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**OVERVIEW OF ARGONNE PROGRESS IN DEVELOPING LEU-BASED
PROCESSES FOR THE PRODUCTION OF MO-99**

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ABSTRACT

Argonne continues to develop technology that will be useful for (1) the conversion of current ⁹⁹Mo production from high-enriched uranium (HEU) to low-enriched uranium (LEU) targets and (2) potential future fission-⁹⁹Mo producers who will be using LEU. This paper presents highlights of our progress during 2009; individual posters and presentations at this meeting will provide details. To assist in conversion of current producers, we have developed an electrochemical ambient-pressure digestion process that would be applicable to base-side producers (IRE, Covidien, and NTP) to allow substitution of LEU-foil targets for the current HEU dispersion targets. For the LEU-Modified Cintichem process that will be used at the Missouri University Research Reactor (MURR) for large-scale production of ⁹⁹Mo, we are developing an understanding of the dissolution/off-gas-collection system to allow dissolution of several targets in a single batch. For development of ⁹⁹Mo recovery from aqueous homogeneous reactors, Argonne is doing research in both (1) solution chemistry and radiolytic gas formation of the reactor during operation and (2) developing a Mo-recovery system. We also continue to work with partners in the IAEA-CRP for Small-Scale Indigenous Production of Mo-99 Using LEU Targets or Neutron Activation, assisting Chile, Libya, Poland, and Romania to implement the LEU-Modified Cintichem process.

1. Introduction

The mission of the Global Threat Reduction Initiative (GTRI) is to reduce and protect vulnerable nuclear and radiological materials located at civilian sites worldwide. The Highly Enriched Uranium (HEU) Reactor Conversion subprogram supports the conversion of domestic and international civilian research reactors and isotope production facilities from the use of weapons-of-mass-destruction-(WMD)-usable HEU fuel to LEU fuel. These efforts result in permanent

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threat reduction because the use of WMD-usable HEU in the civilian fuel cycle is minimized or eliminated. The main technology components of the program are: (1) the development of advanced LEU fuels, (2) design and safety analysis for research reactor conversion, and (3) development of targets and processes for the production of the medical isotope Molybdenum-99 without using HEU.[1] In the scope of the last technology component of the program:

- GTRI makes technical expertise available, on a non-proprietary basis, to global medical isotope producers to assist with converting their ^{99}Mo processes to use LEU.
- GTRI provides technical support in a number of areas, including foil rolling, target fabrication, target irradiation, target disassembly, target dissolution, product recovery and purification, and waste treatment.
- These alternative LEU-based processes can replace the current technologies and increase the ^{99}Mo extraction efficiency and reduce the waste volumes generated.

Currently ~95% of all ^{99}Mo is produced using HEU, but the GTRI-Conversion program is making real progress to lower that fraction, both by developing technology to allow conversion of current HEU processes and by assisting new producers to process using LEU targets. Production of fission-product ^{99}Mo can be characterized in five steps: (1) target fabrication, (2) target irradiation, (3) dissolution or digestion of the uranium fuel and, in some cases, the entire target, (4) recovery and purification of molybdenum from all other target components, and (5) shipment of purified ^{99}Mo solutions to generator producers. Recovery of ^{99}Mo varies from process to process, as do subsequent purification steps. However, the equipment is generally small-scale, with solution volumes being 0.1 to 6 liters. The use of chromatographic columns for the recovery of Mo is widespread in these processes, which have between two and six recovery/purification steps. The final product is sodium molybdate in a solution of 0.2 M NaOH, which is the required feed for loading the Mo into a commercial $^{99\text{m}}\text{Tc}$ generator. Total processing times vary between 4 and 14 hours. Converting to LEU from HEU will necessitate changes in the first four steps. The GTRI goal has been to find the means to make this conversion possible, both technically and economically.

The National Academies released a report (National Academies Report on Medical Isotope Production without Highly Enriched Uranium) in January 2009 that addressed five topics mandated by the US Congress.[2] These topics and short summaries of their findings follow:

- Feasibility of procuring supplies of medical isotopes from commercial sources that do not use HEU
Production of ^{99}Mo on a large scale using LEU targets is technically feasible. Converting current producers to LEU would require a significant cost and time. Not enough ^{99}Mo is currently produced from LEU to meet US demand, but no technical reasons exist for that not being true in the future.
- Current and projected demand and availability of medical isotopes in regular current domestic use

The current US demand for ^{99}Mo is 5000-7000 6-day-Ci/week. Future demand growth is likely 3-5%/year. Reliability of supply is a current problem that should continue with or without conversion. New foreign or domestic sources are several years away.

- Progress being made by the Department of Energy and others to eliminate all use of HEU in reactor fuel, reactor targets, and medical isotope production facilities

The GTRI program has made substantial progress in converting reactor fuels and targets, but much is still left to do. It was recommended that the GTRI focus on removing HEU waste from ^{99}Mo production by either downblending or returning US-origin material to the US.

- Potential cost differential in medical isotope production in the reactors and target processing facilities if the products were derived from production systems that do not involve fuels and targets with HEU

The cost of conversion to LEU targets would be less than 10% of the current cost of HEU-produced ^{99}Mo . While determining the absolute cost of conversion is difficult to quantify in such a complex production/distribution system, the report concluded that conversion cost would have a negligible impact to the cost to the patient.

- Identify additional steps that could be taken by the Department of Energy and medical isotope producers to improve the feasibility of such conversions

Mo-99 producers should commit to conversion and take steps to move forward. The Department of Energy should (1) assist producers with the technical expertise of its laboratory system, (2) examine options to share R&D costs with existing and new producers, and (3) remove disincentives to conversion by maintaining the cost of LEU so it is competitive with HEU. The Department of State should intensify diplomatic pressure on countries that still use HEU targets and fuel. The U.S. Food and Drug Administration should work with industry and DOE technical experts to (1) ensure a common understanding of LEU-based production from a regulatory perspective and (2) promote a good understanding of likely FDA requirements for obtaining approval.

The United States currently has no domestic production of ^{99}Mo . However, that will change over the next several years. The University of Missouri Research Reactor (MURR) is in the process of designing a ^{99}Mo -processing plant based on irradiation of LEU-foil targets. The Babcock and Wilcox Technical Services Group (B&W) is developing the use of the Medical Isotope Production System (MIPS) to produce ^{99}Mo in a critical solution of LEU uranyl nitrate; after five days of irradiation, molybdenum will be milked from the fuel solution, which will then be returned to the reactor for further irradiation. Some of the Argonne activities in support of MURR and B&W are summarized below.

The technical work underway at Argonne in support of MURR using the LEU-Modified Cintichem process is applicable to the International Atomic Energy Agency (IAEA) Coordinate Research Project (CRP) on Developing Techniques for Small-Scale, Indigenous Production of Mo-99 Using Low-Enriched Uranium (LEU) or Neutron Activation (T1.20.18), where Argonne

is assisting Chile, Libya, Poland, and Romania to implement the LEU-Modified Cintichem process using annular LEU-foil targets.

2. Conversion Technology

Conversion to LEU usually necessitates changes in the target, in dissolution/digestion, and the Mo-recovery step. Once the uranium is removed, the remaining purification steps will be identical for HEU and LEU targets. The Reduced Enrichment for Research and Test Reactors (RERTR) website is a source for presentations by Argonne National Laboratory and others at yearly international meetings.[3] A separate paper at his meeting will present our progress in developing an ambient pressure dissolver for substitution of LEU-foil targets in alkaline-based processes, such as those used in Argentina, Belgium, the Netherlands, South Africa, and Australia, employing a two-step process.[4] In the first step, the Al fission-recoil barrier is dissolved in alkaline solution. The second step is anodic oxidation of the uranium metal into basic bicarbonate media, with consequent removal of uranium and carbonate from the solution by precipitation through the addition of calcium oxide. None of the molybdenum precipitates under these conditions, and the filtrate can be fed directly into a BioRad AGMP-1 ion-exchange column, as is done for the current Argentine process. The development of this method has reached the point that we are designing and will fabricate a dissolver that the Argentine Comisión Nacional de Energía Atómica, Argentina (CNEA) has volunteered to test with an irradiated LEU foil target in 2010.

3. LEU-Modified Cintichem Process

In the LEU-Modified Cintichem process, the first processing step in extracting ⁹⁹Mo is dissolving the irradiated uranium foil in nitric acid. A dissolver system, designed at Argonne [5, 6] and tested at MURR is currently being scaled up for larger uranium throughput. Two key technical challenges involved in scaling-up the dissolver system are ensuring that (1) the dissolver vessel can contain the gas pressure produced during the exothermic dissolution of the uranium foil and (2) the off-gas produced during the dissolution (NO_x, H₂O, and fission-products isotopes of I, Xe, Kr) can be removed from the dissolver vessel and trapped in a separate volume. Our approach to meeting these challenges is to perform thermodynamic modeling and experimental studies to first establish the required pressure rating of the dissolver vessel and to ultimately develop a predictive understanding of the chemistry of the dissolver solution and gas phase. It is particularly important to quantify the volume and chemical speciation of the off-gas so that an efficient gas trap can be designed and optimized.

The pilot-scale dissolver (Fig. 1) is constructed of 304 Stainless Steel with a volume of 360 cm³. Based on uranyl-nitrate solubility (~600 g-U/L), this size vessel could dissolve up to 120 g of irradiated foil per batch. It consists of a cylindrical body and a separate lid assembly. Hydrostatic pressure tests have established the dissolver vessel pressure rating at 800 psig at 25°C. The dissolver is supported within a cylindrical steel sleeve with an open base and a flange at the top. The bottom of the sleeve has a window cut out to allow hot air to flow in and around the dissolver. An electric heat gun blows hot air into the support sleeve to increase and maintain the temperature. The heat gun (heater turned off) also provides the air for cooling upon shutdown. The temperature of the dissolver is monitored by two thermocouples (one to indicate

temperature, and one for temperature overrun). The dissolver, containing the uranium foil, is evacuated before the nitric acid is added (through the septum) to start the dissolution process.

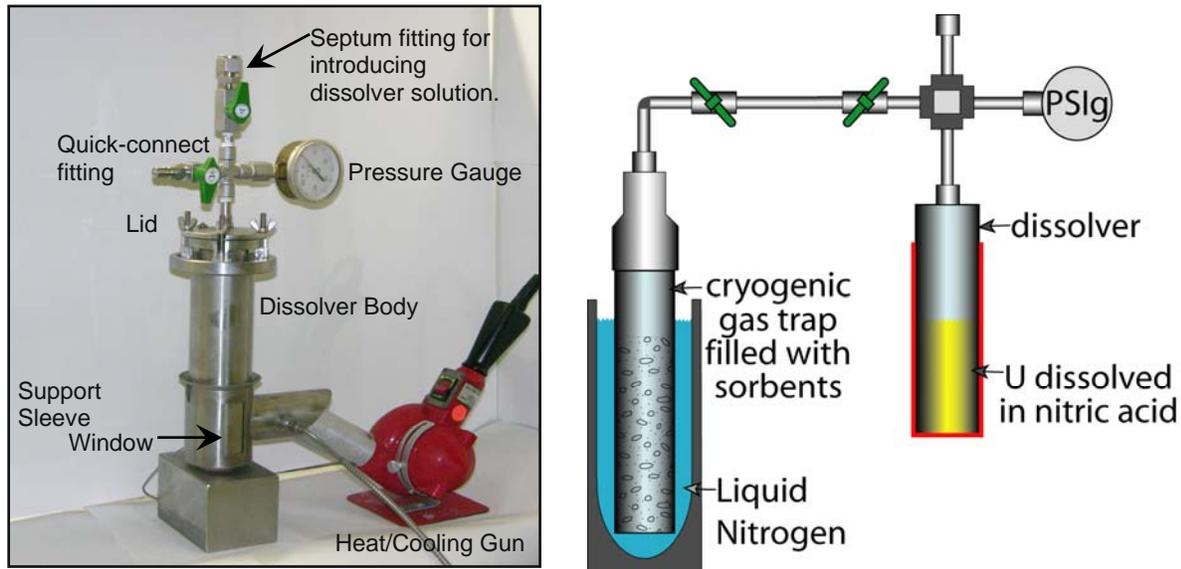


Figure 1. Photograph of dissolver (left) and schematic drawing of the dissolver set-up showing the cryogenic gas trap (left).

The gas trap consists of a seamless, type-L copper tube that is sealed with a copper cap at one end and with a series of copper and brass fittings at the other. Prior to and during use, the gas trap rests in a vertical position, within a Dewar of liquid nitrogen. The sorbents that have been used in the gas trap include 13X molecular sieve pellets, a desiccant (such as Drielite), and calcium oxide. The modeling and experimental studies being performed as part of this project will optimize the gas-sorbent mixture in the cold trap for the increased gas volumes associated with larger uranium throughput. At the end of a dissolution run, the dissolver is cooled to near ambient temperature, and the valves between the gas trap and dissolver are opened. The gas trap is immersed in liquid nitrogen throughout the dissolution; therefore, once the valves are opened, the off gas from the dissolver is cryo-pumped into the sorbent-filled gas trap and thus removed from the dissolver solution.

The next step will be design a production dissolver that can dissolve up to 250 g of irradiated uranium and accompanying Ni fission-recoil barrier to be used at MURR for large-scale production. The dissolver will be heated and cooled by means other than a heat gun to allow rapid heat-up and cool-down. A poster will be presented at this meeting detailing our progress.[7]

4. Aqueous Homogeneous Reactors for Mo-99 Production

Argonne scientists and engineers are collaborating with personnel from the Babcock and Wilcox Technical Services Group (B&W) and Purdue University to optimize the design of the B&W MIPS.[8, 9] The major components of the MIPS are: an aqueous homogeneous solution reactor (AHR) containing uranyl-nitrate fuel (LEU), a molybdenum-extraction system using a chromatographic column, and the reactor off-gas system. The use of AHRs presents an

attractive alternative to the conventional target-irradiation method for producing ^{99}Mo in that solutions eliminate the need for targets and can operate at much lower power than required for a reactor irradiating targets to produce the same amount of ^{99}Mo . The two areas of the Argonne R&D that will be discussed at this meeting are (1) radiolytic gas formation of the fuel solution and its effect on reactor-solution chemistry[10] and (2) sorbents for recovery of molybdenum from the irradiated fuel solution.[11] Additional information on solution chemistry of the AHR and the MIPS can be found elsewhere.[6, 12, 13]

The first solution reactors earned the name "water-boilers" because of the observed bubbling or frothing that result from the radiolytic decomposition of water by fission fragments and subsequent evolution of radiolytic gases (hydrogen and oxygen). Because nitrate ion also undergoes radiolytic decomposition, uranyl-nitrate-based AHRs will also generate N_2 and NO_x in the off gas. The radiolytic decomposition of nitrate ion will also have the effect of increasing the pH of the fuel solution. The rate and composition of the radiolytic gas generation is of practical importance for the design and operation of AHR for two reasons. First, the design of the reactor off-gas system depends on the generation rate and the composition of the gas stream. Second, an increase of the fuel-solution pH can lead to the formation of the precipitates and, therefore, must be controlled.

The aim of this project is to obtain reliable data for radiolytic gas formation in a model nitrate solution (1M NaNO_3 and 0.1M HNO_3), and, subsequently, to expand experiments to the uranyl-nitrate solution that is of practical interest to the AHR.[9] We are using 3-MeV electron Van de Graaff to irradiate the test solution. The gaseous products of radiolysis are being analyzed using a SRI 8610 gas chromatograph with a high-sensitivity Thermal Conductivity Detector (TCD) and Helium Ionization Detector (HID). Helium was used as a carrier gas for all experiments. The main products of radiolysis of 1M solution of NaNO_3 in 0.1M HNO_3 are hydrogen and oxygen; NO_2 , N_2O , NO and N_2 are also present (Figure 3). Dose dependence of the yield of those gasses is shown on Figure 2. Yield for NO was not calculated because it depends on the concentration of the oxygen (due to the reaction of NO with O_2) and conditions set for the separation column (level of saturation with NO_2). Radiolytic gas formation is dominated by hydrogen and oxygen while NO_2 is generated ten fold less, and N_2O and N_2 hundred times less. Nevertheless these preliminary results shows decomposition of the nitrate in the solution that have to be taken into account when designing gas handling system and control of the pH of the solution during irradiation.

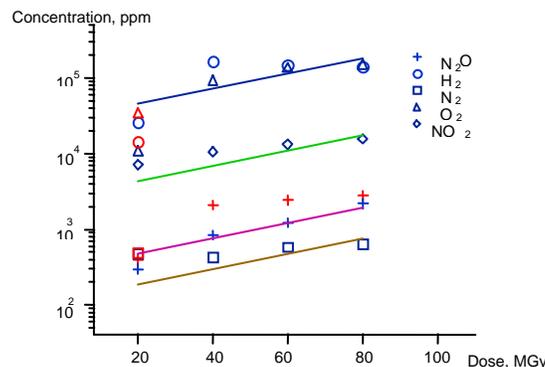


Figure 2. Relative radiolytic-gas formation vs. dose for irradiation of 1M NaNO_3 /0.1M HNO_3

Predicting the speciation and oxidation state of molybdenum in the fuel solution is critical to optimizing molybdenum recovery. The current recovery strategy is to use a column loaded with an inorganic sorbent. Suitable sorbents have been identified and tested at Argonne. Recent experimental data from UV-Vis and Raman spectroscopy as well as density functional theory calculations confirm that, at molybdenum concentrations lower than 10^{-3} molar in dilute nitric acid (pH 1.5 - 4), the species $\text{H}_2\text{MoO}_4(\text{aq})$ and MoO_4^{2-} are favored over polymolybdates such as $\text{Mo}_8\text{O}_{26}^{4-}$. [14] The neutral species H_2MoO_4 was found to dominate at $\text{pH} < 3$. At $\text{pH} < 1$ the molybdenyl species MoO_2^{2+} or its nitrate-coordinated equivalent $[\text{MoO}_2(\text{NO})_3]^+$ were found to dominate. Although the data analysis is not complete, initial results from an Extended X-ray Absorption Fine Structure (EXAFS) study of molybdenum speciation in nitric acid performed at Argonne indicate the presence of molybdenyl with O-Mo-O bond lengths of 1.7 angstroms at $\text{pH} = 0$. The bond lengths increase with increasing pH (from 0 - 2), as would be expected if the species in the higher pH samples was H_2MoO_4 . The distribution of molybdenum species using an updated thermodynamic database is shown in Figure 3, which also shows the speciation of molybdenum in an unirradiated solution (left) and as a function of oxidation/reduction potential (Eh). The Eh-pH condition for the unirradiated MIPS fuel is shown as a yellow dot. If radiolysis causes a decrease in the redox potential (Eh) of the solution (blue dotted line) Mo(VI) will be reduced and form a Mo(V) cation or a Mo(IV) solid. This could complicate the extraction of molybdenum and thus constrains another important operational boundary condition ($\text{Eh} > 0.7$ volts) for the solution reactor. Further refinement of the Argonne thermodynamic database will allow us, in collaboration with B&W personnel, to provide a thermodynamics-based computational tool for optimizing the design and operation of the B&W Medical Isotope Production System.

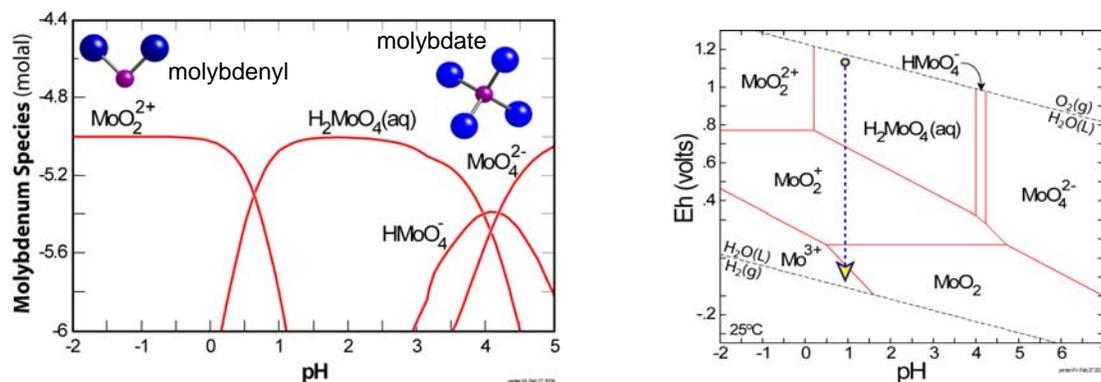


Figure 3. Equilibrium models of molybdenum speciation. Left: Mo(VI) speciation for 10^{-5} molal. Right: redox potential vs. pH for 10^{-5} molal dissolved molybdenum. Conditions of interest are marked by a yellow circle. The blue-dotted line is a hypothetical reduction reaction pathway.

To recover ^{99}Mo from a concentrated uranium solution, a number of sorbents are being evaluated to adsorb Mo(VI) from 60°C solutions containing ppm concentrations of Mo(VI) and 30-300 g-U/L (as uranyl nitrate) in 0.1 M HNO_3 . The bulk of our studies has been to evaluate T-52 (25 mole % of SnO_2 and 75 mole % TiO_2) and T-5M (5 mole % of ZrO_2 and 95 mole % TiO_2), both manufactured by Termoxid Scientific and Production Company (Zarechnyi, Russia). We are also assessing pure- TiO_2 sorbents and alumina. Our studies thus far have been evaluating the partitioning of Mo(VI) as the concentrations of Mo, U, and nitric acid, temperature, and contact

time are varied. We have also studied the chemical and radiolytic stability of the sorbents under predicted process conditions through batch and small-scale column testing. Details of this study are presented elsewhere in this conference.[11]

Given what is known at this time, Argonne proposes a down select to two sorbents; T52 and a pure TiO₂, as the preferred candidates for Mo recovery for irradiated AHR fuel solutions. Because it has less affinity for sorbing uranyl ion and other fuel components, which would lead to a lower column-wash volume, T52 would be our leading candidate. During the coming year, prototypical-column testing will be performed to verify our initial results and provide verification of the column models being developed from our batch studies by Purdue University using their VERSE code.[15].

4. IAEA-CRP

Argonne continues to work with partners in the IAEA-CRP for Small-Scale Indigenous Production of Mo-99 Using LEU Targets or Neutron Activation, assisting Chile, Libya, Poland, and Romania to implement the LEU-Modified Cintichem process.

In 2009, Argonne fabricated and sent dissolvers to Libya and Poland to allow them to demonstrate the LEU-Modified Cintichem process. We are also sending an advanced target-disassembly tool designed and fabricated at MURR to Libya. In September, staff from Argonne and MURR visited POLATOM to assist them in a tracer demonstration of the process. We are planning similar trips to Romania and Libya in the near future. We will continue to work with the IAEA and all participants in the coming years.

5. Acknowledgements

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