DEVELOPMENT AND PROCESSING OF LEU TARGETS FOR ^{99}Mo PRODUCTION*

J. L. Snelgrove, G. F. Vandegrift, and G. L. Hofman

Argonne National Laboratory
Argonne, Illinois U.S.A.

James L. Snelgrove
Coordinator for Engineering Applications, RERTR Program
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 207
Argonne, IL 60439-4841 U.S.A.
Phone: (630) 252-6369
Fax: (630) 252-5161
E-mail: jimsnelgrove@anl.gov

To Be Presented at the
1st International Topical Meeting on
Research Reactor Fuel Management (RRFM)

February 5-7, 1997
Bruges, Belgium

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

DEVELOPMENT AND PROCESSING OF LEU TARGETS FOR ^{99}Mo PRODUCTION

J. L. Snelgrove, G. F. Vandegrift, and G. L. Hofman

Argonne National Laboratory
Argonne, Illinois U.S.A.

INTRODUCTION

Technetium-99m, the daughter of ^{99}Mo, is the most commonly used medical radioisotope. 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. Reduced Enrichment for Research and Test Reactors (RERTR) program's goal of reducing world commerce in HEU is the development of means to produce ^{99}Mo using LEU.

Substituting LEU for HEU in targets for the production of fission-product ^{99}Mo requires changes in both target design and chemical processing. Three major challenges have been identified: (1) to modify targets and processing as little as possible, (2) to assure continued high yield and purity of the ^{99}Mo product, and (3) to limit economic disadvantage. Keeping the target geometry the same, thereby minimizing the effects of LEU substitution on target irradiation, necessitates modifying the form of uranium used. Changing the amount and form of the uranium in the target necessitates modifying at least one or, possibly, two target processing steps--dissolution and initial molybdenum recovery. Our progress in target and process development is summarized in this paper.

One of the issues always raised in connection with using LEU to produce ^{99}Mo is the effect on product purity of the ~30 times greater amount of ^{239}Pu generated through neutron capture by the ^{238}U of an LEU target yielding the same amount of ^{99}Mo as the HEU target it replaces. However, because significantly more ^{234}U is present in HEU than in LEU as a consequence of the enrichment process, total alpha contamination of an irradiated LEU target is less than 20% higher than that of an equivalent HEU target.

TARGET DEVELOPMENT AND TESTING

One way to categorize the world's ^{99}Mo-production is by the type of target used. We know of only one producer of fission product molybdenum that does not use an HEU target--the Australian Nuclear Science and Technology Organization (ANSTO); their target consists of slightly enriched UO_2 pellets. Targets for the production of ^{99}Mo from HEU are generally either (1) miniature Al-clad fuel plates containing U-Al alloy or UAl_x dispersion fuel [Argentine National Atomic Energy Commission (CNEA), the Atomic Energy Corporation of South Africa Limited (South African AEC), National Institute of Radioelements (IRE) of Belgium, and Mallinckrodt in the Netherlands] [1-9], (2) pins containing U-Al alloy [Atomic Energy of Canada, Limited (AECL)] [10,11], or (3) a thin film of UO_2 coated on the inside of a stainless steel tube [the National Atomic Energy Agency (BATAN) of Indonesia, and, in the near future, the U.S. Department of Energy's Sandia National Laboratories (SNL)]. Use of an electrodeposited UO_2 layer on the inner surface of a stainless steel cylinder, which is used as both a target and a dissolver, is part of the so-called Cintichem process developed by Union Carbide [12,13].

Research Reactor Fuel-Type Targets

The first two types of targets listed above, U-Al alloy and UAl_x dispersion, are the fuels which were being used in the reactors at the time ^{99}Mo production was begun. These targets are miniature versions of the reactor fuel plates or pins and are fabricated in the same manner by "commercial" fuel fabricators. The U_3Si_2-Al dispersion fuel already developed for reactor conversion by the RERTR program [14] offers, from the fabrication and irradiation performance points of view, a suitable high-density alternative for the research 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 other fuel materials are also being considered, e.g., UO_2 dispersed in aluminum and the uranium-metal foils discussed below.

Replacement for Cintichem Targets

The UO_2-coated target was used in the U.S. by Cintichem until 1989, when a reactor problem forced a halt in production. As mentioned above, this process is currently being used in Indonesia by BATAN. During the late 1980s we had shown that the UO_2 coating thickness could not be increased nearly enough to produce an LEU target with an equivalent ^{235}U content, and we had begun to develop electrodeposited metallic uranium targets [15]. However, since we were seeking a target which could be fabricated in developing countries using "low-tech" methods, we have developed a concept using uranium metal foils [16,17]. We have concentrated on the design illustrated in Fig. 1, where a thin (125-μm-thick) uranium metal foil is sandwiched between slightly tapered inner and outer tubes. In our preferred design the inner tube is made of a material with a larger thermal expansion coefficient than that of the outer tube material in order for differential thermal expansion to assist in maintaining good thermal contact between the foil and the tubes. The taper and the greater shrinking of the inner tube upon cooling after irradiation facilitate disassembly. We would like to separate the irradiated foil from the tubes, so that only the foil need be dissolved to recover the molybdenum, thereby minimizing waste volume. Thin oxide layers were produced on the inner and outer tubes to serve as diffusion barriers to inhibit diffusion bonding of the uranium to the tubes. Several targets of this type have been irradiated in the Indonesian RSG-GAS reactor operating at 22.5 MW, and postirradiation examinations have been performed in the adjacent BATAN hot.cell facility, under a cooperative research agreement between BATAN and Argonne National Laboratory.

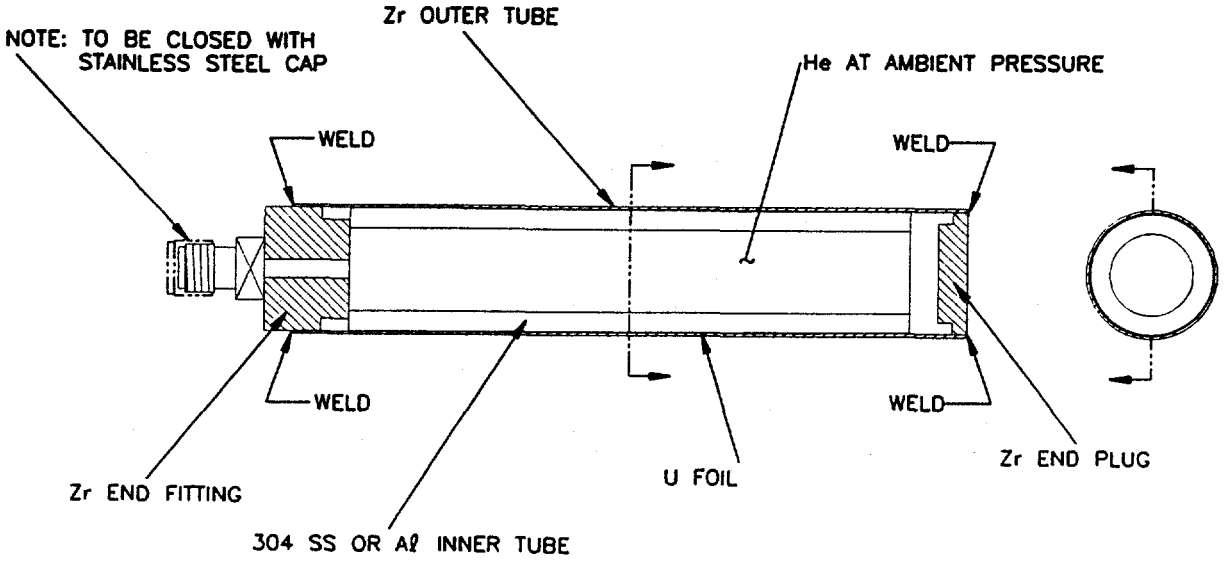

Fig. 1. Drawing of U-Metal Foil Target Being Tested in Indonesia

One such target, with a zirconium outer tube and an aluminum inner tube, was irradiated and examined during the summer of 1995. In spite of a thin aluminum oxide barrier between the uranium foil and the inner tube, which had proven to be sufficient to prevent reaction during thermal testing at elevated temperature, the uranium reacted with the aluminum during irradiation and could not be removed from the inner tube. Metallography showed no apparent interaction of the uranium with the zirconium outer tube, on which a thin zirconium oxide barrier had been placed. Therefore, we assumed that zirconium was a suitable target tube material.

Three additional test targets were irradiated between November 1995 and March 1996 to explore different materials for the inner tube of the target. In one we coated the aluminum with zirconium by flame spraying, thereby retaining all the features of the first design while adding a zirconium layer between the uranium and aluminum to prevent interaction. In a second target the inner tube was made from magnesium, which also has a larger expansion coefficient than zirconium but forms no compounds with uranium. The third target had a zirconium inner tube. Obviously, the thermal expansion difference feature was not present in this combination; however, we believed that adequate thermal contact was assured by the assembly process with the tapered tubes. This test was added to verify the apparent nonbonding of uranium foil and zirconium.

Postirradiation examinations performed during April and May of 1996 showed that the uranium foil was bonded to the inner tube of each of these targets also. The tentative explanation is that the high fission rate in the uranium and correspondingly high recoil atom flux at the uranium-target tube interface leads to an efficient atomic intermixing at the interface. It appears that bonding by this mechanism will occur with any material.

Based on the experience gained thus far, a third set of irradiations was performed during August 1996. We irradiated four targets to test two basic concepts:

1. The inner tube material was changed to austenitic stainless steel. This material was chosen because it will not dissolve in the acid used to dissolve the uranium and because its use will retain the thermal expansion difference feature since 300 series stainless steel has 2 to 2.5 times the expansion coefficient of zirconium. We expected the uranium foil to bond to the stainless steel inner tube and to be pulled loose from the zirconium outer tube during cooling and disassembly (as was the case for the targets with aluminum and magnesium inner tubes), so that the uranium could be dissolved off the inner tube by placing the entire inner tube into the dissolver. However, the inner tube and foil could not be extracted from the outer tube, indicating some amount of bonding of the uranium foil to the zirconium outer tube.

2. Thin recoil-absorbing barrier foils of ~10-μm thickness were placed between the uranium and one or both target tubes. We expected these barrier foils to bond to the uranium by recoil mixing but not to the target tubes, since the fission fragments will not penetrate the barrier. Since the barrier foils must be dissolved with the uranium foil, only certain materials such as nickel, copper, iron, and zinc are allowed. We tested both nickel and copper. In one target an aluminum tube with unoxidized surfaces was used, and nickel foils were placed on both sides of the uranium foil. The inner tube with foils was easily extractable, but the foils could not be removed, indicating bonding, presumably by diffusion, of the nickel to the aluminum. We think that introduction of an aluminum oxide layer will prevent such bonding. The other two targets used a stainless steel inner tube. In one a nickel barrier foil was introduced only between the uranium and the zirconium outer tube. The inner tube with foils was easily extractable, and, as expected, the uranium bonded to the inner tube. The uranium and nickel could be dissolved as described above. The final target contained copper barrier foils were placed on both sides of the uranium foil. The inner tube with foils was easily extractable, and the foil sandwich was easily removed from the inner tube.

The latter two targets demonstrated the viability of the fission-fragment barrier concept. We will proceed now to optimize the target. We will be studying the use of aluminum or other low-

neutron-absorbing materials for the inner tube in order to decrease the reactivity penalty of the target, minimizing the thicknesses of the target tubes in order to minimize waste, and deposition of barrier materials rather than using foils in order to minimize fabrication costs.

CHEMICAL PROCESSING DEVELOPMENT AND TESTING

Processing of irradiated uranium targets for ^{99}Mo can be divided into two broad areas by the target dissolution method. Acid dissolution is currently practiced by AECL, BATAN, and SNL. Dissolution by strong base is practiced by the CNEA, South African AEC, IRE, and Mallinckrodt.

Processing LEU Targets Using Strong Base

The ^{99}Mo is extracted from the current HEU targets by first dissolving the entire Al-clad fuel plate and then performing a series of extraction and purification steps. As discussed previously, we have pursued the substitution of LEU for HEU in plate-type targets by the use of U_3Si_2 dispersed in aluminum. However, the U_3Si_2 is far more difficult to dissolve, and the silicon in the target complicates molybdenum recovery steps. Our development has been centered on this dissolution step [18,19].

We have developed a two-step process for dissolving the target to recover the ^{99}Mo. The first step is dissolving the aluminum-alloy cladding and the matrix aluminum by a solution of NaOH and $NaNO_3$. The second step is U_3Si_2 dissolution by NaOH and hydrogen peroxide. Enough ^{99}Mo is lost to the matrix by fission recoil that it must be recovered from both solutions. We foresee dissolution being carried out in a plug flow reactor and have developed a model for predicting the rate of dissolution under a variety of conditions. This model is being used to design a dissolver. Once dissolution is developed, we will turn to optimizing ^{99}Mo recovery from the dissolver solution. Because U(VI) precipitates from the dissolver solution, only the effects of silicate on the primary recovery step must be analyzed. We must also assure that decontamination from plutonium is sufficient to meet product purity requirements. Future work on this process will concentrate on developing improved mechanical means to break up the fuel meat wafer and, perhaps, more powerful dissolution agents. We may also decide to abandon research in this area and concentrate on metal foil targets, as discussed below.

Because of the difficulties associated with dissolving and processing the uranium silicide targets, we have also pursued an alternative--alkaline-peroxide dissolution of an LEU metal-foil target [19]. Although the target design would need to be altered from that currently used with reactor-type fuels, the uranium metal foil can be dissolved using alkaline hydrogen peroxide in a manner similar to that used for the U_3Si_2 fuel plates. Use of the uranium metal foil eliminates the problems associated with silicon. We have also modeled the dissolution of this material and are currently in the process of designing a dissolver for it. We have completed a preliminary study of possible fission-fragment barrier materials and have selected zinc for further study.

Modified Cintichem Processing of LEU-Metal Targets

To replace the HEU-oxide target, we are also planning to use an LEU foil target. The LEU foil can be dissolved using a cocktail of HNO_3 and H_2SO_4, much like that now being used to dissolve the HEU oxide [20,21]. We have recently developed the dissolution using nitric acid alone. This innovation should significantly improve waste treatment and disposal over that currently used. The products of the nitric-acid dissolution of UO_2 and uranium metal are the same: UO_2^{2+}, NO gas, and water. However, because (1) dissolution of uranium metal requires a six-electron oxidation rather than a two-electron oxidation for UO_2 and (2) approximately five times more uranium is required for an LEU target, considerably more gas is formed during LEU target dissolution. Also, the LEU foil will be removed from the target following irradiation for dissolution in separate piece of equipment. Design of a closed dissolver system, which includes off-gas collection, is part of our conversion development.

The principal recovery and decontamination step of the Cintichem process is precipitation of molybdenum from the spent dissolver solution by α-benzoin oxime. This is a standard analytical method for molybdenum and, therefore, has essentially 100% Mo recovery and a molybdenum precipitate with very little impurities. Results from tracer demonstrations run at the University of Illinois at Urbana/Champaign (UIUC) and in Indonesia have shown that the additional uranium mass and the higher concentration of ^{239}Pu in the irradiated target should not affect product purity. With the exception of ^{103}Ru, the purity requirements for gamma-emitting isotopes in the ^{99}Mo product, <0.1μCi/mCi-^{99}Mo, are easily met for the LEU process. The alpha contamination level of $<10^{-7}$ μCi/mCi-^{99}Mo was also met in tracer-level experiments. Table 1 shows typical decontamination factors for the recovery and two proprietary purification steps. In addition, we have shown that the introduction of the barrier materials does not interfere with molybdenum recovery and that they should be adequately removed without further changes to the process.

Both the dissolution and processing of uranium-metal foils have been developed to the point of demonstration using slightly irradiated LEU targets [22-24]. We are planning a full-scale demonstration in Indonesia early in 1997.

Table 1. Decontamination of the ^{99}Mo Product During Tracer-Level Demonstration of Modified Cintichem Processing of an LEU-Metal Target

Nuclide	Predicted Activity[a] (Ci)	DF Values			Impurity Level μCi/mCi-^{99}Mo
		a-BO Ppt.[b]	Purification 1	Purification 2	
Ba-140	292	>516	>162	>165	<3.6E-05
Ce-141	121	>1116	328	419	<1.3E-06
Ce-143	685	>3354	313	641	<1.7E-06
I-131	186	51	28	41	5.3E-03
I-133	628	91	36	51	6.3E-03
I-135	104	121	38	43	8.8E-04
La-140	224	>2409	>104	>149	<1.0E-05
Mo-99	697	1.04	1.05	1.08	---
Nb-95	4.7	4	>13	>9.5	<1.6E-02
Nb/Zr-97	480	11	56	1410	9.2E-04
Nd-147	119	208	>62	>59	<2.6E-04
Np-239	1610	>1770	>247	>333	<1.9E-05
Pm-151	45	103	>16	>22	<2.1E-03
Rh-105	102	>276	>34	>46	<4.0E-04
Ru-103	54	113	1.3	3.7	1.7E-01
Sb-127	13.6	>41	1.3	>10.0	<4.3E-02
Sr-89[c]	65.7	-	-	-	<2.3E-07
Sr-90[c]	0.39	-	-	-	<1.4E-09
Sr-91	209	>3452	235	>586	<7.4E-07
Sr-92	2.65	>2101	>71	>63	<4.7E-07
Te-132	464	>5083	327	657	<7.1E-07
Zr-95	70	13	27	>49	<6.8E-03
Zr-97	447	17	23	>41	<4.6E-02

[a]Predicted from an ORIGEN2 code calculation for an 18-g target 24-hours after removal from the Indonesian RSG-GAS reactor following a 120-h irradiation at full power.

[b]α-benzoin oxime precipitation.

[c]Predicted from Sr-91 behavior.

SUMMARY AND CONCLUSIONS

We have made significant progress in developing targets and chemical processes for the production of ^{99}Mo using LEU. Target development has been concentrated on a uranium-metal foil target as a replacement for the coated-UO_2 Cintichem-type target. Although the first designs were not successful because of ion mixing-induced bonding of the uranium foil to the target tubes, recent irradiations of modified targets have proven successful. We have shown that only minor modifications of the Cintichem chemical process are required for the uranium-metal foil targets. A demonstration using prototypically irradiated targets is anticipated by the end of 1996. Progress has also been made in basic dissolution of both uranium-metal foil and aluminum-clad U_3Si_2 dispersion fuel targets, and work in this area is also continuing.

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 235U 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, Williamsburg, Virginia, September 18-23, 1994, ANL/RERTR/TM-20, in preparation.

[10] R. T. Jones, "AEC-2 Experiments in Support of ^{99}Mo Production in NRU," AECL-7335 (1982).

[11] K. A. Burril 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] U.S. Nuclear Regulatory Commission, "Safety Evaluation Report Related to the Evaluation of Low-Enriched Uranium Silicide-Aluminum Dispersion Fuel for Use in Non-Power Reactors," NUREG-1313 (July 1988).

[15] 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, San Diego, California, September 18-24, 1988, ANL/RERTR/TM-13, CONF-8809221, pp. 443-450 (July 1993).

[16] 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 International Meeting on Reduced Enrichment for Research and Test Reactors, September 18-23, 1994, Williamsburg, Virginia, ANL/RERTR/TM-20, in press.

[17] G. L. Hofman, T. C. Wiencek, E. L. Wood, and J. L. Snelgrove, "Irradiation Tests of ^{99}Mo Isotope Production Employing Uranium Metal Foils," paper presented at the 19th International Meeting on Reduced Enrichment for Research and Test Reactors, October 6-10, 1996, Seoul, Korea.

[18] 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," Proceedings of the XVIII Reduced Enrichment for Research and Test Reactors International Meeting, Paris, France, September 17-21, 1995, paper no. 3-6 (May 1996).

[19] D. Wu, S. Landsberger, and G. F. Vandegrift, "Progress in Chemical Treatment of LEU Targets by the Modified Cintichem Process," paper presented at the 19th International Meeting on Reduced Enrichment for Research and Test Reactors, October 6-10, 1996, Seoul, Korea.

[20] 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 Reduced Enrichment for Research and Test Reactors International Meeting, Paris, France, September 17-21, 1995, paper no. 3-2 (May 1996).

[21] L. Chen, D. Dong, B. A. Buchholz, and G. F. Vandegrift, "Progress in Alkaline Peroxide Dissolution of Low-Enriched Uranium Metal and Silicide Targets," paper presented at the 19th International Meeting on Reduced Enrichment for Research and Test Reactors, October 6-10, 1996, Seoul, Korea.

[22] 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," Proceedings of the XVIII Reduced Enrichment for Research and Test Reactors International Meeting, Paris, France, September 17-21, 1995, paper no. 3-3 (May 1996).

[23] 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," Proceedings of the XVIII Reduced Enrichment for Research and Test Reactors International Meeting, Paris, France, September 17-21, 1995, paper no. 3-4 (May 1996).

[24] D. Wu, S. Landsberger, and G. F. Vandegrift, "Application of Neutron Activation Analysis in a Fission Molybdenum Separation Study," *J. Radioanal Nucl. Chem*, accepted for publication.