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OVERVIEW OF PROGRESS RELATED TO IMPLEMENTATION OF THE LEU-MODIFIED CINTICHEM PROCESS

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ABSTRACT

The primary method for producing ^{99}Mo with a high-specific activity is irradiation of uranium targets. Uranium-235 in a target undergoes fission, yielding ^{99}Mo and other fission products. The irradiation of LEU foils contained in annular targets has been thoroughly described and demonstrated. The associated chemical processing scheme (target dissolution, Mo recovery, and Mo purification steps) - the Modified Cintichem Process - has also been extensively described and demonstrated. A brief review of the issues likely to effect the advancement of this approach beyond research and into the industrial realm is given. This paper is also an overview of the recent technology developments moving this approach toward deployment.

1. Introduction

1.1. Background

Cintichem Inc. was a major supplier of medical ^{99}Mo for the US until 1989, when production was shut down due to operational issues and associated costs of repair. Cintichem's established production process (the "Cintichem Process") started with irradiation of HEU oxide coated on the inside of a steel tube target in a 5 megawatt open-pool reactor at Tuxedo N.Y. The irradiated uranium oxide was then dissolved in a solution of nitric and sulfuric acid. The Mo was purified by precipitation with alpha-benzoine oxime followed by two column purification steps to yield a high purity, high activity product.[1] This established process served as a starting point for the development of an LEU based ^{99}Mo process as part of the RERTR (Global Threat Reduction-Conversion) program [1].

When designing an LEU target to replace an existing HEU target, it must contain an equivalent amount of ^{235}U. LEU contains less than 20% ^{235}U relative to total U, whereas HEU generally contains over 90% ^{235}U relative to total U. Therefore, to yield the same amount of ^{99}Mo, an LEU target must contain nearly five times as much total uranium as the HEU target that it is meant to replace. In order to convert the original Cintichem Process from HEU to LEU targets, a denser form of uranium was required if the target geometry was to be similar. A target design containing LEU metal foil was developed at Argonne along with modified dissolution and purification steps.[2] This target was a key technology for the development of the LEU Modified Cintichem Process, and has been extensively described and reviewed.[3]

Several organizations are moving toward large scale production of medical ^{99}Mo using the LEU Modified Cintichem Process. A vital part of this cooperative development has been the establishment of the IAEA's Coordinated Research Project "Developing techniques for small-scale indigenous production of Mo-99 using LEU or neutron activation" that assists member countries to pursue ^{99}Mo production without the use of HEU.[4]

1.2. Review of Scale-up Issues

In order to discuss the scale-up issues of deploying the Modified Cintichem process, we will assume that approximately 5,000 20-g foils (120 6-day Ci ^{99}Mo/target) are required per year to meet 100% of the US demand. The Missouri University Research Reactor is working towards large-scale ^{99}Mo production using the LEU Modified Cintichem Process, and projects that they can produce 50% of the US demand.[5] Another promising approach is to employ a purpose built isotope production reactor systems based on homogeneous liquid core technology.[6] Such systems are currently being studied for large scale production.[7]

Accordingly, production of the full US demand would require the irradiation of around 100 kg of LEU foil each year. The foil fabrication procedure will further require that the LEU metal in the foils be composed of small, randomly-oriented grains.[3] These characteristics are thought to be critical for acceptable irradiation behavior.[3, 8] Several approaches to scale-up of both foil production and target fabrication has been investigated.[8, 9, and 10] Machining, welding, and inspection procedures can be adapted from standard industrial practice.

Once the target is removed from the reactor, the product yield is very dependent on the processing time (i.e., about 1% of product is lost every hour), so the optimization of the target disassembly, dissolution, as well as the recovery and purification operations will be critical to the product yield. El-Gizawy et al. [11] will describe the issues for minimizing the time required for target disassembly. In addition, they have reviewed the existing equipment designs. Dissolution of the irradiated metal foil is quite fast, and the heat-cool cycle time determines the time required for this step. Argonne's new dissolver was designed to minimize the heating cycle time.[12] The size of the dissolver will be matched to the volume of dissolver solution that depends on the size and number of

targets to be processed in one batch. The volume of the dissolver solution is limited by the solubility of uranium (about 500 g-U/L of solution).

Purity, yield, and speed are the important factors in the product recovery and purification steps. Purity of the product is rarely an issue due to the remarkable selectivity of the alpha-benzoine oxime precipitation for Mo. Yield is maximized by minimizing the time that the Mo product is in the solid the alpha-benzoine oxime form, because the organic precipitate degrades in the high radiation fields. Observations from demonstrations suggest that this degradation forms material that irreversibly binds or traps the Mo.

Waste storage, treatment, and disposition are factors that will be critical to the efficient and cost effective deployment of the Modified Cintichem Process. The storage strategy will be specific to each facility, and will need to take into account the volume, chemical, and radiological properties of the waste. One important factor will be the amount of time the waste is allowed to decay before treatment.[13] Because the burnup of targets is very low, recycling the LEU into new targets can be considered. Recycling would require processes for recovering clean LEU and for reducing it to metal. The initial cost of these operations could be minimized by utilizing an existing facility, rather than designing, building and licensing a new facility. These costs would be offset by reduced raw materials costs.

2. Discussion

2.1. Preparation of Bulk LEU Metal

As part of our ongoing work with BATAN, Indonesia, Argonne is shipping a total of 1 kg of LEU to BATAN [8]. The LEU was poured as 75 g ingots to match their production plans, and make for convenient rolling. BATAN will use this raw material to fabricate foils using the hot rolling techniques developed at Argonne. The resulting foils will be placed in targets for irradiation.

2.2. Characterization of LEU Foils

The Korean Atomic Energy Research Institute (KAERI) has developed a method to fabricate thin uranium foils economically using a direct casting method.[14] This method can produce a continuous polycrystalline LEU foil with a thickness range of 100 to 150 μm and a width of about 5 cm, exceeding 5 m in length per batch. Due to this large potential production capacity, this method shows great promise for providing a significant portion of the LEU foil required for large-scale deployment of the Modified Cintichem Process.

The direct cast foil is somewhat rougher than previously observed in rolled foils (Figure 1). A typical transverse cross section had a minimum thickness of 65 μm (0.0026 in.) and a maximum thickness of 205 μm (0.0082 in.). This characteristic roughness could affect (1) target fabrication, where the U foil, or the Ni foil might be damaged during drawing, and (2) irradiation behavior, where gaps between the target walls and the U metal might affect cooling of the targets. Argonne has an ongoing R&D effort to study

the roughness of these foils, potential means to smooth them by rolling techniques, and any effects that the observed uniformity had on target fabrication[8].

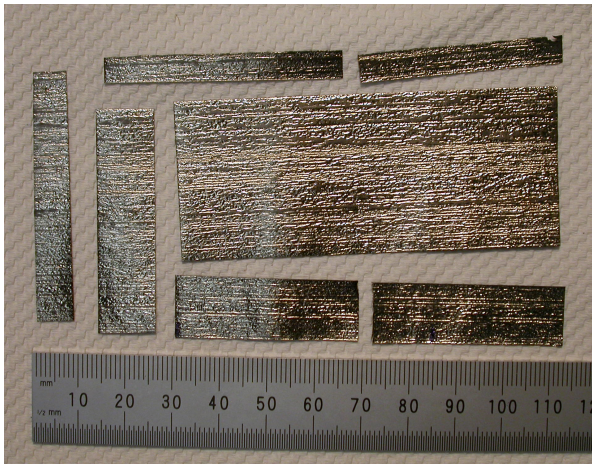

Figure 1. Photograph of direct cast LEU foils (KAERI)

2.3. Target Fabrication with Direct Cast Foils

A series of annular mock targets were produced using direct cast uranium foils. As can be seen from Figure 2, where the LEU foil (dark area) is uniform in thickness, the contact is quite good between the foil, the Ni recoil barrier (light grey) and the aluminum tubes. However, gaps between the direct-cast foil and the Ni recoil barrier were also observed in different areas of the same sample (Figure 3). Currently, we are studying means to eliminate these gaps. Calculations done by ANSTO [15] and MURR [16] show small gaps within the annular targets will have little effect on the heat transfer out of the

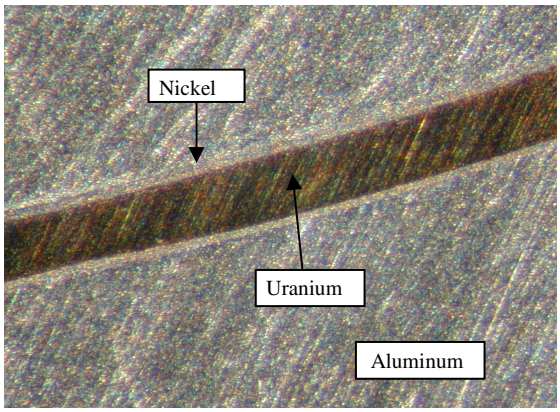

Figure 2. Optical micrograph of a cross section of a target using direct cast foil with excellent contact along each interface

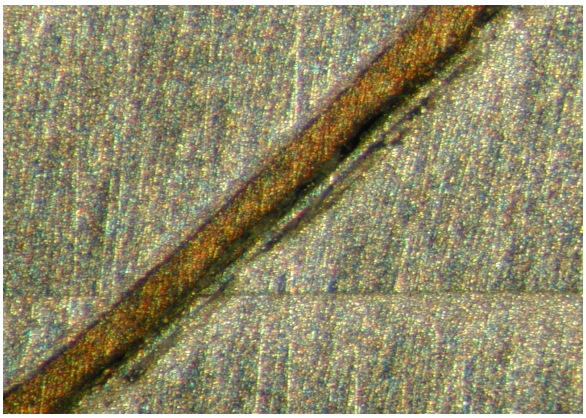

Figure 3. Optical micrograph of a cross section of a target using direct cast foil with poor contact along the U/Ni interface.

uranium during irradiation. Given this, and our determination that the grains in the direct cast foils are random, good irradiation behavior of such targets is possible. However, no irradiation data of direct-cast foils is currently available.

2.4. Irradiation

Several rolled foils have been irradiated and processed in Indonesia [17]. The last two targets irradiated were fabricated by BATAN using LEU foils prepared at Argonne. In addition ANSTO [18] and CNEA [12, 19] have irradiated annular LEU foil targets.

MURR is preparing to irradiate a 5-gram (total uranium) LEU foil annular target soon. Two targets are being prepared, one using a foil rolled at Argonne, and one using a direct cast foil from KAERI. These irradiations will be important demonstrations of the facilities at MURR, and of the irradiation behavior of the KAERI foil.

2.5. Target disassembly

Several groups have developed equipment and procedures for disassembling the irradiated annular foil targets. El-Gizawy et al [11] have described the issues for minimizing the time required for this operation. In addition, they have reviewed the existing equipment designs.

2.6. Foil dissolution

The dissolver design and fabricated at Argonne (Figure 4) [12] and tested at MURR. Initial testing showed that no major modifications were needed to dissolve 40 g of uranium foil. The Argonne dissolver will be used in the upcoming MURR demonstration.

2.7. Product recovery and purification

Table 1 shows the results of a demonstration done by BATAN in 2005. Activities of the dissolver solution are directly compared with activities of the purified product solution. The ^{99}Mo activity shows that the product recovery is relatively high at 86%. When production facilities and procedures are used, rather than the experimental ones used here, then the recovery is expected to be higher. Comparison of the impurity activities show that the Modified Cintichem Process is very effective in removing these impurities while giving a good recovery.

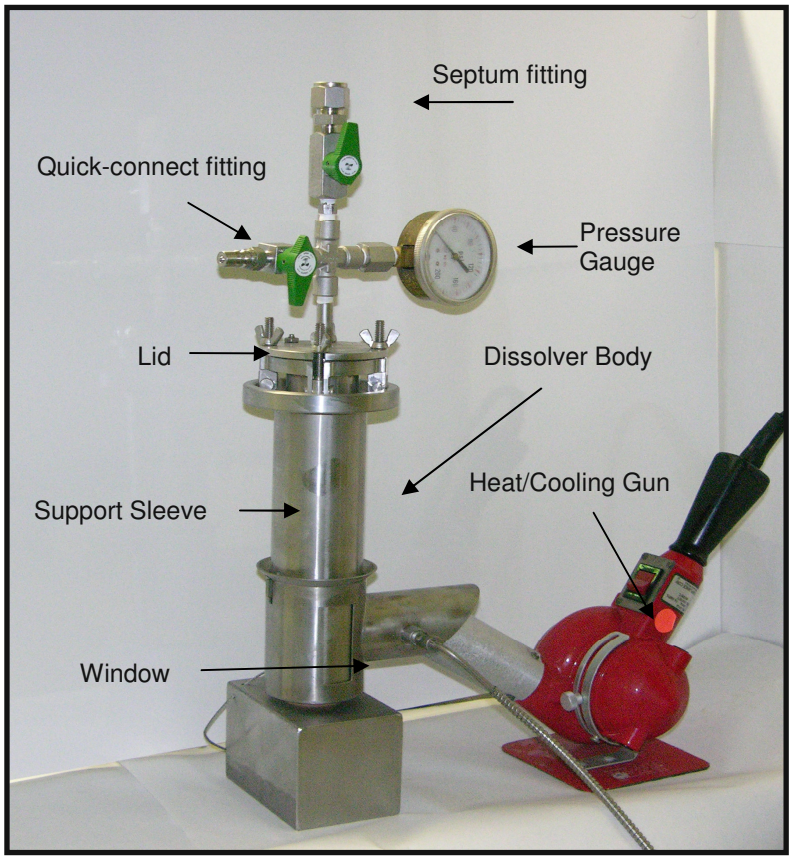

Figure 4. Photograph of new dissolver designed and fabricated at Argonne and being demonstrated at MURR

Table1. Results from 2005 demo at BATAN

Isotope	Dissolver solution impurity mCi/mCi ^{99}Mo	Product solution impurity mCi/mCi ^{99}Mo
^{99}Mo Activity	86.9 Ci	77.5 Ci (86%)
^{131}I	0.426	1.01e-5
^{103}Ru	0.181	8.39e-7
^{140}Ba	0.980	<9.31e-3
^{132}Te	0.933	9.27e-8

2.8. Process Waste

Table 2 shows a general description of the routine waste generated by the dissolution, recovery and purification of ^{99}Mo from a 24 g (total U) LEU metal target using the Modified Cintichem Process. Most of the fission products are contained in about 135 ml of dilute HNO_3. Most of the activity 30 days of cooling is contained in short-lived isotopes [e.g., ^{141}Ce (33d), and ^{143}Pr (14 days)] [13]. After one year of cooling, the total activity has dropped to less than 3% of the total activity after 30 days, and most of the

activity is contained in isotopes with longer half lives [e.g., ^{144}Ce (284 days), ^{95} Zr (65 days), and ^{91}Y (59 days)] [13]. Therefore, the waste handling requirements will depend strongly on the age of the waste. Long term storage will simplify waste handling and disposal, but storage space will limited in some facilities.

Table 2. Wastes from the Modified Cintichem Process (per 24 g Target)

Waste description	**Volume**
High Activity Waste: Dissolved uranium (150 gU/L or 0.62 M) 40 ml 0.75 HNO_3 25 mL 1M HNO_3 4 mg of NaI in 4 mL liquid 0.5 ml 10% Ag NO_3 in 0.1M HNO_3 0.5 mL of Mo carrier (10 mg/mL) ~20 mL of 2.5% $KMnO_4$ in DIW 1.5 ml of Rh carrier (8 mg/mL of 0.3 M HNO_3) 2.0 mL of Ru carrier (5 mg/mL) 20 mL of 2% ABO in 0.4 M NaOH 20 mL of 0.1 M HNO_3	133.5 mL
Low Activity Waste 0.1 M HNO_3	90 mL

3. Conclusions

A great deal of progress has been made toward large-scale implementation of the Argonne annular target and LEU foil Modified Cintichem process. These advancements include: 1) characterization and target fabrication with a direct cast uranium foil produced by KAERI, 2) target disassembly, and 3) waste characterization.

4. Acknowledgements

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