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B. Srinivasan, J. C. Hutter, G. K. Johnson, and G. F. Vandegrift  
Chemical Technology Division

Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 60439

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# DEVELOPMENT OF DISSOLUTION PROCESS FOR METAL FOIL TARGET CONTAINING LOW ENRICHED URANIUM

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## ABSTRACT

About six times more low enriched uranium (LEU) metal is needed to produce the same quantity of  $^{99}\text{Mo}$  as from a high enriched uranium (HEU) oxide target, under similar conditions of neutron irradiation. In view of this, the post-irradiation processing procedures of the LEU target are likely to be different from the Cintichem process procedures now in use for the HEU target. We have begun a systematic study to develop modified procedures for LEU target dissolution and  $^{99}\text{Mo}$  separation. The dissolution studies include determination of the dissolution rate, chemical state of uranium in the solution, and the heat evolved in the dissolution reaction. From these results we conclude that a mixture of nitric and sulfuric acid is a suitable dissolver solution, albeit at higher concentration of nitric acid than in use for the HEU targets. Also, the dissolver vessel now in use for HEU targets is inadequate for the LEU target, since higher temperature and higher pressure will be encountered in the dissolution of LEU targets. Our desire is to keep the modifications to the Cintichem process to a minimum, so that the switch from HEU to LEU can be achieved easily.

## INTRODUCTION

In October 1992, the United States Congress passed an amendment to the Atomic Energy Act of 1954. This amendment prohibits export of high enriched uranium (HEU) for use as fuel or target in a research or test reactor unless several conditions are met: (1) no alternative low enriched uranium (LEU) fuel or target can be used, (2) the recipient 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.

In this report, we discuss our continuing research and development (R&D) activities on the substitution of LEU-metal foil target in the place of HEU- $\text{UO}_2$  for the production of  $^{99}\text{Mo}$  [1-3]. This isotope is the precursor to  $^{99\text{m}}\text{Tc}$ , an important nuclide in diagnostic nuclear medicine. Specifically, we report the results of our experiments on the dissolution of uranium metal foil in a mixture of nitric and sulfuric acids, which is the first step in the isolation of  $^{99}\text{Mo}$  from

neutron-irradiated targets. The report also contains a comparison of LEU-metal foil targets and HEU-UO<sub>2</sub> targets and summarizes the processing chemistry used to isolate <sup>99</sup>Mo from irradiated HEU-UO<sub>2</sub>.

### PRODUCTION OF <sup>99</sup>MO

Molybdenum-99 ( $t_{1/2} = 66$  h) is produced with about 6% yield in the thermal neutron-induced fission of <sup>235</sup>U:



It can also be produced by neutron capture reaction of <sup>98</sup>Mo according to:



Molybdenum-99 is commercially produced through the fission reaction rather than by neutron absorption. The specific activity of the nuclide that can be obtained from the former reaction is much higher than the latter. The HEU (~93% <sup>235</sup>U) targets used in the production of <sup>99</sup>Mo contain either uranium compounds (e.g., UO<sub>2</sub>) or uranium alloys (e.g., UAl<sub>x</sub>) in the form of fuel plates [4-7], rods [8], or cylinders [9,10]. After irradiation, the cladding is removed either by mechanical or chemical means, and the uranium is dissolved. The <sup>99</sup>Mo in the dissolver solution is separated from unconverted uranium, other fission products, and activation products (<sup>239</sup>Np and <sup>239</sup>Pu). The separation procedures are based upon a combination of chromatographic separation, solvent extraction, and/or precipitation methods.

Technetium-99m ( $t_{1/2} = 6$  h) is the daughter product from beta decay of <sup>99</sup>Mo. The technetium isomer emits 140 keV gamma-rays to form <sup>99</sup>Tc ( $t_{1/2} = 2.1 \times 10^5$  y). In diagnostic nuclear medicine, the usual practice is to allow the <sup>99m</sup>Tc to grow from the decay of <sup>99</sup>Mo contained in a column, and elute the <sup>99m</sup>Tc as needed.

In the U.S., until the end of February 1990, <sup>99</sup>Mo was produced by thermal neutron irradiation of cylindrical HEU-UO<sub>2</sub> targets in a reactor operated by the Union Carbide Corporation in Sterling Park, New York. The production was stopped at that time because of the closure of the reactor facilities.

At Sterling Park, the separation and purification of the <sup>99</sup>Mo generated in the HEU-UO<sub>2</sub> target were done by a procedure known as the "Cintichem process." At the time of closing and decommissioning of the reactor facilities, the proprietary rights governing the process were transferred to the U.S. Department of Energy (DOE). The DOE is considering use of the Cintichem process to produce <sup>99</sup>Mo at Sandia National Laboratories. At present, Nordion of Canada is the primary supplier of <sup>99</sup>Mo to the U.S. The Cintichem process is also being used by BATAN (Badan Tenaga Atom Nasional) in Indonesia to produce <sup>99</sup>Mo from HEU-UO<sub>2</sub> targets. A formal agreement between Indonesia and the U.S. is in the final stages of negotiation to test the replacement of HEU-UO<sub>2</sub> target with the LEU-metal foil target, and also to test the modifications to the Cintichem process to produce <sup>99</sup>Mo from LEU targets.

At Argonne National Laboratory (ANL), under the aegis of the Reduced Enrichment for Research and Test Reactors (RERTR) program, we are working toward developing a LEU-metal

foil target to replace the HEU-UO<sub>2</sub> target. The work also includes developing chemical procedures to separate <sup>99</sup>Mo from neutron irradiated LEU-metal foil targets. The various steps in the procedure will resemble the steps in the original Cintichem process. In this manner, <sup>99</sup>Mo production facilities can make a smooth switch from HEU to LEU targets with minimal process changes.

In the sections to follow, we shall describe the similarities and differences between the HEU-UO<sub>2</sub> and LEU-metal foil targets, outline the Cintichem process, and report progress made by us in developing a dissolution procedure for the LEU-metal foil target.

### COMPARISON OF HEU-UO<sub>2</sub> AND LEU-METAL FOIL TARGETS

To develop a satisfactory dissolution and separation process for the LEU-metal foil targets, we must understand the similarities and differences between the HEU-UO<sub>2</sub> and the LEU-metal foil targets. The two targets are compared in Table 1.

Table 1. Properties of HEU-UO<sub>2</sub> and LEU-Metal Foil Targets

	HEU-UO <sub>2</sub>	LEU-Metal Foil
Chemical Composition	UO <sub>2</sub>	U metal
Total uranium	about 16 g	about 94 g
<sup>235</sup> U enrichment	~93%	slightly less than 20%
<sup>235</sup> U	15 g	18.5 g
<sup>99</sup> Mo	532 Ci (1.11 mg)	545 Ci (1.13 mg)
<sup>239</sup> Pu	28 μCi (0.44 mg)	722 μCi (11.8 mg)

The HEU and LEU targets produce about the same amount of <sup>99</sup>Mo at the end of irradiation, since both targets contain about the same amount of fissionable <sup>235</sup>U. However, the activation products (e.g., <sup>239</sup>Pu) are about twenty-six times more abundant in the LEU target relative to HEU, because of the higher amount of <sup>238</sup>U in the former. The fission products abundance remain about the same in the two targets.

With regard to acid dissolution, six times more LEU will have to be dissolved relative to HEU, 94 g versus 16 g. The HEU dissolution involves oxidizing U(IV) in the target to U(VI) in the solution (two-electron transfer), whereas the LEU dissolution involves a change from the zero oxidation state in the target to the VI state in the solution (six electron transfer). At least three times more oxidant will be needed for the LEU target relative to HEU. Furthermore, the rates of dissolution, the heats of reaction, and the products (especially the gases) from the dissolution of metal foil and UO<sub>2</sub> are likely to be different.

### THE CINTICHEM PROCESS

As stated earlier, the U.S. DOE owns the proprietary rights for the Cintichem process and also possesses detailed documentation describing the process. The main features of the Cintichem process are based on a 1974 U.S. Patent [9]. It appears that for the commercial production of <sup>99</sup>Mo, modifications and improvements have been made to the procedures described in the patent.

We have contacted the U.S. DOE to obtain copies of the Cintichem process documents. We hope to use them in designing post-irradiation chemistry procedures for the LEU-metal foil targets which are similar to the Cintichem process. However, the documents are not yet available, and therefore, we are unable to describe here the exact details of the Cintichem process. In its place, we substitute the information that is available in the patent.

The patent by Arino et al. [9] describes the methods of preparation for the target itself and the various steps involved in the separation of  $^{99}\text{Mo}$  from the irradiated HEU- $\text{UO}_2$  target. Here, we are concerned with the dissolution procedure of the irradiated target and subsequent separation of  $^{99}\text{Mo}$  from the dissolver solution.

As described in the patent, the HEU- $\text{UO}_2$  target contained 7 g of  $^{235}\text{U}$  (~93% enriched) in the form of  $\text{UO}_2$ , deposited electrolytically on the inner side of a stainless steel cylinder. Note that for commercial production of  $^{99}\text{Mo}$ , the target contains about twice the amount of  $^{235}\text{U}$ . The procedures described below are for the 7 g  $^{235}\text{U}$  target.

The volatile elements (fission product gases) that escaped from the target during irradiation were removed first. The  $\text{UO}_2$  was then dissolved in 60 mL of a mixture of 1M sulfuric acid and 0.7M nitric acid. The stainless steel cylinder target served as the dissolver vessel. The pressure during dissolution was a maximum of about 6 atm (70 psi gauge). The dissolution was complete in about 45 min. The concentration of uranium in the dissolver solution was about 0.5M.

The volatile fission products (e.g., iodine, noble gases) released by the dissolution process were then removed to an alumina trap and a cold finger containing suitable absorbents (calcium oxide, calcium sulfate, and zeolite). The acid solution containing molybdenum along with other non-volatile fission and activation products was transferred to another container. The cylinder was washed with dilute sulfuric acid, and the washings also were transferred. After the addition of  $\text{Na}_2\text{SO}_3$ , the molybdenum in the solution was precipitated by the addition of alpha benzoinoxime solution in the presence of hold-back carriers for other fission products. The precipitate was washed with dilute sulfuric acid, and then it was dissolved in alkaline hydrogen peroxide solution. Further purification and additional decontamination were achieved through re-precipitation (again from an acidic solution) using alpha benzoinoxime, followed by dissolution of the precipitate in sodium hydroxide solution. Finally, the alkaline solution containing molybdenum was passed through a silver-coated charcoal column, an inorganic ion exchanger column, and an activated charcoal column. The column purification procedures were repeated to obtain a highly pure product. The specific activity of the final  $^{99}\text{Mo}$  product was >1000 mCi/mL. The total of other fission products was less than 1  $\mu\text{Ci}$  per curie of  $^{99}\text{Mo}$ .

## R&D WORK ON LEU-METAL FOIL TARGET AND MOLYBDENUM SEPARATION

At ANL, the R&D work on the LEU-metal foil target is focused on developing suitable targets and post-irradiation chemical procedures for the production of  $^{99}\text{Mo}$ . The new chemical procedures are expected to resemble closely the Cintichem process procedures used for HEU targets. Our program goals are as follows:

1. Develop a suitable LEU-metal foil target.
2. Establish acid dissolution procedure for the irradiated target.
3. Establish separation and purification procedure for  $^{99}\text{Mo}$  from the acid solution.

4. Provide guidance to the commercial producers to gain acceptance from the U.S. Federal Drug Administration (FDA) and other government agencies for the  $^{99}\text{Mo}$  product from LEU-metal foil targets.

The target design work is being done by our colleagues in the Energy Technology Division of ANL. Their work is reported in a companion paper [11]. Our work on the dissolution of LEU targets and separation procedures for  $^{99}\text{Mo}$  is being done in the Chemical Technology Division of ANL and at the University of Illinois in Urbana. The work toward gaining approval from FDA and other government agencies is yet to begin. We have made initial contacts with the FDA to learn about preparing the application for human use of  $^{99\text{m}}\text{Tc}$  derived from irradiation of LEU targets.

The work on the dissolution of unirradiated samples of uranium metal foil is reported in the following sections. In these preliminary experiments, depleted uranium metal foil samples were used in place of LEU samples. The experiments dealt with the following four aspects:

1. Dissolution rates for uranium metal foil in nitric-sulfuric acid mixtures.
2. Oxidation state of uranium in the dissolved solution.
3. Calorimetry experiments to determine the heat evolved during the dissolution reaction.
4. Gas analysis experiments to determine the nature and abundance of gases evolved during dissolution. These experiments have not been completed yet.

#### NITRIC-SULFURIC ACID DISSOLUTION OF URANIUM METAL FOIL

We have stated earlier that three times more oxidant is needed for the metal foil dissolution relative to  $\text{UO}_2$ . Therefore, the nitric acid concentration in the dissolver mixture must be increased for the LEU-metal foil target, relative to the Cintichem process solution, in order to dissolve the foil in a minimum amount of acid. We studied of the dissolution rate of (depleted) uranium metal foil in various nitric-sulfuric acid mixtures and also in pure nitric acid. The nitric acid concentration was  $4\text{M}$  to  $16\text{M}$ , which is higher than the  $0.7\text{M}$  nitric acid used in the Cintichem process.

Samples of depleted uranium metal foil (0.3%  $^{235}\text{U}$ ) were used in the dissolution experiments; the foil thickness was  $127\ \mu\text{m}$  (0.005 in.) and the surface density was  $203\ \text{mg}/\text{cm}^2$ . An unknown amount of surface oxide layer was present on the foil. The oxide layer was not removed prior to dissolution, since in the actual production of  $^{99}\text{Mo}$  the oxide layer is expected to be present.

Uranium metal foil samples weighing between 30 and 80 mg were dissolved in about 3 to 6 mL of the acid at temperatures of  $25\text{--}95^\circ\text{C}$ . The temperature during dissolution was kept nearly constant by immersing the dissolution tubes in a constant temperature bath. During dissolution, gas bubbles evolved from the surface of the foil in a steady stream. The end of dissolution was marked by the cessation of gas evolution. It is certain that  $\text{NO}_2$  is one of the gaseous products, as seen by the characteristic brown color of the fumes. Other products are likely to be a mixture of other oxides of nitrogen ( $\text{NO}$  and  $\text{N}_2\text{O}$ ). It is known that in nitric acid dissolution, hydrogen gas is not one of the products [12]. Whether hydrogen gas is evolved in nitric and sulfuric acid mixtures will be a subject of our study in the gas analysis experiments.

The rates of dissolution of uranium metal foil in nitric acid, and in a mixture of nitric and sulfuric acids are shown in Table 2. Note that two surfaces of the thin foil are exposed simultaneously to the acids. For example, a  $203\ \text{mg}$  foil presents  $2\ \text{cm}^2$  surface for dissolution.

In the units of mg/min/cm<sup>2</sup> given in Table 2, this factor of two is taken into account in calculating the surface area from the surface density of the foil given above.

Table 2. Rate of Dissolution of Uranium Metal Foil in Nitric Acid and in Mixture of Nitric and Sulfuric Acids

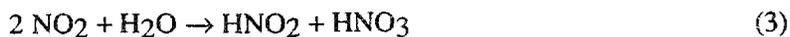
Acid (mol/L)		Rate (mg/min/cm <sup>2</sup> ) <sup>a</sup>				
Nitric	Sulfuric	25°C	40°C	59°C	84°C	95°C
4		Very slow <sup>b</sup>				0.76
4	0.56	≥0.03			3.1	
8		0.09	0.15	≥0.42 <sup>c</sup>	1.5	
8	0.56	0.29	0.70	1.7	4.0	
8	1.1	0.52	1.5	4.7		
12		≥0.2 <sup>c</sup>	0.73	1.6	4.0	
12	0.56	1.81	5.64	9.3	21	
12	1.1	5.9	12.6	35		
16		≥0.2 <sup>c</sup>			6.0	
16	0.56				102	

**Notes:**

- <sup>a</sup>The rates of dissolution represent an average value. The samples were not stirred during dissolution. Where determined, the initial rates for dissolution were found to be higher than the average values.
- <sup>b</sup>The dissolution rate in 4M nitric acid at 25°C is very low. There is no appreciable change in the mass of the foil even after 164 h.
- <sup>c</sup>The ≥ sign means that the exact time for complete dissolution was not known. Several of these experiments were done overnight or over the weekend, and complete dissolution had occurred during this period.

The data in Table 2 are semi-quantitative for the following reasons: First, the foil was not pure uranium metal; a surface oxide layer was present. Therefore, the rates correspond to the dissolution of a mixture of metal and its oxide. Second, the time required for dissolution was determined by visual inspection of the total disappearance of the foil, which invariably coincided with the cessation of gas evolution. Such visual observations yield only approximate values.

In a separate experiment, we studied the rates of dissolution of the metal foil by bubbling air or nitrogen through the dissolver solution (mixture of 12M nitric acid + 0.56M sulfuric acid). The bubbling removed the oxides of nitrogen from the solution as soon as they formed. The dissolution slowed down by a factor of five relative to quiescent condition. It appears that dissolved NO<sub>2</sub> accelerates the dissolution process, possibly due to reconversion to nitrous and nitric acid according to



Additional experiments are necessary to understand the kinetics and mechanism of the dissolution reaction.

Despite the semi-quantitative nature of the data given in Table 2, some general conclusions are possible. For a given nitric acid concentration, the rate of dissolution is higher in nitric-sulfuric acid mixtures than in pure nitric acid alone. An earlier study [13] showed that the rate of dissolution of uranium metal in the mixture is about 30 times higher when the nitric acid contained 3 vol % sulfuric acid (0.56M) as compared with pure nitric acid of the same concentration. However, our study showed that the rate increase is only a factor of two or three higher. Also, the rate of dissolution increases with increasing temperature.

The solution at the end of dissolution is greenish yellow, which upon heating to about 90°C is converted to a yellow solution. Concentration of this solution to a very low volume yielded crystals of uranium compounds. These could be redissolved very easily in a minimum amount of water to yield concentrated solutions of about 200 g of uranium/per Liter. This is comparable to the 0.5M solution that was obtained in the Cintichem process. We have not completed our experiments on the crystallization temperature of the dissolved uranium compounds in the various acid mixtures. These experiments will be done after we decide upon the exact composition of the dissolver solution.

A desirable rate of dissolution for the actual target is about 3 mg/min/cm<sup>2</sup>. At this rate, a LEU-metal foil target (see Table 3) will require about 30 min for complete dissolution. Note that the dissolution time is independent of mass, since higher mass of foil has correspondingly higher surface area.

Table 3. Time Required for Complete Dissolution of LEU-Metal Foil Target

Mass of Foil	15.7 g
Dimensions	10.2 cm x 7.6 cm x 0.013 cm (thick)
Surface Area for Dissolution	155 cm <sup>2</sup>

Dissolution Rate (mg/min/cm <sup>2</sup> )	Dissolution Time (min)
1	101
3	34
10	10

The data shown in Table 2 can be used to define the concentration of the acids and temperature needed to obtain a dissolution rate of 3 mg/min/cm<sup>2</sup>. If the dissolution is to take place at 25°C, then the preferred dissolver solution is a mixture of 12M nitric acid and 1.1M sulfuric acid; the dissolution will be complete in about 17 min. If the acid mixture is to resemble the Cintichem dissolver solution, then the mixture of 4M nitric acid and 0.56M sulfuric acid at 84°C may be used. If the mixture is made up from 1.1M sulfuric acid instead of 0.56M, then dissolution can be carried out at <84°C. We plan to carry out dissolution experiments using larger quantities of uranium metal than reported here in order to duplicate commercial processing conditions.

## OXIDATION STATE OF URANIUM IN DISSOLVED SOLUTION

Depleted uranium metal foil samples (70 to 130 mg) were dissolved in a mixture of nitric and sulfuric acid (3 to 4 mL), and the visible absorption spectra of these solutions were recorded by a Cary Recording Spectrophotometer. The different experimental conditions for the dissolution are as follows:

- a) 8M nitric acid + 0.56M sulfuric acid
- b) 12M nitric acid + 0.56M sulfuric acid
- c) 12M nitric acid + 0.56M sulfuric acid; nitrogen bubbled during dissolution
- d) 12M nitric acid + 0.56M sulfuric acid; air bubbled during dissolution
- e) 12M nitric acid + 1.1M sulfuric acid
- f) 12M nitric acid + 1.1M sulfuric acid; air bubbled during dissolution.

The absorption spectra in all cases were identical. A typical example is shown in Figure 1. The peak and shoulders in the region of 420 to 470 nm are due to the absorption by the uranyl species ( $\text{UO}_2^{2+}$ ). The absence of U(IV) is indicated by no appreciable absorption in the region around 630 nm. If dissolved  $\text{NO}_2$  exists in the solution, then the  $\text{UO}_2^{2+}$  absorption is masked by the absorption continuum at the short wavelength region (below 450 nm). Bubbling air or nitrogen during dissolution did not change the oxidation state of uranium in the dissolved solution; in both cases, only  $\text{UO}_2^{2+}$  was present in the solution, with negligible amounts of U(IV). The solution obtained from the dissolution of uranium metal appears to be similar to the solution from  $\text{UO}_2$  dissolution; uranyl sulfate is expected to be the major species in both cases. No studies were done to determine the exact nature of the species and their abundance.

## CALORIMETRY EXPERIMENTS

The heat evolved during the dissolution of depleted uranium metal foil in a mixture of nitric acid and sulfuric acid was determined at 30, 40 and 50°C by using a LKB 8700 precision calorimetry system. A chemical standard (reference material 724, tris-hydroxymethyl aminomethane or simply tris, from the National Bureau of Standards) was used to verify that the system was working satisfactorily. It also served as a calibration standard for the calorimeter. This material reacts with 0.100N HCl and releases 245.76 J/g of heat at 25°C, at a concentration of 5 g per 1000 cm<sup>3</sup> of solution. In our experiments 500 mg of tris was dissolved in 100 mL of 0.100N HCl, causing a 0.27°C temperature rise in the solution, at 30°C. In the temperature range of 20 to 30°C, the heat of reaction may be corrected for the change in heat capacity with temperature by using the following value:  $\Delta C_p = 1.435 \text{ J}/(\text{g}\cdot^\circ\text{C})$ . But the temperature regime of our experiments was 30 to 50°C. This is outside the limits for which the correction is valid. However, as a first approximation, we have used the above correction factor for all our experiments.

The heat evolved by the dissolution of the depleted uranium metal foil was determined by dissolving 30 to 200 mg of the metal in 100 mL of the 12M nitric acid and 1.1M sulfuric acid mixture at 30, 40, and 50°C. The temperature rise observed in the experiments is given in Table 4. Approximate values for the heat of reaction calculated from the observed temperature rise are also included. The following assumptions were made in calculating the heat of reaction:

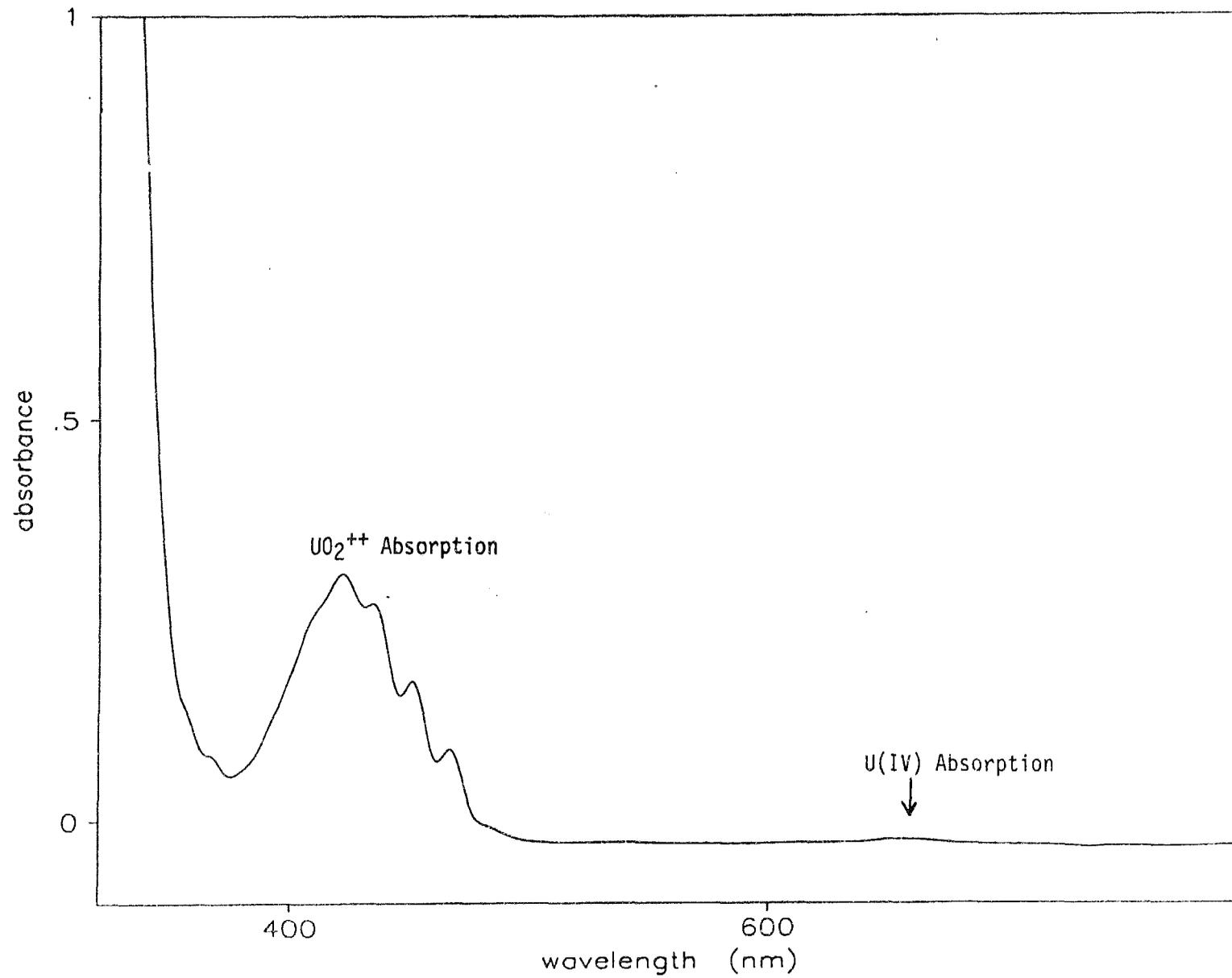


Figure 1. Absorption Spectrum in the Visible Region of Uranium Metal Dissolved in a Mixture of 12M HNO<sub>3</sub> and 1.1M Sulfuric Acid. Uranium concentration is about 0.1M.

1. The results of the tris standard experiment were used to evaluate the quantity of heat that is used up to heat the glass calorimeter and the stirrer to the desired temperature, in addition to the 100 mL HCl present in the calorimeter. The heat capacity of 0.100N HCl was taken to be 4.15 J/(g•°C) at 25°C, as obtained from the National Standard Reference Data Series [14]. No corrections were made for heat capacity variation with temperature.
2. The heat capacity of 12M nitric acid solution was calculated from the data provided by the National Standard Reference Data Series [14]. The calculated value was 2.72 J/(g•°C), at 25°C. The same value was assumed for the nitric and sulfuric acid mixture at all temperatures.

Table 4. Results from Calorimetry Experiments on Dissolution of Depleted Uranium Metal Foil in 100 mL of Mixture of 12M Nitric Acid and 1.1M Sulfuric Acid

Mass of Foil (mg)	Temperature (°C)	Temperature Rise (°C)	Heat of Reaction (kJ/mol)
31.44	30	0.40	1200
30.52	40	0.36	1100
62.47	40	0.74	1100
110.42	40	1.28	1100
204.74	40	2.39	1100
28.32	50	0.34	1100

The heat of reaction appears to be about 1100 kJ/mol (average of the six values in Table 4). The heat of reaction not only includes the dissolution of uranium metal in the acid, but also the heat of dissolution of gases evolved. The dissolved gases may participate in other reactions, such as the production of nitrous and nitric acid from dissolved nitrogen dioxide. No corrections were made for these side reactions or for the heat removed by the escaping gases. Making appropriate corrections for these factors would yield a more precise heat of dissolution of uranium metal. In addition, the heat capacity of the nitric-sulfuric acid mixtures at different temperatures must be obtained. We plan to gather the relevant data in the near future. Nevertheless, the data given in Table 4 are useful in predicting the temperature rise of the reaction mixture in a dissolution vessel that is similar to the one used in the Cintichem process.

The Cintichem process dissolution vessel is a stainless steel cylinder measuring 45.7-cm long, 2.5-cm diameter, and 0.25-cm thick. The volume of the vessel is about 230 cm<sup>3</sup>. If such a vessel is used to dissolve the same amount of uranium metal foil (7.5 g) and in the same volume (60 mL) as used in the Cintichem process, the temperature rise is expected to be about 60°C. In this calculation, the heat capacity of the system (vessel and the dissolver solution in a mixture of 12M nitric acid and 1.1M sulfuric acid) is assumed to be 2.76 J/(g•°C).

In the actual production of <sup>99</sup>Mo, about six times more LEU-metal foil is needed relative to HEU to obtain the same amount of <sup>99</sup>Mo. The dissolution will require a corresponding increase in the amount of the acid, so that the final uranium concentration (0.5M) remains the same in both cases. The Cintichem dissolver is not sufficiently large to hold the higher volume of acid needed

for LEU. A new dissolver is needed. The temperature rise expected in the new dissolver can be calculated from the experimental heats of reaction reported in Table 4. The new dissolver must be designed to accommodate the temperature rise in the dissolution reaction and also safely contain the gases released during dissolution. The results of gas analysis experiments, in progress, will help in calculating the expected pressure inside the new dissolver vessel.

## SUMMARY

At ANL, we are developing a LEU-metal foil target to replace the HEU-UO<sub>2</sub> target for the production of <sup>99</sup>Mo. About six times more uranium will be needed in the LEU target in order to produce the same amount of <sup>99</sup>Mo from the LEU as from the HEU (assuming same duration of irradiation at the same neutron fluence). Our work reported here is confined to studies on the post-irradiation dissolution procedures for the LEU target. Our desire is to design the chemistry procedures along the same lines as the Cintichem process procedures, making minimal changes and modifications. In this manner, the switch from HEU to LEU can be easily accomplished when the latter target becomes available for commercial production of <sup>99</sup>Mo.

The dissolution studies show that LEU-uranium metal foil dissolves easily within 30 min in 12M nitric and 1.1M sulfuric acid mixtures at 25°C, in 12M nitric and 0.56M sulfuric acid mixtures at 40°C, or in 4M nitric and 0.56M sulfuric acid mixtures at 84°C. The reaction takes place smoothly with steady evolution of gases from the surface of the foil. Other combinations of acid concentrations and temperature can also be used to achieve a quick dissolution. The final selection of the dissolver solution will be made by taking into account the ease of dissolution, the final concentration of uranium in the dissolver solution, and the similarity between this solution and the corresponding Cintichem process solution. Uranyl ions are primarily present in the dissolver solution with no evidence for U(IV) species.

Calorimetric experiments show that the heat of dissolution of uranium metal is about 1100 kJ/mol. This result can be used to predict the temperature rise that will accompany the dissolution of the LEU-metal foil in the acid mixture.

A new dissolver vessel, which is different from the Cintichem vessel, is needed for the dissolution of LEU-metal foil targets. The new design must take into account the expected temperature rise during dissolution, as well as the pressure increase due to the release of gases. Gas analysis experiments are in progress to determine the nature and abundance of gases released by the dissolution process.

## REFERENCES

- [1] G. F. Vandegrift, D. J. Chaiko, R. R. Heinrich, E. T. Kucera, K. J. Jensen, D. S. Poa, R. Varma, and D. R. Vissers: Preliminary Investigations for Technology Assessment of <sup>99</sup>Mo Production from LEU Targets, 1986 International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), November 3-6, 1986, Gatlinburg, Tennessee, ANL/RERTR/TM-9, CONF-861185, pp. 64-79.
- [2] G. F. Vandegrift, J. D. Kwok, S. L. Marshall, D. R. Vissers, and J. E. Matos: Continuing Investigations for Technology Assessment of <sup>99</sup>Mo Production from LEU Targets, presented at the 1987 International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), September 28-October 2, 1987, Buenos Aires, Argentina.
- [3] G. F. Vandegrift, J. C. Hutter, B. Srinivasan, J. E. Matos, and J. L. Snelgrove: Development of LEU Targets for <sup>99</sup>Mo Production and Their Chemical Processing,

presented at the 16th Int. Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), October 3-7, 1993, Oarai, Ibaraki, Japan.

- [4] J. Konrad: Facilities for the Irradiation of  $^{235}\text{U}$  for the Production of  $^{99}\text{Mo}$  at the HFR Petten, Irradiation Technology, Proc. of the Int. Topical Meeting, Grenoble, France, pp. 677-683 (1982).
- [5] J. Salacz: Production of Fission Mo-99, I-131 and Xe-133, Revue IRE Tijdschrift, Vol. 9, No. 3 (1985).
- [6] C. J. Fallais, A. Morel de Westgaver, L. Heeren, J. M. Bagnat, J. M. Gandolfo, and W. Boeykens: Production of Radioisotopes with BR2 Facilities, BR2 Reactor Meeting, Mol, Belgium, INIS\_MF\_4426, pp. IX-1 to -11 (1978).
- [7] A. A. Sameh and H. J. Ache: Production Techniques of Fission Molybdenum-99, Radichimica Acta 41 (1987) 65-72.
- [8] R. T. Jones: AEC-2 Experiments in Support of  $^{99}\text{Mo}$  Production in NRU, AECL-7335 (1982).
- [9] 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).
- [10] H. Arino, F. J. Cosolito, K. D. George, 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).
- [11] T. C. Wiencek, G. L. Hofman, E. L. Wood, C. T. Wu, and J. L. Snelgrove: LEU  $^{99}\text{Mo}$  Production-Overview, Status and Plans, Proc. of the 17th Int. Meeting on Reduced Enrichment for Research and Test Reactors, September 18-22, 1994, Williamsburg, Virginia, U.S.A.
- [12] R. E. Blanco and C. D. Watson: Head-End Processes for Solid Fuels in Reactor Handbook, 2nd edition, eds. S. M. Stoller and R. B. Richards, Interscience Publishers Inc., New York, Vol. II (1961) pp. 60.
- [13] B. Elliot: Process Development Quarterly Report MCW-1407, as cited in Nuclear Science Abstracts 14 (1960) 15669.
- [14] V. B. Parker: Thermal Properties of Aqueous Uni-univalent Electrolytes, National Standard Reference Data Series, National Bureau of Standards 2, U.S. Government Printing Office, Washington D.C. (1965) pp. 44.