dissolving solution. In addition bubbles formed on the surface of the matrix and further inhibited dissolution of the matrix, preventing the silicide particles from dispersing. Use of a sonicating bath did not improve dispersion time because the reaction temperature could not be maintained at 88°C with the existing apparatus. More powerful focused sonic energy and selected surfactants are being investigated to dislodge bubbles and enhance matrix aluminum dissolution.

URANIUM-METAL-FOIL TARGETS AND PROCESSING

The UO₂-coated target was used in the U.S. by Cintichem until 1989, when a reactor problem forced a halt in production. This process is currently being used in Indonesia by BATAN. During

the late 1980s we had shown that an increased UO_2 coating thickness was not feasible, and had begun to develop electrodeposited metallic uranium targets [14,20,21]. Since we were seeking a target which could be fabricated in developing countries using "low-tech" methods, we developed several concepts using uranium metal foils [15,22,23]. Prototype targets of two designs were produced and subjected to out-of-reactor thermal testing last year [23]. This year we have begun irradiation testing one of these targets, as reported below in this paper. Results of previous dissolution studies were reported last year [24]. This year, dissolution and other chemical processing studies have been performed at ANL and in Indonesia, as reported in several papers at this meeting [25-27].

LEU Foil Target Fabrication and Irradiation Testing

The targets discussed in Refs. 22 and 23 rely on diffusion barriers to inhibit bonding of the uranium foil to the zirconium and/or aluminum tubes encasing the foil so that the foil can be removed for processing. One of the designs sandwiches the uranium between an outer zirconium tube and an inner aluminum tube and relies on the different thermal expansion coefficients of aluminum and zirconium to maintain good contact with the uranium foil for heat transfer. The surfaces of the zirconium and aluminum were oxidized to provide the diffusion barrier. One target of this type was irradiated for six days during July of this year in the central irradiation position of the Indonesian RSG-GAS reactor operating at 22.5 MW. Preliminary postirradiation examination results indicate that the uranium did not bond to the zirconium but that it did bond to the aluminum. The afore-mentioned out-of-reactor thermal tests had shown that a thin aluminum oxide layer prevented any interdiffusion between the uranium foil and the aluminum tube during a six-day test at 400°C [23]--a temperature substantially higher than expected to occur during irradiation of the target. It seems that radiation rendered the oxide layer ineffective and also enhanced interdiffusion, resulting in what appears to be a substantial conversion of uranium to UAl_3 . Various fixes are being considered, and we expect to perform another irradiation test in the near future. We are highly confident that a suitable target will be developed.

Processing of LEU Metal-Foil Targets Using the Cintichem Process

Substitution of LEU for HEU in the Cintichem process requires modifications of dissolution and processing steps. Modifications are necessary due to (1) the change of target design, (2) the greater amount of uranium required, (3) the oxidation state of uranium in the target, and (4) the greater amount of transuranic isotopes produced in LEU. The following describes our progress in modifying the process.

Dissolution of Metal Foil by Nitric/Sulfuric Acid Solutions

The irradiated LEU-metal foil target will be processed similarly to the current HEU- UO_2 target, using the Cintichem process to recover the ^{99}Mo product. However, some modifications are needed for the LEU targets, especially in the first step of dissolution by a solution of nitric

and sulfuric acids. The LEU target requires about three times more of the oxidant (i.e. nitric acid) than the HEU target because of the differences in the oxidation states of uranium in the targets, U(0) in LEU in contrast to U(IV) in HEU; both targets yield U(VI) in the solution. Moreover, the heat evolved during dissolution will be higher for the LEU case. We measured the heats of reaction and pressures to provide the necessary information for the design of a suitable dissolver vessel for processing LEU targets.

We carried out a systematic study of dissolution of depleted uranium-metal foil in solutions of nitric and sulfuric acids of various concentrations and at different temperatures. The rate of dissolution was found to be directly proportional to the acid concentrations and temperature. From these laboratory experiments, the dissolver cocktail composition was chosen to be a mixture of 3M nitric acid and 2M sulfuric acid, and the dissolution temperature was chosen to be ~90°C. Using this dissolver solution composition in an open system, an LEU-metal foil target of ~15 g can be dissolved in 65 mL of the acid mixture in about 100 minutes. The abundance of gaseous products released in the dissolution of depleted uranium metal in 3M nitric acid and 2M sulfuric acid mixture was measured, under different experimental conditions. These experiments showed that both NO and NO₂ are released.

Dissolver Tests for Uranium-Metal Foil

A stainless-steel dissolver was designed, built, and tested for 125- μ m-thick uranium foils with weights from 0.2 to 18 g. For the new dissolver the current Cintichem design was modified in such a way that existing jigs can be used for heating and rotating the dissolver. The modified design allows the uranium foil, which is contained inside the dissolver, to be dissolved quickly (~30 minutes), thereby minimizing the ⁹⁹Mo decay losses during this process step. Remote-handling features were incorporated into the modified dissolver, making it usable in a shielded-cell facility. As with the original design, this dissolver minimizes the amount of nitric and sulfuric acid used. This in turn minimizes the solution volume that must be processed to recover the ⁹⁹Mo from the uranium, fission products, and other materials. A mathematical relationship was developed to predict dissolution rates in the dissolver.

Future work on the dissolver includes (1) improving the model for the dissolution process, (2) determining the best orientation for the dissolver, (3) optimizing the dissolver for the amount of LEU to be charged to a production dissolver, and (4) identifying the best materials of construction for a production dissolver.

Processing of LEU Dissolver Solutions

During 1995, we studied the effects on irradiated target processing of modifying the dissolver solution. Experiments were done using tracers obtained by irradiating natural molybdenum and LEU in the University of Illinois TRIGA reactor. Analyses were developed to follow many fission products and ²³⁷Np by their gamma ray spectra.

Most of the effort has involved the primary step to recover and purify the ^{99}Mo by removing molybdenum, and little else, from the dissolver solution. The effects on yield and decontamination of ^{99}Mo have been measured as a function of the concentrations of nitric acid, sulfuric acid, and uranium in the dissolver solution. Means to increase the envelope of possible dissolver compositions have been developed. The recovery and decontamination of ^{99}Mo for various processing steps were measured, and the effects of LEU substitution in the Cintichem process were analyzed.

Demonstration of Cintichem Processing in Indonesia

Two mock demonstrations of the Cintichem process for LEU were run in Indonesia. Because the problems associated with the irradiated LEU target, a demonstration of the process using a spike from the dissolved irradiated LEU was not possible. However, an HEU spike was used for both demonstrations, one with a dissolver solution containing natural uranium and one from dissolving an 18-g DU foil in the ANL-designed dissolver. The mock demonstrations were done in a fume hood. Gamma ray analyses were performed on solutions from various stages of processing.

Dissolution of LEU Metal Foil by Alkaline Peroxide

Dissolution of uranium metal foil is a promising alternative to that of U_3Si_2 targets--eliminating the dissolution and process problems due to the presence of silicon. In this process, an irradiated LEU-metal-foil target is dissolved in sodium hydroxide/hydrogen peroxide solutions. Then, the molybdenum is separated and purified from the dissolved solution. During the past year our research has focused on the rate and mechanism of uranium-metal dissolution in the basic peroxide system. We have thoroughly investigated the effects of sodium hydroxide concentration, hydrogen peroxide concentration, and temperature on the rate of uranium dissolution. These kinetics studies will allow us to develop a mechanistic model for predicting the products and the rate of uranium dissolution under any process conditions.

Future work will develop means to (1) destroy peroxide remaining following the dissolution of the target, (2) remove the hydrated hydroxide precipitate containing uranium and insoluble fission products, and (3) recover molybdenum from the resultant solution.

FUTURE ACTIVITIES

Most of our work this year concentrated on the uranium-metal-foil target alternative to the Cintichem target and process. We expect to solve the uranium foil separation problem and perform several processing tests during this next year. We also expect to increase our effort on the dissolution and processing of U_3Si_2 targets in cooperation with one or more partners. We would also like to begin work on dissolution and processing of UO_2 pellet targets. One final initiative is related to the Babcock & Wilcox Medical Isotope Production Reactor (MIPR) [28].

We have requested funding from DOE to study a number of chemical processing issues in collaboration with the University of Virginia.

REFERENCES

- [1] J. Konrad, "Facilities for the Irradiation of ^{235}U for the Production of ^{99}Mo at the HFR Petten," Irradiation Technology, Proc. of the Int. Topical Mtg., Grenoble, France, pp. 677-683 (1982).
- [2] J. Salacz, "Production of Fission Mo-99, I-131 and Xe-133," Revue IRE Tijdschrift, Vol. 9, No. 3 (1985).
- [3] C. J. Fallais, A. Morel de Westgaver, L. Heeren, J. M. Baugnet, J. M. Gandolfo, and W. Boeykens, "Production of Radioisotopes with BR2 Facilities," BR2 Reactor Mtg., Mol, Belgium, INIS MF 4426, pp. IX-1 to -11 (1978).
- [4] A. A. Sameh and H. J. Ache, "Production Techniques of Fission Molybdenum-99", Radiochimica Acta 41, 65-72 (1987).
- [5] 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, pp. 23-33 (June 1989).
- [6] A. A. Sameh and H. J. Ache, "Production Techniques of Fission ^{99}Mo ," 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, pp. 47-64 (June 1989).
- [7] J. Salacz, "Processing of Irradiated ^{235}U for the Production of ^{99}Mo , ^{131}I , and ^{133}Xe Radioisotopes," 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, pp. 149-154 (June 1989).
- [8] A. A. Sameh and A. Bertram-Berg, "HEU and LEU MTR Fuel Elements as Target Materials for the Production of Fission Molybdenum," Proc. of 1992 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, Roskilde, Denmark, September 27 - October 1, 1992, ANL/RERTR/TM19, CONF-9209266, pp. 313-333 (July 1993).
- [9] H. Cols, P. R. Cristini, and R. O. Marques, "Preliminary Investigations on the Use of Uranium Silicide Targets for Fission Mo-99 Production," Proc. 1994 Int. Mtg. on

Reduced Enrichment for Research and Test Reactors, September 18-23, Williamsburg, Virginia, in preparation.

- [10] R. T. Jones, "AEC-2 Experiments in Support of ^{99}Mo Production in NRU," AECL-7335 (1982).
- [11] K. A. Burrell and R. J. Harrison, "Development of the ^{99}Mo Process at CRNL," 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, pp. 35-46 (June 1989).
- [12] H. Arino, H. H. Kramer, J. J. McGovern, and A. K. Thornton, "Production of High Purity Fission Product Molybdenum-99," U.S. Patent 3,799,883 (1974).
- [13] H. Arino, F. J. Cosolito, K. D. George, and A. K. Thornton, "Preparation of a Primary Target for the Production of Fission Products in a Nuclear Reactor," U.S. Patent 3,940,318 (1976).
- [14] G. F. Vandegrift, J. D. Kwok, S. L. Marshall, D. R. Vissers, and J. E. Matos, "Continuing Investigations for Technology Assessment of ^{99}Mo Production from LEU Targets," Proc. X Int. Mtg. on Reduced Enrichment for Research and Test Reactors (RERTR), September 28-October 2, 1987, Buenos Aires, Argentina (1990).
- [15] G. F. Vandegrift, J. D. Kwok, D. B. Chamberlain, J. C. Hoh, E. W. Streets, S. Vogler, H. R. Thresh, R. F. Domagala, T. C. Wiencek, and J. E. Matos, "Development of LEU Targets for ^{99}Mo Production and their Chemical Processing--Status 1989," Proc. XIIth Int. Mtg. on Reduced Enrichment for Research and Test Reactors, Berlin, September 10-14, 1989, pp. 421-433 (1991).
- [16] J. D. Kwok, G. F. Vandegrift, and J. E. Matos, "Processing of Low-Burnup LEU Silicide Targets," Proc. 1988 Int. Mtg. on Reduced Enrichment for Research and Test Reactors," September 18-24, 1988, San Diego, California, ANL/RERTR/TM-13, CONF-8809221, pp. 434-442 (July 1993).
- [17] G. F. Vandegrift, J. C. Hutter, B. Srinivasan, J. E. Matos, and J. L. Snelgrove, "Development of LEU Targets for ^{99}Mo Production and Their Chemical Processing Status 1993," Proc. 16th Int. Mtg. on Reduced Enrichment for Research and Test Reactors, October 4-7, 1993, Oarai, Japan, JAERI-M 94-042, pp. 394-400 (March 1994).
- [18] J. C. Hutter, B. Srinivasan, M. Vicek, and G. F. Vandegrift, "Production of Mo-99 Using Low-Enriched Uranium Silicide," Proc. 1994 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, September 18-23, Williamsburg, Virginia, in preparation.

- [19] B. A. Buchholz and G. F. Vandegrift, "Processing of LEU Targets for ^{99}Mo Production-- Dissolution of U_3Si_2 Targets by Alkaline Hydrogen Peroxide," these proceedings.
- [20] G. F. Vandegrift, D. J. Chaiko, R. R. Heinrich, E. T. Kucera, K. J. Jensen, D. S. Poa, R. Varma, and D. R. Vissers, "Preliminary Investigations for Technology Assessment of ^{99}Mo Production from LEU Targets," 1986 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, November 3-6, 1986, Gatlinburg, Tennessee, ANL/RERTR/TM-9, CONF-861185, pp. 64-79 (May 1988).
- [21] S. L. Marshall, L. Redey, D. R. Vissers, G. F. Vandegrift, and J. E. Matos, "Continuing Investigations on Electrochemical Preparation of LEU Targets for ^{99}Mo Production," Proc. 1988 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, September 18-24, 1988, San Diego, California, , ANL/RERTR/TM-13, CONF-8809221, pp. 443-450 (July 1993).
- [22] T. C. Wiencek and G. L. Hofman, "Development of Uranium Metal Targets for ^{99}Mo Production," Proc. 16th Int. Mtg. on Reduced Enrichment for Research and Test Reactors, October 4-7, 1993, Oarai, Japan, JAERI-M 94-042, pp. 385-393 (March 1994).
- [23] T. C. Wiencek, G. L. Hofman, E. L. Wood, C. T. Wu, and J. L. Snelgrove, "LEU ^{99}Mo Target Fabrication and Testing: Overview, Status, and Plans," Proc. 1994 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, September 18-23, Williamsburg, Virginia, in preparation.
- [24] B. Srinivasan, J. C. Hutter, G. K. Johnson, and G. F. Vandegrift, "Development of Dissolution Process for Metal Foil Target Containing Low Enriched Uranium," Proc. 1994 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, September 18-23, Williamsburg, Virginia, in preparation.
- [25] 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," these proceedings.
- [26] D. Wu, B. A. Buchholz, S. Landsberger, and G. F. Vandegrift, "Processing of LEU Targets for ^{99}Mo Production--Testing and Modification of the Cintichem Process," these proceedings.
- [27] Z. Aliluddin, A. Mutalib, A. Sukmana, Kardarisman, G. F. Vandegrift, D. Wu, B. Srinivasan, and J. L. Snelgrove, "Processing of LEU Targets for ^{99}Mo Production-- Demonstration of a Modified Cintichem Process," these proceedings.

[28] R. M. Ball, "Use of LEU in the Aqueous Homogeneous Medical Isotope Production Reactor," Proc. 1994 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, September 18-23, Williamsburg, Virginia, in preparation.