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A CONCEPTUAL CELL FOR
ELECTROWINNING LIQUID URANIUM

MASTER

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Abstract

A production-scale cell is proposed for electrowinning liquid uranium from uranium dioxide feed in a molten fluoride electrolyte. The design is based on the development work of several investigators. Features of the design include a vertical cathode, a terraced, electrically floating hearth, isolation of the metal pool from the oxide feed, and provision for rapid removal of the molten metal.

The paper analyzes problems of other researchers in achieving high current efficiencies and the importance in the cell design of feeding sufficient oxide to the anode area and of maintaining ample metal-to-anode spacing.

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INTRODUCTION

Uranium metal is presently produced commercially by a batch metallothermic method (1) in which uranium dioxide is converted to UF_4 and the UF_4 is reduced with magnesium to yield a uranium regulus. The high cost of this process is due principally to (a) the chemical step in which anhydrous HF is used to produce the UF_4 , (b) the use of magnesium as a reactant, and (c) the inability to recover the magnesium from the MgF_2 slag. An alternate reduction process employing a continuous electrowinning cell shows promise as a replacement for the metallothermic process for the commercial production of uranium.

Driggs and Lilliendahl (2) reported an early attempt to electrowin solid uranium in a molten salt cell. During the Manhattan Project, uranium metal dendrites were electrowon from various uranium oxides and halides in chloride electrolytes (3). This process, however, is inherently complex and inefficient, and it was subsequently replaced by the currently used metallothermic method. Later research at the Knolls Atomic Power Laboratory demonstrated that liquid uranium could be prepared by the electroreduction of uranium oxides in fluoride systems (4). Based on this work, Niedrach et al. (5) estimated the cost of producing electrolytic liquid uranium and concluded that it would be economically feasible. However, in these investigations, consistently good coalescence of the metal in the cathode hearth was not attained because of contamination of the product by oxide-bearing materials.

This paper describes a proposed production-scale electrowinning cell for uranium. This design, by workers at the National Lead Company of Ohio, is based on earlier work at the Reno Metallurgy Research Center of the U. S. Bureau of Mines using laboratory-scale cells. Operating costs of this proposed cell are compared with those of the present metallothermic reduction method.

RECENT INVESTIGATIONS

Mallinckrodt Chemical Works

Piper, et al. (6,7) at the Mallinckrodt Chemical Works, Uranium Division, investigated various alternative approaches to the electrowinning of liquid uranium. Hall-type cells were used in which the graphite crucible (hearth) served as the cathode where liquid uranium was formed and collected. Both $\text{BaF}_2\text{-LiF-UF}_4$ all-liquid electrolytes and $\text{CaF}_2\text{-LiF-UF}_4$ frozen-crust electrolytes were investigated with the direct feeding of UO_2 or UF_4 . Rod and slotted graphite anodes, as well as UO_2 -carbon composite anodes, were used. A number of experimental parameters were evaluated in this work, but

critical difficulties were also uncovered. Pilot-scale cells of 10,000 and 35,000 ampere capacity were tested (8). The work was terminated when the facility closed in 1966.

Contrary to the comparable conditions in a Hall aluminum cell, uranium dioxide is both denser than the fluoride electrolyte and much less soluble in it than alumina in cryolite. In the Mallinckrodt research using a crucible cathode, large direct additions of UO_2 to the all-liquid electrolyte resulted in poor metal quality as a consequence of the settling and entrapment of the dense oxide. When lower UO_2 feeding rates were used, insufficient oxide was dissolved in the electrolyte, and CF_4 evolved at the anode instead of CO . Continued operation with the evolution of CF_4 gas resulted in an interruptive "anode effect." For cells with the Hall-type geometry, the limiting (highest) anodic current densities consistent with good metal quality and the avoidance of the anode effect were lower than 5 amperes per square inch, ~~a value that would yield an uneconomically low rate of uranium production.~~ The use of UF_4 as feed and the machining of graphite anodes to increase the anode area further added to processing costs. The English are continuing research with cells of similar geometry.

U. S. Bureau of Mines

As part of a broad rare-earth electrowinning program (9), investigators at the U. S. Bureau of Mines in Reno have further studied the preparation of liquid uranium by the direct electrolysis of UO_2 dissolved in fluoride melts (10,11). However, in the research at Reno, the cell design included a rod-type vertical cathode and an electrically floating hearth.

The essential features of the most acceptable electrowinning cell designed by the U. S. Bureau of Mines are shown in Figure 1. The cell consisted of a compartmented crucible 8-inches in inside diameter with two rod-type anodes and a single cathode. The electrodes were encircled by a graphite barrier 4-3/4 inches in inside diameter which was perforated with vertical slits on a 120-degree arc. Uranium dioxide was fed into the space outside the barrier directly behind the anodes. Nearly complete utilization of UO_2 was achieved.

Heat for melting the electrolyte and for maintaining the requisite thermal balance during electrolysis was obtained from a graphite resistor located beneath the crucible. The electrolyte composition was 35 wt % UF_4 , 5 wt % LiF , and 60 wt % BaF_2 . The operating conditions and results are given in Table 1.

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Gas samples taken from above the electrolyte were analyzed for CO, CO₂, and fluorocarbons. The product gas was predominantly CO. Less than 1% CF₄ was generated, and occasionally C₂F₆ was detected. An increase in fluorocarbons in the off-gas during electrolysis indicated a deficiency of dissolved oxide in the bath. This was compensated for by increasing the UO₂ feed rate.

Oxidation of the anode rods during electrolysis, with the resultant decrease in surface area, caused a gradual increase in anode current density up to the limit imposed by the anode effect. Anode current densities were 14 to 15 amperes per square inch at the start of electrolysis and increased to 24 to 30 amperes per square inch as the experiment progressed.

The immersed portion of the cathode was maintained as the hottest point in the cell by using cathode current densities of 80 to 110 amperes per square inch. These conditions produced a highly fluid deposit that dripped from the cathode to the bottom of the cell. The uranium product collected on the crucible bottom as a completely coalesced regulus. Almost 2,200 grams of metal was recovered at a current efficiency of 38%. However, the hearth geometry was not optimized to provide adequate isolation of the uranium pool from the anode.

Examination of the vertical cross-sections of the recovered metal regulus showed a small amount of included electrolyte near the top and a thin carbide layer at the bottom. The specific gravity of the metal was 18.9 grams per cubic centimeter, compared with 19.05 for high-purity uranium. Vickers hardness numbers ranged from 216 to 282. Metallographic examination showed dendritic inclusions identified as uranium carbide. Metal purity of 99.8% was attained; a typical analysis is shown in Table 2. Major impurities were carbon and aluminum. The use of the feed barrier and the resulting absence of an oxide sludge layer were responsible for the low oxygen content. This work pointed out the requirement that undissolved oxide be restricted as much as possible from the site of metal collection. To limit the back-reaction of the metal, it was further suggested that the zone of metal collection be designed to limit the contact area between the metal and the electrolyte.

National Lead Company of Ohio

Because of the complexity of experimentation with molten salts at elevated temperatures, some experiments were conducted at National Lead using a room-temperature aqueous solution analog to the electrowinning of uranium in a vertical rod cathode cell. A mercury cell was chosen because of its similarity to the molten uranium electrolytic process with respect to the multivalent cations in the

electrolyte and the production of liquid metal at the cathode. These experiments were undertaken to observe the deposition of metal and the reactions at a vertical rod cathode and to gain a better understanding of current efficiency and its relationship to cyclic reactions, side reactions, and electrode arrangement.

A sketch of the experimental apparatus is shown in Figure 2. The experiments were performed in glass containers, using platinum gauze as the anode, and a 1/8-inch-diameter graphite rod as the cathode. The surface area of the cathode could be varied by sliding a glass tube over the rod. Electrolysis experiments were performed either with mercuric nitrate [$\text{Hg}(\text{NO}_3)_2$] solutions in equilibrium with excess solid mercuric oxide (HgO) or with mercuric chloride (HgCl_2) solutions containing excess solid HgCl_2 to maintain Hg^{++} ion concentration constant during electrolysis.

In both solutions during electrolysis, minute drops of mercury metal formed at the vertical rod cathode. As the drops grew, they rolled down the rod and collected at the base of the electrode as tiny spheres. Coalescence of the spheres depended on cathode current density and the concentration of Hg^{++} ions. Higher cathode current densities were required for coalescence as the concentration of Hg^{++} ions increased in the two electrolytes. In the HgCl_2 solution, it was evident that a high cathode current density was necessary for coalescence because at low cathode current density partial reduction to mercurous chloride occurred. The insoluble mercurous chloride prevented the coalescence of the mercury droplets.

As the cathode current density was increased, hydrogen was evolved concurrently with the deposition of mercury metal. Two distinct reaction areas were observed on the vertical rod cathode as illustrated in Figure 3. An upward flow of electrolyte was observed in the vicinity of the cathode. The flow was probably caused by a change in the density of the solution in the vicinity of the electrode.

The use of a vertical rod cathode in aqueous mercury electrolysis may not be precisely analogous to molten salt- UO_2 electrolysis; nevertheless, this experiment gave insight into potential problems involved in the use of a vertical cathode. For example:

1. Simultaneous Reactions

Simultaneous reactions in the mercury electrolysis indicate that the diluent electrolyte (LiF , BaF_2) used in UO_2 electrolysis may be coreduced if the cathode current density is high enough. The rapid carbide formation noted in previous studies (7,10) of UO_2

electrolysis could result from the reduction of alkali or alkaline earth metal and its subsequent reaction with CO or CO₂ from the anode. Some simultaneous reduction of an alkali or alkaline earth cation may be beneficial, as discussed below.

2. Coalescence of the Metal Formed

Problems with coalescence of uranium metal during UO₂ electrolysis using a vertical rod cathode have been reported (11). If uranium metal forms as tiny spheres during the electrolysis of UO₂ in molten salt, as did mercury metal in mercury electrolysis, the coreduction of barium (or calcium) ions from the electrolyte would produce barium (or calcium) metal in the vicinity of the uranium droplets. Both metals should reduce the fluoride film on the uranium droplets and calcium would reduce the oxide film thereby aiding coalescence.

Current efficiency was studied in solutions containing weighed amounts of Hg(NO₃)₂ · H₂O in the presence of excess solid HgO. This system was selected because the Hg⁺⁺ concentration could be held constant during electrolysis by the dissolution of solid HgO.

The results of these electrolysis experiments are given in Table 3. The data indicate that current efficiency in the mercury electrolysis was affected by two types of cyclic reactions. The Type I reaction resulted in the formation of partially reduced mercurous ions at the cathode and the reoxidation of these ions at the anode.

Table 3 shows that the Type I cyclic reaction, as measured by current efficiency, depends upon:

- a. Electrolyte composition - the current efficiency decreased with increased Hg⁺⁺ ion concentration.
- b. Cathode current density - the current efficiency increased with increased cathode current density.
- c. Cathode-anode spacing - the current efficiency increased with increased spacing.

The Type II reaction resulted when mercury droplets collected beneath the cathode and reacted with the electrolyte.

The back-reaction increased rapidly when the vertical rod cathode was raised so that the mercury droplets were allowed to fall freely through the electrolyte.

Experiments on the loss of mercury by back-reaction to the electrolyte were also performed by placing a given weight of mercury in 250 cm³ of electrolyte. The mercury was placed in the electrolyte as a single sphere or as multiple spheres for 20 minutes, and the weight-loss was determined. The results are shown in Table 4. These data indicate that the back reaction $\text{Hg}^0 + \text{Hg}^{++} \rightarrow 2\text{Hg}^+$ is dependent on:

- a. Electrolyte composition - the reaction increased with increased Hg^{++} ion concentration.
- b. Metal product surface area - the reaction increased with increased surface area between the product and the electrolyte.
- c. Temperature - the reaction increased with increased temperature.

These studies of current efficiency and back-reaction indicated that electrolyte composition, temperature, cathode current density, cathode-anode spacing, and cathode-metal pool spacing are all interrelated. The most promising approaches to the maximization of current efficiency would appear to be the study and optimization of cathode-anode spacing and isolation of the metal pool.

BASIC DESIGN CONSIDERATIONS

In the design of the production cell for electrowinning liquid uranium, certain theoretical and physical conditions had to be satisfied. These conditions were mostly established by the previous research at Mallinckrodt (6-8) and the U. S. Bureau of Mines (9-11).

Theoretical Conditions

In the choice of an all-liquid electrolyte composition for the production of pure uranium, only those cations may be considered which are less readily reduced than uranium. Using room temperature aqueous-solution electrode potentials (in the absence of data for molten salts at 1200°C) only the alkali and alkaline-earth cations seem suitable. Electrolyte mixtures of BaF_2 , MgF_2 , CaF_2 , and LiF with UF_4 have been evaluated. Generally, the chlorides have been excluded because of their excessive vapor pressures and limited

solubility for UO_2 . A CaF_2 addition generally results in a higher liquidus temperature and is used when a frozen crust is desirable. LiF raises the conductivity and lowers the liquidus temperature but may result in excessive vapor losses at high concentrations. Based on previous research, an electrolyte composition of 60 wt % BaF_2 , 35 wt % UF_4 , and 5 wt % LiF seems most suitable.

Identification of the uranium ionic species in fluoride solutions at 1250°C has not been accomplished. However, it is known that trivalent uranium ions are predominant in equilibrium with metallic uranium; at much higher oxygen activities, tetravalent uranium ions are predominant. For this discussion, the presence of uncomplexed U^{+3} , U^{+4} and O^{--} ionic species is assumed. The existence of two valence states for uranium is significant in determining many characteristics of both the laboratory and the production cells: current efficiency, electrolyte composition and thereby the oxide solubility, cell geometry, scale-up considerations, etc.

In an electrowinning cell using a UO_2 feed, the oxidation reaction at the carbon anode according to the reaction

results in the evolution of carbon monoxide gas. The oxygen ions are supplied by the chemical dissolution of the UO_2 feed in the electrolyte

At the cathode, the sequence of reduction reactions

and

results in the deposition of liquid uranium. Summing reactions 1 through 4 gives the total (net) cell reaction

From standard free energy data for reaction 5, the equilibrium cell voltage is 0.923 volts at 1200°C .

In the uranium electrowinning cell, various processes result in a decrease in current efficiency. The rapid stirring of the melt by the evolution of CO at the anode causes the transport of U^{+3} ions from the cathode to the

anode, where reaction 3 occurs in the reverse direction. This cyclic electrochemical reaction requires the flow of electrons through the external circuit but does not contribute to the deposition of metallic uranium. The cyclic reaction therefore reduces current efficiency and is particularly deleterious in laboratory-scale cells and Hall-type cells where the anode-to-cathode separation is small.

Chemical back-reactions may also contribute to current inefficiency. Porter, et al. (12) studied the reaction

The rate of reaction increased with increasing temperature. As with the cyclic reaction, the influx of U^{+4} ions to the metal and the transport of U^{+3} ions away from the metal are aided by turbulence in the molten electrolyte. Despite the loss of metal, reaction 6 alone does not represent current inefficiency because the formation of U^{+3} ions is a necessary intermediate step to the deposition of uranium. However, if the U^{+3} ions formed by reaction 6 are transported to the anode, the reverse of reaction 3 will again return the U^{+3} ions to U^{+4} ions at the expense of input power. The minimization of metal/electrolyte contact area, the maximization of metal-to-anode spacing, and the retention of the metal in a turbulence-free location are design requirements dictated by these considerations. None of these conditions can be satisfied in a Hall-type cell.

The chemical back-reaction of uranium with the CO gas liberated at the anode can also contribute to current inefficiency by the consumption of product uranium. Again, maximization of the metal-to-anode spacing is required. Current efficiencies up to 44% were reported by Piper (7) for a Hall-type laboratory cell at 1170°C. For a vertical-cathode laboratory cell with a relatively unprotected metal pool, Kesterke et al (11). reported a 38% current efficiency for operation at about 1300°C. There is general agreement that higher temperatures result in lower current efficiencies principally because of reaction 6 and the cyclic reaction.

The solubility of UO_2 in BaF_2 - UF_4 - LiF solutions was measured at 1150°C by Varwig (13) and at 1250°C by Porter and Brown (14). This work indicated that the UO_2 solubility is essentially proportional to the UF_4 content of the melt. Further, the solubility is very temperature dependent; for the 60 wt % BaF_2 , 35 wt % UF_4 , 5 wt % LiF electrolyte, the UO_2 solubility would equal about 1.5 wt % at 1150°C and about 4.0 wt % at 1250°C. These values are far lower than those for the solubility of alumina in cryolite (15) in the Hall cell process. Furthermore, the kinetics of dissolution

are not rapid; from 10 to 30 minutes were required to saturate an electrolyte melt with UO_2 at 1250°C (14).

For an electrowinning cell, the rate of metal production (in moles/hour) at steady-state must equal the rate of UO_2 dissolution (in moles/hr), or else UF_4 additions must be made to the bath with CF_4 evolution from the anode. In view of the low UO_2 solubility and the slow rate of UO_2 dissolution, the cell must be designed to provide a continuous supply of finely divided UO_2 particles to the immediate vicinity of the anodes. However, because its density exceeds that of the electrolyte, excess UO_2 would tend to settle onto the metal pool. This must be prevented because the UO_2 would interfere with product coalescence and quality.

The previous operation of uranium electrowinning cells of laboratory size has been limited to anodic current densities below that at which an interruptive "anode effect" occurs. This phenomenon has its analogy in the aluminum Hall cell (16,17). The anode effect is the result of an insufficient supply of oxygen ions to the anode where CO gas is being liberated. The critical anodic current density is raised by factors which increase the concentration of dissolved oxygen in the electrolyte: higher UF_4 content and higher temperature. Unfortunately, both of these factors also result in a decrease in current efficiency, so that the temperature and electrolyte composition are chosen for the best compromise of limiting anodic current density and current efficiency.

It is believed that in uranium cells, the initiation of the "anode effect" is preceded by a large evolution of CF_4 vapor. A cell is returned to normal operation by increasing the UO_2 feed to the electrolyte. The anode for a production cell must have a large area readily available to the UO_2 feed. It must burn uniformly with the easy release of CO gas.

Previous research (7,11) indicated that very high cathodic current densities (over 100 amps/in²) could be used without significant cathodic polarization. Because the cathode vicinity is a principal source of U^{+3} ions for the cyclic reaction which is completed at the anode, the use of a small cathode area is advantageous in reducing the cyclic reaction. The increase of the cathodic current density has resulted in higher current efficiencies.

Physical Conditions

In addition to the chemical and electrochemical requirements and limitations which have been discussed, the prospective uranium production cell must stay within certain

physical or material limitations. A temperature of about 1250°C would insure sufficient UO_2 solubility and sufficient fluidity for the coalescence of the liquid uranium (melting temperature of 1132°C).

In the choice of construction materials, the temperature and the corrosive nature of the molten fluorides excludes from consideration most materials except graphite (carbon). Fortunately, the reaction between uranium and carbon is held to a negligible level by the formation of an adherent and protective film of UC on the graphite. Unfortunately, however, with the use of a vertical cathode, the electronically conducting graphite hearth cannot be held neutral but will assume some potential between that of the anode and the cathode. The relative proximity of the anode and cathode to the hearth will determine the exact potential. In any case, the cell geometry must be designed such that the cathodic reactions 3 and 4 are minimized at the hearth. These hearth reactions would only contribute to the cyclic reaction and decrease the current efficiency. A slight cathodic polarity would afford some degree of cathodic protection to the product.

In the electrowinning of uranium intended for nuclear applications, special strict requirements on metal purity must be met. In particular, the metal may contain no more than 0.25 ppm boron. This restriction requires the use of only high purity salts and selected, specially purified graphite materials. These requirements add to the cost of the cell materials.

Perhaps the most critical design feature in the vertical-cathode production cell is the manner in which the liquid uranium is collected and protected. To prevent contamination, the liquid uranium pool should be physically separated from the slowly dissolving and settling UO_2 feed. To reduce back-reaction and dissolution of the metal, both the area of contact with the electrolyte and turbulence near the metal must be minimized. A withdrawal system must be provided to remove the secluded pool of metal from the cell.

An annoying problem was experienced in previous laboratory and pilot-plant cells (7,8,11). A conductive layer of mixed uranium, electrolyte, and carbon formed at the top of the cathode and grew out toward the anode. This "extended" cathode would collect more metal resulting in further growth, a reduction in current efficiency, and ultimately a shorting out of the cell. There is disagreement whether the carbon particles resulted from mechanical separation from the graphite (11) or from a chemical back-reaction of the CO

product (7). In the Mallinckrodt pilot plant cell (8), these layers were manually removed by periodically skimming the electrolyte surface with tools inserted through special ports. In the final laboratory cell of Kesterke et al. (11), the floating carbon particles were trapped in a "splash trough" along the hearth wall. Provisions to handle this problem are necessary in the production cell.

THE DESIGN OF THE CONCEPTUAL ELECTROWINNING CELL

Figure 4 shows top and cross section views of the proposed cell. Mechanical and structural details are omitted from this conceptual design. The cell is conservatively rated at 25,000 amperes. In practice, however, it could be operated at currents as high as 50,000 amperes to obtain basic design data. This amperage probably is an upper limit because cathode heat dissipation and excessive electrode voltage drop pose severe problems. Features of the design include:

- (1) A vertical cathode with current density of 50 amp/in².
- (2) Six fluted anodes extruded from carbon low in boron; current density = 4-6 amp/in².
- (3) A small diameter (8-inch) molten metal pool.
- (4) A slotted secondary wall as a "crud" catcher.
- (5) Bottom and sidewall terraces which retain and distribute undissolved UO₂ in the vicinity of the anode.
- (6) A vacuum lift withdrawal system for removing molten metal.
- (7) An electrolyte comprising 35 wt % UF₄, 5 wt % LiF, and 60 wt % BaF₂, capable of dissolving about 3 wt % UO₂, and providing an electrode submergence of up to 20 inches.
- (8) An estimated current efficiency of 50% which, at 25,000 amperes, results in the production of 61.25 lb uranium/hr.
- (9) Feeding of UO₂ into the annular space between cell wall and anodes.
- (10) Auxiliary heating on bottom and sidewalls.
- (11) Total enclosure of cell in an argon atmosphere with provision for removing off-gases.

COST ANALYSIS

Figure 5 shows the operations required to produce uranium metal by the present metallothermic route. Also shown is the route visualized for the electrowinning process.

The cost analysis is summarized in Table 5 and is based on the following assumptions:

Both Routes

1. One hundred tons of metal are produced.
2. Power costs are 9 mils per kilowatt hour.
3. Labor and maintenance costs are equal. (These costs would probably be higher in the present route because of more operations.)

Metallothermic

1. Anhydrous HF at a cost of \$275 per ton (\$0.14/lb) converts UO_2 to UF_4 by the reaction

2. Magnesium (one hundred and four percent of theoretical) costing \$800 per ton (\$0.40/lb) converts the UF_4 to metal by the reaction

3. The power required to cause equation 2 to go to completion is based on plant practices of using 30 kilowatts for 4 hours to make a 330-pound derby of uranium.
4. The cost of recovery of uranium values in the slag (MgF_2) is estimated at \$1360. Nitric acid and labor are included.

Electrolytic

1. Premium grade carbon, low in neutron absorbers like boron, is extruded into anodes for \$200 per ton (\$0.10/lb). Seventy-five percent of the anode is utilized.

Here, 13.4 tons of carbon anodes are required to make 100 tons of uranium.

2. The cell operates at 10 volts (a conservative value) and a current efficiency of 50%. The power required to operate such a cell to produce 100 tons of metal is calculated as follows:

$$\text{KW-Hr per 100 tons} = \frac{C \cdot Z \cdot E \cdot W}{A (C E) (1000)}$$

Where C is constant of 12,159
amp-hrs/lb. equivalent

Z is no. of equivalents/mol of U

A is atomic wt of U

E is operating cell voltage

C E is current efficiency

W is weight produced (pounds)

Or

$$\text{KW-Hr/100 Tons} = \frac{12159 (4) (10) (200,000)}{(238) (.50) (1000)}$$

$$\text{KW-Hr/100 Tons} = 817,200$$

Thus, from Table 5, the direct cost savings based primarily on raw materials, amounts to \$18,180 for 100 tons of product or a 64 percent reduction in costs compared to the metallothermic process.

CONCLUSIONS

The proposed prototype cell described in this report should more fully demonstrate the feasibility of electrowinning molten uranium from the oxide in a molten fluoride bath.

The features considered most important in this cell design include:

1. Methods for assuring an ample supply of oxide near the anodes.
2. A terraced hearth for assisting dissolution of the oxide into the molten salt.
3. A small cavity in the hearth to contain the molten metal and provide maximum isolation of the metal from the electrolyte, feed, and anode gas. The metal could be withdrawn from the cavity by vacuum.
4. A slotted wall near the outside of the cell to entrap floating impurities and prevent short circuits.

The hearth of a cell this size (Figure 4) could be made from one piece of graphite. Larger cells would probably require the assembly of graphite blocks.

It is believed that the operation of a prototype cell of the type described would permit the defining of operating parameters. Subsequent production cells should then be most competitive with other processes presently under investigation for the production of nuclear fuels and for the recovery and recycle of partially spent fuel.

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TABLE 1 - Operating Conditions and Results for Electro-winning Uranium from Uranium Dioxide*

Direct current.....amp	300-400
Voltage.....	15-17
Weight of electrolyte.....kg	13.0
Initial anode immersion.....inches	3
Initial cathode immersion.....inches	2-1/4
Initial anode current density....amp/sq in	14.8
Initial cathode current density..amp/sq in	110.0
Approximate oxide feed rate.....g/min	5.0
Supplemental external heat.....kw	3.3-4.2
Cell bottom temperature.....°C	1,350-1,360
Bath surface temperature.....°C	1,275-1,300
Product yield.....grams	2,200
Current efficiency**.....%	38

* U. S. Bureau of Mines data from compartmented cell containing two anodes and one cathode. See Figure 1.

** Calculated according to Faraday's Law, assuming the reduction of U^{+4} to U^0 .

TABLE 2 - Typical Analysis of Massive Uranium*

Impurity element	Parts per million
Aluminum.....	300
Barium.....	20
Calcium.....	50
Chromium.....	50
Copper.....	10
Iron.....	200
Lithium.....	1
Magnesium.....	5
Manganese.....	40
Molybdenum.....	80
Nickel.....	15
Potassium.....	9
Silicon.....	50
Sodium.....	7
Vanadium.....	15
Carbon.....	740
Oxygen.....	50

*Metal Produced by U. S. Bureau of Mines.

TABLE 3 - Effects of Cathode Current Density, Hg^{++} Ion Concentration, and Cathode-Anode Spacing on Current Efficiency*

Electrolyte Composition	Current (amp)	Temp. ($^{\circ}\text{C}$)	Wt of Hg Deposited (grams)	Current Efficiency (%)	Cathode-to-Anode Spacing (inches)
50g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	3	45	2.58	69	1.75
500 ml H_2O	6	56	5.69	76	1.75
Excess solid HgO	8	42	7.76	78	1.75
100g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	3	56	2.65	71	.75
500 ml H_2O	6	56	5.57	75	.75
Excess solid HgO	6	56	5.79	78	1.75
150g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	6	56	4.56	61	.75
500 ml H_2O	6	56	4.89	66	1.75
Excess solid HgO					
200g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	6	56	3.38	45	.75
500 ml H_2O	6	52	3.40	46	.75
Excess solid HgO	6	45	3.63	49	1.75
	8	50	5.10	51	1.75
	8	50	4.96	50	1.75
	8	50	5.15	52	1.75
	12	50	9.16	61	1.75
	12	50	9.61	64	1.75
Saturated solution of $\text{Hg}(\text{NO}_3)_2$ with excess solid HgO	10	55	2.66	21	1.75
	10	52	0.71	5.7	.75

*National Lead Company of Ohio data

NOTE: All tests were of 20 minutes duration.
Cathode: 1/8-inch-diameter rod immersed 1.75 inches.

TABLE 4 - Back Reaction of Mercury with $\text{Hg}(\text{NO}_3)_2$ Electrolyte*

Electrolyte Composition	Temp ($^{\circ}\text{C}$)	Initial Weight (grams)	Final Weight (grams)	Loss (%)	Condition of Hg (sphere)
Saturated $\text{Hg}(\text{NO}_3)_2$ ·	46	2.096	1.118	47	Single
H_2O in 500 ml H_2O	33	2.229	1.389	38	Single
Excess HgO	20	1.972	1.506	24	Single
200g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$,	56	2.016	1.616	20	Single
500 ml H_2O	40	2.003	1.684	16	Single
Excess HgO	40	2.008	1.617	19	Multiple
	28	2.009	1.810	10	Single

*National Lead Company of Ohio data

NOTE: All tests were of 20 minutes duration.

TABLE 5 - Cost Comparison of Metallothermic Process with Proposed Electrowinning Process for Producing 100 Tons of U from UO_2

<u>Raw Material</u>	<u>Assumption</u>	<u>Amount</u>	<u>Unit Cost</u>	<u>Total Cost</u>
<u>Metallothermic Route</u>				
Anhydrous HF	0% excess	33.6 tons	\$275/ton	\$ 9,240
Ground Mg	4% excess	21.2 tons	\$800/ton	16,960
Chemicals and labor	slag leach	----	----	1,360
Power	----	72,600 kw hr	0.009/kw hr	<u>660</u>
			TOTAL	\$28,220
<u>Electrowinning Route</u>				
Carbon	75% utilization	13.4 tons	\$200/ton	\$ 2,680
Power	10V; 50% current efficiency	817,200 kw hr	0.009/kw hr	<u>7,360</u>
			TOTAL	\$10,040
		NET RAW MATERIAL SAVINGS		\$18,180

FIGURE 1 Two Anodes, One Cathode in Compartmented Cell
(U. S. Bureau of Mines Design)

FIGURE 2 Mercury Cell Used at NLO

FIGURE 3 Simultaneous Reduction at Vertical Electrode

FIGURE 4 Conceptual Electrowinning Cell for Producing Liquid Uranium From UO_2 Feed