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**PROGRESS IN DEVELOPING ELECTROCHEMICAL
DISSOLUTION OF LEU FOILS**

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ABSTRACT

Argonne National Laboratory is developing an alternative method for digesting irradiated LEU foil targets to produce ⁹⁹Mo in neutral/alkaline media. This method consists of the electrolytic dissolution of irradiated uranium foil in sodium bicarbonate solution, followed by precipitation of carbonate, base-insoluble fission and activation products, and uranyl species with CaO. The addition of CaO is vital for the effective anion exchange separation of MoO₄²⁻ from the fission products, since most of the interfering anions (e.g., CO₃²⁻) are removed from the solution, while molybdate remains in solution. An anion exchange column is used to retain and to purify the ⁹⁹Mo from the filtrate. The electrochemical dissolver has been designed and is in the fabrication stage. The advantages and disadvantages of various alkaline dissolution methods will be discussed.

1. Introduction

The Global Threat Reduction Initiative--Conversion Program develops technology necessary to enable the conversion of civilian facilities using high enriched uranium (HEU) to low enriched uranium (LEU) fuels and targets. The main technology components of the program are:

- the development of advanced LEU fuels,
- design and safety analysis for research reactor conversion, and
- development of targets and processes for the production of the medical isotope Molybdenum-99 with LEU

Instead of -HEU-aluminide dispersion target, an LEU metal-foil target was devised. However, the change of the target form has an impact on contemporary chemical processing methods that

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use sodium-hydroxide digestion of the target. Under normal conditions, uranium metal is only slowly digested in NaOH. High-temperatures are needed to accelerate the digestion with sodium hydroxide alone, which necessitate the use of a high pressure vessel to reach temperature of $\sim 275^\circ\text{C}$ [2]. With the aid of H_2O_2 , the digestion can be accelerated and performed at ambient pressure, but the digestion is cumbersome and difficult to control [1].

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

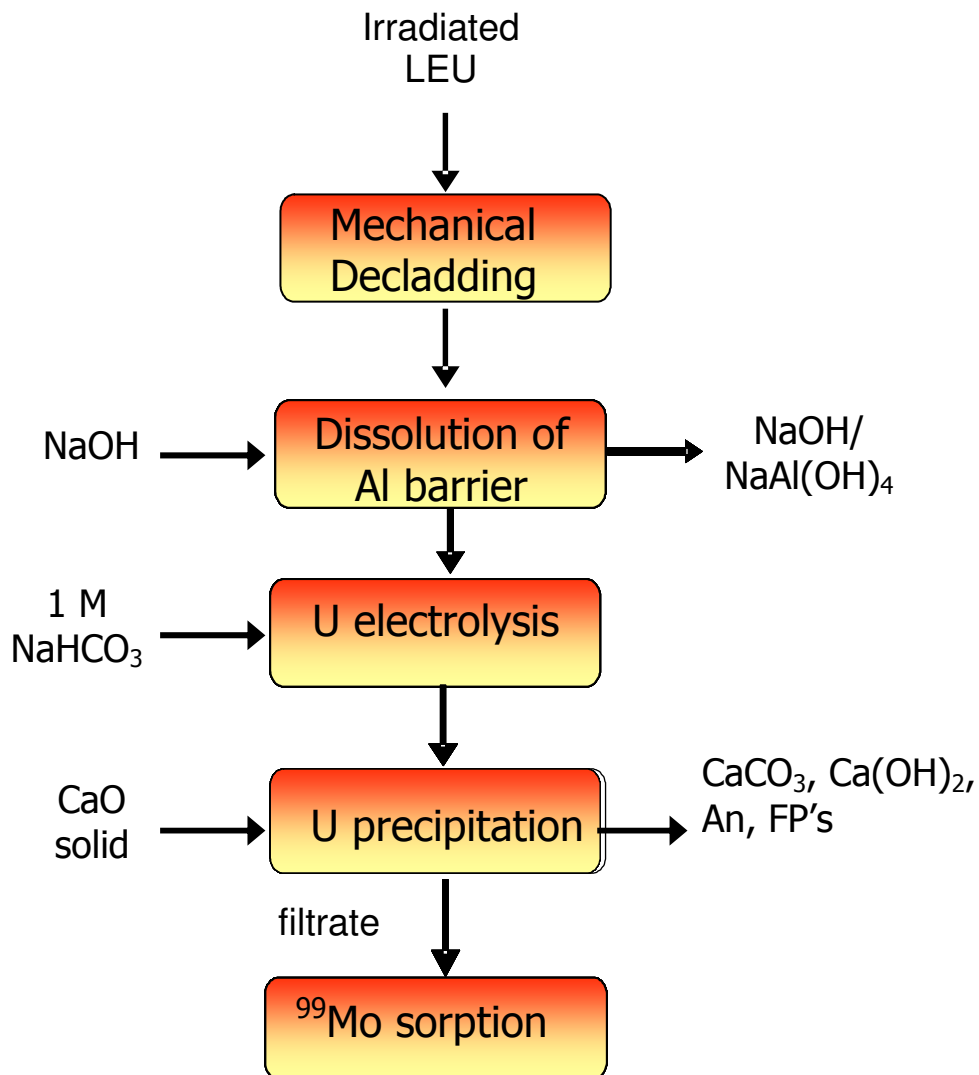


Figure 1. Block-diagram of a novel process for the Mo-99 production via LEU-foil electro-dissolution.

2. Electrolysis Experiments

The electrolytic setup consisted of a four-electrode system, a working electrode, a reference electrode, an auxiliary electrode, and a sense electrode, connected to a Princeton Applied Research VersaSTAT 4 potentiostat with a 20 Amp power booster. The reference and the sense electrode were connected to the potentiostat, while the working and the auxiliary electrodes were connected to the power booster. The working electrode was a depleted uranium (DU) foil placed in Ni anode baskets, immersed in the electrolyte solution. The auxiliary electrode was a piece of nickel foil 10x12 cm. The reference electrode was a Hg/HgO/0.1 M NaOH electrode by CH Instruments. The electrolyte solution used was 1 mol/L sodium bicarbonate (NaHCO_3). A clear plastic 0.5 L beaker was used as a cell. Gravimetric analysis was used for proving and correlating the coulometric measurements.

Linear sweep voltammetry (LSV) has been performed for the systems with and without 22 g DU foil in the potential range between -1 and 2.2 V vs. reference electrode (Figure 2). Oxidation of water occurs on the Ni anode at the potential above 1.3-1.4 V, while the U foil oxidation reaches nearly maximum (20 A) allowable current of the setup at 1.45 V.

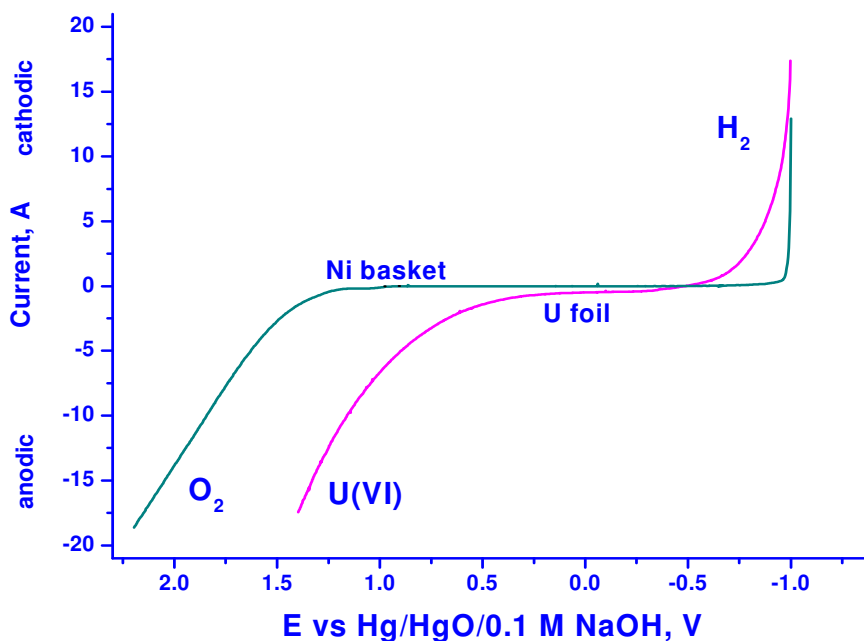


Figure 2. Linear sweep voltammetry of a 160 cm^2 uranium working electrode (blue line) and the Ni basket (red line) in 1 mol/L NaHCO_3 with a Ni counter electrode; Hg/HgO/0.1 M NaOH Ref. electrode, scan rate 0.1 V/s.

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.[3] Hexavalent uranium has rather high solubility in the presence of carbonate/bicarbonate ions.[4] The dissolution occurs when

these negative ions reach the positively charged surface of the uranium anode. Therefore, an effective mass-transfer of the solution species to the U surface is needed for the efficient electrolysis. We were able to dissolve a 22 g DU target in less than 50 min.

3. CaO precipitation experiments

In order to use ion exchange to separate and concentrate molybdate, it is necessary to remove carbonate and bicarbonate from solution. The concentrations of these anions are at much higher concentrations in solution than molybdate and, therefore, would compete for sites on the column, leading to poor retention of MoO_4^{2-} . Therefore, their removal from the solution by precipitation of calcium carbonate is performed by addition of calcium oxide (CaO). Along with the carbonate and bicarbonate being precipitated, the uranyl cations and base-insoluble activation and fission products are also precipitated. A 5-10% CaO excess over carbonate concentration is used to precipitate all the uranyl ions. The resulting suspension is saturated with $\text{Ca}(\text{OH})_2$; only traces of uranium are present in the filtrate. The pH of the filtrate was measured to be 12.7. The precipitate had a yellow color and was easily filtered through a medium coarse filter paper under gravity.

The sorption of ^{99}Mo added to the bicarbonate solution prior the DU foil electrolysis, was proven to be efficient; the K_d values are in the range of 340-350 [5].

4. Conceptual Design of a Production Dissolver

A conceptual design for the two-step dissolver required for this procedure has been completed. Previously [5], the digester consisted of two chambers. However, to minimize the physical dimensions of the apparatus, we have changed it to a one chamber dissolver with a stirring rod coming through the bottom. After the first step to remove the Al fission-recoil barrier from the uranium foil, the $\text{Al}(\text{OH})_3$ containing solution will be sucked out through a dip tube. After washing, a sodium bicarbonate solution is added in the dissolver, and the uranium foil electrolysis begins. Figures 3 and b illustrate the dissolver.

5. Future work

We 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 from this front end step, including the formation of radiolytic gasses, and the means for their disposition.

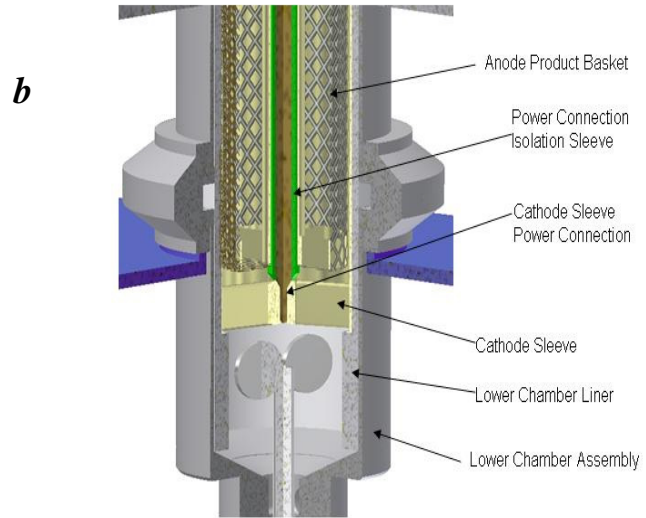
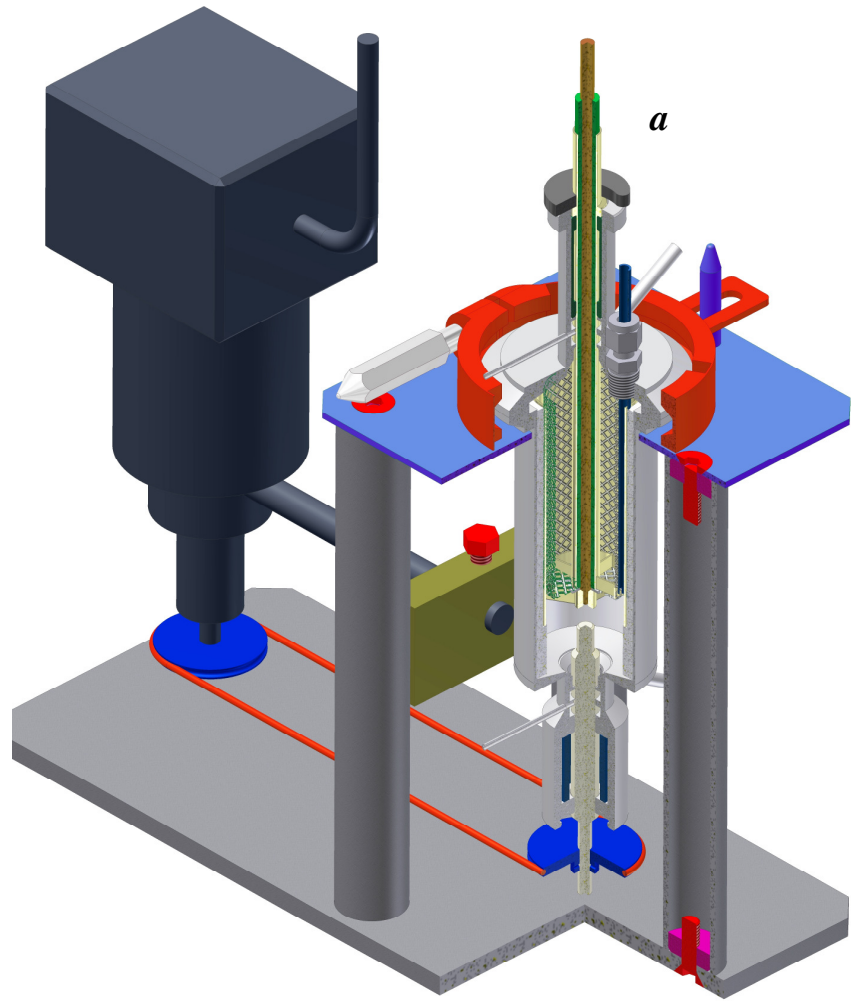


Figure 3 (a and b). (a)--Electrochemical dissolver with a motor and (b) Ni anode basket and cathode sleeve

6. Acknowledgements

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7. References

- [1] G. F. Vandegrift, A. V. Gelis, S. B. Aase, A. J. Bakel, E. Freiberg, Y Koma and C. Conner “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 2002
 - [2] A. V. Gelis, G. F. Vandegrift, S. B. Aase, A. J. Bakel, J. R. Falkenberg, M. C. Regalbuto, and K. J. Quigley “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, October, 2003, Chicago, IL, USA
 - [3] S. Sunder, L.K. Strandlund, and D.W. Shoesmith: Anodic Dissolution of UO₂ in Slightly Alkaline Sodium Perchlorate Solutions. AECL 1144. 1996.
 - [4] J.A. McLaren, W.D. Cline, H.S. Clinton, J.J. Finley, J.H. Goode and J.A. Westbrook, *The electrolytic dissolution of metallic uranium*, ORNL K-587, 1950
 - [5] Artem V. Gelis, Allen Bakel, James Jerden, Martin Precek¹, Kevin Quigley, Stan Wiedmeyer and George F. Vandegrift. *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, October, 2009, Beijing, China
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