

RERTR 2009 — 31st INTERNATIONAL MEETING ON
REDUCED ENRICHMENT FOR RESEARCH AND TEST REACTORS

November 1-5, 2009
Kempinski Hotel Beijing Lufthansa Center
Beijing, China

EXPERIMENTAL RESULTS ON THE DEVELOPMENT OF ANODIC DISSOLUTION OF LEU FOILS FOR USE IN ALKALINE-DIGESTION PROCESSES

Artem V. Gelis, Allen J. Bakel, James L. Jerden, Martin Precek¹,
Kevin J. Quigley, Stan G. Wiedmeyer and George F. Vandegriff

*Chemical Sciences and Engineering Division
Argonne National Laboratory
9700 S Cass Ave. Argonne, IL 60439 USA*

ABSTRACT

An alternative method for digesting irradiated LEU foil targets to produce ⁹⁹Mo in neutral/alkaline media is being developed. 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 product, and uranyl species with CaO. The addition of CaO is vital for the effective anion exchange separation of ⁹⁹MoO₄²⁻ 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 is used to retain and to purify the ⁹⁹Mo from the filtrate. This novel method is very promising for low-temperature dissolution of irradiated LEU foils.

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

In the scope of the last technology component of the program, a new LEU target was adopted. Instead of aluminum-HEU alloy, an 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 an aid of H₂O₂, the digestion can be accelerated, but the digestion is

¹ Oregon State University graduate student

cumbersome and difficult to control.[1] High-temperatures are needed to accelerate the digestion with sodium hydroxide, which necessitate the use of a high pressure vessel to reach temperature of $\sim 275^\circ\text{C}$. [2]

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.

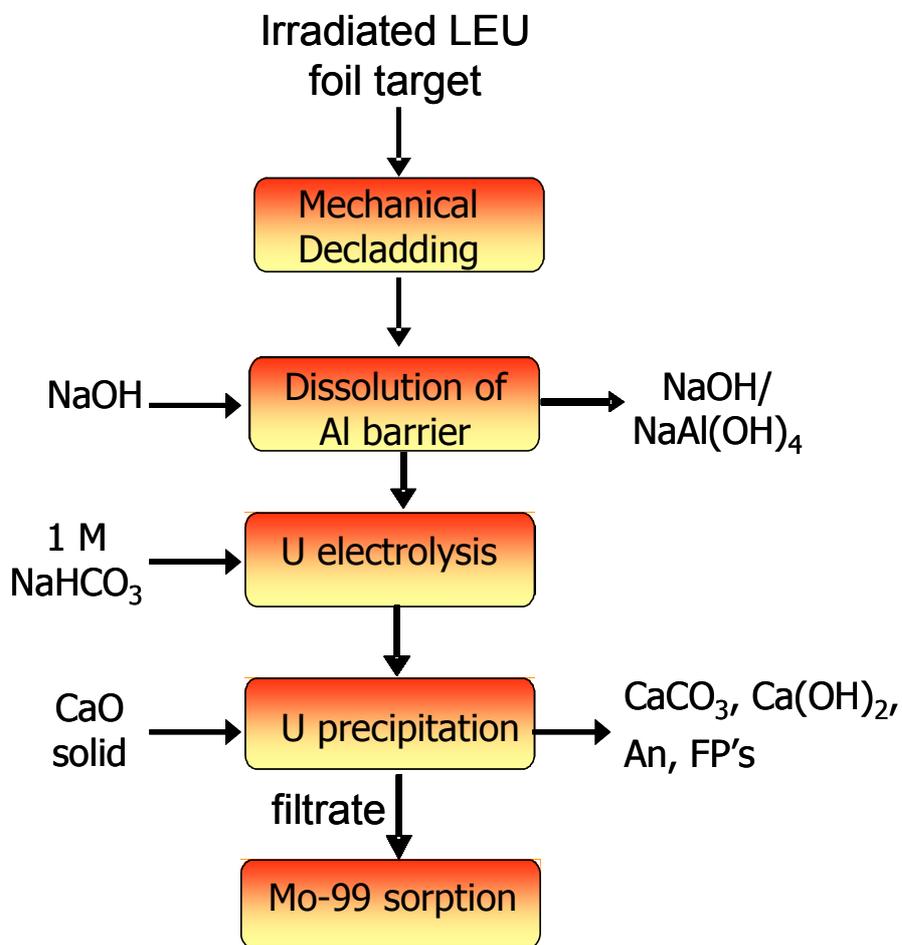


Figure 1. Block-diagram of a novel process for the Mo-99 production via LEU-foil electro-dissolution.

2. Electrolysis Experiments

The electrolytic setup consisted of a four-electrode system (Figure 2), a working electrode, a reference electrode (not shown), an auxiliary electrode, and a sense electrode (not shown), 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 3). 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.

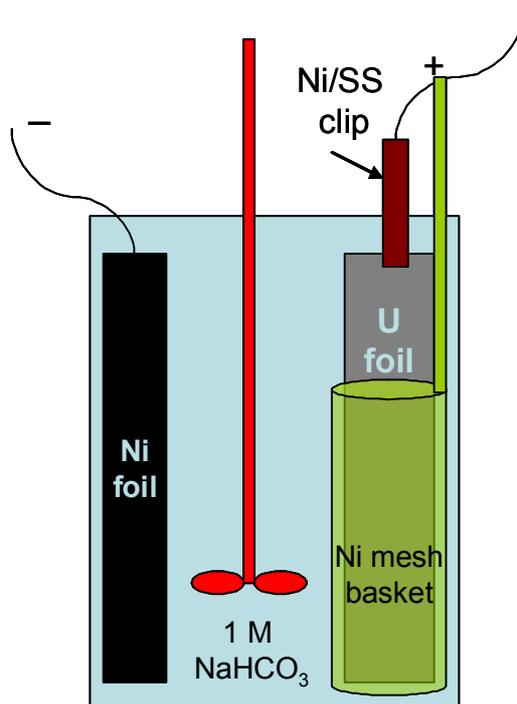


Figure 2. A schematic of the electrolysis setup for the U foil dissolution

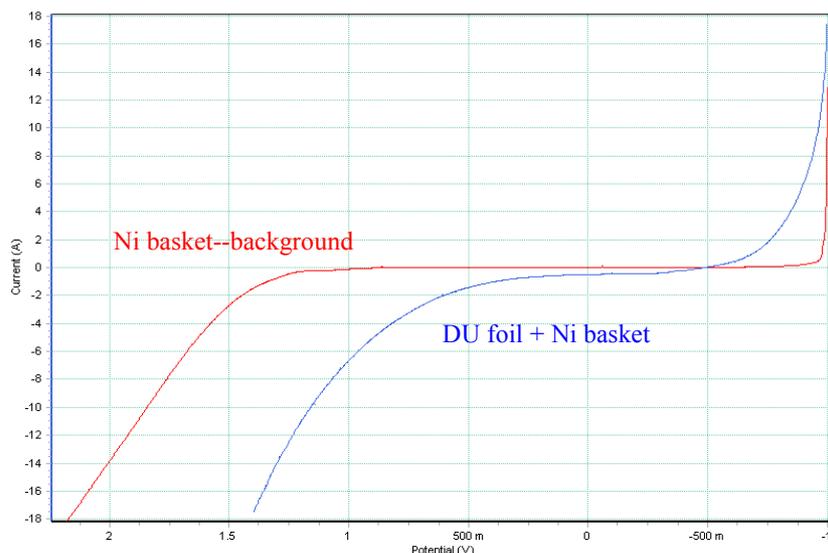


Figure 3. Linear sweep voltammetry of a 160 cm² uranium working electrode (blue line) and the Ni basket (red line) in 1 mol/L NaHCO₃ with a Ni counter electrode; Hg/HgO/0.1 M NaOH Ref. electrode, scan rate 0.1V/s (American sign notation).

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 UO₂ proceeds through the formation of UO_{2+x} species on the surface until UO₃·2H₂O 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.

If significant stirring is utilized, a high uranium dissolution rate can be achieved. For a smaller piece of U foil, the current density may rise to 170-180 mA/cm², which results in 0.0042 g/min·cm² initial dissolution rate. An 8.8 g U foil (60 cm²) was completely dissolved in less than 45 min. If a full-size foil is used at this current density, the total current would exceed the 20-A limit of our experimental electrochemical setup. However, even at lower current density, we were able to dissolve a 22 g target in less than 1.5 hours. A more powerful potentiostat/booster will be used to demonstrate the process for production-scale foils.

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 MoO₄²⁻. Therefore, their removal from the solution by precipitation of calcium carbonate is performed by addition of calcium oxide (CaO).

Calcium oxide dissolves in water, forming dissolved calcium hydroxide $[\text{Ca}(\text{OH})_2]$, which reacts with the carbonate present and precipitates it. The solubility of calcium carbonate is substantially low ($K_{\text{sp}} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] = 8.7 \times 10^{-9}$ at 25 °C); therefore, it is possible to reduce the carbonate concentration from 1 mol/L to < mmol/L. Along with the carbonate and bicarbonate being precipitated, the uranyl cations and activation and base-insoluble 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.

Samples of the solid precipitate were subjected to X-ray powder diffraction analysis. Although the major constituents of the precipitate, calcium carbonate and calcium hydroxide were clearly identified, the identification of the precipitated form of uranium was not successful. The most promising candidate for the uranium form was a mineral co-precipitate of uranyl carbonate and calcium carbonate called *fontanite* $\text{Ca}[(\text{UO}_2)_3(\text{CO}_3)_4] \cdot 3 \text{H}_2\text{O}$.

4. Mo Separation and Estimation of the Distribution Constant

A set of experiments was performed to prove the separation of molybdenum from uranium and carbonate by the CaO precipitation method. The uranium solution was produced by electro-dissolution of 596.9 mg of uranium in 40 mL of 1 mol/L sodium bicarbonate. The uranium concentration was therefore 14.92 g U/L (0.0627 mol/L). The solution was altered by an addition of sodium molybdate labeled with ^{99}Mo . The concentration of molybdenum in the solution submitted for precipitation was 0.001 mol/L. A 0.5 mL sample was taken in an LSC vial from the solution for subsequent gamma-spectrometric analysis.

A 110%-stoichiometric amount of 2.5 g CaO was used to ensure complete precipitation of carbonate from the solution; it was added to the solution during mixing at room temperature. The resulting supernatant was filtered, and a 0.5 mL sample was taken from it into an LSC vial.

From the supernatant, two 4 mL samples were transferred to centrifuge tubes, which contained 41,3 mg and 51,2 mg of BioRad AGMP-1 anion exchange resin in OH^- form (Dowex-1 type resin). After an overnight equilibration, most of the liquid phase above the resins was transferred into the body of a syringe and pressed through its tip equipped with a filter into another vial in order to remove all resins. In the end, 3.4 mL of the filtered solution was pipetted into an LSC vial for each of the two samples.

The original bicarbonate solution, filtered solution after precipitation (supernatant/filtrate), and the two solutions obtained after equilibration with anion exchanger were subjected to gamma-counting on high-purity germanium detector HPGe, characteristic peak of ^{99}Mo at 739.47 keV was used for analysis. From the known sorbent mass m_s and specific activity before (a_0) and after (a_1) equilibration, the distribution constant K_d in units of mL/g was calculated as:

$$K_d = [(a_0 - a_1)/a_1] \times (4 \text{ mL} / m_s)$$

The results of the analysis are summarized in the Table1.

Table 1. Results of gamma-counting of ⁹⁹Mo samples for the an-ex in OH⁻ form

Sample	Activity (739.47 keV, μCi)	Volume (mL)	Specific Activity (μCi/mL)	Sorbent mass (g)	K _d (mL/g)
1 - before precipitation	2.038	0.5	4.0760		
2 - after precipitation	2.052	0.5	4.1040		
3 - supernatant 41.3 mg	3.076	3.4	0.9047	0.0413	342.5
4 - supernatant 51.2 mg	2.589	3.4	0.7615	0.0512	342.9

As can be seen from the specific activity of the first two samples, the precipitation did not remove any measurable quantity of molybdenum from the solution. The average of the distribution constant value was established as $K_d = 343$ mL/g. These distribution coefficients will be sufficient for a design of a successful ⁹⁹Mo-recovery process.

5. Conceptual Design of a Production Dissolver

A conceptual design for the two-step dissolver required for this procedure has been completed. In the top chamber of this apparatus, the Al fission-recoil barrier attached to the uranium foil, which prevents bonding of the foil to the aluminum cladding, is removed using NaOH solution. Once the Al fission-recoil barrier is removed, the LEU foil is lowered into the bottom stage, where the uranium metal is electrochemically oxidized to U(VI), which is soluble in the bicarbonate solution. Figures 4-6 illustrate the dissolver. We are planning to build this dissolver and ship it to Argentina for testing by the CNEA with an irradiated LEU-foil target.

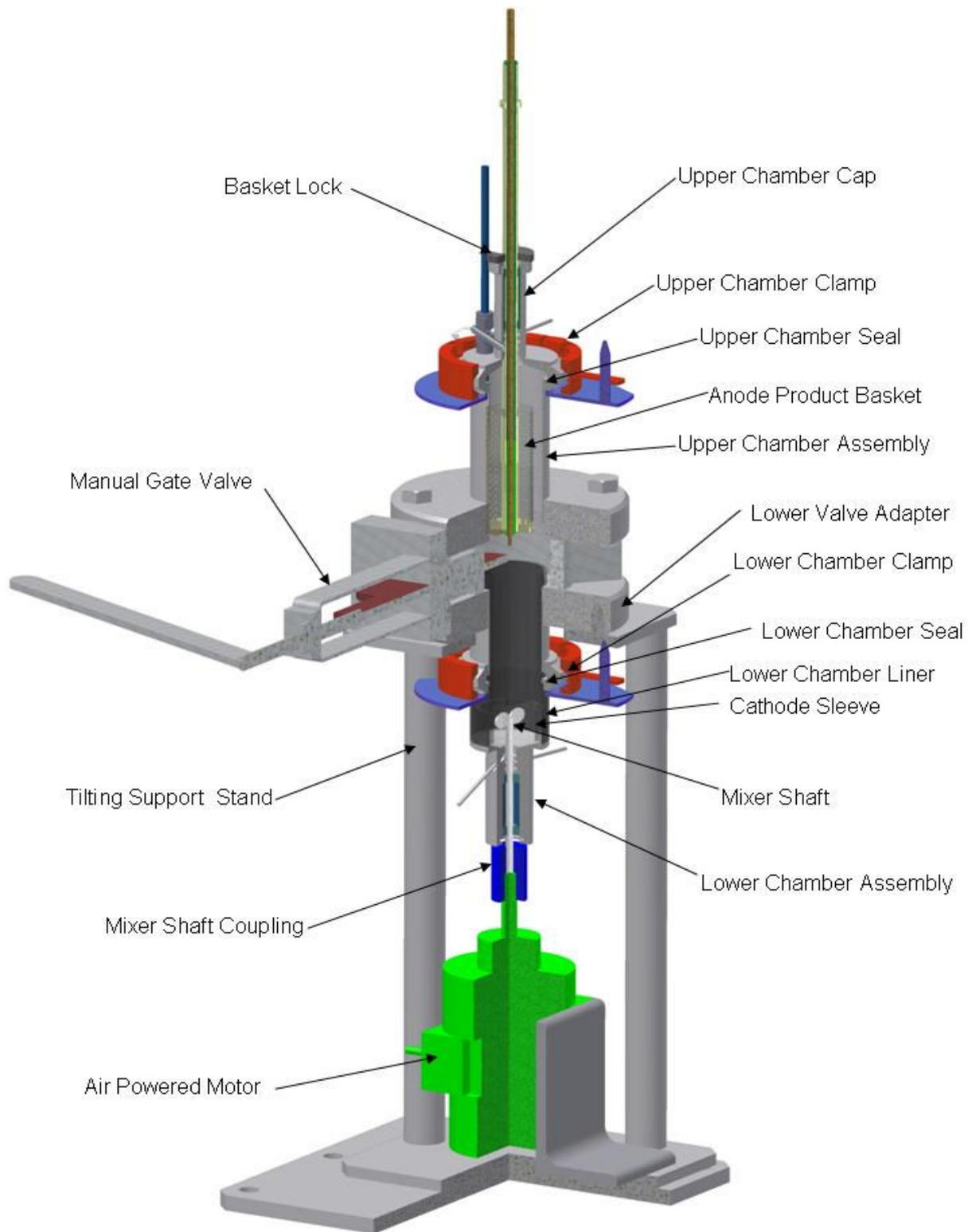


Figure 4. Dissolution Apparatus Main Components

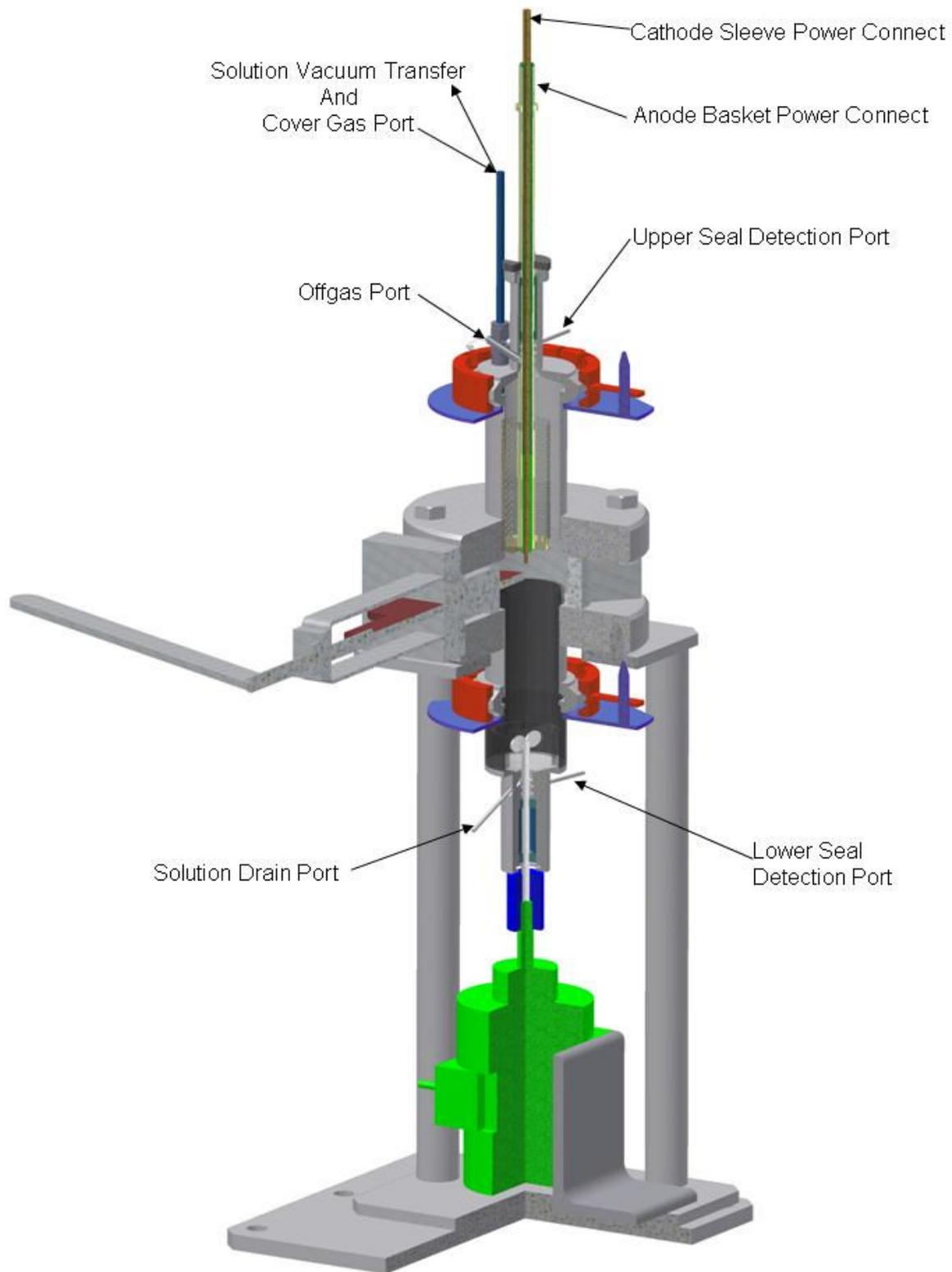


Figure 5. Dissolution Apparatus Connections

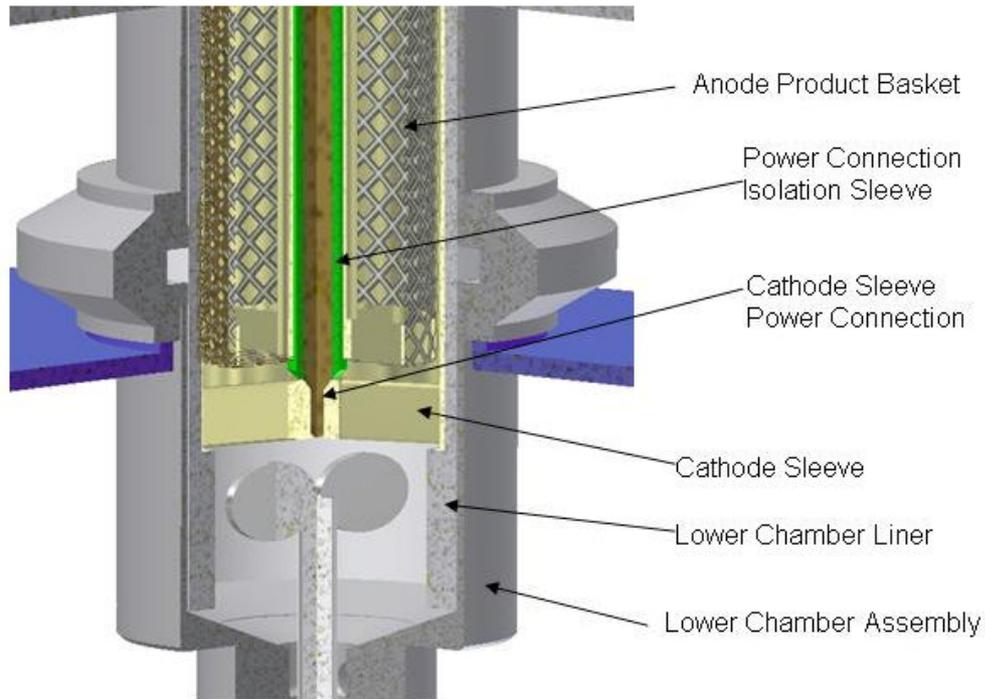


Figure 6. **Cathode Sleeve Electrical Connection**

Aluminum dissolution is performed in the upper chamber. With the manual gate valve closed and the foil sealed inside the upper chamber, the dissolving fluid (NaOH solution) is vacuum transferred into the upper chamber (see **Figure 5** and 5). As soon as the solution is in the chamber, a cover gas is introduced using the same port. To capture the off gas of the process, a port is provided with an in-line filter to prevent any foam or by product from leaving the chamber. A small leak-detection port has been provided between the o-ring seals both above and below the valve to monitor the seal integrity. After completing of the aluminum dissolution, the solution is vacuum-transferred out of the upper chamber into a separate vessel, while the cover gas is bleeding in. Once empty, the upper chamber may be flushed with water and then evacuated.

Uranium Dissolution then begins. Following the above process, without opening the upper chamber, the manual valve is opened. The anode rod with the basket is then lowered into the lower chamber. When seated properly, the basket-lock mechanism may be rotated to secure the anode basket in place. The power connections for the anode and the cathode are concentric in the anode basket shaft. By seating the basket in the basket lock (Figure 6), the cathode sleeve can be powered from outside the chamber through the cathode power rod. The positive connection can then be made directly onto the basket rod. Solution is added using the same port as above. The off gas is also collected using the same port. Agitation is provided using a mixer blade under the anode basket. This is powered by a gas-powered motor for variable speed and explosion-proof performance. At the end of the process, the lower solution drain port can be opened and the solution gravity-transferred to another container.

6. Acknowledgements

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357.

Government License Notice

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

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