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ELECTROWINNING PLUTONIUM METAL

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ELECTROWINNING PLUTONIUM METAL

by

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ABSTRACT

Plutonium metal was produced by electrolysis of PuO_2 in molten LiF-BaF_2-PuF_3 salt systems. Conditions favoring efficient cell operation were determined, and a sequence of probable cell reactions was developed.

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ELECTROWINNING PLUTONIUM METAL

INTRODUCTION

The production of plutonium metal by electrowinning from molten salts is a potentially attractive plant process. This method offers the advantages of continuous operation and the generation of a minimum of plutonium-bearing scrap or residues that require recovery. In addition, an electrolytic process that uses plutonium oxide as feed would avoid or minimize the costly production of plutonium halides. Metal of a high degree of purity can be produced by an electrolytic process.

This report summarizes the laboratory investigation of the electrowinning of molten plutonium metal from molten fluoride electrolytes with plutonium dioxide as feed. The primary objective of the investigation was to establish the feasibility of the method rather than to develop and demonstrate a complete process. Preliminary to this investigation, a study of the electrowinning of cerium metal — as a stand-in for plutonium — was undertaken(1) to define the important electrochemical phenomena.

The electrochemical preparation of milligram quantities of plutonium metal was reported in 1944 by Kolodney,(2) who obtained the metal by the electrolytic reduction of $PuCl_3$ in a fused electrolyte of $BaCl_2$-KCl-NaCl. The development of the method was not completed because of the successful demonstration of the bomb reduction method at about the same time.(3) More recently, the electrowinning of molten plutonium metal from fused chloride salts was developed into a workable process by Curtis and his co-workers.(4) This process reportedly operates best with pure $PuCl_3$ as feed, although operation with significant amounts of PuO_2 in the $PuCl_3$ feed is satisfactory. Also recently, a plutonium metal electrorefining process that utilizes fused chloride salts was developed by Mullins, et al.(5) No previous investigation of the electrowinning of molten plutonium metal from fused fluoride salts utilizing PuO_2 feed has been reported. However, a similar study for thorium was reported by Meyer,(6) and a similar process for uranium has been developed for large scale application by Piper and Leifield.(7)

There are both advantages and disadvantages inherent in the use of either fluoride or chloride melt systems for electrowinning plutonium metal. Chloride salts melt at lower temperatures and are less corrosive toward electrolysis cell components than fluoride salts. However, $PuCl_3$ and the usual chloride salt diluents are hygroscopic and require special preparation and handling techniques not necessary with fluoride salts. The PuF_3 and PuO_2 required for electrowinning in a fluoride system can be produced readily by processes and equipment that have been developed. Likewise, residues from fluoride electrolysis cells can be recovered by an aqueous process in conventional stainless steel equipment, using Al(III) to complex the fluoride ion. The undesirable generation of neutrons via the $^{19}F(\alpha,n)^{22}Na$ reaction is encountered with fluoride melt systems, but essentially the same problem is incurred in the bomb reduction of plutonium fluorides to metal. Perhaps the greatest problem with the fluoride system is the difficulty of obtaining rapid and complete assimilation of the PuO_2 feed into the melt.

SUMMARY

Techniques were developed for electrowinning molten plutonium metal from fused fluoride electrolytes with PuO_2 as feed. Electrolytes containing approximately 50 wt % LiF, 20 wt % BaF_2, and 30 wt % PuF_3 gave best cell performance, but other compositions were satisfactory.

A maximum production rate of about 40 grams of plutonium metal per hour could be sustained in a laboratory cell, which consisted of a tantalum crucible, 2-5/8 inches ID by 5-1/2 inches tall. The crucible served as the cathode. Laboratory tests led to the development of a specially shaped carbon anode that promoted stirring of the melt by the anodic gases. The cell was operated at 1000°C and at a current of 100 amperes. PuO_2 powder was added at a controlled rate to the melt, and molten plutonium metal deposited in a pool in the bottom of the crucible. Under these conditions, utilization of the PuO_2 was essentially 100%, and current efficiencies were 10 to 20%.

The purity of the electrolytically produced plutonium metal was comparable to that of metal produced by bomb reduction, with the exception that the product usually contained ~3500 ppm of tantalum, derived from the crucible.

The plutonium metal was produced in a molten form that could be tapped directly into molds, but this operation was not attempted in the present investigation, which was concerned primarily with the electrochemical behavior of the cell. A valve mechanism or weir arrangement would permit periodic or continuous removal of the metal during cell operation.

The following conditions were important for the electrowinning of plutonium metal from fluoride melts:

- Low anode current density (<1 amp/cm^2) to prevent the "anode effect"

- High cathode current density (>1 amp/cm^2) to favor metal production over cyclic oxidation-reduction between oxidation states of plutonium
- A cathodic potential on the reduced metal to prevent loss by reaction with the electrolyte
- A slow, uniform rate for addition of the PuO_2 feed to ensure its complete assimilation into the system.

DISCUSSION

EXPERIMENTAL METHODS

Equipment

The general features of the experimental cell are shown in Figure 1. Specific design details and design variations are described in later sections. The tantalum crucibles for the cell were 2-5/8 inches ID by 5-1/2 inches tall. Crucibles with a 0.050-inch wall thickness were fabricated by a drawing technique by the Fansteel Metallurgical Corporation. Other crucibles with a 0.100-inch wall thickness were fabricated at the Savannah River Laboratory (SRL) by welding rolled tantalum sheet. Molybdenum and tungsten crucibles were also tested. The crucibles were contained within a stainless steel sheath to confine the contents in the event of leakage.

Graphite was used as the anode material; several designs, shown in Figures 2, 3, and 4, were tested. The characteristics of the different anodes are described in the section, Cell Design and Performance.

The cells were enclosed in a 3-inch-ID "Vycor"* tube; the ends of the tube were sealed to stainless steel or aluminum plates with silicone rubber gaskets. Helium could be admitted through an inlet in the end plate to provide an inert atmosphere and to sweep the off-gas from the cell for analysis. Ports in the top plate were provided for the off-gas, a thermocouple, a feed chute, and stainless steel rods that supported the crucible and electrodes. These rods also served as electrical connections. "Swagelok"** fittings fabricated of "Teflon"*** provided gas-tight insulating seals between the rods and the top plate.

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* Trademark of Corning Glass Works, Corning, N. Y.

** Trademark of Crawford Fitting Co., Cleveland, Ohio.

***Trademark of E. I. du Pont de Nemours & Co., Wilmington, Delaware.

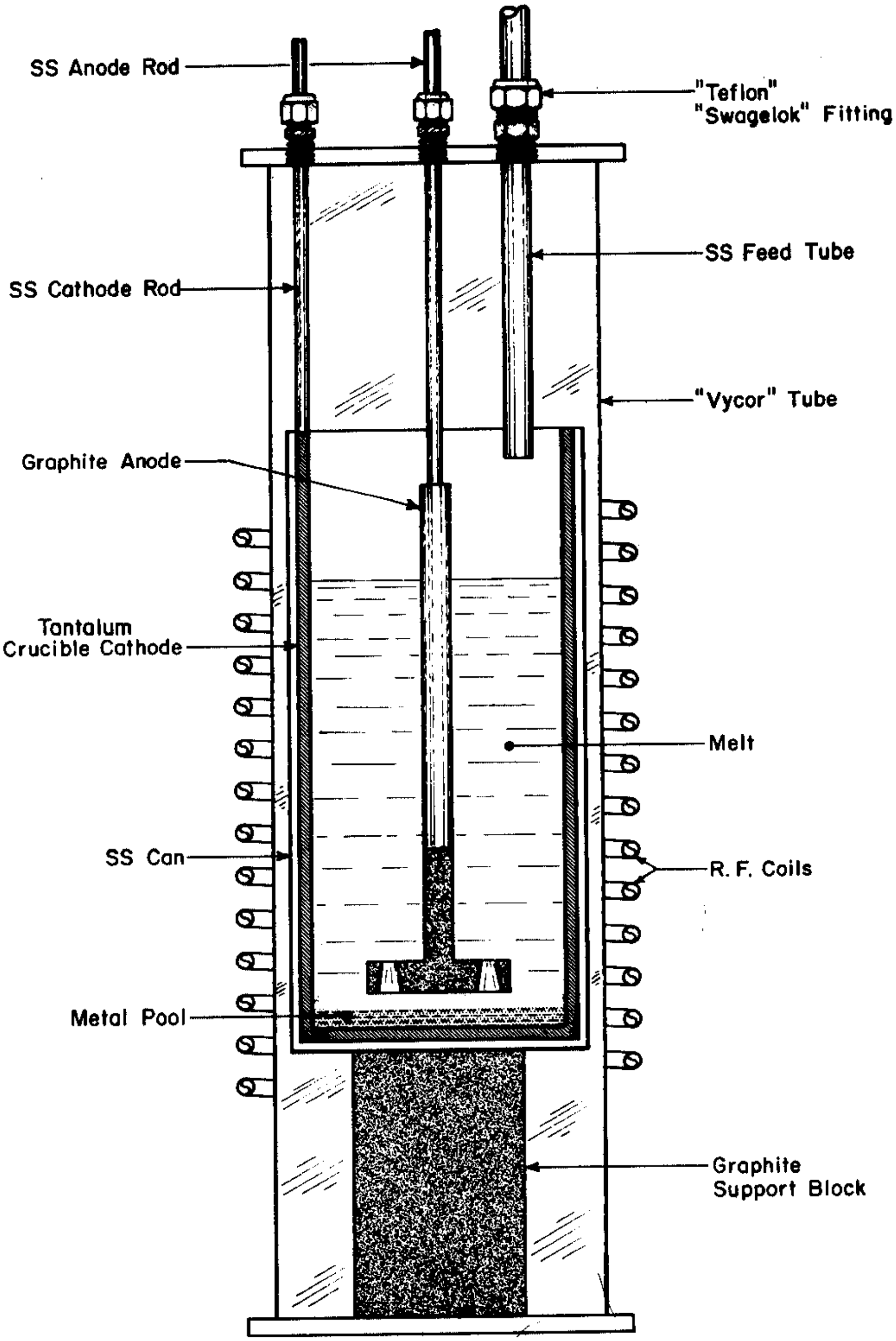

FIG. 1 ELECTROWINNING CELL ASSEMBLY

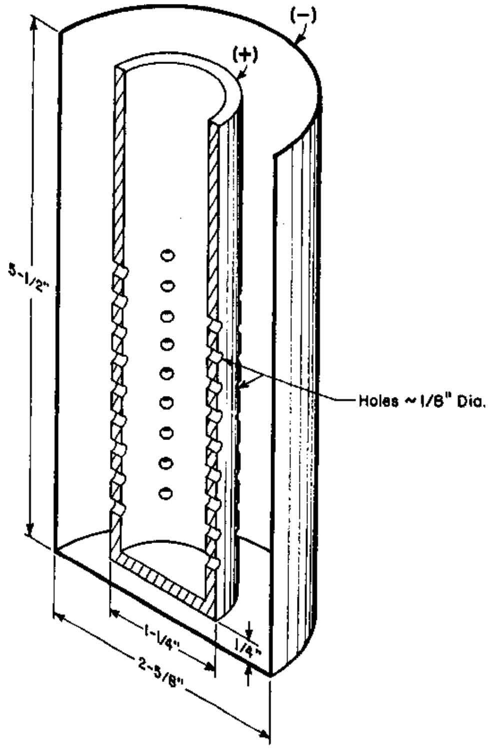

FIG. 2 ELECTROWINNING CELL WITH BASKET ANODE

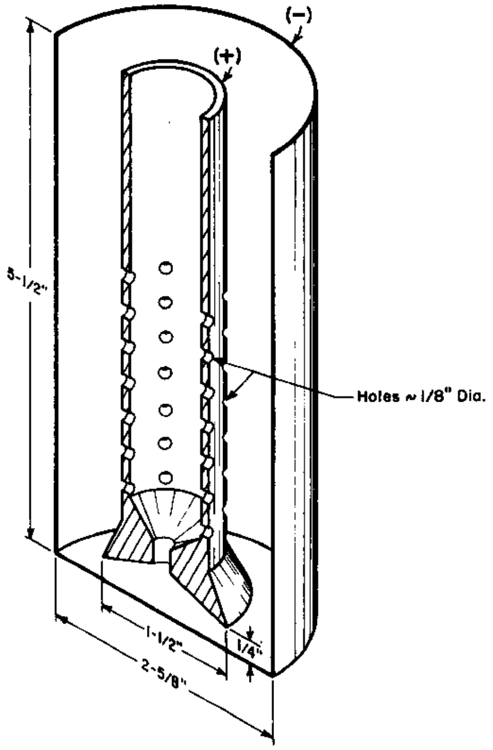

FIG. 3 ELECTROWINNING CELL WITH MODIFIED BASKET ANODE

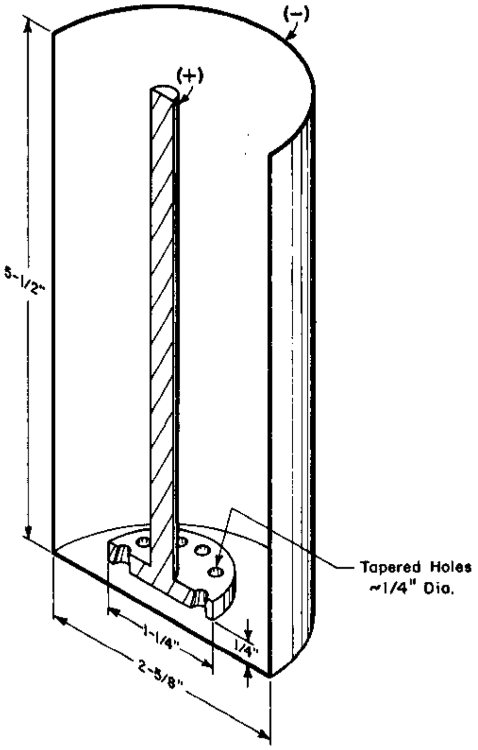

FIG. 4 ELECTROWINNING CELL WITH DISC ANODE

The device shown in Figure 5 was constructed to feed PuO_2 to the cell at uniform, controlled rates. The rate of feed could be adjusted by varying the speed of rotation of the spiral brush. A 60-cycle vibrator attached to the feed device promoted uniform flow of the oxide to the cell. The oxide entered the cell through a 1/2-inch ID stainless steel tube.

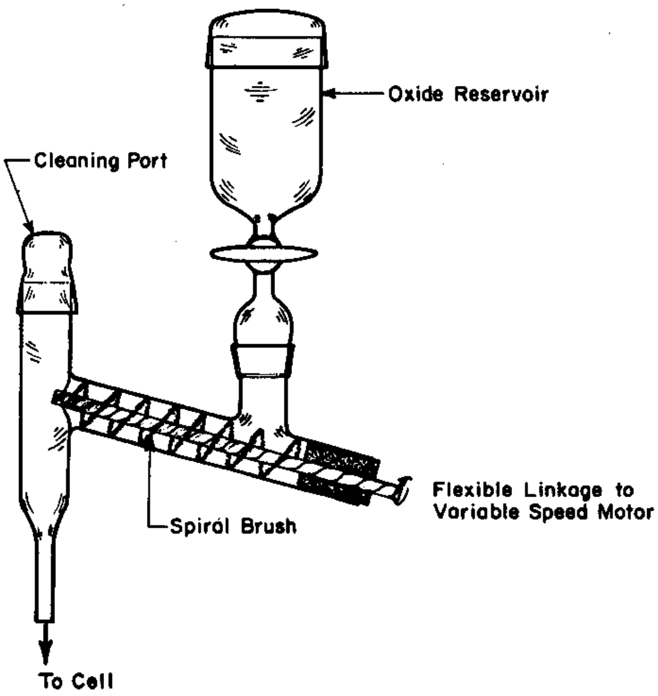

FIG. 5 FEED ADDITION DEVICE

The cell was heated and maintained at the operating temperature with a 10-kc, 15-kw "Tocco"* induction heater. The cell temperature was sensed with a chromel-alumel thermocouple placed between the crucible and the stainless steel sheath. The cell assembly was located in a stainless steel glove-box.

The electrolysis current was supplied by a Hanson-Van Winkle-Munning DC power supply rated at 100 amperes and 12 volts. The current and voltage were continuously recorded.

The off-gas from the cell was analyzed with a Fisher Gas Partitioner, Model 25. Gas samples were taken with a hypodermic needle through a rubber diaphragm in the off-gas line. The quantitative analysis of a sample for O_2, N_2, CO, CO_2, and CF_4 could be completed within five minutes after withdrawal.

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* Trademark of Ohio Crankshaft Co., Cleveland, Ohio.

Materials

The diluent components of the fluoride electrolyte were reagent-grade, and were vacuum dried at 300°C before use. The PuF_3 was production-grade material obtained from the Savannah River Plant, and was dried under argon at 300°C. The PuO_2 feed was prepared by precipitation of Pu(III) oxalate from acid solution and calcination at about 450°C with procedures already described(8).

Operating Procedures

Operating procedures were adapted from the previous cerium studies(1) in SRL and from the uranium studies of Piper and Leifield(7). The general procedure for the plutonium electrowinning runs was the following:

- Prior to assembly of the cell, all components were heated to about 800°C in a flowing helium atmosphere to remove volatile impurities.
- The cell was assembled, and diluent components of the melt were added to the crucible and melted under a helium atmosphere.
- The cell was cooled, and the PuF_3 component of the melt was added and melted.
- The electrodes were positioned, and the electrolysis was started. A uniform flow of inert gas to the cell was maintained throughout the run, and the off-gas was analyzed periodically.
- An initial period of electrolysis was performed before the addition of PuO_2 feed to strip the system of residual oxides in the fluoride salts. This helped to prevent the accumulation of excess, undissolved PuO_2 in the system which could settle to the bottom of the cell and interfere with the coalescence of the molten plutonium metal. During this period the operating temperature and current were stabilized at the desired values.
- When the off-gas analysis showed the system to be stripped of oxide (by the absence of CO or CO_2), the PuO_2 feed was started. Feed rate was correlated with the rate of CO and CO_2 evolution (as determined by off-gas analysis) to ensure that excess oxide did not accumulate in the system.
- At the conclusion of a run, electrolysis was continued for a period after the PuO_2 feed addition was stopped, to strip residual oxide from the system. The cell was cooled to near the freezing point of the melt before the electrolytic current was discontinued and the anode was removed.

- After the cell cooled to room temperature, the melt was broken out and the metal product was examined. The results of the run were evaluated on the basis of analyses and visual observations.

The plutonium metal product wetted and adhered strongly to the tantalum crucible. Since casting facilities were not available, the metal was dissolved with hydrochloric acid. The metal yield was determined by weighing the crucible and by analysis of the dissolved plutonium. The purity of the metal product was determined by spectrochemical analysis of small, free beads of metal that had not coalesced in the main body of the product.

PRELIMINARY STUDIES

Scouting experiments were performed in cells of simple design to evaluate materials of construction, to test melt compositions, and to define cell reactions. The cells in these experiments consisted of graphite, molybdenum, tantalum, or tungsten crucibles to contain the melt; a graphite rod anode; and usually a molybdenum, tantalum, or tungsten rod as the cathode. In some experiments the crucible served as the cathode. The cells were operated at 800 to 1000°C and at low currents, although the electrode current densities were varied over a wide range. Run duration was usually about 1 hour.

The tests showed tantalum to be the best crucible material to contain fluoride melts and molten plutonium metal, although it was attacked to a slight degree. Molybdenum was attacked rapidly. Tungsten appeared to be the most inert of the refractory metals, but a satisfactory tungsten crucible could not be obtained. Tungsten crucibles fabricated by powder metallurgy and by flame-spraying were porous and fragile. Graphite was excellent for use in contact with the fluoride melts, but carbide formation occurred when graphite contacted molten plutonium metal. Common ceramic materials in contact with fluoride melts were attacked rapidly.

Fluoride melts containing NaF or KF could not be used for electrowinning plutonium metal because the alkali metals were preferentially deposited. Melts containing various compositions of $LiF-PuF_3$, $LiF-CaF_2-PuF_3$, and $LiF-BaF_2-PuF_3$ were all operable. Electrolytes containing these components melt above 750°C, which is sufficiently above the 640°C melting point of plutonium to ensure the production of molten metal product. Only minor differences were discernible in the operating characteristics of these melts. The $LiF-BaF_2-PuF_3$ system was used most extensively in the continuing studies because it provides lower melting points over a range of compositions than the other systems. The $LiF-BaF_2$ eutectic (82 mole % LiF) melts at 765°C; the melting point of the system is altered only slightly by small quantities of PuF_3.

The effect of electrode current density on the efficiency of metal production was studied in the preliminary tests. At cathode current densities below ~0.5 amp/cm^2, the current efficiency for metal production was near zero; at cathode current densities between 0.5 and ~1 amp/cm^2, efficiencies were 15 to 20%. When the cathode current density was 2 to 3 amp/cm^2, the current efficiency approached 50%. Electrodeposition of Li or Ba metal occurred at cathode densities near 5 amp/cm^2. The anode current density had little effect on cell operation as long as the current density did not exceed ~1 amp/cm^2, at which point the "anode effect" occurred. The "anode effect", which is a common problem in the electrolytic production of aluminum, is the interruption of the cell current by the formation of a nonconducting film of gas on the anode. The current density values cited above for producing a given effect varied somewhat with changing operating conditions. In general, increased current densities were required to produce the same effect at increased temperatures or with increased concentrations of PuF_3 in the melt, and vice versa.

Melts from runs in which the electrolytic current was continued until the melt cooled below its freezing point showed color gradients which indicated that Pu(III) was present in the region of the cathode and Pu(IV) in the region of the anode. Thus, the cyclic oxidation-reduction of plutonium between its oxidation states is probably responsible for the nonproductive consumption of current, as discussed in the following section. Extrapolations of current-voltage curves showed the decomposition potential for PuO_2 to be 2.2 to 2.4 volts in the fluoride melts at ~1000°C. Back emf's of the same value were observed when the cell current was interrupted. The appearance of this back emf was established as a criterion of successful cell operation.

Another phenomenon was the loss of plutonium metal product by reaction with the melt. Free metal in frozen melts was surrounded by a Pu(III)-rich layer of melt, indicating reaction between metal and Pu(IV) in the melt. Metal maintained at the cathode potential was not subject to loss by this mechanism. Loss of the metal product by simple dissolution in the melt appeared to be insignificant, but solubility data to verify this conclusion are not available.

Assimilation of PuO_2 feed into the fluoride melt was relatively slow. No obvious reaction occurred when PuO_2 was added to the melt, in contrast with the behavior noted(1) in the analogous cerium system. Carefully controlled, slow addition rates were required to prevent accumulation of settled oxide in the bottom of the cell. The accumulation of settled oxide was deleterious to cell operation because, (1) the oxide was largely unavailable for electrolysis, and (2) metal coalescence was inhibited.

CELL REACTIONS

The operational behavior of the plutonium electrowinning cells in the scouting experiments was similar in many respects to the behavior of the previously studied cerium cells. Similar cell reactions are postulated to describe the operation of the plutonium process. The reactions are written below in ionic form, but the species actually involved may be complex.

Cathode Reactions

1) $Pu^{4+} + e^- \rightarrow Pu^{3+}$

2) $Pu^{3+} + 3e^- \rightarrow Pu^0$

Anode Reactions

3a) $O^{2-} + C \rightarrow CO + 2e^-$

3b) $2O^{2-} + C \rightarrow CO_2 + 4e^-$

4) $Pu^{3+} \rightarrow Pu^{4+} + e^-$

5) "Anode Effect"

$4F^- + C \rightarrow CF_4 + 4e^-$

Other Reactions

6) $Pu^0 + 3Pu^{4+} \rightarrow 4Pu^{3+}$

7) $PuO_2 + 3Pu^{4+} \rightarrow 4Pu^{3+} + O_2$

8) $O_2 + C \rightarrow CO_2$

9) $O_2 + 2C \rightarrow 2CO$

Upon electrolysis of a $LiF-BaF_2-PuF_3$ melt before addition of PuO_2, the initial cell reactions are probably the reduction of Pu(III) to metal at the cathode (reaction 2) and the oxidation of Pu(III) to Pu(IV) (reaction 4) at the anode. Electrolysis of small amounts of oxide impurities also occurs until the oxide is consumed (reactions 1, 2, 3a and 3b). These reactions proceed initially with high efficiency, but as the concentration of Pu(IV) increases, the reduction of Pu(IV) to Pu(III) (reaction 1) becomes a competing cathode reaction. Eventually, steady-state concentrations of Pu(III) and Pu(IV) are established.

If the cell is operated at low electrode current densities, essentially all of the current is consumed by the cyclic oxidation-reduction of plutonium species (reactions 1 and 4). Operation of the cell at increased current densities causes increased polarization, and the electrode potentials required for electrolysis of plutonium fluoride are attained. Plutonium is produced by reaction 2, and CF_4 by reaction 5. Although plutonium metal may be produced under these conditions, the limitation on the current densities that is imposed by the "anode effect" renders this mode of operation inefficient and generally unsatisfactory.

If PuO_2 is added to the LiF-BaF_2-PuF_3 melt, fluoride electrolysis ceases because of the depolarizing action of the oxide, and plutonium metal is produced by electrolysis of the oxide (reactions 1, 2, 3a, and 3b). When oxide is present in the system, higher current densities are required for fluoride electrolysis. To ensure efficient electrolysis of the oxide feed, operation at current densities as high as possible without electrolyzing fluoride is desirable. Under this condition, the required degree of polarization for oxide electrolysis is most likely to be maintained. The anode reactions during oxide electrolysis (reactions 3a and 3b) produce both CO and CO_2. The proportion of CO increases at higher operating temperatures. The off-gas from the laboratory cell typically contained about 70% CO_2 and 30% CO when operating at about 1000°C.

Reaction 6 describes the loss of metal product by reaction with the melt. As previously stated, this reaction can be minimized by maintaining the metal at cathode potential.

The mechanism by which PuO_2 feed is assimilated into fluoride melts is an important consideration in cell design. The usual concept for the operation of oxide-fluoride systems is that the oxide is first dissolved in the melt, and then is electrolyzed. The solubility of PuO_2 in fluoride melts is unknown, but based on studies(9) of the similar uranium system it is probably no greater than 1 to 2 wt %, and the rate of oxide dissolution should be slow. However, since Pu(IV) is present in the melt, PuO_2 may be assimilated by reaction 7, in addition to simple dissolution. If the feed were assimilated mainly by this reaction, the primary cathode process would be reduction of Pu(III) to metal (reaction 2) and the primary anode process would be oxidation of Pu(III) to Pu(IV) (reaction 4). Reaction 7 would not only provide for oxide assimilation, but would also consume the anode product, Pu(IV). The oxygen produced by reaction 7 would react with graphite cell components to produce CO and CO_2 (reactions 8 and 9). Upon summation of these reactions, however, the over-all cell reaction is the same as (and thereby indistinguishable from) the case in which dissolved oxide is electrolyzed.

Assimilation of oxide feed by the above type reaction, rather than by dissolution, was important in the analogous cerium system.(1) CeO_2 reacted vigorously and almost instantaneously upon contact with fluoride melt containing Ce(IV); traces of unreacted oxygen were detected in the off-gas. A similar vigorous reaction of PuO_2 with fluoride melts containing Pu(IV) was not observed. However, when PuO_2-PuF_4-PuF_3 mixtures were heated in graphite crucibles with diluent fluoride salts at 1000°C, the Pu(III)/Pu(IV) ratio was increased substantially. In a test with the LiF-BaF_2 eutectic, the Pu(III)/Pu(IV) ratio increased from 0.2 to 3.3 upon heating at 1000°C for 30 minutes. Although the reaction did not proceed to completion and the rate appeared to be slow, the occurrence of reaction 7 was indicated.

A comparison of the standard free energy change for reaction 7, written for cerium, plutonium, and uranium, leads to essentially correct predictions about the occurrences of these reactions in fused salt systems. Of course, the actual free energy change for the reactions in the fused salt systems may be significantly different from the calculated values. The approximate standard free energy change for reaction 7 at 1250°K, calculated from available data(10) for cerium, plutonium, and uranium, is -120, -16, and +196 kcal/mole respectively. On the basis of these calculations, the cerium reaction should occur spontaneously, the plutonium reaction is marginal, and the uranium reaction should not occur. Additional chemical potential may be derived from scavenging of the oxygen product by reaction with carbon. Other phenomena, such as the complexing of reactants, may decrease the chemical potential.

In accord with these thermodynamic estimates, the cerium reaction occurs readily, but the uranium reaction shows little tendency to occur(1,7). The only indication of the occurrence of the uranium reaction is that melts containing UF_4 dissolve more UO_2 than melts containing UF_3(9). However, the solubility of UO_2 is still quite low, and the increase cannot be attributed definitely to the reaction. Also, in agreement with the predictions, the plutonium reaction does occur, but is slow and incomplete. Other investigators(11) who have studied the solid-state reaction of PuO_2 with PuF_4 have shown that the reaction is reversible.

CELL DESIGN AND PERFORMANCE

The preliminary experiments defined several important design criteria for a plutonium electrowinning cell: the cell should provide high cathode current density, low anode current density, and should maintain the deposited metal at cathode potential. In addition, the PuO_2 must be fed in a manner that ensures its complete utilization. Of the many conceptual cell designs considered, none fulfills all of these conditions completely and simultaneously. Hypothetically, the ideal cell design would consist of an electrically nonconductive crucible, a pool of molten plutonium metal in the bottom of the crucible to serve as the cathode, and a large graphite anode immersed in the melt. The lack of a suitable crucible material has prevented the testing of such a cell.

Three cell designs which partially meet the above criteria and which were tested rather extensively will be described. These cells were similar in most respects to the design shown in Figure 1, except that the anode configurations were as shown in Figures 2, 3, and 4.

Cell with Basket Anode

The basket anode design shown in Figure 2 was successfully used in cerium electrowinning cells and was tested for use in the plutonium cell. This graphite anode was a 1-1/4-inch-OD, thin-walled cylinder with a closed bottom. The walls were perforated with many 1/8-inch-diameter holes. The oxide feed was added to the center cavity of the anode. The intent of this design was to confine the solid oxide during the time required for its dissolution, and thus avoid contamination of the metal product.

Plutonium cells incorporating this anode, with a tantalum crucible as the cathode, were tested with several of the melt compositions already described at temperatures in the 850-1000°C range and at currents up to 100 amperes. At a current of 100 amperes, the cathode and anode current densities for this cell were ~0.6 and 1.3 amp/cm^2, respectively; the computation was based upon only the external surface of the anode. This cell design maintained the metal product at cathode potential, and the anode current density was only slightly higher than the desired value of 1 amp/cm^2; however, the cathode current density was undesirably low and low current efficiency was expected. The performance of the cell with this design was extremely poor; only thin metal films or occasional small metal nodules were produced, and current efficiencies and feed utilization efficiencies were near zero. Most of the PuO_2 feed remained undissolved and accumulated within the anode basket. The lack of rapid circulation of melt throughout the cell to transport the oxide in the absence of a vigorous feed assimilation reaction (as with cerium oxide) was responsible for the poor performance.

Cell with Modified Basket Anode

The modified basket anode design shown in Figure 3 was more successful. The graphite anode was similar to that in the previous basket design, except that the bottom was in the shape of an inverted funnel. The anode gases, electrolytically generated on the bottom of the anode, rose through the opening in the anode and caused circulation of the melt and agitation of the PuO_2. The oxide feed was added continuously to the anode cavity. Plutonium cells with this anode design and a tantalum crucible as the cathode were tested under the conditions described for the previous cell. The cathode and anode current densities tested were about 0.6 and 1.3 amp/cm^2, respectively, the same as for the previous cell design. This cell successfully produced coalesced molten plutonium metal. However, successful operation required that the anode was centered in the tantalum crucible and spaced approximately 1/4" from the bottom. This placement provided a shorter path for current flow at the cell bottom than at the sides, and presumably the effective current densities were substantially higher at the cell bottom than elsewhere. With the larger proportion of the anode gases generated at the bottom and rising through the anode, the desired flow pattern was achieved. Also, nearly all of the plutonium metal product was deposited directly beneath the anode in the region of high current density. A thin film of plutonium metal was observed to form on the crucible walls, but this metal apparently reacted with the melt or with anode products almost as rapidly as it was deposited. The usefulness of this cell design was limited by the slow growth of an electrically conductive deposit from the cathode toward the anode at the melt surface. This deposit eventually disrupted operation by bridging between the electrodes and short-circuiting the cell.

Typical performance data for the modified basket anode design are shown in Table I. Cell performance was judged on the basis of the percent metal yield (percent utilization of the added feed) and the degree of coalescence of the metal product. The current efficiency was a less meaningful basis for evaluation because for a given current the maximum efficiency theoretically attainable depended upon the feed rate. The optimum run conditions for this cell design to produce reliably high percent yields of coalesced metal product (prior to short-circuiting) were as follows: 1) PuO_2 feed rates no greater than about 40 g/hr, 2) operating temperatures near 1000°C, and 3) melts not highly enriched in BaF_2. These conditions are illustrated by run 3A (Table I), which was highly successful. Except for the short-circuiting problem, the operational characteristics and problems of the modified basket anode design were similar to those of the disc anode design, which are discussed in the following section.

TABLE I

Performance of Plutonium Electrowinning Cell with Modified Basket Anode

Run[a]	Melt Composition, wt %			Run Temp., °C	Run Duration[b]		PuO_2 Feed		Metal Yield		Current Efficiency[d], %	Product Form
	LiF	BaF_2	PuF_3		hours	amp-hours	grams	g/hr	grams	%[c]		
1	26	41	33	925	1.9	171	106	56	92	99	24	Partly coalesced
2	28	42	30	950	4.1	416	222	54	66	34	7	Nodules
3A	28	42	30	1000	4.3	421	149	35	126	96	14	Fully coalesced
B	28	42	30	1050	2.9	282	163	56	128	90	21	Partly coalesced
4	10	60	30	950	1.1	97	63	60	25	45	12	Nodules-black solids

(a) Lettered runs denote sequential operation with the same melt.
All runs were made with approximately 4" depth of melt in cell (600 to 1000 grams).
Cells operated usually at 90 to 100 amperes and 6 to 7 volts.
Cathode current density ~0.6 amp/cm; anode current density ~1.3 amp/cm^2.

(b) Time required for feed addition. Pre- and post-electrolysis times about 0.5 hour each.

(c) Percent yield based on quantity of PuO_2 feed added.

(d) Excluding current consumed before and after addition of PuO_2.

Cell with Disc Anode

The most successful anode design that was tested is shown in Figure 4. This graphite anode consisted of a flat disc, about 1/4" thick and 1-1/4" in diameter, and a small diameter riser rod. The electrolytic gases generated on the bottom of the anode rose through a number of holes drilled in the disc. When this anode was spaced about 1/4" from the bottom of the tantalum crucible cathode, the anode gases caused considerable agitation of the melt in an effective flow pattern. The PuO_2 feed was added to the body of the melt, and while the anode did not provide confinement of the oxide, the rising gas bubbles provided the necessary suspension and mixing during assimilation.

Cells with this anode design and operating at 100 amperes provided anode and cathode current densities of ~1.5 amp/cm^2 each (these values were calculated on the basis of the disc area and the crucible area immediately surrounding the disc). The cell of this design successfully produced coalesced plutonium metal. Nearly all of the metal product was deposited on the crucible bottom directly beneath the anode in the area of highest current density. The growth of electrically conductive deposits at the melt surface did not occur with this cell design, presumably because of adequate electrode separation at that point.

Typical performance data with the disc anode design are shown in Table II. The optimum run conditions for reproducible, good performance with this design were the same as with the modified basket anode design: 1) PuO_2 feed rates no greater than ~40 g/hr, 2) operating temperatures near 1000°C, and 3) melts not highly enriched in BaF_2. These conditions are illustrated in runs 10B through 13C, excepting 12C. Very good performance was demonstrated in runs 5B, 7B, and 9 under unfavorable conditions. These exceptional runs were not reproducible, and the specific conditions responsible for their occurrence is unknown. Undoubtedly, these runs are an indication that further studies would lead to substantially improved cell performance.

Purity data for typical samples of metal product are shown in Table III. These samples were produced in runs of the same number reported in Table II. Except for tantalum, the purity of the product was usually comparable to that of plutonium metal produced by bomb reduction. The tantalum content of the samples analyzed was quite variable; apparently the tantalum segregated as the product cooled in the cell. However, the data indicated that the quantity of tantalum present was approximately that which would be predicted on the basis of solubility. The solubility of tantalum in plutonium metal is reported to be 3594 ppm at 1000°C.(12) Tantalum contamination should be lower with cells that provide for continuous product removal, because of the short residence time.

TABLE II

Performance of Plutonium Electrowinning Cell with Disc Anode

Run[(a)]	Melt Composition, wt %			Run Temp, °C	Run Duration[(b)]		PuO_2 Feed		Metal Yield		Current Efficiency[(d)], %	Product Form
	LiF	BaF_2	PuF_3		hours	amp-hours	grams	g/hr	grams	%[(c)]		
5A	28	42	30	950	5.5	426	111	20	87	89	9	Partly coalesced
B	28	42	30	950	4.7	422	177	38	159	102	17	Fully coalesced
C	28	42	30	950	5.0	429	111	22	101	97	11	Mostly nodules
D	28	42	30	950	3.5	300	265	76	109	47	17	Mostly nodules
6	26	44	30	950	3.5	322	187	53	48	29	7	Black solids
7A	15	52	33	950	2.5	245	100	40	17	19	3	Metal film
B	15	52	33	950	1.3	120	100	80	116	132	44	Fully coalesced
C	15	52	33	950	.8	75	100	133	87	99	53	Nodules-black solids
8A	11	59	30	925	2.5	245	100	40	28	32	5	Nodules-black solids
B	11	59	30	950	1.7	167	100	60	79	90	22	Nodules
9	25	42	33	1000	1.3	128	100	87	91	103	32	Fully coalesced
10A	60	0	40	925	1.3	91	50	40	Trace	Low	Low	Metal film
B	60	0	40	1020	2.5	250	50	22	42	95	8	Mostly coalesced
C	60	0	40	1010	2.8	280	50	18	42	95	7	Mostly coalesced
11	48	20	32	1010	2.8	250	50	18	36	82	7	Fully coalesced
12A	55	17	28	1010	2.0	200	50	25	36	82	8	Fully coalesced
B	55	17	28	1015	1.7	170	50	30	43	98	11	Fully coalesced
C	55	17	28	990	1.0	100	50	50	9	20	4	Nodules-black solids
13A	44	21	35	1005	3.5	350	98	28	66	77	9	Fully coalesced
B	44	21	35	1015	5.0	500	104	20	84	92	8	Fully coalesced
C	44	21	35	1050	4.4	440	100	23	72	82	7	Fully coalesced
D	44	21	35	1015	6.0	660	180	30	66	41	3	Fully coalesced-excess oxide
14	27	41	32	990	0.9	90	100	109	32	36	18	Nodules-black solids
15	25	42	33	990	1.5	150	100	67	41	47	12	Nodules-excess oxide

(a) Lettered runs denote sequential operation with the same melt.
All runs were made with approximately 4" depth of melt in cell (600 to 1000 grams).
Cells operated usually at 90 to 100 amperes and 6 to 7 volts.
Cathode and anode current densities both ~1.5 amp/cm^2.

(b) Time required for feed addition. Pre- and post-electrolysis times about 0.5 hour each.

(c) Percent yield based on quantity of PuO_2 feed added.

(d) Excluding current consumed before and after addition of PuO_2.

TABLE III

Purity of the Plutonium Metal Product[a]

Element	Pu Metal Sample No. 9	No. 12C	No. 13D[b]	No. 14	No. 15	PuO_2 Feed No. 13D
Al	77	35	10	>800	22	48
Ca	<10	<10	<10	<10	<10	35
Cd	<10	<10	<10	<10	<10	-
Cr	<10	<10	<10	25	<10	<10
Cu	<2	<2	<2	5	<2	3
Fe	20	<10	<10	60	60	15
Ga	<10	<10	<10	<10	<10	<10
Mg	30	<10	<10	<10	<10	-
Mn	20	<10	<10	<10	<10	-
Ni	<10	<10	<10	<10	<10	<10
Pb	<10	<10	<10	10	<10	75
Si	<5	5	<10	<5	<5	100
Sn	<10	<10	<10	<10	<10	<10
Ta	-	3000-3500[c]	1500	5000-10,000[c]	-	-
Zn	<50	<50	<50	<50	<50	<50
Density, g/cc	19.2	19.7	-	18.6	19.5	-

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[a] Impurities were determined spectrographically and are reported in ppm.
[b] Metal sample No. 13D was produced from PuO_2 feed No. 13D.
[c] Range of four samples.

The optimum run conditions for the modified basket and disc anode designs minimize several disruptive phenomena to which the small laboratory cells were highly vulnerable. The high density PuO_2 feed tended to settle rapidly from the small volume of melt in these cells. With high feed rates, the oxide was not completely assimilated into the melt and settled to the bottom of the cell where it was unavailable for electrolysis and where it also interfered with the coalescence of the metal product and the proper directional flow of current. Another disruptive effect occurred if the cell operating temperature was less than ~1000°C; "black solids" formed and accumulated in the bottom of the cell. The composition of the "black solids" was variable and could not be definitely established by X-ray diffraction and chemical analysis. However, the material was predominately dispersed plutonium metal and a plutonium-rich salt, possibly a double salt or solid solution of plutonium fluoride and barium fluoride. The formation of the "black solids" apparently involved first the precipitation of the high melting plutonium-rich salt, followed by its settling to the cell bottom where it mixed with or reacted with the plutonium metal product. This phenomenon occurred less often in the melts with lower BaF_2 content, and was seldom a problem when the operating temperature was maintained near 1000°C. Once formed, the "black solids" were not re-assimilated into the system. After mechanical separation, the remainder of the melt was reusable.

At cell operating temperatures near 1000°C, severe corrosion of the tantalum crucible occurred at the melt surface. The attack was quite rapid, and complete penetration of the thin-walled crucible usually occurred after several hours. This problem was eliminated by inserting a protective graphite sleeve that extended slightly below the melt surface. The corrosive agent was not identified, but was probably either oxygen released from the added oxide feed or electrolytically generated lithium or barium metal. Generalized corrosion of the tantalum crucible was not significant at 1000°C, but became noticeable at temperatures above 1050°C; the major corrosive agent was plutonium metal, as determined by inspection of the crucible.

The above problems were intensified by inability to heat the laboratory cells uniformly. With melt surface temperatures of ~1000°C, the temperature of the cell bottom was ~925°C. This gradient occurred because the small size and the configuration (the crucible was the susceptor for the inductive heating) of the experimental equipment did not permit adequate thermal insulation.

RECOMMENDATIONS

Further studies of the plutonium electrowinning process should lead to substantially improved performance. The use of cells slightly larger than those tested in the present investigation is recommended for such studies; larger cells generally operate more efficiently and with less sensitivity to minor process variations. The development of improved cell designs, the optimization of operating conditions, and the demonstration of continuous removal of product in runs of long duration will be greatly facilitated with larger cells. The maximum diameter of plutonium cells must be restricted to about 4 inches because of criticality considerations, unless the height is severely restricted or the batch size is controlled. However, a 4-inch-diameter cell will probably be sufficiently large to achieve a high performance plutonium process. The volume of melt in a 4-inch cell would minimize the settling problem with the oxide feed. With adequate thermal insulation and uniform heating to minimize the temperature gradients, the operating temperature of the cell could probably be reduced below 1000°C without the disruptive occurrence of "black solids". Another significant benefit of lower operating temperature would be to decrease the corrosion of tantalum cell components and thereby the tantalum-content of the plutonium product. The temperature-dependence of the solubility of tantalum in plutonium(12) is indicated by the following data:

Temperature, °C	Ta Solubility, ppm
700	400
800	955
900	1955
1000	3594

These data also suggest that the tantalum content of the plutonium product could be decreased to a low level by heat treatment at a temperature slightly above the melting point of plutonium (640°C), followed by filtration to remove the segregated tantalum. The most desirable solution to the problem of product contamination is the development of more resistant materials for cell construction.

Basic chemistry studies could also lead to improvements in the electrowinning process. A knowledge of the phase diagrams of potentially useful salt systems, the solubility of PuO_2 and plutonium metal in such systems, and identification of the plutonium species in fluoride melts would be particularly valuable.

BIBLIOGRAPHY

1. J. A. Porter and L. P. Fernandez. Electrowinning Cerium Metal. USAEC Report DP-802, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1963).

2. M. Kolodney. Production of Plutonium by Electrolysis. USAEC Report LA-148, University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. (1944).

3. R. D. Baker. Preparation of Plutonium Metal by the Bomb Method. USAEC Report LA-473, University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. (1946).

4. M. H. Curtis. Continuous Electrowinning of Plutonium Metal: Progress Report. USAEC Report RL-SEP-30, General Electric Co., Hanford Atomic Products Operation, Richland, Wash. (1964).

5. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman. Plutonium Electrorefining. USAEC Report LA-2666, University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. (1962).

6. L. H. Meyer. "Electrolytic Reduction of Thorium Oxide." J. Electrochem. Soc., 107, 1, 43-47 (1960).

7. R. D. Piper and R. F. Leifield. "Electrolytic Production of Uranium Metal from Uranium Oxides". Ind. Eng. Chem. Process Design Develop. I, 3, 208-212 (1962).

8. J. A. Porter and A. E. Symonds. Precipitation of Plutonium (III) Oxalate and Calcination to Plutonium Dioxide. USAEC Report DP-981, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1965).

9. J. W. Varwig. Solubility of UO_2 in Molten Salt. USAEC Report MCW-1490, Mallinckrodt Chemical Works, Uranium Division, Weldon Spring, Mo. (1964).

10. A. Glassner. The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K. USAEC Report ANL-5750, University of Chicago, Argonne National Laboratory, Chicago, Ill. (1957).

11. S. Fried and N. R. Davidson. "Studies in the Dry Chemistry of Plutonium Fluorides". The Transuranium Elements, Nat'l Nuclear Energy Ser. Div. IV, 14B, 784, McGraw-Hill Book Co. New York (1949).

12. D. F. Bowersox and J. A. Leary. The Solubility of Selected Elements in Liquid Plutonium. V. Revisions to the Tantalum Study. USAEC Report LA-3338, University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. (1965).