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PROGRESS IN CONVERTING ^{99}Mo PRODUCTION FROM HIGH- TO LOW-ENRICHED URANIUM--1999*

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ABSTRACT

Over this past year, extraordinary progress has been made in executing our charter to assist in converting Mo-99 production worldwide from HEU to LEU. Building on the successful development of the experimental LEU-foil target, we have designed a new, economical irradiation target. We have also successfully demonstrated, in collaboration with BATAN in Indonesia, that LEU can be substituted for HEU in the Cintichem target without loss of product yield or purity; in fact, conversion may make economic sense. We are interacting with a number of commercial producers--we have begun active collaborations with the CNEA and ANSTO; we are working to define the scope of collaborations with MDS Nordion and Mallinckrodt; and IRE has offered its services to irradiate and test a target at the appropriate time. Conversion of the CNEA process is on schedule. Other papers presented at this meeting will present specific results on the demonstration of the LEU-modified Cintichem process, the development of the new target, and progress in converting the CNEA process.

INTRODUCTION

In mid-1993, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) program embarked on a major effort to develop targets and associated chemical processing to produce fission-product ^{99}Mo using low-enriched uranium (LEU) in response to an amendment passed by the U.S. Congress in October 1992 to the Atomic Energy Act of 1954. This amendment prohibits export of HEU for use as a fuel or target in research or test reactors unless several conditions are met: (1) no alternative low-enriched uranium (LEU) fuel or target can be used, (2) the U.S. is actively developing an LEU fuel or target for that reactor, and (3) the proposed recipient of the HEU provides assurances that, whenever possible, an LEU fuel or target will be used in that reactor.

Our progress has been reported at each of the last six RERTR International meetings. In addition, our past work through spring of 1998 has been summarized in a recent IAEA TECDOC [1]. When we met one year ago, we had developed an LEU-metal-foil target and had demonstrated its viability in collaboration with the Indonesian National Nuclear Energy Agency (BATAN) that began in November 1994. Through that collaboration, we had also developed and tested a modified Cintichem (acid-dissolution) process for the LEU foils. A collaboration agreement had been signed in December 1996 with the Korea Atomic Energy Research Institute (KAERI), although no joint work had begun. We also reported that we were discussing

additional collaborations with the Argentine National Atomic Energy Commission (CNEA) to address alkaline processing and with the Australian Nuclear Science and Technology Organisation (ANSTO) to address issues of target design and acid processing.

International cooperation is important to the success of our efforts for at least two reasons. First, producing ^{99}Mo is becoming a rather widespread international activity, as shown in Table 1—and this table lists only those current or potential producers with whom we have held discussions about collaboration. Second, currently there is no facility in the U.S. suitable for ^{99}Mo target and process testing—we are dependent on our international colleagues. We have made extraordinary progress this year in developing relationships with partners and, through these collaborations, in advancing the technical aspects of the program.

This paper contains an overview of our significant progress during the past year. Three additional papers presented at this meeting will discuss our process demonstration activities with the BATAN [2], development and testing of an improved, economic LEU-foil target [3], and progress in developing an LEU alternative for the CNEA [4].

OVERVIEW OF TECHNICAL PROGRESS

During this year, our emphasis in target development has shifted from developing and proving a target concept to developing a commercially viable target. The design work has been carried out at ANL, and the testing has been carried out in Indonesia. Our collaborations with ANSTO and the CNEA will afford additional opportunities to refine target design and perform irradiation tests. Our work with BATAN on a modified Cintichem process has moved to the demonstration phase, while our development focus has shifted to alkaline-digestion processes in collaboration with the CNEA. In the following, we will summarize the results of our work with our three active partners this past year.

BATAN

BATAN personnel performed two series of target irradiations and processing during the past year—one set in March and the other during August/September 1999. The second series of targets were of the new, improved design discussed in another paper in this session [3]. Details of the process demonstration are discussed separately [2]. Overall, this collaboration has been highly successful, and the capability of the Indonesians to irradiate new target designs and test changes to their ^{99}Mo recovery and purification procedure has led to our swift progress. We are particularly indebted to the Indonesians' willingness to allow us to broaden the scope of our tests to include fission-recoil barriers compatible with alkaline digestion.

During March 1999, eight targets of the design described in earlier meetings [1,5,6] were irradiated in the RSG-GAS reactor for ~120 hours at 15 MW reactor power. Most of the targets were produced for testing target performance, but two targets were processed for ^{99}Mo recovery. Table 2 describes each target and summarizes its behavior during irradiation and disassembly. Several parameters were tested during this series, including:

- Materials used for target inner and outer walls (304 stainless steel (SS), type-702 zirconium, or anodized type-1100 aluminum)

Table 1. Summary of the RERTR Program's Interactions with Producers and Potential Producers of ^{99}Mo

Organization	Country	Status		
		^{99}Mo Production	Conversion	Form of Cooperation
BATAN	Indonesia	HEU-oxide Cintichem targets	Plans to convert	Ongoing technical cooperation; irradiating and processing LEU targets
CNEA	Argentina	HEU/Al alloy plates	Plans to convert within 3 years	3-year R&D plan actively underway to meet goal
ANSTO[a]	Australia	Currently are using 2.2%-enriched UO_2 pellets	Are evaluating 19.75%-enriched metal-foil targets to increase productivity	Active cooperation with the RERTR program with emphasis on development and testing of LEU-metal-foil targets
SNL[b]	USA	HEU-oxide Cintichem targets. Start of production on hold	ANL plans to test LEU once HEU production is underway	Active cooperation for conversion awaits funding for SNL production
IRE[c]	Belgium	HEU-aluminide dispersion plates	Have expressed interest in converting when target technology is proven	Have expressed willingness to irradiate and process LEU targets
MDS Nordion/ AECL[d]	Canada	Currently, HEU/Al alloy rods. Plans to convert to HEU oxide targets	Have expressed a willingness to convert if economics are positive	Developing scope of cooperation
Mallinckrodt	Netherlands	HEU-aluminide dispersion plates	Have expressed interest in conversion	Discussions are in progress to define cooperative activity
AEC[e]	South Africa	HEU/Al alloy plates	Have expressed willingness to evaluate the possibility of conversion	Preliminary discussions have been held
KAERI[f]	South Korea	Studying various production options and facility needs	Evaluating Mo production technology using LEU	A cooperative agreement with the ANL RERTR program is in place with emphasis on LEU target development

[a] Australian Nuclear Science and Technology Organisation
[b] Sandia National Laboratories
[c] Institut National des Radioéléments
[d] Atomic Energy of Canada Limited
[e] Atomic Energy Corporation of South Africa Limited
[f] Korean Atomic Energy Research Institute

Table 2. Description and Behavior of LEU-Foil Targets Irradiated during March 1999 in the BATAN RGS-GAS Reactor

Target	Description			Disassembly Performance	Notes
	Outer Tube	Inner Tube	Barrier/ Uranium[a]		
1-A	Zr	SS	Ni/*A*	Good	Inner tube was relatively easy to extract. Foil was not brittle and easily handled.
1-B	Zr	SS	Ni/*P*	Good	Inner tube was relatively easy to extract; the differential thermal expansion of the SS inner tube vs. the Zr outer tube seemed to constrain the growth of the pure U foil in this target. However, there were some obvious changes in the surface texture of the foil.
2-A	Al	Al	Ni/*P*	Good	Inner tube was relatively easy to extract. Some changes in the surface texture of the foil were evident. (Target irradiated for only 7 hours.[b])
2-B	Al	Al	Al/*P*	Good	Inner tube was relatively easy to extract. Some changes in the surface texture of the foil were evident. (Target irradiated for only 7 hours.[b])
3-A	Zr	SS	Zn/*A*	Good	Inner tube was relatively easy to extract. Foil was slightly brittle but much less so than Zn-plated foils from previous irradiations. Removal of entrapped hydrogen gas following electroplating seemed to work.
3-B	Zr	SS	Zn/*P*	Good	Inner tube was relatively easy to extract; the differential thermal expansion of the inner vs. outer tube seemed to constrain the growth of the pure-U foil. However, some obvious changes in the surface texture of the foil were noted. This foil was plated using a $ZnCl_2$ bath and seemed to perform well. However, absolute performance was difficult to determine because of grain growth in the pure-U foil.
4-A	Zr	Zr	Ni/*P*	Moderate	Inner tube was relatively easy to extract but the foil was stuck to outer tube. During cutting the target longitudinally, the foil came free of the outer tube. Some changes in the surface texture of the U foil were evident.
4-B	Zr	Zr	Al/*P*	Not Attempted	A white teardrop-shaped spot was observed on the target's outer wall following irradiation. Target was cut longitudinally without trying to push out the inner tube to facilitate examination of the spot. The U foil near the spot had been completely consumed (as if it had melted). The remainder of the foil was recovered in small pieces; parts of it were stuck to the inner tube or outer tube.

[a] *A* = Adjusted with 450 ppm iron and 1000 ppm aluminum or *P* = pure

[b] Examination of the white spot detected on target 4-B, which was removed from the reactor at the same time these targets began their irradiation, caused us to pull these targets from the reactor before they had their full 120-hour irradiation.

- Fission-barrier material (electroplated nickel, zinc electroplated from either a sodium zincate or zinc chloride bath, or aluminum-foil wrapped)
- Composition of uranium (pure or adjusted with 450 ppm iron and 1000 ppm of aluminum)

We learned the following during test target fabrication:

- Avoid anodizing aluminum parts near weld joints. The oxide layer makes it difficult to produce a gas-tight weld.
- The tapered-target design is very difficult to assemble properly. It is also difficult to know if it was assembled properly. It is impossible to tell if the fission-recoil barriers were damaged during assembly (see irradiation results below). Also, the tolerances on the target tubes and foils must be very tight in order for these parts to fit together properly. Deviations from specification as small as 20 μm in the target-tube tapered diameter or in the foil thickness can make it impossible to properly assemble the target.
- Type-1100 aluminum is not a good alloy choice. It was chosen because it can be fusion welded (i.e., no filler rod) to a gas-tight condition. However, the alloy is extremely soft, which makes it very easy to scratch and nick the surfaces. Also, its softness made it far too easy to strip threaded parts during assembly.

We learned the following during irradiation and disassembly of the test targets:

- It appears that one of the aluminum-foil barriers (target #4B) tore during target assembly. This target showed a very pronounced white spot (~ 3-cm teardrop shape) on the outside of the zirconium cladding when it was withdrawn from the reactor. Later examination of this target showed that the uranium foil had completely reacted with aluminum barrier material in this spot. It is hypothesized that a rip in the aluminum-foil barrier caused the uranium foil not to be in contact with the cladding at that spot, owing to the galling of the torn aluminum foil. Without sufficient heat removal, the uranium foil in that area heated up and then reacted exothermically with the galled-up aluminum foil. When the galled-up aluminum foil was consumed, the uranium foil obtained good thermal contact with the target walls, and the reaction stopped.
- Adjusted uranium should be used instead of pure uranium. Even after being given a beta-quench heat treatment to get the proper grain size and orientation [7], pure uranium behaved poorly. The pure-uranium foils underwent extensive dimensional changes during irradiation.
- The adjusted-uranium foils that had been zinc- or nickel-plated performed very well. Following past irradiations, zinc-plated foils were extremely friable. We surmised this owed to the low plating-efficiency of the sodium zincate bath that led to hydrogen-gas entrapment inside the zinc barrier. This in turn led to embrittlement of the uranium foil during irradiation. We developed two means to solve this problem. The first was to change the plating solution to $ZnCl_2$. The plating efficiency from this solution is considerably higher, >90%. The second means was to heat the zinc-plated foil from the sodium zincate bath at 150-175°C for two hours in a slow-flowing stream of 99.999+%

argon. Although both methods greatly improved the behavior of the foils, they were still a little more brittle than their nickel-plated counterparts.

Owing to the recognized potential poor performance during irradiation of pure uranium and to our not having yet understood the cause of the problem encountered with target #4B, we decided to remove the two aluminum-clad targets (#2A and #2B) from the reactor after just 7 h of irradiation. We were concerned that the growth of the pure uranium foil in these targets could cause a fuel breach if they were irradiated for the complete 120 hours. Consequently, we learned little about the performance of aluminum target tubes from these tests.

Lessons learned from this and earlier irradiations were incorporated into the design of our new target tubes. With the information gained from tests of nickel, zinc, and aluminum fission-recoil barriers, we feel confident that the new targets can be used for both acid-based and alkaline-based processes.

Foils from two of these targets (#1A and #3A) were successfully processed for ^{99}Mo recovery. Based on our process-demonstration work in Indonesia, we can make several positive statements concerning the conversion of the Cintichem process to LEU. Conversion to LEU targets will:

- Increase the ^{99}Mo yield per target by increasing ^{235}U loading in the target, thus decreasing the number of targets that need to be irradiated and processed to meet commitments.
- Decrease target fabrication and irradiation costs by use of easily fabricated LEU-foil aluminum annular-tube targets. Although target fabrication itself is easy and assuredly will be economical, we must also show that uranium foils can be produced economically. During the past year we have held discussions with several potential vendors of uranium foils. We are preparing a specification for uranium foils, and soon we will issue a request for proposals to produce LEU-metal foils for use in targets for testing in collaboration with several partners.
- Provide a higher yield of ^{99}Mo owing to a decrease of 1.5 to 2.0 hours in the processing time and potentially higher processing efficiency.
- Cut waste treatment and disposal costs by the combination of less targets processed, less liquid waste per target, and elimination of sulfuric acid.
- Eliminate safeguards concerns of storage and disposal of HEU.

Future activities will include further irradiations and processing demonstrations, eventually leading to a decision on conversion to LEU.

CNEA

ANL and CNEA have agreed on the scope and schedule of our cooperation to develop a target and processing to the point that CNEA could convert to LEU in three years. Currently, CNEA produces ^{99}Mo by alkaline digestion of small uranium-aluminum alloy fuel plates. Jointly we are investigating the feasibility of an interim solution based on substitution of more-highly loaded uranium aluminide dispersion fuel plates, as well as the longer-term solution using LEU-metal foils. It is through this cooperation that we plan to demonstrate the feasibility of the uranium-

metal-foil targets for conversion of alkaline-based processes. Tasks to be performed during 1999 are:

- Defining loading and geometry of LEU targets and geometry of the irradiation rig.
- Defining target fabrication techniques (metal-foil cylindrical targets and high-density LEU/Al dispersion plates).
- Developing LEU-foil alkaline-digestion procedure.
- Studying effects on the initial molybdenum-recovery step of the presence of zinc (and/or any other component changes) owing to LEU-target conversion.

Both partners began work immediately after the collaboration agreement was signed in February of this year. Thus far, no serious problems have been identified for the processing of the uranium-metal foils. As discussed previously, the viability of annular targets has already been demonstrated in Indonesia. The schedule calls for the first LEU-foil-target irradiation to be performed in the first quarter of 2000, and the first of a series of entire LEU process demonstration will be performed in the second quarter of 2001. At the CNEA, dimensions have been defined for an annular target that will meet transport requirements, and an irradiation rig is being designed. Results of activities performed by ANL are presented separately [4].

The Argentines are considering major changes to their current process to take full economic advantage of their conversion to LEU. Such changes will necessitate a revision of our joint tasks and schedule. Nevertheless, the CNEA has agreed to continue far enough down our current path to demonstrate the viability of using LEU-metal-foil targets with small modifications to their current process.

ANSTO

Our active cooperation with ANSTO began officially in April 1999. With plans for a replacement reactor and increasing ^{99}Mo sales, ANSTO saw this as a perfect time to assess their current target (2.2%-enriched UO_2 pellets) and (acid) process. Having become aware of our success using 19.75%-enriched metal-foil targets and their dissolution in nitric acid under pressure, ANSTO approached the RERTR program about cooperating. For our part, having another reactor in which to test our targets and another research and production organization helping us to improve, test, and evaluate these targets offered an attractive opportunity. Thus far, ANSTO has developed some preliminary target designs and done thermal-hydraulic calculations for targets to be irradiated in HIFAR. ANL has provided advice on targets and processing based on our experience. The schedule calls for irradiation of test targets in HIFAR beginning in mid-2000 after completion of an extended HIFAR maintenance shutdown. Demonstration of a viable HIFAR target and process is scheduled for completion at the end of June 2002. It is envisioned that design of a target for ANSTO's replacement reactor will also be jointly undertaken.

PROGRESS IN DEVELOPING FURTHER COLLABORATIONS

As noted in Table 1, we have had contact with a number of other present or aspiring producers. Our activities with these organizations are briefly discussed below.

SNL

For several years, the U.S. Department of Energy (DOE) has been engaged in a project to set up and operate a ^{99}Mo production facility at SNL in Albuquerque, NM, using the Cintichem process with HEU targets. Approximately two years ago we reached an informal agreement with SNL and DOE to collaborate to obtain FDA approval for ^{99}Mo produced using LEU-metal-foil targets and the modified Cintichem process we have been developing with the help of BATAN. Completion of the facility at SNL and beginning of production has been put on hold pending identification of a private entity to take over the work from DOE. We plan to renew our pursuit of a formal collaboration with SNL if the project is restarted.

IRE

During discussions more than one year ago, IRE offered to irradiate and process an LEU target when we were ready for that step. Our successful development of the new annular uranium-metal-foil target has brought that time much closer.

MDS Nordion/AECL

Last October, MDS Nordion initiated discussions with the RERTR program on assessing the feasibility of converting to the use of LEU targets in the new MDS Nordion reactors and production facility under construction at the AECL site at Chalk River. Confidentiality (or nondisclosure) agreements were signed with both MDS Nordion and AECL, and discussions were held in November and January. We agreed to perform a brief (paper) feasibility study to address the key issues of dissolving approximately five times as much LEU oxide as HEU oxide and the effect of the greater amount of uranium on the first molybdenum separation step. In order to avoid some problems related to intellectual property, MDS Nordion and AECL subsequently decided that AECL should perform this initial study. The results of the initial study should be available soon, after which discussions will be held on further joint activities.

Mallinckrodt

Mallinckrodt, through its Mallinckrodt Medical subsidiary in the Netherlands, produces ^{99}Mo at Petten. Several months ago, we were approached by Mallinckrodt to begin discussions about converting to LEU. A meeting is scheduled at Petten on September 30 to discuss collaboration.

AEC

The South African AEC is producing a significant amount of ^{99}Mo using small 45%-enriched uranium-aluminum fuel plates irradiated in the SAFARI-I reactor. Very preliminary discussions have been initiated about possible conversion of ^{99}Mo production to LEU within the broader context of conversion of the SARARI fuel to LEU.

KAERI

KAERI has been studying the possibility of producing ^{99}Mo using its new HANARO reactor. ANL signed a collaboration agreement with KAERI in December 1996 under which we would pursue joint research in the use of LEU to produce ^{99}Mo in Korea. KAERI's initial interest was

to develop its own target. Unfortunately, the issue of the availability of a hot cell for ^{99}Mo production coupled with Asian economic problems has not allowed technical work to begin. We anticipate that active work can begin later this year.

CONCLUSION

The key to our meeting the RERTR program's goal of complete conversion to LEU is tied to open dialog and active cooperation with all producers. BATAN's willingness to allow us to test new target concepts and processing has led to our success in developing the annular, metal-foil targets. CNEA's open sharing of information and active development activities will make their successful conversion to LEU a reality. ANSTO's openness and willingness will also lead to their success. IRE commitment to irradiate and test LEU targets when we are ready for them is gratifying. The open technical sharing over the years and recent overtures for active cooperation from Mallinckrodt bodes well.

An activity that started five years ago against heavy opposition now appears to be on a solid road to success. We will continue to cooperate with producers as our resources allow. Our goal continues to be to provide a benefit to humankind by ending the use of HEU for ^{99}Mo production, and to do it in a way that provides an economic benefit to the producer as well.

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