STATUS REPORT ON TECHNICAL PROGRESS FOR LEU-BASED ^{99}MO PRODUCTION AT ARGONNE NATIONAL LABORATORY

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ABSTRACT

Currently, most of the world's supply of ^{99}Mo is produced from the fissioning ^{235}U in high-enriched uranium (HEU) targets. Conversion of these targets to low-enriched uranium (LEU) would ease worldwide concern over the use and transport of this weapons-grade material. This paper documents our progress in three development areas: (1) the chemistry of iodine and its recovery from irradiated uranium targets, (2) alternate uranium metal target dissolution methods compatible with existing alkaline ion exchange processes and, (3) a small-foot-print dissolver for the LEU-modified Cintichem process.

1. Introduction

Technecium-99m is the most commonly used radioisotope in nuclear medicine [1]. It is produced from the decay of its parent ^{99}Mo. Nearly all of the ^{99}Mo is produced in research, test or isotope production reactors by irradiation of highly enriched uranium (HEU) targets. The utilization of HEU causes worldwide concerns over the protection and transport of this weapon grade material [2].

Production of ^{99}Mo utilizing LEU instead of HEU targets eliminates the concerns over proliferation, criticality, and transportation of the weapons-grade material. However substitution of LEU for HEU in most process will require some modifications [3]. Because ^{99}Mo is a product of ^{235}U fission, five times more total uranium as LEU is required to yield equivalent amount of ^{99}Mo. Consequently, substituting LEU for HEU might require changes in chemical processing to efficiently separate ^{99}Mo from high concentrations of uranium while obtaining a product of equal purity [1, 3].

2. Results from LEU Demonstration at CNEA

The Comisión Nacional de Energia Atómica in Argentina (CNEA) has been a strong partner of the RERTR program for many years [4]. It is currently working in cooperation with ANL on development of a process using LEU-foil targets [5]. One of the problems encountered with the CNEA conversion using LEU-foil targets is the unpredictable behavior of iodine during ^{99}Mo recovery from uranium solution.

During target processing at CNEA in December 2006 a target was irradiated in a relatively low flux position in the reactor [$5x10^{13}$ neutrons/(cm^2 sec)], therefore, yielded only 53.87 Ci of ^{99}Mo and 22.62 Ci of ^{131}I (based on gamma analyses of the dissolved target). The irradiated LEU-foil (24.35 g of LEU-total; 4.87 g of ^{235}U) was digested in a dissolution vessel heated to 280ºC and 100 bar. The digestion required 400 mL of 1 M NaOH and $KMnO_4$ oxidant.

The gamma counting results (Table 1) showed that 92% of the ^{99}Mo was recovered in the product stream. However, less than 10% of the total ^{131}I was recovered in the wash and product streams. The low yield of ^{131}I is unexpected because iodide species are expected to be oxidized by $KMnO_4$ to iodate. Iodate has low K_d values and therefore is not retained by the resin and should be present in the aqueous streams.

Table 1. The results from gamma spectrometry performed on the samples from the test performed by CNEA and ANL on December 11, 2006.

Isotope	**Activity in Digester Solution**	**Activity in Elution**	**Activity in Product**
^{137}Cs	0.0819 Ci	0.0722 Ci (88%)	0.0007 Ci (< 1%)
^{134}Cs	0.0405 Ci	0.0396 Ci (98%)	0.0039 Ci (9%)
^{95}Zr	0.0089 Ci	0.0096 Ci (108%)	0.0006 Ci (6%)
^{131}I	22.62 Ci	1.820 Ci **(8%)**	0.1136 Ci **(<1%)**
^{99}Mo	53.86 Ci	< detection limit	49.68 Ci **(92%)**

3. Iodine Chemistry

The speciation of iodine in solution varies depending on chemical nature of the environment. Due to this complexity, the solution chemistry of iodine is not fully understood. Stable oxidation states in a basic solution consist of iodide, iodate, periodide and iodine [6]. However, the prevalence of individual iodine species in alkaline solution varies widely with their concentration and the pH of the solution. Lin has measured radiation induced oxidation products of iodide in solution as a function of radiation dose, pH and total iodine concentration [6]. He has shown that iodide converts nearly quantitatively to IO_3^- when the initial I^- concentration is 10^{-6} M or less and pH ranges from 3 to 9. At the same concentrations but higher pH values, presence of iodate diminishes significantly. In 0.01 N NaOH, only 22.1 % of iodine species is present as iodate and 77.5 % as iodide. In 0.1 N NaOH, 1.7 % of iodine is in form of iodate and 97.9 % as iodide. When the concentration of iodide is 10^{-5} M, iodide converts nearly quantitatively to iodate only in a pH range of 7-8. The presence of iodate in irradiated solutions further diminishes with increasing concentration. When iodide concentration is 10^{-3} M, less than 5 % of iodate species is present in alkaline solutions after irradiation.

The concentration of iodine in the uranium target dissolved at CNEA was assumed to be about 10^{-4} M. Under the CNEA digestion/dissolution conditions, all iodine should be present as iodate due to oxidation with $KMnO_4$. However, due to the high radiation dose from the dissolved target, iodate species are unstable in the solution. As a result, most of the iodine produced under irradiation adsorbs on an AG MP-1 column

Formation of iodide in irradiated solutions of iodate is consistent with observations made by Lin [6]. Upon irradiations of 10^{-5} M iodate solutions at pH 7, 99.3 % of iodine remains in the solution as iodate. However, at pH 10, only 2.7 % remains as iodate and the rest is present as iodide. Clearly these results suggest that at iodine concentrations $\geq 10^{-4}$ and high pH more reductions than oxidations occur in irradiated solutions and the iodide species predominates.

We have investigated the effect of adjusting pH on iodine speciation in the concentration range of 10^{-4} M. Between 7 and 10, pH has a small effect on the speciation and iodide is the predominant species in all solutions. In the presence of 10 times excess of $KMnO_4$, iodate species remain in the solution after 40 minutes of irradiation (4 x 10^6 rad). These results suggest that by adding an appropriate amount of oxidant, iodate species can be maintained in an irradiated solution. We have investigated ClO_3^-, OCl^-, $S_2O_8^-$ and H_2O_2 for oxidation of iodide to iodate. We have found that OCl^- oxidizes iodide to iodate. Oxidation with H_2O_2 and ClO_3^- was not successful and $S_2O_8^-$ only partially oxidized iodide to iodate.

Alternatively, separation of I can be achieved by collecting iodide on a pre-column. To ensure that all of ^{131}I is present as iodide, a reducing agent can be added to the solution. Toward this, we have investigated the effect of NO_2^-, SO_3^-, Sn^{2+} and N_2H_4 as reducing agents for iodate and found that only hydrazine reduces iodate to iodide.

Iodide and iodate species dominate alkaline solutions and their ratio in irradiated solutions is dependent on concentration and pH. In the CNEA process, the concentration of iodine is about 10^{-4} M and therefore, iodate species are expected to be reduced to iodide in the irradiated target solution. Iodide can be oxidized to iodate with addition of an oxidizer such as $KMnO_4$ or NaOCl. Alternately, iodate reduction can be completed by addition of hydrazine. Iodide can then be separated on a pre-column.

4. Alternative Uranium foil Dissolution Experiment

This study began with a literature review and some exploratory equilibrium thermodynamic modeling (Gibbs free energy minimization). The modeling, which involved simulations of dissolution and precipitation processes, was performed using the code "The Geochemist's Workbench®" Release 3.0 and a slightly adapted version of the database "thermo.com.V8.R6.full" [7]. The modeling results are valuable as guides to speciation in solution and precipitation of solids in the systems of interest.

The three criteria by which a potential dissolution processes are evaluated are: (1) compatibility of the dissolver solution with the separation process (i.e. molybdenum speciation must be appropriate for anion exchange and the concentrations of interfering species must be insignificant), (2) kinetics of target dissolution at or below the boiling point (fast kinetics will

allow the dissolution to be carried out at ambient pressure, negating the need for a pressurized dissolver, and processing time needs to be minimized), (3) volume of liquids to be used (liquid waste volumes need to be minimized)

For operational reasons, it is desirable to avoid pressurized systems used in the process demonstrated at CNEA [8]. Therefore, an effort at Argonne is focused on identifying rapid, non-pressurized alternative methods for dissolving uranium metal targets to produce a solution from which molybdenum can be extracted by anion exchange. For the anion exchange process to work, the dissolution step must produce a solution in which molybdenum is present as molybdate anion (MnO_4^-). Therefore, the dissolution procedure must either be done in an alkaline solution (NaOH + oxidant) or in an acid solution that is later adjusted to higher pH.

Criterion number one is particularly important in this discussion because it provides a specific guideline for the chemistry of the dissolution methods that can be considered. The BioRad AG®1, AG MP-1 or AG2 resins have relatively high selectivity for HSO_4^-, NO_3^-, NO_2^-, HCO_3^- and HPO_4^-. Therefore, high concentrations of these or similar species may interfere with uptake of molybdate on the resin. This makes the search for a low pressure dissolution method challenging because many inorganic uranium complexants that would aid in low pressure dissolution of uranium (e.g., carbonate, phosphate and sulfate) interfere with the anion exchange extraction of molybdenum. Our approach to this problem was not to avoid such complexants, but rather to investigate ways of removing them from solution (e.g., by precipitation) prior to the anion exchange step.

Of the types of uranium metal dissolution methods described in the literature we have chosen (based on the criteria listed above) to focus on: (1) a non-pressurized, two step acidic process and (2) a non-pressurized, two step alkaline processes.

The proposed acidic process involves dissolving the uranium target in an oxidizing acidic solution (i.e. dilute nitric acid) containing a complexant, followed by the addition of base to precipitate the uranium, lanthanides and any complexant anions that might interfere with the molybdenum extraction process. The main advantage of this method is that it achieves rapid dissolution at relatively low temperature and at ambient pressures. The disadvantage of this method is that the dissolver solution must be converted to a base to facilitate molybdenum separation by anion exchange. The addition of NaOH to convert the acid dissolver solution to base increases the amount of liquid waste.

The proposed alkaline process involves dissolving the uranium target in a mixture of sodium hydroxide and a strong oxidant (e.g. persulfate). The alkaline process would require a step in which the excess sulfate (from the decomposition of the persulfate) is removed from solution by the precipitation of barium sulfate. The main advantage of this method is that it avoids the titration step. The disadvantage is that it proceeds slowly at ambient pressure and requires the addition of an oxidant, which may necessitate further treatment of the solution before the molybdenum extraction step (e.g., precipitating excess sulfate from a persulfate oxidant).

Phosphate was chosen as an additive to the dissolver solution because it forms strong complexes with uranium and thus facilitates (speeds up the kinetics of) the dissolution of uranium metal and

uranium oxides. Our calculations suggest that soluble uranyl phosphate species dominate uranium speciation up to a pH of approximately 9. This further suggests that phosphate is a good complexant for uranium and might increase the kinetics of uranium metal dissolution. Calculations also suggest that titration of the acidic solution containing phosphorus and uranium with NaOH will lead to the precipitation of the uranium phosphate solids or UP_2O_7.

Sulfate was chosen as an additive to the dissolver solution because it also forms strong uranium complexes and thus facilitates the dissolution of uranium metal and uranium oxides. Calculations show that soluble uranyl sulfate species dominate below a pH of approximately 4; above 4, uranyl hydroxide species dominate. At high Eh and low pH, a uranyl sulfate complex is predominant. At higher pH, U(IV) and U(VI) solids are expected to form. Thus, titrating an acidic solution containing sulfate and uranium with NaOH will lead to precipitation of sodium uranate or UO_{2+x}, depending on the redox conditions. Further calculations suggest that residual sulfate in solution can be precipitated as the sparingly soluble mineral barite ($BaSO_4$) as long that the pH is in the range 4 – 10.

The addition of persulfate as an oxidant within a basic dissolver solution (e.g. 1 molal NaOH) is also being investigated. Persulfate will be added to the dissolver solution as $Na_2S_2O_8$. The total dissolution reaction may thus be generalized as follows:

$$U_{(metal)} + 3S_2O_8^{2-} + 2H_2O \rightarrow 4H^+ + UO_2^{2+} + 6SO_4^{2-}$$

The excess sulfate in this alkaline dissolution system will not combine with uranium to form uranyl sulfate complexes, as these species are not stable at high pH. Therefore, persulfate serves only as an oxidant during dissolution. As discussed above, the excess sulfate in this process can be removed from solution by the addition barium.

5. Development of a Dissolver for LEU-Modified

As part of our commitment to support the International Atomic Energy Agency (IAEA) Coordinated Research Project (CRP) "Developing Techniques for Small-Scale, Indigenous Production of ^{99}Mo Using Low-Enriched Uranium (LEU) or Neutron Activation (T1.20.18)," we designed and fabricated a small-foot-print dissolver for the LEU-modified Cintichem process. The new dissolver (Figure 2) is constructed of 304 Stainless Steel [schedule 40 nominal 3.8 cm (1.5 inch) pipe, 22.9 cm (9 inches) tall with a welded cap bottom], has a volume of 360 cm^3, and rated limits of 900°C and 670 Pa (2000 psig). The top is a flanged lid with an o-ring seal, and a "cross" fitting with a pressure gauge, a plug valve attached to a quick-connect plug, and a plug valve attached to a septum.

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The dissolver support sleeve (Figure 1) is a cylinder with an open base and a flange at the top. The sleeve is 22.9 cm (9 inches) tall and 6 cm (2.38 inch) diameter, and is constructed of 1.6 mm (1/16inch)-thick 304 stainless steel. It is used to support the dissolver during heating. The bottom of the sleeve has a 6.4 cm (2.5 inch) tall window cut out to allow hot air to flow in and around the dissolver.

The temperature of the dissolver is monitored by two thermocouples (one to indicate temperature, and one for temperature overrun). 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. To heat the dissolver and dissolve the foil will take about 30 minutes, and the cool-down will take about 20 minutes. The dissolver is currently being tested and will be sent to MURR in mid October.

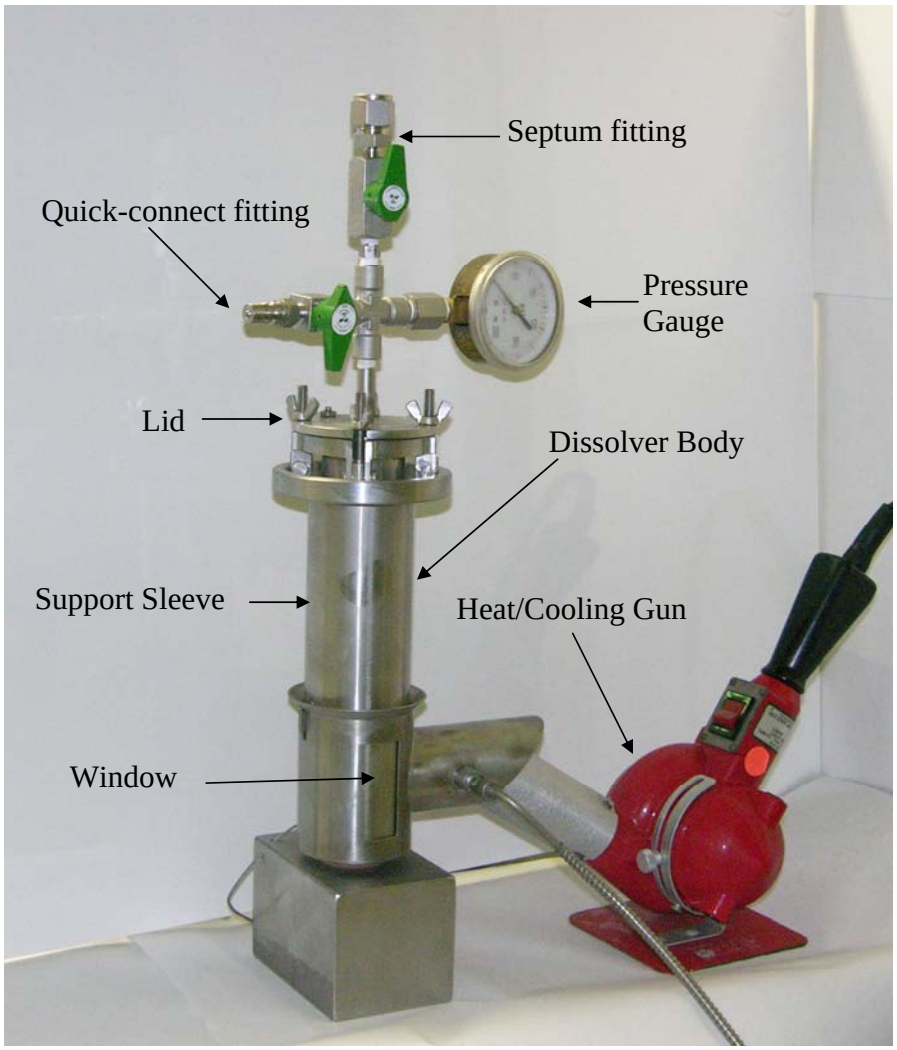

Figure 1. Photograph of the new dissolver with labels.

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6. Conclusions

The work shown here leads us to the following conclusions:

(1) the observed behavior of iodine in production demonstrations show the importance of controlling the redox of iodine in process liquids. We believe that the recovery of iodine can be improved by controlling its oxidation state during the purification steps.
(2) current alkaline dissolution methods, such as the one demonstrated in conjunction with CNEA, are operationally difficult due to the need for an elevated-pressure vessel. Two alternate alkaline uranium metal target dissolution methods compatible with existing alkaline ion exchange processes are discussed and proposed for testing. The first method dissolves in nitric acid and raised the pH in a separate step. The second method dissolves in base, with a complexant added, followed by a second step to remove the complexant.
(3) a new, small-foot-print dissolver for the LEU-modified Cintichem process is shown, and described.

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8. References

[1] George F. Vandegrift, Facts and Myths Concerning ^{99}Mo Production with HEU and LEU Targets, Proceedings of the 2005 International Meeting on Reduced Enrichment for Research and Test Reactors, November, 2005, Boston, USA.

[2] A. J. Kuperman, Weaker U.S. Export Controls on Bomb-grade Uranium: Causes, Consequences, and Prospects, Proceedings of the 2005 International Meeting on Reduced Enrichment for Research and Test Reactors, November, 2005, Boston, USA.

[3] R. W. Brown, The Radiopharmaceutical Industry's Effort to Migrate Toward Mo-99 Production Utilizing LEU, Proceedings of the 2005 International Meeting on Reduced Enrichment for Research and Test Reactors, November, 2005, Boston, USA.

[4] P. R. Cristini, H. J. Cols, R. Bavaro, M. Bronca, R. Centurión, D. Cestau " Production of Molybdenum-99 from Low Enriched Uranium Targets" Proceedings of the 2002 International Meeting on Reduced Enrichment for Research and Test Reactors, San Carlos de Bariloche, Argentina, November 2002.

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[5] A. J. Bakel, D. C. Stepinski, G. F. Vandegrift, A. A. Leyva, A. V. Gelis, A. H. Bond, and H. Mayes, "Progress in Technology Development for Conversion of ^{99}Mo Production—BATAN's (Indonesia) Conversion Program, Progress in the CNEA (Argentina) LEU foil-Baseside Process, and Development of Inorganic Sorbents for 99Mo Production, Proceedings of the 2005 International Meeting on Reduced Enrichment for Research and Test Reactors, November, 2005, Boston, USA.

[6] Lin C. C. Chemical Effects of Gamma Radiation on Iodine in Aqueous Systems. *J. Inorg. Nucl. Chem*., **1980,** *42*, 1101-1107.

[7] Wolery, T. J. and Daveler, S. A., 1992, EQ6, A computer program for reaction path modeling of aqueous geochemical systems: Theoretical manual, user's guide, and related documentation (Version 7.0): Lawrence Livermore National Laboratory Report UCRL-MA- 110662 PT IV.

[8] A. V. Gelis, K. J. Quigley, S. B. Aase, A. J. Bakel, A. Leyva, M. C. Regalbuto, and G. F. Vandegrift, ANL Progress On the Cooperation with CNEA for the Mo-99 Production: Base-Side Digestion Process, Proceedings of the 2003 International Meeting on Reduced Enrichment for Research and Test Reactors, November, 2004, Vienna, Austria.

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