Laboratory-Scale Study of Electrolytic Reduction of Uranium Oxides

by D. S. Poa, L. Burris, R. K. Steunenberg, and Z. Tomczuk

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Chemical Technology Division

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OF URANIUM OXIDES

by

D. S. Poa, L. Burris, P. K. Steunenberg, and Z. Tomczuk

ABSTRACT

An exploratory study was undertaken to investigate potential improvements in the electrolytic reduction of uranium oxide to the metal. Advantages of the electrolytic procedure over existing chemical reduction processes are (1) lower operating temperatures, (2) removal of most impurities, and (3) elimination of solid by-product wastes. The results showed that $\text{UO}_2$ can be reduced electrolytically in a molten LiF-KF-NaF-CaF$_2$-UF$_4$ electrolyte at 975°C, and at current densities from 500 to 900 mA/cm$^2$. The metallic uranium product was collected as a solid deposit on a molybdenum or uranium cathode rod.

I. INTRODUCTION

Uranium oxides constitute both the chemical used in the head end of the uranium fuel cycle as well as the nuclear reactor fuel. Metallic uranium and its alloys are important components of fast reactor fuel elements, particularly as used in EBR-II and the Integral Fast Reactor (IFR) concept. Metallic uranium is also employed in the advanced isotope separations process by laser interaction with atomic vapor (AVLIS), and is also recycled in various scrap operations. Handling of metallic uranium very often generates oxidic scrap owing to the reactive nature of metallic uranium. Processes for reducing oxides to metal are therefore of broad interest.

Electrolytic reduction of uranium oxides to metal was investigated in the early 1960's by workers at the Mallinckrodt Company [1-4]. The more recent requirements for efficient reduction of uranium oxides made it desirable to reexamine electrolytic procedures that would be compatible with the IFR and other processes, and take advantage of information obtained since the Mallinckrodt studies. Successful development of an efficient electrolytic reduction step could also open up other applications, e.g., reclamation of enriched uranium from scrap and residues, and reduction of spent oxide fuels.

Uranium oxides can be reduced to the metal by a variety of methods. The commercial method for production of uranium metal consists of converting uranium oxides to UF$_4$, and then reducing the UF$_4$ to metal with calcium using a thermo-chemical reduction process. The uranium oxides can also be reduced by electrolytic methods using a molten salt as the electrolyte [1-5]. In both cases, the process is carried out at a high temperature (1200°C or higher) and the product is collected as liquid uranium metal. Chemical reductions involving a liquid such as zinc-magnesium alloy as the reductant at temperatures of 700-800°C have been demonstrated on a laboratory scale [6-7]. In this case, the uranium metal product was recovered by vaporizing off the solvent metals in a distillation or retorting operation.

*Preliminary scouting studies were supported by the Y-12 Development Division of Martin Marietta Energy Systems, Oak Ridge, TN. Subsequent work reported here was supported by Argonne Experimental Development Funds.
In this study, an exploratory research effort was directed to the electrolytic reduction of uranium oxides to produce uranium metal, using molten LiF-KF-NaF-CaF\(_2\) (45.6 - 41.2 - 11.7 - 1.5 mol %) eutectic salt plus 7 to 8 mol % UF\(_4\) as the electrolyte. This quarternary eutectic was chosen because of its low melting point (444.0°C), chemical stability, and oxide solubility.

The approach taken in this study was to deposit solid uranium metal directly on a solid cathode at temperatures below the melting point of uranium (1132°C). The lower temperature electrolytic reduction process has several advantages over the existing uranium reduction processes: (1) It lessens materials problems and special heating and insulating requirements associated with high-temperature operations. (2) It removes most impurities. (3) It does not produce the large quantities of byproduct oxide wastes typical of chemical reduction processes.

In a complete process, electrolytic deposition of a uranium metal product on a cathode would be followed by stripping the uranium product mechanically from the cathode and consolidating it into an ingot by melting. A uranium cathode is a possible alternative.

II. BACKGROUND LITERATURE

A. Early Studies on Electrolytic Reduction of Uranium Oxides

The earliest work on direct electrolysis of uranium oxides was done by Niedrach and Dearing [1] at Knolls Atomic Power Laboratory in 1958. They developed a process for the production of molten uranium by reduction of its oxides, based on the concept of the Hall process for producing molten aluminum from its oxides. They investigated the effects of current, salt-bath composition, and other variables on efficiency and cell operation. An electrolyte bath containing 20 mol % UF\(_4\) diluted with a 50:50 mol % mixture of BaF\(_2\) and MgF\(_2\) was found to be satisfactory, and sufficient metal was obtained to prove the process concept. Poor coalescence of the metal deposit caused by oxide contamination and low yields were the major unsolved problems. Both resulted from the low solubility of uranium oxides in the fluoride electrolyte.

To solve the problems of low yield and poor coalescence, Piper and Leifield [2] at the Mallinckrodt Chemical Works (MCW) initiated laboratory-scale studies in 1959. They developed the concept of incorporating the uranium oxides in a consumable oxide-carbon anode. The laboratory-scale demonstration of this approach was successful and production of well-coalesced uranium metal was achieved. However, because of the added cost of preparing the sintered UO\(_2\)-carbon anode and the difficulty of scale up, Piper [3-4] then adopted the approach of feeding the uranium oxide directly into the cell, using the crucible as the cathode as proposed by Niedrach and Dearing [1]. Electrolytes composed of an equimolar mixture of BaF\(_2\) and LiF with varying amounts of UF\(_4\) were used by Piper [3-4] in most of his work.
Concurrent with the MCW development, workers at the Federal Bureau of Mines [8] developed a process that employed a neutral crucible with a graphite cathode rod.

The electrolytic reduction of uranium oxides suffers from several difficulties not encountered in the Hall process for aluminum production, all of which are directly or indirectly associated with the low solubility of the uranium oxides in the electrolyte. Varwig [9], who measured the solubility of UO₂ in various electrolytes, found that the solubility of UO₂ was increased by the presence of UF₄ in molten halide electrolytes. For example, the solubility of UO₂ in molten BaF₂-LiF electrolyte of equimolar ratio at 1170°C is about 1 wt % with a UF₄ concentration of 20 wt %, and it reaches a maximum of 4 wt % at a UF₄ concentration of 45 wt %. Recently, Greenfield and Hyde [10] measured the solubility of UO₂ in molten UF₄ and in several binary and ternary mixtures of dilute fluorides containing UF₄. These systems are typical of those used as electrolytes in electrolytic cells. Greenfield and Hyde's solubility values are in general agreement with those obtained by Varwig [9].

Poa and Steunenberg [11] have reported the results of a preliminary experimental study on the electrolytic reduction process. A graphite rod anode and a molybdenum rod cathode were used for the electrolysis. The electrolyte was molten LiF-KF-NaF-CaF₂ (45.6 - 41.2 - 11.7 - 1.5 mol %) eutectic salt plus 7 to 9 mol % UF₄. Although the results of that investigation had demonstrated that uranium oxides can be reduced electrolytically to produce a solid uranium metal deposit at an operating temperature of about 950°C, the estimated current efficiency was very low (about 15 to 20%). In that study, achieving continuous and stable operation of the cell was not possible in the rudimentary cell system that was employed. For improvement of cell operation, the following areas were identified as worthy of future investigations.

A well designed larger cell system and improvements of the associated facilities were considered to be the key factors for successful development of the electrolytic reduction process. Furthermore, incorporation of several essential cell structures and components, including the compartmentalization of the cathode zone, the shielding of the anode rod, and the installation of a gas-sparging system and a paddle stirrer were suggested.

B. Process Chemistry

The basic reactions in this process are:

At the anode:

\[
UO_2 + C \rightarrow U^{4+} + CO_2 + 4e^- \quad (1)
\]

or

\[
UO_2 + 2C \rightarrow U^{4+} + 2CO + 4e^- \quad (2)
\]

At the cathode:

\[
U^{4+} + 4e^- \rightarrow U \quad (3)
\]
Overall:
\[ \text{UO}_2 + \text{C} \rightarrow \text{U} + \text{CO}_2 \]  \hspace{1cm} (4)

or
\[ \text{UO}_2 + 2\text{C} \rightarrow \text{U} + 2\text{CO} \]  \hspace{1cm} (5)

Uranium dioxide is the only important oxide because all the higher oxides such as \( \text{UO}_3 \) and \( \text{U}_3\text{O}_8 \) are thermally decomposed to \( \text{UO}_2 \) at the cell operating temperature (900 to 1000°C).

The actual electrode processes are more complicated. The cathode reaction may be preceded by electron-transfer processes involving uranium fluoride complex ions.

The anode process may be even more complicated than the cathode reaction. Uranium dioxide dissociates by dissolution in the molten electrolyte so that electroactive species undergoing discharge at the anode are either oxygen ions, \( \text{O}^{2-} \), or some kind of oxygen-containing uranium oxyfluoride complex ions. Reaction (2) is favored thermodynamically. Oxygen depositing onto carbon at the cell operating temperature should form essentially all \( \text{CO} \) with very little \( \text{CO}_2 \). However, experimental research evaluation and industrial cell data strongly indicate that \( \text{CO}_2 \) is the predominant anode product. Thonsad and Hove [12] pointed out that reaction kinetics cause the discharged oxygen to form \( \text{CO}_2 \) rather than thermodynamically favored \( \text{CO} \).

In general, the actual electrode processes are not well understood and numerous side reactions are possible, e.g., [3, 10].

(1) formation of \( \text{UF}_3 \) by the reaction of uranium at the cathode with \( \text{UF}_4 \) in the electrolyte,
\[ U + 3\text{UF}_4 \rightarrow 4\text{UF}_3 \]  \hspace{1cm} (6)

(2) formation of \( \text{CF}_4 \) at the anode at higher current densities, especially when there is a depletion of oxygen-containing ions at the anode surface,
\[ \text{UF}_4 + \text{C} \rightarrow U^{4+} + \text{CF}_4 + 4\text{e}^- \]  \hspace{1cm} (7)

(3) back reaction of \( \text{CO} \) at the cathode,
\[ U + 2\text{CO} \rightarrow \text{UO}_2 + 2\text{C} \]  \hspace{1cm} (8)

(4) back reaction between uranium dissolved in some form in the electrolyte and carbon dioxide formed at the anode,
\[ U + 2\text{CO}_2 \rightarrow \text{UO}_2 + 2\text{CO} \]  \hspace{1cm} (9)

This reaction accounts for most of the carbon monoxide in the anode gases.
(5) parasitic cyclic reactions

\[ U^{4+} + e^- \rightarrow U^{3+} \text{ (cathode)} \quad (10a) \]
\[ U^{3+} \rightarrow U^{4+} + e^- \text{ (anode)} \quad (10b) \]

The cyclic reaction results from the formation of trivalent uranium at the cathode. The trivalent uranium then migrates to the anode where it is reoxidized to the quadrivalent uranium.

The last three reactions account for most of the loss in the current efficiency in the electrolytic reduction process.

III. EXPERIMENTAL

A. Glove-Box Facility

Because the molten fluorides used in the electrolytic reduction process react with gaseous impurities such as oxygen and moisture, the experiments were conducted in a glove-box facility in which a high-purity helium atmosphere was maintained. The glove box is of a standard modular design developed earlier at ANL [13] for maintaining high-purity inert atmospheres or for containing radioactivity. The helium glove-box atmosphere was purified by a cryogenic system consisting of molecular sieves and activated charcoal cooled by liquid nitrogen [14]. The moisture level of the helium was kept below 3 ppm during the experiments, and the oxygen level was below 15 ppm.

B. Electrochemical Cell

1. Overall Cell Configuration

The basic design of the cell that was used for the electrolytic reduction experiments is shown schematically in Fig. 1. The cell vessel was a graphite (Union Carbide "UCAR" Grade CS) crucible having an outside diameter of 10.16 cm, a depth of 11.43 cm, and a wall thickness of 0.63 cm. A photograph of the crucible is shown in Fig. 2.

The graphite crucible contained the electrolyte, a shielding tube housing the graphite rod anode and a gas-sparging tube, a paddle stirrer, the cathode rod, and a smaller graphite crucible that served to compartmentalize the cathode zone in the cell.

The cell was placed inside a secondary tantalum container, which had an outside diameter of 12.07 cm, a depth of 29.20 cm, and a wall thickness of 0.05 cm. This secondary container was then positioned in the furnace chamber. The furnace was placed inside the glove box.

A closed-end graphite tube housing a calibrated Chromel-Alumel thermocouple was positioned in the space between the cell vessel and the tantalum secondary container.
Fig. 1. High-Temperature Cell for the Electrolytic Reduction of Uranium Oxides.
The more important cell components and the associated facilities are discussed in greater detail below.

2. Electrodes

The anode was a graphite rod (Grade ECV, Union Carbide Corp. Cleveland, OH) of 1.27 cm diameter. The rod was positioned inside a shielding tube of 2.54 cm inside diameter and 0.32 cm wall thickness. The upper section of the tube (about 25 cm in length) was made of alumina (Grade 998 Al₂O₃, McDanel Refractory Co., Beaver Falls, PA), while the lower section (about 9 cm in length) of the tube that was immersed in the molten fluorides during the electrolysis was made of boron nitride (Grade HBR, Union Carbide Corp. Cleveland, OH). This shielding tube served as: (1) a shield to reduce the back reaction of CO at the cathode; and (2) an off-gas outlet channel for releasing the gases such as CO₂, CO, and CF₄ generated in the cell.
The cathode used in all the electrolytic reduction tests was a 0.635 cm diameter molybdenum rod, with the exception of one test in which a uranium rod of 0.56 cm diameter was used. The diameter of the cathode rod was about half that of the corresponding graphite-rod anode. This was done to provide a high ratio of anode-to-cathode areas for the purpose of obtaining a relatively low anode current density that might alleviate the "anode effect," which is the blockage of the anode surface by a gas film. A gas film will inhibit the current transfer between the anode and the melt.

The cathode rod was encased tightly in an insulation tube. The upper section of the tube was made of alumina, while the lower section was made of boron nitride (BN). A well-defined length of the cathode rod, which gave an apparent electrode surface area of approximately 8 cm$^2$, was exposed to the molten fluoride electrolyte during electrolysis. The exposed lower end of the cathode rod was positioned inside the smaller graphite crucible (Union Carbide "UCAR" Grade AGSX, of 5.08 cm OD, 0.635 cm wall thickness, and 6.35 cm depth. See Fig. 2). As shown in Fig. 1, this smaller crucible was attached to the inside wall and seated on the bottom of the cell vessel (the larger graphite crucible), and it was fixed in position with graphite cement (Union Carbide, C-34 cement). The position of the inner small crucible in the cell served to compartmentalize the cathode zone, and thus helped to avoid oxide contamination of the metallic uranium deposit by limiting access of undissolved oxide to the cathode compartment.

3. Gas Sparger

The main length of the gas-sparging tube was 0.32 cm OD copper tube. Since copper is slowly attacked by the molten fluorides, a BN tube of about 0.42 cm outside diameter and 12.8 cm long was connected to the gas-outlet end of the copper tube. Therefore, only a section of the BN tube was immersed in the molten electrolyte during electrolysis.

The other end of the gas-sparging tube system was connected to the compressed helium gas cylinders (Grade 5 helium gas containing a maximum impurity level of 10 ppm, supplied by Airco Industrial Gases, Chicago, IL) located outside the glove box. The helium gas was purified by the same cryogenic system as that used for the glove-box atmosphere [14]. Glass tube rotameters (Model Omega FL-1703, Omega Engineering, Inc. Stamford, CT) were used to monitor and control the flow of gas to the electrolyte within the space between the anode rod and its shielding tube (see Fig. 1).

Before it was admitted to the cell, the helium sparging gas was preheated in a 250-cm-long preheating section of the copper tube. The length of preheating copper tube was coiled and heated in a furnace well at about 500°C. This furnace well was built into the floor of the glove box and extended downward into a resistance-heated furnace.

The helium sparging assembly was tested in water outside the glove box before it was incorporated into the cell system in the box.
The maximum helium gas flow rate was about 6 to 7 standard liters/hour. The test results demonstrated that a higher flow rate would cause splashing of the molten fluorides. Furthermore, if the gas flow rate were higher, the helium gas entering the cell might be insufficiently preheated, and therefore, cause the formation of cold spots in the electrolyte adjacent to the anode surface.

4. **Paddle Stirrer**

The paddle stirrer used to provide agitation of the bulk-phase electrolyte had two pairs of blades. Each of the molybdenum blades was 0.5 cm wide and 0.95 cm long. The stirrer shaft was a molybdenum rod with a diameter of 0.64 cm and a length of 38.1 cm.

5. **Furnace**

The furnace used in this work was a Mellen Model C3-401 (Mellen Company, Inc., Penacook, NH), single-zone, crucible-type, top-loading, high-temperature furnace capable of operation at temperatures up to 1300°C in an air atmosphere. The furnace chamber was 12.7 cm inside diameter with a heated length of 30.5 cm. The outside dimensions were approximately 35.6 cm OD by 47.8 cm high. Power requirements for the furnace were 57 volts, single phase, 60 Hz with a capacity of approximately 3,000 watts.

Power and control for the furnace were provided by a Mellen Model PS-400-240-25T, single-zone, SCR control and power supply. The lowest set point of the temperature controller was 600°C and the increment was 100°C.

The furnace was placed in the glove box for the electrolytic reduction experiments. Because the thermal conductivity of helium gas is higher than that of air, two layers of ceramic fiber insulation blanket (Fiberfrax Durablanket, the Carborundum Co., Niagara Falls, NY) were wrapped around the furnace to prevent excessive heat loss and to maintain the outer surface temperature below 70°C during high-temperature operations. This was also done in accord with ANL safety requirements.

The secondary tantalum container for the electrolytic cell also served as a furnace liner for protecting the furnace insulation material and the heating element from molten fluoride salt attack (see Fig. 1).

C. **Materials**

The molten salt electrolyte used in these studies was the quaternary eutectic salt LiF-KF-NaF-CaF$_2$ (45.6 - 41.2 - 11.7 - 1.5 mol %, mp, 444.0°C) plus 7 to 8 mol % UF$_4$. The quaternary fluoride eutectic was polaro-graphic-grade material obtained from the Anderson Physics Laboratories, Urbana, IL. The depleted UF$_4$ powder, which contained 75.8 wt % uranium, was provided by the Special Materials Department of Argonne National Laboratory. Uranium oxides were obtained from two different sources: (1) the Martin Marietta Energy Systems, Inc. (Y-12 plant), which supplied 911.4 g U$_3$O$_8$ powder, the analysis of which is given in Table I; and
(2) the Special Material Department of Argonne National Laboratory, which supplied UO₂ pellets (1.0 cm in length and 0.5 cm in diameter). The anodes used in these studies were Grade ECV graphite rods obtained from Union Carbide Corp., Cleveland, OH.

| TABLE I. Analytical Results for Uranium Oxide Obtained from Martin Marietta, Inc. (Y-12 Plant) |
| Uranium content by chemical analysis ----- 0.859 g(U)/g |
| Theoretical for U₃O₈ -------------------- 0.848 g(U)/g |
| X-ray Diffraction ------------------------ Pure U₃O₈ |

<table>
<thead>
<tr>
<th>Other Impurities</th>
<th>Concentration (ppm)</th>
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<tr>
<td>Carbon</td>
<td>442</td>
</tr>
<tr>
<td>Iron</td>
<td>80</td>
</tr>
<tr>
<td>Tungsten</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Silicon</td>
<td>48</td>
</tr>
<tr>
<td>Aluminum</td>
<td>22</td>
</tr>
<tr>
<td>Manganese</td>
<td>19</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>18</td>
</tr>
<tr>
<td>Nickel</td>
<td>16</td>
</tr>
<tr>
<td>Niobium</td>
<td>11</td>
</tr>
<tr>
<td>Sodium</td>
<td>10</td>
</tr>
<tr>
<td>Others</td>
<td>Not read, or &lt; 10 ppm</td>
</tr>
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D. Instrumentation

A Model 6282 A DC power supply (Hewlett Packard, Palo Alto, CA) was used to provide the DC current for the electrolytic reduction tests. The cell voltage and current were monitored with a Model 197 Autoranging DMM and a Model 177 Microvolt DMM (Keithley Instrument, Inc., Cleveland, OH), respectively. The cell voltage and current were also recorded by a Model 110 strip-chart recorder (Gould, Inc., Cleveland, OH). The paddle stirrer was driven by a Model R-4370-00 bench stirrer motor (Cole-Parmer Instrument and Equipment Co., Chicago, IL).
E. Procedure

1. Degassing and Preheating of Cell Components

Several operations, including degassing and preheating, were performed on the cell prior to introducing the process materials into the system. The tantalum secondary container was cleaned by sand blasting to remove surface oxides and any other foreign materials.

The graphite crucibles were degassed in a AVS Model No. HMF-12-12-12-1300 Horizontal Vacuum Furnace (Advanced Vacuum Systems, Inc., Ayer, MA). The crucibles were heated at 1100°C under vacuum for about three hours. Then, with the furnace still under vacuum, the heater was turned off and the furnace was allowed to cool to room temperature overnight. Argon was admitted to the furnace, and the crucibles were withdrawn from the furnace and transferred to the glove box.

After the cell system was assembled in the furnace chamber inside the helium-atmosphere glove box, it was heated overnight at about 600°C under helium gas. The cell was then heated to the temperature of 1200°C at a rate of 100°C/h. Various small alumina and BN parts were treated similarly to eliminate as much moisture from the system as possible. The cell system was allowed to cool to room temperature and the assembly was withdrawn from the furnace chamber and visually examined.

2. Electrolytic Reduction Procedure

The general procedure for the electrolytic reduction experiments consisted of the following steps:

(a) The electrolyte salt, consisting of about 600 g LiF-KF-NaF-CaF$_2$ eutectic and 350 g of UF$_4$ (about 7 to 8 mol % UF$_4$ in the electrolyte) was added to the graphite crucible. The crucible containing the salt was then lowered into the tantalum secondary container in the furnace chamber.

(b) The top opening of the furnace chamber was covered with the fire-brick cover and three layers of ceramic fiber insulation blanket.

(c) The cell was heated to about 580°C to melt the electrolyte salt. After the salt had melted, about 60 g of uranium oxide (approximately 6 wt % of the electrolyte) was added to the crucible through a fill tube (which was the same tube that later would be used as the shielding tube of the anode rod).

(d) The cell was heated overnight at about 580°C. The electrodes, gas sparger, the anode shielding tube, and the paddle stirrer were then installed in the cell, and the crucible contents were stirred.
(e) The cell temperature was increased to the predetermined operating temperature of 775 to 975°C, and the electrical connections to the cell were made.

(f) Gas sparging of the electrolyte adjacent to the anode surface was started. The helium flow rate was adjusted to about 7 standard liters/hour. The rotational speed of the paddle stirrer was adjusted to about 200 rpm.

(g) After about 30 minutes on open circuit, electrolysis was initiated.

(h) At the completion of a run (ranging from 5 to 6 hours), the stirring and gas sparging of the electrolyte were discontinued, the electrolysis circuit was opened, and the cell was allowed to cool to about 700°C.

(i) With the insulation cover still on the top of the furnace chamber, the electrodes, the gas-sparger, the anode shielding tube, and the paddle stirrer were moved out of the molten salt electrolyte, which required raising them vertically 4 to 5 inches, and suspended in the upper space of the furnace chamber.

(j) The power to the furnace was cut off.

(k) The furnace and the cell system were allowed to cool to ambient temperature, after which the insulation cover was removed from the top of the furnace chamber. The electrochemical cell was withdrawn from the furnace chamber at this time, completing the experiment.

(l) The metal deposit on the cathode surface, and the conditions of the electrochemical cell and its associated components were examined visually.

IV. RESULTS AND DISCUSSIONS

Three series of experimental runs were made in this study. A new cell and a fresh electrolyte salt were used for each series of runs. However, the electrolyte salt composition was essentially the same for all these series of experiments, i.e., about 600 g of quarternary fluoride eutectic plus about 350 g of UF₄ (approximately 7.0 mol % UF₄ in the electrolyte).

A. Effects of Operating Conditions

The first series of four experiments were made to establish the operating conditions and to examine the effects of several important operating parameters, including cell temperature, agitation of the bulk phase electrolyte, and sparging of the electrolyte adjacent to the anode surface with helium gas on the electrolytic reduction process.
The uranium oxide added to the cell for this series of experiments was about 60 g of UO₂ pellets.

1. Temperature

To determine the lowest possible temperature for the electrolytic reduction process, three experimental runs (Run 1A, 1B, and 1C) were made at three different temperatures: 775, 875, and 975°C. The flow rate of sparging gas was maintained at about 7 standard liters/hour, and the rotational speed of the paddle stirrer at about 200 rpm.

The results of these tests showed that at the lower temperatures of 775 and 875°C, the cell voltage was high (4.5 to 7.0 V) and unstable even at a low current density of about 50 mA/cm² (based on the apparent cathode surface area of about 8.0 cm²). As evident from Fig. 3, which presents the cell voltage vs time curves for the reduction test performed at 875°C (Run 1B), the cell voltage was unstable during the entire period of electrolysis.

The two runs made at 775 and 875°C (Runs 1A and 1B) failed to produce any observable metallic uranium deposit on the cathode.

As shown in Fig. 4, at a higher temperature of 975°C, the electrolytic reduction process could be carried out at a much higher current density of about 115 mA/cm². The cell voltage was much lower (2.3 to 2.6 V), relatively stable, and showed no oscillations during electrolysis. Most importantly, a metallic uranium deposit was obtained from this run (Run 1C). A photograph of this cathode deposit is shown in Fig. 5. Failure to electrolytically deposit uranium at the two low temperatures could be related to the solubility of uranium oxide in the molten fluoride electrolyte.

2. Gas Sparging and Bulk Phase Electrolyte Agitation

The effects of bulk phase electrolyte agitation and gas sparging on the electrolytic reduction process were studied in a special test, Run 1D, made at 975°C.

The test was made by starting the electrolysis with both the gas sparger (helium gas flow rate of 7 standard liters/hour) and the paddle stirrer system (rotational speed of 200 rpm) on. After about 45 min., when the operating conditions and the cell voltage were stabilized, either the gas-sparging system or the paddle stirrer was turned off alternatively for a period of time. As shown in Fig. 6, which presents the cell-voltage-vs-time curves recorded during this test, the responses of the cell voltage to these operating variables were clear and definite. Figure 6 shows that, when the paddle stirrer used for agitating the bulk phase electrolyte was turned off, the cell voltage rose to a much higher level (by a difference of 2 to 3.5 V, as shown by points A, B, and D in Fig. 6) and then stabilize at that level. However, when the sparging gas was cut off, as shown by point C in Fig. 6, the cell voltage showed a very steep increase up to a level above the preset cell voltage control limit of 10.0 V. This sharp increase in cell voltage caused immediate interruption of the current flow through the cell.
Fig. 3. Cell Voltage and Current vs. Time for Run 1B at 875°C.
Fig. 4. Cell Voltage and Current vs. Time for Run IC at 975°C.
Fig. 5. Photograph of the Cathode Metal Deposit from Run 1C. Temperature = 975°C; cathode = 0.635 cm diameter Mo rod.
Fig. 6. Effects of Bulk-Phase Electrolyte Agitation and Helium Sparging on Cell Voltage during Electrolysis.
These results indicate clearly that gas sparging of the electrolyte adjacent to the anode surface is critical for continuous and stable operation of the electrolytic reduction process.

B. Reproducibility of the Electrolytic Reduction Process

After the important operating parameters had been established as described in Section A, a second series of five experiments, Runs 2A to 2E, were performed. All these five tests were made under the same established operating conditions: a cell temperature of 975°C, a helium flow rate of 7 standard liters per hour for the gas-sparging system, and a rotational speed of about 200 rpm for the paddle stirrer.

The objectives of this series of experiments were: (1) to test the reproducibility of the electrolytic reduction process at the established operating conditions, and (2) to determine whether the cathode product of uranium metal was derived mainly from the reduced uranium oxides or from the reduction of uranium tetrafluoride (UF₄) dissolved in the molten fluorides.

To partially accomplish the second objective, the first electrolytic experiment of this series of tests, Run 2A, was made without adding any uranium oxide to the electrolyte contained in the cell. It was an electrolytic reduction test carried out on the blank molten electrolyte. The cell-voltage-vs-time curve recorded for this test is presented in Fig. 7, which shows that, during the electrolysis, only a very low current density (~25 to 37 mA/cm²) could be maintained at a relatively high cell voltage of 4.5 to 6.0 V. The cell voltage curve also shows strong oscillation and cyclic patterns.

At the completion of this run, no metallic deposit could be observed on the cathode surface. As evident from the characteristic patterns of the cell voltage curve shown in Fig. 7, the small current passed through the cell during electrolysis might have been consumed by the parasitic cyclic reactions involving reduction of U⁴⁺ to U³⁺ at the cathode and oxidation of U³⁺ back to U⁴⁺ at the anode.

The results of this test indicate that the electrolytic reduction of UF₄ to produce a uranium metal deposit under the stated operating conditions is very difficult.

Before the start of the other four test runs (Runs 2B to 2E) made in this series of experiments, approximately 60 g of UO₂ pellets was added to the cell. The cell contents were stirred for about two hours. Runs 2B through 2E were then carried out in sequence.

It should be noted here that instead of the molybdenum rod (0.635 cm in diameter) cathode used in all of the other tests, the cathode used for Run 2D was a uranium rod of 0.56 cm diameter. This was done to study the effect of different substrate materials on the adherence of the metallic deposits.
Fig. 7. Cell Voltage and Current vs. Time for Run 2A. (Blank electrolyte electrolysis at 975°C.)
The results of these four tests demonstrated that the electrolytic reduction process is reproducible under the established operating conditions.

As shown in Figs. 8 to 11, the cell-voltage-vs-time curves for Run 2B to 2E indicate that, during electrolysis, a relatively higher current density (~75 mA/cm²) could be maintained, and the cell voltages were relatively low (2.3 to 2.9 V) for these tests. Furthermore, the cell voltages were very stable during the entire period of electrolysis. Run 2B, 2C, and 2D showed no cell voltage oscillation. However, cell voltage oscillations did occur during the last half of Run 2E (Fig. 11). These oscillations were probably due to the gradual depletion of uranium oxide in the electrolyte near the end of a series of electrodepositions. The lower concentrations of the dissolved uranium oxide in the electrolyte might have caused a decrease in the mass-transfer rate of uranium ions from the electrolyte to the electrode surface.

A good metallic cathode product was obtained from each of these test runs. Figures 12 to 15 show the photographs of these four cathode deposits. The morphology of the metallic uranium deposits was dendritic. Because of the adhering and occluded electrolyte, the cathode products showed a dark green color with a shade of brown.

A total of about 23 g of cathode products was recovered from these four deposits. Samples of the cathode products were submitted for instrumental and chemical analyses by the ANL Analytical Chemistry Laboratory. Results of the analyses are presented in Table II. The major conclusions from these results are:

1. The metallic uranium contained in the cathode products was about 60 wt % on the average (excluding uranium in UF₄ contained in the occluded or adhering electrolyte); the balance was essentially electrolyte.

2. The metal products were α-uranium of high purity and showed no oxide contamination.

3. The total uranium metal actually produced from these four runs was approximately 13.8 g (which is 60% of the gross weight of the total cathode products of 23 g). However, the total amount of electricity passed through the cell during these tests was about 11.35 Ah, which, based on the cathode reaction of Equation (3), should theoretically have produced 25.197 g uranium metal. Therefore, the average current efficiency for these four electrolytic reduction tests was approximately 53%, which compares with efficiencies generally below 40% reported by other investigators [1-4].

Before and after Runs 2B through 2E, three dip samples of the electrolyte, weighing 1 to 2 grams each were taken from different locations in the cell and analyzed for oxygen. The purpose of these samples was to determine the consumption of uranium oxide during electrolysis.
Fig. 8. Cell Voltage and Current vs. Time for Run 2B.
Fig. 9. Cell Voltage and Current vs. Time for Run 2C.
Fig. 10. Cell Voltage and Current vs. Time for Run 2D.
Fig. 11. Cell Voltage and Current vs. Time for Run 2E.
Fig. 12. Photograph of Cathode Metal Deposit from Run 2B. Temperature = 975°C; cathode = 0.635 cm diameter Mo rod.

Fig. 13. Photograph of Cathode Metal Deposit from Run 2C. Temperature = 975°C; cathode = 0.635 cm diameter Mo rod.
Fig. 14. Photograph of Cathode Metal Deposit from Run 2D. Temperature = 975°C; cathode = 0.56 cm diameter uranium rod.

Fig. 15. Photograph of Cathode Metal Deposit from Run 2E. Temperature = 975°C; cathode = 0.635 cm diameter Mo rod.
TABLE II. Analytical Results of the Cathode Products from Test Runs 2B to 2E

<table>
<thead>
<tr>
<th>Element</th>
<th>Deposit I (wt %)</th>
<th>Deposit II (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium⁹⁰,³⁰</td>
<td>74.12 ± 0.003</td>
<td>60.70 ± 0.003</td>
</tr>
<tr>
<td>Potassium⁹⁰</td>
<td>10.61</td>
<td>14.95</td>
</tr>
<tr>
<td>Lithium⁹⁰</td>
<td>2.15</td>
<td>2.97</td>
</tr>
<tr>
<td>Calcium⁹⁰</td>
<td>0.44</td>
<td>0.59</td>
</tr>
</tbody>
</table>

a By X-ray diffraction, deposited uranium metal was determined to be α-uranium.
b Includes uranium in UF₄ contained in the electrolyte adhering or occluded in the dendritic deposit.
c From the electrolyte adhering or occluded in the dendritic deposit (estimated uncertainty is 5%).

The two sets of electrolyte samples, along with a sample of blank fluoride eutectic salt were submitted for oxygen analysis by the ANL Analytical Chemistry Laboratory (see Table III). Based on the analytical data, material balance calculations were made on UO₂ in the electrolytic cell system. The calculated results indicated that, within the limits of

TABLE III. Analytical Results of the Oxygen Concentration in the Electrolyte (Weighted average)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank fluoride eutectic:</td>
<td>0.16 ± 0.07 wt %</td>
</tr>
<tr>
<td>Initial oxygen concentration: (before electrolysis)</td>
<td>0.92 ± 0.10 wt %</td>
</tr>
<tr>
<td>Final oxygen concentration: (after electrolysis)</td>
<td>0.51 ± 0.08 wt %</td>
</tr>
</tbody>
</table>

Notes: 1 Calculated initial oxygen concentration attributed to the added UO₂ in the electrolyte = 0.71 wt %.
2 Total uranium metal deposited on the cathodes = 14 g.
3 Total weight of the electrolyte (including UO₂) = 1005 g.
the estimated uncertainties of the analytical data of oxygen, the amount of UO$_2$ lost from the electrolyte (based on oxygen analysis) agrees with the total amount of uranium metal deposited on the cathodes in these electrolytic reduction tests (Runs 2B-2E). It is evident from this agreement that the uranium metal from the cathode products obtained from these tests was derived from the reduction of UO$_2$ dissolved in the electrolyte. This argument is reinforced by the results of Run 2A, a blank run made without UO$_2$, which demonstrated that no uranium metal was produced from reduction of UF$_4$ under the operating conditions used in this study.

The results of these tests also showed that, judged by the mechanical force needed to remove the deposits from the cathode surface, the adherence of the metallic uranium deposits to the molybdenum cathode was strong. However, the adherence of the uranium metal deposits to the uranium cathode was even stronger. These two different cathode substrate materials (uranium and molybdenum) showed no other significant effect on the electrolytic reduction process.

C. Electrolytic Reduction of U$_3$O$_8$

The third series consisted of only two experiments, Run 3A and 3B. The electrolyte salt composition and the operating conditions used for these tests were exactly the same as those used in the second series of experiments. However, the uranium oxide used for these two electrolytic reduction tests was the U$_3$O$_8$ powder (60 g was added to the cell) supplied by Y-12 plant of Martin Marietta Energy System, Inc. (see Table I).

Figures 16 and 17 show the current and cell-voltage-vs-time curves recorded during these two runs. In comparison with the cell voltage curves for Run 2B to 2E (Figs. 8-11), the voltage curves shown in Figs. 16 and 17 indicate that, in these two tests, the cell voltage during electrolysis was generally higher (2.5 to 3.7 V). It was also relatively unstable. It showed periods of ups and downs, small oscillations, and instantaneous short circuits in the cell. The U$_3$O$_8$ powder and its impurities might have been responsible for the unstable character of the cell voltage during these tests. Because it was observed that, after adding U$_3$O$_8$ powder to the cell, a film of powder formed at the surface of the electrolyte, it was believed this powder film caused intermittent shorting between the anode and cathode. It was also observed that, with the U$_3$O$_8$ powder, dewetting of the surfaces of the electrodes and the inside wall of the electrolytic cell occurred (an effect possibly caused by impurities), which could account for the higher electrolysis voltages required.

Unstable operation of the cell caused, for example, by conductive surface films could possibly be avoided by improved cell designs such as the use of isolated cathode collectors, or pretreatment of the feed oxide, e.g., oxidation of free carbon or fabrication of the oxide into sintered consumable oxide-carbon anodes.
Fig. 16. Cell Voltage and Current vs. Time for Run 3A.
Fig. 17. Cell Voltage and Current vs. Time for Run 3B.
Photographs of the cathode deposits obtained from Runs 3A and 3B are shown in Figs. 18 and 19. These deposits had the same dendritic character and overall appearance as observed in Runs 2B to 2E. The current efficiencies estimated for these two runs were lower, about 40% for Run 3A, and 30% for Run 3B. However, these values are less accurate than the value of 53% obtained for Run 2B-2E, because of the intermittent short circuits.

A sample of the cathode products from these runs was submitted for a determination of the carbon content by the ANL Analytical Chemistry Laboratory. The reported carbon content of the deposits was below 200 ppm, the lower limit of detection of the analytical procedure that was employed. The original carbon content of the U₃O₈ powder was about 442 ppm (see Table I).

D. General Observations

Following are some of the important observations common to all the three series of electrolytic reduction tests:

1. The photographs shown in Fig. 20 are pictures of a graphite anode before and after use in an electrolytic reduction experiment. The reacted anode exhibits the shape change typical of the graphite anodes used in these tests.

2. Post-test visual examination of the electrochemical cell system revealed that the graphite crucibles, the tantalum secondary container, the molybdenum-rod cathodes, and other associated cell components were all in good condition, except the molybdenum paddle stirrer, which appeared to be slightly attacked by the molten fluoride electrolyte.

V. SUMMARY AND RECOMMENDATIONS

A. Summary of the Results

A cell, containing a graphite rod anode and a molybdenum (or uranium) rod cathode, has been designed, built, and successfully operated to produce uranium metal by the electrolytic reduction of uranium oxides. Solid deposits of metallic uranium were obtained on the cathodes at 975°C, and at current densities from 500 to 900 mA/cm². The electrolyte was molten LiF-KF-NaF-CaF₂ (45.6 - 41.2 - 11.7 - 1.5 mol %) eutectic salt plus about 7 mol % UF₄. The tests were conducted in a graphite crucible located in a high temperature furnace chamber in a high-purity helium-atmosphere glove box.

The important conclusions from these investigations are summarized below:

1. The incorporation of several new (novel) design features in the electrochemical cell system contributed to the success of the electrolytic reduction process:
Fig. 18. Photograph of Cathode Metal Deposit from Run 3A. Temperature = 975°C; cathode = 0.635 cm diameter Mo rod.

Fig. 19. Photograph of Cathode Metal Deposit from Run 3B. Temperature = 975°C; cathode = 0.635 cm diameter Mo rod.
Fig. 20. Photograph of a Used Graphite Anode Rod (B) in Comparison with a New One (A).

(a) Stirring of the bulk phase electrolyte during electrolysis. This helped to maintain a saturation concentration of uranium oxides in the molten salt electrolyte by preventing settling of the oxides. Stirring of the electrolyte lowered the cell voltage by 2 to 3.5 V during electrolysis.

(b) Sparging the electrolyte adjacent to the anode surface with pre-heated helium gas. This reduced the overpotential for anodic gas evolution, and, most importantly, alleviated the "anode effect."

(c) Installation of an anodic shielding tube and compartmentalization of the cathode zone in the cell. This helped to avoid losses in current efficiency by back reactions of CO and CF₄. Compartmentalization of the cathode zone also helped to avoid oxide contamination of the metallic uranium deposit by limiting access of undissolved oxide to the cathode compartment.

With these cell structure improvements, continuous and stable operation of the electrolytic deposition process was achieved.
Satisfactory operating conditions have been established at a cell temperature of 975°C, a helium gas flow rate of 7 standard liters per hour for the gas-sparging system, and a rotational speed of about 200 rpm for the paddle stirrer. Under these operating conditions, a sequence of seven electrolytic reduction tests have been successfully completed. Cathode products of metallic uranium have been obtained from the reduction of UO₂ as well as U₃O₈.

The morphology of the metallic uranium deposit was dendritic. The metallic portion of the deposits was identified as α-uranium by X-ray diffraction. The results of chemical analyses indicated that the metal product was of high purity, and showed no oxide contamination.

The carbon content of the uranium metal (produced from the electrolytic reduction of U₃O₈ powder) was determined to be below 200 ppm, which was the lower limit of detection of the analytical procedure that was employed. The process reduced the carbon content from 442 ppm to < 200 ppm in spite of the graphite components of the cell.

The current efficiency obtained in this process was about 50%, which compares with efficiencies generally below 40% reported by other investigators.

Based on the data of chemical analyses, material balance calculations were made on UO₂ in the electrochemical cell system. The results showed that, within the limits of the estimated uncertainties of the analytical data of oxygen, the amount of UO₂ lost from the electrolyte roughly agrees with the total amount of uranium metal deposited on the cathode in the electrolytic reduction process. Besides, under the conditions of these experiments, no uranium was deposited unless uranium oxide was present in the electrolyte. That is, uranium was not deposited by reduction of UF₄ contained in the electrolyte.

Taken together, these two observations provide convincing evidence that uranium metal deposited on the cathode resulted from the reduction of uranium oxides.

B. Recommendations for Further Studies

It is recommended that further work be done with the main objective of resolving the questions concerning the reactive species and their reactions in the fluoride melt raised by the findings of this study as well as by the work of others. It is suggested that the following areas be investigated:

1. A study of the variations of the off-gas composition during electrolysis under various conditions should be made.
A knowledge of the precise composition of the gases such as CO, CO\textsubscript{2}, and CF\textsubscript{4} generated in the cell under various operating conditions would assist in the determination of appropriate reaction mechanisms and kinetics of the electrode reactions occurring during electrolysis. A sealed cell system would be required to accomplish this study. Experimental facilities and an environment that permit the electrolytic reduction test run to be continued for 48 hours or longer at a high temperature of about 1000°C would also be required.

(2) A study of the relative merits of different anode designs, such as a basket anode and a sintered consumable oxide-carbon anode. This is particularly important when the uranium oxide to be processed is of fine powder form and contains significant amount of lower density impurities such as carbon.

(3) Other fluoride or mixed chloride-fluoride electrolytes should be investigated as an alternative to the quarternary fluoride eutectic used in this study. The objective would be: (a) to find a compatible electrolyte that can dissolve uranium oxides significantly (> 4 wt %) at temperatures lower than 800°C, and (b) to study the effect of UF\textsubscript{4} or UCl\textsubscript{4} concentration on the solubility of uranium oxides.

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