Uranium Anodic Dissolution under Slightly Alkaline Conditions Progress Report— Full-Scale Demonstration with DU Foil

Chemical Science and Engineering Division

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by

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prepared for

U.S. Department of Energy, National Nuclear Security Administration,
Office of Defense Nuclear Nonproliferation

February 2013

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URANIUM ANODIC DISSOLUTION UNDER SLIGHTLY ALKALINE CONDITIONS PROGRESS REPORT—FULL-SCALE DEMONSTRATION WITH DU FOIL

ABSTRACT

Argonne National Laboratory (Argonne) is developing an alternative method for digesting irradiated low enriched uranium (LEU) foil targets to produce ^{99}Mo in neutral/alkaline media. This method consists of the electrolytic dissolution of irradiated uranium foil in sodium bicarbonate solution, followed by precipitation of base-insoluble fission and activation products, and uranyl-carbonate species with CaO. The addition of CaO is vital for the effective anion exchange separation of $^{99}\text{MoO}_4^{2-}$ from the fission products, since most of the interfering anions (e.g., CO_3^{2-}) are removed from the solution, while molybdate remains in solution. An anion exchange is used to retain and to purify the ^{99}Mo from the filtrate. The electrochemical dissolver has been designed and fabricated in 304 stainless-steel (SS), and tested for the dissolution of a full-size depleted uranium (DU) target, wrapped in Al foil. Future work will include testing with low-burn-up DU foil at Argonne and later with high-burn-up LEU foils at Oak Ridge National Laboratory.

1 INTRODUCTION

Instead of aluminum high enriched uranium (HEU) alloy, a low enriched uranium (LEU) metal-foil target was devised. However, the change of the target form has an impact on contemporary chemical processing methods that use sodium-hydroxide digestion of the target. Under normal conditions, uranium metal is only slowly digested in NaOH. With the aid of H_2O_2 , digestion can be accelerated, but the digestion is cumbersome and difficult to control (Vandegrift et al. 2002). High temperatures are needed to accelerate the digestion with sodium hydroxide, which necessitates the use of a high-pressure vessel to reach a temperature of $\sim 275^\circ\text{C}$ (Gelis et al. 2003).

A low-temperature, low-pressure procedure employing anodic oxidation of the uranium metal into basic bicarbonate media is under development, with consequent precipitation of uranium and carbonate from the solution by the addition of calcium oxide, followed by the sorption of ^{99}Mo on an anion exchanger (e.g., BioRad AGMP-1) (Figure 1). The goal of this study was to verify the feasibility of this method and to identify key optimizing factors for the development of an industrial-scale procedure.

FIGURE 1 Block-Diagram of a Novel Process for the ^{99}Mo Production via LEU-Foil Electro-dissolution

2 ELECTROLYSIS EXPERIMENTS

The oxidation of uranium metal is assumed to proceed quickly through U(III), producing U(IV) oxide. Then, according to literature data, the oxidation of UO_2 proceeds through the formation of UO_{2+x} species on the surface until $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ is formed (Sunder et al. 1996). Hexavalent uranium has rather high solubility in the presence of carbonate/bicarbonate ions (McLaren et al. 1950). The dissolution occurs when these negative ions reach the positively charged surface of the uranium anode.

Our preliminary tests showed that 20–22 g DU foils are completely dissolved in 1-M $\text{NaHCO}_3/90^\circ\text{C}$ within 1.5 h. The foils were connected to anode lead via a clip, hanging freely in the solution, while the solution was intensively stirred. However, hanging the irradiated foils during the dissolution may not be practical, because there is a chance of dropping the foil in the dissolution vessel. Therefore, an anode basket or a cage should be utilized.

The following dissolution tests were conducted using a high-current direct-current (DC) power supply by Magna Power with a voltage range of 0–32 V and a current range of 0–62 A. The foil was placed in the anode basket between two SS coarse screens, which were tightened together (Figure 2).

The vertical bolt pushes the outer frame with the welded screen toward the inner frame with the attached screen, thus providing the necessary contact between the anode lead and the foil. The authors have shown that, using a basket, it takes about 2.5 h to dissolve nearly 99% of the full-size foil due to the partial reduction of the free foil surface area, caused by the mesh interference.

A dissolver required for this process has been designed and fabricated. The material used for the prototype is the 304 SS (Figure 3). Nitrogen gas will be used to sweep the dissolver. The fission gases will be collected; hydrogen gas, which is generated during the electrolysis, will need to be recombined.

The first step is the dissolution of Al barrier in 1-M NaOH as $\text{NaAl}(\text{OH})_4$. Then the solution is drained through a ball valve on the side of the dissolver (Figure 3). After a wash step, a sodium bicarbonate solution is added in the dissolver through one of the ports on the lid, and the uranium foil electrolysis is conducted at elevated temperature ($85\text{--}95^\circ\text{C}$) and intense stirring. Heating is provided by a heat gun (not shown).

A photo of the dissolver in the shroud and the anode basket is presented in Figure 5.

FIGURE 2 Prototype Anode Basket for U Foil Dissolution

FIGURE 3 Sketch of the Electrochemical Dissolver with a Motor and the Anode Basket

The approximate volume of the solution required to cover a 24-g uranium foil ($10\text{ cm} \times 8\text{ cm}$) is about 1.2 L. However, the solution/U-metal ratio will be significantly smaller if a batch of several foils is dissolved in a vessel modified for the full-scale process. The solubility of uranium in bicarbonate medium is 80 g-U/L (it is soluble as neutral and anionic complexes of uranyl carbonate) (McLaren et al. 1950), so for a 225-g batch of U foils at least 3 L of the solution is required. A concept of the dissolver with the anode for 225-g batch dissolution has been conceived; however, its implementation is pending the experimental results of the dissolver shown above.

The detailed drawing of the assembled prototype dissolver including the stand, the heat gun, and the stirring motor is shown in Figure 4. The stand also serves as a shroud for the hot/cool air direction in order to control the temperature. For the full-size dissolver, the anode basket(s) will be fabricated from nickel or nickel alloys, which are resistant to oxidation in alkaline mediums. 304 SS is acceptable for several applications, so it was chosen to minimize the cost of the prototype. The cathode and the dissolver body of the production dissolver can be made from stainless steel, as there should be no significant corrosion during the processing.

FIGURE 4 Assembled Dissolver with a Stand (Detailed Drawing)

FIGURE 5 Fabricated Anode Basket and the Dissolver, Inserted in the Shroud

A 23.7-g piece of DU foil, 0.125 mm thick (10 cm $\times$ 7.5 cm) was wrapped in 0.1-mm Al foil (W = 4.5 g) and was placed in the anode basket (Figure 6).

To dissolve the Al recoil barrier, 1.2 L of 1.1-M NaOH was added to the dissolver. The solution was intensely stirred and heated up to 60°C using a heat gun. The temperature was maintained for 5 minutes, then heating was stopped and the resultant solution was drained by gravity. The basket was removed from the dissolver to ensure the completeness of Al dissolution. No Al foil remained in the basket. A small amount of black solids, presumably hydrous UO_2 , was found in the solution. The UO_2 was likely removed from the DU foil surface due to the agitation. No significant UO_2 formation is expected in alkaline medium under the experimental conditions.

For the tests with the irradiated U foil, the $\text{NaOH}/\text{NaAl}(\text{OH})_4$ solution will be analyzed for ^{99}Mo content. It could be combined with the filtrate (the feed to the purification process) to prevent any loss of the product from the Al dissolution step.

To dissolve the uranium foil, 1.2 L of 1-M NaHCO_3 was added to the dissolver after a 100 mL H_2O rinse. The solution was heated up to 85°C, and the electrolysis was started. Nitrogen gas was continuously used for sweeping the dissolver head space. The temperature was maintained at $90 \pm 5^\circ\text{C}$. For the first hour, the current was maintained at 29 A, while the voltage was in the 6.0–6.3 V range. After 1 h, the process was stopped and the foil removed from the

FIGURE 6 Anode Basket with DU Foil, Wrapped in Al

basket, washed with water, dried, and weighed on the scale. Exactly 10 g was dissolved. This dissolution rate was considered to be unsatisfactory, so for the remaining time the experiment was conducted at ≈ 8.5 V and 40–45 A. After 1.5 h from the restart (2.5 h total) the electrolysis was terminated. After inspection, only a small piece (0.78 g) of DU was left. Therefore, about 97% of the foil was dissolved in 2.5 h, although the rate can be further improved by applying a higher voltage all the time.

After the dissolution, the uranium-containing solution was transferred to a stirring tank under vacuum, then while stirring solid CaO was added to it through a funnel. About 86 g (1.5 mol) of CaO was used to ensure a complete precipitation of uranyl carbonates and CaCO_3 . After 10 min of stirring, the suspension was filtered through a 1- μm Whatman filter with a 2000- cm^2 surface area under vacuum. The filtration setup at the end of the process is shown in Figure 7.

FIGURE 7 Filtration Setup (Uranium was collected on the filter.)

3 FUTURE WORK

The authors are planning to conduct a series of tests using depleted uranium foil as well as the low-burn-up irradiated foil. We will study molybdenum recovery and the behavior of fission products including iodine to find the ways to separate it from the other fission products. The study will also focus on the waste characterization including the formation of fission-product gasses and the means of their storage, utilization, and/or disposal. We will also test the prototype system operations in a hot cell mock-up facility at Argonne.

Once these laboratory studies are completed, our plans are to test this process in a hot cell at Oak Ridge National Laboratory using a fully irradiated foil.

4 REFERENCES

Gelis, A.V., G.F. Vandegrift, S.B. Aase, A.J. Bakel, J.R. Falkenberg, M.C. Regalbuto, and K.J. Quigley, 2003, "ANL Progress in Developing a Target and Process for Mo-99 Production: Cooperation with CNEA," *Proceedings of the 2003 International Meeting on Reduced Enrichment for Research and Test Reactors*, Chicago, IL, October.

Gelis, A.V., A. Bakel, J. Jerden, M. Precek, K. Quigley, S. Wiedmeyer, and G.F. Vandegrift, 2009, "Experimental Results on the Development of Anodic Dissolution of LEU Foils for Use in Alkaline-Digestion Processes," *Proceedings of the 2009 International Meeting on Reduced Enrichment for Research and Test Reactors*, Beijing, China, October.

McLaren, J.A., W.D. Cline, H.S. Clinton, J.J. Finley, J.H. Goode, and J.A. Westbrook, 1950, *The Electrolytic Dissolution of Metallic Uranium*, ORNL K-587, Oak Ridge National Laboratory.

Sunder, S., L.K. Strandlund, and D.W. Shoesmith, 1996, *Anodic Dissolution of UO_2 in Slightly Alkaline Sodium Perchlorate Solutions*, AECL 1144.

Vandegrift, G.F., A.V. Gelis, S.B. Aase, A.J. Bakel, E. Freiberg, Y. Koma, and C. Conner, 2002, "ANL Progress in Developing a Target and Process for Converting CNEA Mo-99 Production to Low-Enriched Uranium," *Proceedings of the 2002 International Meeting on Reduced Enrichment for Research and Test Reactors*, San Carlos de Bariloche, Argentina, November.

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