

## **ANL PROGRESS ON THE COOPERATION WITH CNEA FOR THE MO-99 PRODUCTION: BASE-SIDE DIGESTION PROCESS.**

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### **ABSTRACT**

Conversion from high-enriched uranium (HEU) to low-enriched uranium (LEU) targets for the Mo-99 production requires certain modifications of the target design, the digestion and the purification processes. ANL and the Argentine Comisión Nacional de Energía Atómica (CNEA) are collaborating to overcome all the concerns caused by the conversion of the CNEA process to use LEU foil targets. A new digester with stirring system has been successfully applied for the digestion of the low burn-up U foil targets in  $\text{KMnO}_4$  alkaline media. In this paper, we report the progress on the development of the digestion procedure utilizing effective stirring and focusing on minimization of the liquid radioactive waste.

### **1. Introduction**

To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) program is working to limit the use of high-enriched uranium (HEU) by substituting low-enriched uranium (LEU) fuel and targets. Low-enriched uranium contains <20%  $^{235}\text{U}$ . Technetium-99m, the daughter of  $^{99}\text{Mo}$ , is the most commonly used medical radioisotope in the world. Currently, most of the world's supply of  $^{99}\text{Mo}$  is produced by fissioning  $^{235}\text{U}$  in targets containing HEU, generally 93%  $^{235}\text{U}$ . These producers include Institut National des Radioéléments (IRE), Mallinckrodt, and the South African Nuclear Energy Corporation Limited (NECSA). The Argentine Comisión Nacional de Energía Atómica (CNEA) recently converted to using an LEU-Al dispersion target [1]. Targets for the production of  $^{99}\text{Mo}$  are generally either (1) miniature Al-clad fuel plates or pins containing U-Al alloy or  $\text{UAl}_x$  dispersion fuel or (2) a thin film of  $\text{UO}_2$  on the inside of a stainless steel tube. After irradiation, the  $^{99}\text{Mo}$  is recovered from the irradiated uranium and purified.

To yield equivalent amounts of  $^{99}\text{Mo}$ , an LEU target must contain approximately five times the uranium as does an HEU target. Consequently, substituting LEU for HEU requires changes in both target design and chemical processing. Three major challenges have been identified in the substitution of LEU for HEU: (1) modifying the targets and purification processes as little as possible, (2) assuring continued high yield and purity of the  $^{99}\text{Mo}$  product, and (3) limiting economic disadvantages.

The CNEA process has been described in the literature [1,2] and has much in common with the Mallinckrodt process; both processes are based on that developed by Sameh and Ache [3]. In this process, the irradiated targets are heated in sodium hydroxide solution. The aluminum cladding and meat in the targets are dissolved to form sodium aluminate and the uranium is digested, forming a mixture of  $\text{UO}_2$  and  $\text{Na}_2\text{U}_2\text{O}_7$ . The digestion has to be carried out in 2 L of

1.8-2.0 M NaOH solution to provide enough sodium hydroxide and volume to keep aluminum in solution. If the volume is smaller or less hydroxide is used, aluminum hydroxide will precipitate, clogging the filter and preventing removal of the solution from the digester. Molybdenum is soluble in alkaline solutions as the molybdate ion, but the actinides and many of the metallic fission-products reside in the precipitate as the hydroxides. Following filtration of the dissolver solution, the filtrate is fed onto an anion-exchange column, which retains molybdenum and some other anionic species. A series of separation processes purifies the molybdenum to meet pharmaceutical standards.

We have developed LEU metal foil targets that are wrapped in a thin aluminum-foil fission recoil barrier. The foil is held between two aluminum tubes that have been swaged for good thermal contact and welded closed at each end [4, 5]. The fission recoil barrier is present to prevent interaction between the uranium foil and the material of the target, allowing the foil to be removed from the target before digestion. The aluminum mass to be digested for these targets is significantly lower than for the HEU targets currently used by CNEA. Therefore, the LEU foil target can be digested in less than 400 mL of the alkaline solution, which results in a substantial decrease in the amount of liquid radioactive waste.

## **2. Progress**

Since reporting R&D results at the 2003 International RERTR Meeting [6], we have made progress aimed at the conversion of  $^{99}\text{Mo}$  production to LEU targets in two areas: (1) developing a production digester with stirring system and (2) modifying the process for digesting irradiated LEU foils by alkaline potassium permanganate solution. Each of these is discussed below.

### Prototype Dissolver for CNEA Production

In 2003 ANL purchased a stainless steel vessel from Berghof™ (Fig. 1a).



a)



b)

Figure 1. The Berghof™ pressure vessel (a) and the digester set-up (b).

The vessel is sealed by means of two knobs that require only a force equivalent to hand-tightening. The vessel has been customized to meet the digestion process requirements: (1) the whole vessel is made of stainless steel 316 Ti, (2) the vessel has been rated up to  $T_{\max}=300\text{ }^{\circ}\text{C}$  and  $P_{\max}=3600\text{ psig}$  (250 bar), (3) a  $\frac{3}{8}$ -in. (9.5 mm) dip tube (to the bottom of the vessel) was added in order to remove the liquid and the solids by vacuum without removing the lid after digestion, (4) a  $\frac{1}{4}$ -in. (6.4 mm) port for adding liquids was placed in the cap, and (5) a thermocouple well was added to the cap.

The vessel is heated by an electric heating mantle wrapped around the body of the digester. A shroud fits over the digester body and serves as a stand and for directing air during the cool-down operation, as shown in Fig. 1b.

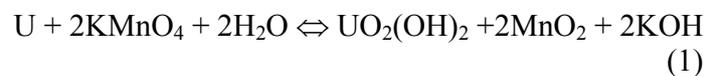
Conducting the tests during 2003, we experienced certain difficulties with the draining of the digester. Occasionally, not all solids were removed. To address this issue and to improve the digestion efficiency, we have purchased a new cap with a magnetic stirrer from Berghof™ (Fig. 2).



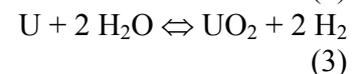
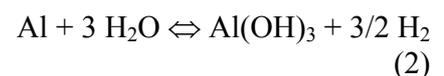
Figure 2. The cap with the magnetic stirrer and the motor.

### Digestion Process Modification

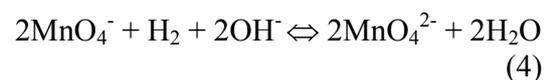
Our major modifications of the digestion process have been described in detail previously [6]. In short, the irradiated LEU foil with Al foil recoil barrier is digested in 0.5 M NaOH in the presence of  $\text{KMnO}_4$  at 285 °C and 90 bar (1400 psig). U metal reacts with  $\text{KMnO}_4$  according to Reaction 1:



However, there are a few side reactions going on during the digestion process:



The hydrogen gas, generated in the digester, reacts with permanganate according to Reaction 4 [7]:



The product of Reaction 4,  $\text{MnO}_4^{2-}$ , is reduced by hydrogen gas, resulting in a formation of  $\text{MnO}_2$  [7]. Therefore, the amount of the potassium permanganate in the digester should be sufficient to react with both U and hydrogen. Otherwise, uranium foil digestion and molybdenum release into the solution may not be complete.

Due to the large amount of the cake and its affinity for sticking to the digester walls, we were not able to consistently drain the digester well without stirring.

Our initial tests to optimize the stirring conditions were conducted with non-irradiated U foil. A typical experimental procedure is presented below:

- Place a target into the digester.
- Add solid  $\text{KMnO}_4$ , stable Mo and I carriers.
- Close the digester.
- Evacuate the digester to 25" Hg vacuum.
- Add 400 mL of 0.5 M NaOH solution through the vacuum line.
- Evacuate the digester to 25" Hg vacuum.
- Turn on the heater and the stirring motor (at maximum setting). Heat to the operating pressure and temperature, paying attention to the design limits (2800 psi, 300 °C).
- After the desired time for digestion, turn off the heater and cool the dissolver to 80-90 °C.
- Vent the gases
- While stirring, remove the suspension using  $\frac{3}{8}$ -in. tube under vacuum.
- Filter the suspension through Whatman™ medium flow filter.

However, the first experiments were discouraging. Only about 20-30% of the solids were removed by draining. Most of the cake, forced by the stirrer, accumulated on the upper part of the digester wall. Additional rinses were not effective, either.

Having tested various stirring rates, time, and temperature, we concluded that the only way to avoid accumulating of the cake on the wall and to drain the digester completely is to stir the suspension only below 120 °C. Therefore, we modified our experimental procedure accordingly. The stirring was applied only at beginning of the digestion to dissolve the solid  $\text{KMnO}_4$  and at the end of the cooling cycle below 100 °C. These conditions provide a complete solids removal with the digestion solution and 100-200 mL of rinse.

The modified procedure was used to digest low-burnup ( $10^{-5}\%$ ) uranium foils. The targets consisted of depleted uranium foil with less than 0.5%  $^{235}\text{U}$ . Weighed DU foils were wrapped in high-purity 0.04 mm Al foil and placed in the two Al capsules. The capsules were welded shut to prevent the escape of fission gases. After two hours of irradiation in a neutron flux of about  $10^{13}$  neutrons/cm<sup>2</sup>·sec and 24 hours of cooling time, both capsules were cut open. The irradiated DU foils wrapped with Al foil were removed from the inner capsule and digested.

The digestion results for the DU-irradiated targets are presented in Table 1. Procedures A and B are the replicates of the modified CNEA process. Procedure C is the modified IRE process that was conducted for comparison. It should be noted that high maximum pressure for procedures A and B is caused by the presence of hydrogen, generated according to Reactions 2 and 3. After cooling, the residual  $\text{H}_2$  pressure in the digester is about 10-15 bar at 60 °C. For procedure C, there is no residual pressure below 100 °C.

The  $^{99}\text{Mo}$  activity in the alkaline filtrate was determined by gamma counting at 739.4 and 777.8 keV. The recovery of  $^{99}\text{Mo}$  was calculated as follows. To determine an amount of Mo remaining in the solid phase, the filtered sludge was placed back in the digester and dissolved at 150 °C in 3-4 M  $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  added. About 20 mg of stable Mo was added to the solution as a carrier,

and alpha-benzoin oxime was added to precipitate both radioactive and stable  $\text{MoO}_2^{2+}$ . The suspension was filtered; the white precipitate was washed with 1 M  $\text{HNO}_3$  and then digested in 0.2 M  $\text{NaOH}/1\% \text{H}_2\text{O}_2$ . The solution was analyzed by gamma counting for  $^{99}\text{Mo}$  content. The  $^{99}\text{Mo}$  recovery was calculated as a ratio of the  $^{99}\text{Mo}$  activity in the alkaline filtrate product to the sum of the  $^{99}\text{Mo}$  activity in the alkaline filtrate and in the digested alpha-benzoin oxime solution.

Table1. Experimental conditions and results for the digestion of the DU-irradiated targets at ANL.

Process	A	B	C
Description	modified CNEA	modified CNEA	modified IRE
Digestion solution	0.4L 0.5 M NaOH	0.4L 0.5 M NaOH	0.4L 1M NaOH/ 4M $\text{NaNO}_3$
DU, g	23.36	23.44	23.04
Al, g	2.05	2.13	2.01
$\text{KMnO}_4$ , g	44.1	45.2	5.05
$T_{\text{max}}$ , °C	$285 \pm 3$	$282 \pm 3$	$282 \pm 3$
Time at max. temperature, min	30	30	15
$P_{\text{max}}$ , bar	90	90	60
$^{99}\text{Mo}$ recovery, %	<b>&gt;99.5</b>	<b>&gt;99.5</b>	<b>&gt;99.8</b>

### CNEA process

Removal of the solids in Process A required one wash of 200 mL. We could not stir the slurry at the maximum stirring rate (7.5 in our case), so we stirred at 6 while we were evacuating the digestion solution (325 mL) and the first rinse (100 mL). The suspension was filtered. After that we opened the digester and found that about a quarter of the solids was not removed. Two hundred milliliters of the filtrate was added back to the digester, the slurry was stirred at 7.5 for 3 minutes and drained under vacuum. All solids were removed. In Process B, all solids were removed with the digestion solution and 100 mL rinse (stirred at 7.5).

Using the alkaline filtrates from procedures A and B, we also did the first step of the  $^{99}\text{Mo}$  purification [6]. The alkaline solutions were passed through a column at 5 mL/min containing 2.1 g of AGMP-1 (BioRad™) anion exchanger in  $\text{OH}^-$  form, which retains  $\text{MoO}_4^{2-}$ . In the first case, no  $^{99}\text{Mo}$  was observed in the effluent. In the second case, the breakthrough occurred after 325 out 425 mL of the filtrate passed through the column. The concentration of Mo in this 100 mL fraction was about 30% of the initial concentration. The second filtrate had a distinct yellow color. The column was washed with 2 bed volumes of 0.5M NaOH solution at the same flow rate.  $^{99}\text{Mo}$  was stripped with 0.5M NaOH/1M  $\text{Na}_2\text{SO}_4$  solution. The strip in the second case (procedure B) was also bright yellow. We have done an ICP MS analysis of the strip solutions, diluted in nitric acid. The data are shown in Fig. 3.

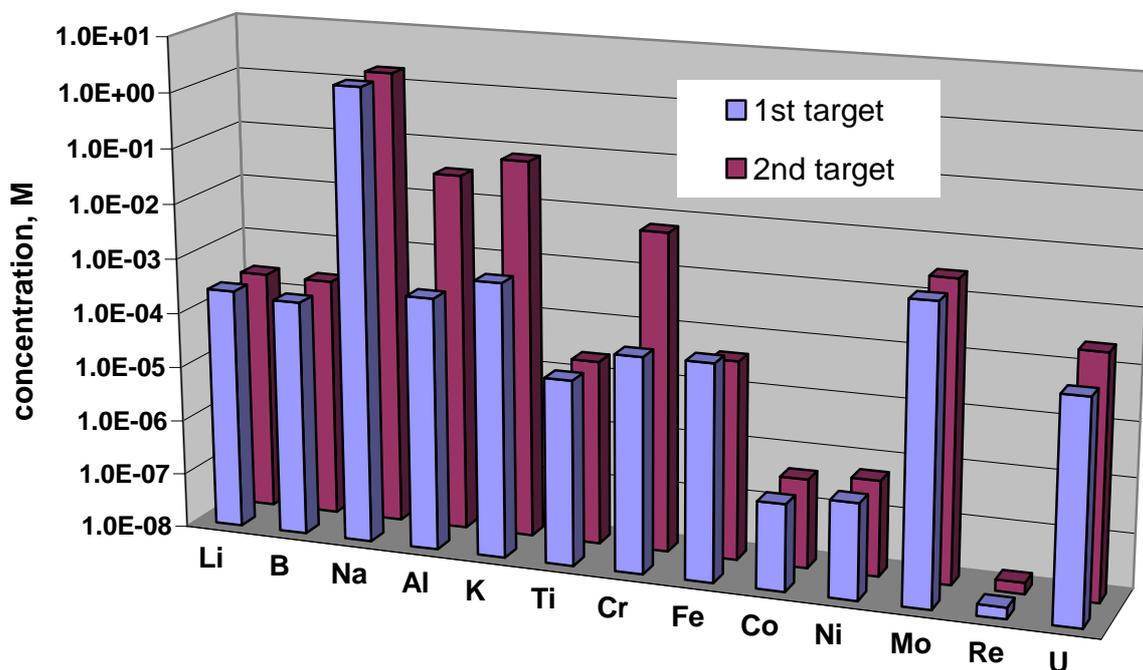


Figure 3. The compositions of the strip solutions (metals only) for the 1<sup>st</sup> and 2<sup>nd</sup> targets

The second strip solution (procedure B) has elevated concentrations of Al, K, Cr and, to a lesser extent, U. Aluminum content in the filtrate did not exceed 1-2 % of its total amount in the system and could be explained by the incomplete wash of the column. Uranium concentration was within its solubility range in 0.5 M NaOH.

In alkaline media chromium may exist as either trivalent hydroxo-complex,  $\text{Cr}(\text{OH})_6^{3-}$  or chromate (yellow),  $\text{CrO}_4^{2-}$ , species. Considering the fact that the solubility of Cr(III) in alkaline solutions is low [8], chromate ion, most likely, is the major chromium species in the second strip solution and, correspondingly, in the second filtrate. Since it is a double charged anion, it has a very high tendency to sorb onto anion exchangers. Therefore, the chromate sorption onto AGMP-1 limits its capacity, resulting in the breakthrough of  $^{99}\text{MoO}_4^{2-}$  in the second filtrate. Both Al and U, being anionic species in base, may also decrease the capacity of the anion exchange column.

Such a high concentration of Cr in the second strip/filtrate can be explained by the chromium release from the stainless steel body of the digester. After the digestion of the first target and the filtration step, we conducted the dissolution of the precipitate in the digester at 150 °C. The  $\text{HNO}_3/\text{H}_2\text{O}_2$  solution, containing also  $\text{MnO}_2$ , is a very strong oxidizing media, which could partially destroy the  $\text{Cr}_2\text{O}_3$  layer of the stainless steel surface [8]. Therefore, during the digestion of the second target, chromium was oxidized by the alkaline permanganate solution generating potassium chromate.

The dissolution of the precipitates was done to determine the yield of  $^{99}\text{Mo}$  and could also be done without using hydrogen peroxide, which should eliminate the chromium release. In any case, the cake dissolution will not be a standard procedure for a production facility.

One of the major concerns in the Mo purification process in alkaline media is the chemical behavior of iodine. There are a few I isotopes produced in the course of the  $^{235}\text{U}$  fission. They have relatively high specific activities and may radiolytically decompose the ion exchange resin if adsorbed. Therefore, we have assayed all the solutions for iodine content.

There are two major chemical forms of iodine in alkaline media – an oxidized species,  $\text{IO}_3^-$ , and a reduced one,  $\text{I}^-$ . The distribution coefficient for  $\text{I}^-$  between the alkaline solution and AGMP-1 is substantially higher than that of  $\text{IO}_3^-$ . Iodide reacts with an oxidizing agent, such as  $\text{KMnO}_4$ , producing iodate,  $\text{IO}_3^-$  [8]. Our preliminary tests showed that the oxidation of  $\text{I}^-$  to  $\text{IO}_3^-$  by permanganate occurs immediately after the addition of  $\text{I}^-$  to the alkaline solution of  $\text{KMnO}_4$  even at ambient temperature. However,  $\text{IO}_3^-$  is unstable under beta radiation and is reduced back to iodide.

The sorption of Mo onto AGMP-1 column was done on the day after the digestion. About 95% and 94% of iodine adsorbed on the column in the first and the second tests, respectively. This indicates, perhaps, that the major fraction of iodine in the filtrate solutions was reduced back to  $\text{I}^-$  in the beta field during the 20 hour time interval between the digestion and the sorption. Additional tests will be carried out to explore the radiochemical reactions of iodine under these conditions.

### IRE process

As reported previously [6], we are working on the optimization of the IRE process for the LEU-foil digestion. Digestion of U foil targets in 3M NaOH/4M NaNO<sub>3</sub> solution generated a suspension that was hard to filter. We carried out a series of tests and found that an addition of 5 grams of  $\text{KMnO}_4$  changes the properties of the slurry significantly, making the filtration step very fast. As for the CNEA digestion,  $\text{MnO}_2$ , generated during the digestion, interacts with Al hydroxide forming a mixed solid phase. This allowed us to conduct the successful digestion of the irradiated target (Table 1, procedure C) at lower base concentration, in 1M NaOH/4M NaNO<sub>3</sub>, which will decrease the volume of the liquid waste for the process [6].

### **3. Future Work**

We plan to ship the digester and all necessary equipment to Argentina for a process demonstration at the CNEA production facility. At ANL, we will continue the study of the  $^{99}\text{Mo}$  purification steps including I sorption, as well as the waste removal and minimization.

### **4. Conclusions**

- A commercial Berghof™ vessel with stirring system was customized and purchased by ANL. This vessel has been successfully used at ANL for the digestion tests of irradiated and non-irradiated uranium foils.

- The digestion procedure has been optimized. It has been used on irradiated low-burnup targets at ANL. Recovery of  $^{99}\text{Mo}$  is over 99.5%.
- In consultation with CNEA, future work will address the existing uncertainties and will optimize the process for use in CNEA's hot cell facilities.
- LEU foil targets can be successfully digested using IRE process conditions. Addition of  $\text{KMnO}_4$  improves the filterability of the slurry, resulting in waste reduction for the whole process.

## 5. Acknowledgments.

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