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DPST-65-432

SEPT. 13, 1965

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ELECTRODEPOSITION OF PLUTONIUM

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ELECTRODEPOSITION OF PLUTONIUM JUL 1960

Equipment for electrolytic deposition of plutonium from molten salt solutions was designed and built, and was tested with cerium as a stand-in for plutonium. The electrolysis cell is a graphite crucible that serves as the anode; the cathode is a molybdenum rod. The cell is heated by induction and is enclosed in a quartz chamber to permit operation in an inert atmosphere.

Buttons of cerium metal were successfully produced by electrolysis of molten mixtures of  $CeF_3$ - $BaF_2$ - $LiF$  (weight ratio 77:13:10) that contained 5 wt % of dissolved  $CeO_2$ . In one experiment the mixture was electrolyzed 13 minutes at  $900^\circ C$ , with 25-35 amperes at a potential of 6 volts. A coalesced 5-g button of cerium metal was formed and about 2 g of additional cerium adhered to the molybdenum cathode. The total cerium indicated a current efficiency of 62%. Electrolysis at about  $800^\circ C$  showed about the same current efficiency, but the cerium metal was dispersed as nodules throughout the melt. Plans were made to use a single charge of the mixed fluorides in repetitive cycles, with periodic addition of the cerium dioxide feed.

The electrodeposition of plutonium metal from fused salt systems has potential advantages over the present process in which batches of plutonium fluoride are reduced with calcium; the electrolytic process could be adapted to continuous operation, and extended use of the same batch of electrolyte for several throughputs of  $PuO_2$  would reduce the amount of plutonium that must be recovered from reduction wastes. Previous study in the laboratory was directed toward the electrodeposition of plutonium from organic solvents; this method was found to be limited both by the solubility of plutonium salts in the solvents tested and by the conductivity of the organic solutions. Electrolysis from fused salts is expected to avoid these problems, but considerable effort will be needed to define satisfactory operating conditions and materials of construction.

ELECTRODEPOSITION OF PLUTONIUM

OCT 1960

Exploratory runs in the electrolysis equipment described in the July report were continued with the object of defining satisfactory operating conditions and materials of construction for electrodepositing plutonium from molten salts. Tests with cerium as a stand-in for plutonium were continued and tests with plutonium were started. Cerium was successfully deposited when  $CeO_2$  was added periodically during 105 minutes to a molten bath of  $CeF_3$ - $BaF_2$ - $LiF$ . About 16 g of cerium was produced; the current efficiency was about 60%. The operating temperature,  $800^\circ C$ , was not high enough to allow the cerium to coalesce in the bottom of the graphite crucible; most of the cerium remained as a spongy, dendritic deposit on the cathode.

Deposition of plutonium from the analogous  $PuF_3$ - $BaF_2$ - $LiF$  system has not yet been tested, but attempts to deposit plutonium from other systems were not successful. When solutions of  $PuF_3$  in  $NaF$ - $KF$  and  $LiF$ - $NaF$  eutectics were electrolyzed, flames appeared at the surface of the solutions. In all experiments in which a flame appeared, the cathode was a molybdenum rod and the flame surrounded the cathode. In these tests the anode gases were probably mixtures of fluorine and carbon-fluorine compounds; these gases may have reacted with the molybdenum or with molten metals at the cathode. To avoid the use of molybdenum, in one experiment a graphite anode was used and the graphite cell served as the cathode. No flaming occurred and the electrolysis was continued for one hour at  $800^\circ C$ . No plutonium metal was found; any plutonium produced may have reacted with the graphite crucible. In an attempt to overcome this problem, the graphite crucible was replaced by a magnesia crucible, and two molybdenum strips were used as cathodes with a graphite rod as the anode. After  $PuF_3$  was added to the  $LiF$ - $NaF$  electrolyte the electrolysis proceeded without flaming, but the run was interrupted by dissolution of the magnesia crucible. Preparations were made for tests with solutions of  $PuO_2$  in various molten salts, including  $KPuF_5$  and  $Cs_2PuF_6$ .

Plutonium was electrodeposited from a molten bath of  $\text{PuF}_3\text{-NaF-LiF}$ , in successful demonstration of an electrolytic process that is being studied as a potential replacement for the present bomb reduction process. The electrolysis was performed at  $800^\circ\text{C}$  in a graphite crucible, which served as the anode. The cathode, a molybdenum rod, was shielded from the atmosphere above the cell by an inverted graphite cup that extended below the surface of the melt. The shield almost completely eliminated the flaming that previously occurred at the

surface of the melt during electrolysis. After electrolysis for 87 minutes, about 2 g of plutonium metal was dispersed as small beads throughout the melt, and about 2 g adhered to the cathode. Preparations were made for tests with solutions of  $\text{PuO}_2$  in various molten salts.

ELECTRODEPOSITION OF PLUTONIUM

FEB 1961

In further study of the electrodeposition of plutonium from molten salts, the flaming that previously occurred at the surface of the melt during electrolysis was eliminated and the evolution of dense vapors from the melt during electrolysis was greatly reduced. Plutonium was deposited satisfactorily in two tests in which the basic procedure summarized in the November report was improved by purifying the argon blanket gas and substituting a melt of  $\text{LiF-CaF}_2\text{-PuF}_3$  for the former  $\text{LiF-NaF-PuF}_3$ .

Two experiments with a  $\text{LiF-NaF}$  bath at  $800^\circ\text{C}$  showed that water vapor in the blanket gas contributed to the formation of flames during electrolysis. When the stream of argon supplied to the electrolytic cell was passed over copper turnings at  $600^\circ\text{C}$  to remove oxygen the melt evolved dense vapors during the electrolysis and flamed during and after the electrolysis. When the argon was also passed through silica gel the vaporization from the  $\text{LiF-NaF}$  melt persisted but flames did not form. The inert atmosphere system was also improved by the use of a new cell assembly that provided more positive control of the flow of argon and the pressure in the cell. In a third test, substitution of a  $\text{LiF-CaF}_2$  melt for the  $\text{LiF-NaF}$  nearly eliminated the formation of vapor; this effect indicated that sodium is electrodeposited and vaporized. Because of its relatively low boiling point and its low reduction potential, sodium is not a desirable constituent of the fluoride melts, which must be operated above  $800^\circ\text{C}$ .

Two successful tests were made with melts of  $\text{LiF-CaF}_2$  that initially contained as much as 5.5 wt % of  $\text{PuF}_3$ . The cell consisted of an insulated graphite crucible with a graphite anode and a molybdenum cathode. The tests proceeded smoothly for as long as three hours without evidence of flaming or vaporization and without serious attack on the cell components. In the longest run, 9.6 g of plutonium was deposited, of which about 4 g coalesced as a button. Plans were made for longer tests, with more  $\text{PuF}_3$ .

MAY 1961

Study was continued of the electrodeposition of plutonium as a potential replacement for the present plant process in which plutonium salts are reduced to the metal by reaction with calcium. The  $\text{LiF-CaF}_2\text{-PuF}_3$  cell system and the operating techniques that were recently developed as described in the February report continued to give relatively stable operation and permitted runs of long duration in which no flaming occurred. The longer runs, however, showed the need for developing conditions for increasing the yield of plutonium metal.

Five runs with  $\text{PuF}_3$  from the plant produced a total of about 12 g of plutonium, which represented an average current efficiency less than 10%. The results are summarized in the following table. The cell temperature in all cases was  $875 \pm 10^\circ\text{C}$ . The cell was an insulated graphite crucible with a graphite anode and a molybdenum cathode, as described previously; the size and shape of the electrodes were varied. At the end of each run the melt was removed from the cell, the plutonium metal was collected, and the melt was then re-used in the subsequent runs. The low yields were attributed to two possible factors: (1) an appreciable quantity of slag accumulated on the surface of the melt and caused arcing and stray currents; the slag probably resulted from impurities in the melt or in the argon blanket; (2) the graphite cell as it was arranged in these runs may sometimes have been anodic with respect to the molybdenum cathode; this condition would cause anodic dissolution of previously deposited plutonium.

Four electrolyses with cerium as a stand-in for plutonium are also summarized in the following table. The cerium is being used to expedite the development of conditions for obtaining higher yields. These runs showed improved yields and confirmed that the salts and the blanket need to be dried more rigorously than was done in the runs with plutonium. In the runs with cerium, the salts were dried by heating in argon and then in vacuum at  $400^\circ\text{C}$ . The argon for the blanket of the electrolysis cell was dried with silica gel and was passed over copper turnings at  $400^\circ\text{C}$  to remove oxygen. The electrolyses were made at  $875^\circ\text{C}$  with a potential of 5.0 to 5.7 volts, and a current of 15 to 20 amperes. Very little slag was formed on the surface of the melts. There was some indication that the average cathode current efficiency is dependent on the cathode current

density and on the duration of the electrolysis. These factors are being explored in further runs with cerium, preparatory to runs with plutonium in which the  $\text{PuF}_3$  will be precipitated in the laboratory and outgassed prior to use.

Electrodeposition of Plutonium and Cerium

Plutonium Runs Melt, 200 g			Current Density, amps/cm <sup>2</sup>		Time, hr	Cathode Current Efficiency, %	Product
wt % LiF	CaF <sub>2</sub>	PuF <sub>3</sub>	Cathode	Anode			
26.7	33.9	39.4	0.2	0.1	2.5	4	4.2-g button
			0.7	0.5	3.0		
31.2	39.5	29.3	2.0	0.2	3.0	3	3-g granules, carried to next run
31.2	39.5	29.3	2.0	0.2	1.0	6	6.9-g Pu, in 1-g buttons
			3.5	0.4	0.5		
31.2	39.5	29.3	3.5	0.4	4.5	-	No Pu collected
34.2	43.2	22.6	3.5	0.8	2.0	2	1.4-g granules
Cerium Runs Melt, 350 g							
wt % LiF	CaF <sub>2</sub>	CeF <sub>3</sub>					
31.0	39.3	29.7	3.0	0.6	2.5	25	9.5-g button
23.6	29.9	46.5	2.5	0.5	4.0	13	17.2-g button
22.0	28.0	50.0	9.0	0.5	3.0	21	21-g button
24.1	30.6	45.3	3.5	0.7	3.0	4	4.3-g button

In the continuing laboratory study of the electrodeposition of plutonium metal as a potential replacement for the bomb reduction process with calcium that is presently used in the plant, additional runs with cerium as a stand-in for plutonium resulted in improved yields and aided in defining the factors that affect the cell efficiency. In three runs, cerium metal was produced with an average cathode current efficiency of 62% and a maximum efficiency of 82%, compared with a previous average of about 16% and a maximum of 25%. In plutonium electrolyses to date the average current efficiency has been less than 10%, as was most recently summarized in the May report.

The most significant improvement in yield was due to the presence of dissolved  $\text{CeO}_2$  in the  $\text{LiF-BaF}_2\text{-CeF}_3$  melt during electrolysis. The results in the following table may be compared with the results of runs without oxide that were described in the May report. In the recent experiments the melt contained initially about 15 wt %  $\text{LiF}$ , 20 wt %  $\text{BaF}_2$ , 60 wt %  $\text{CeF}_3$  and 5 wt %  $\text{CeO}_2$ ; additional  $\text{CeO}_2$  was added periodically during the electrolysis according to the calculated depletion rate. The cell was a graphite crucible with a graphite anode and a molybdenum cathode, as previously described; the size and shape of the electrodes were varied. The operating temperature of the melt was  $825 \pm 10^\circ\text{C}$ . The first three runs summarized in the table show the improved yields under essentially the same conditions that previously gave a maximum cathode current efficiency of 25% with the oxide-free melt. The trend toward lower efficiency as the electrolysis progressed was again noted. The last three runs shown in the table were complicated by short circuits and erratic currents in the cell. In at least one of the runs this behavior was caused by

contact of accumulated cerium with the cell components. In the last AUG 1961 two runs, attempts were made to operate with higher current densities at the anode. Although the results were obscured by shorting in the cell, the experiments indicated that the yield was lower at the higher anode current densities. This observation is consistent with the occurrence of the "anode effect" in aluminum electrolysis, in which the cell efficiency is decreased by the formation of a nonconducting film of fluorocarbon on the anode. Apparently, at anode current densities higher than about 1 amp/cm<sup>2</sup>, or when the oxide content of the bath is depleted, the anode process changes from predominant production of CO and CO<sub>2</sub> to predominant production of fluorocarbon. This effect has been observed by workers at Weldon Spring<sup>(1)</sup> in studies of the electro-deposition of uranium from fused fluorides. The effect will be explored in further runs with cerium, preparatory to runs with plutonium in which PuO<sub>2</sub> will be present in the melt. Changes in cell designs are being studied to eliminate the occurrence of the short circuits.

Electrodeposition of Cerium

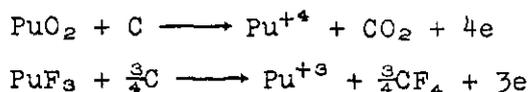
AUG 1961

Current Density, amps/cm <sup>2</sup>		Time, hr	Cathode Current Efficiency, %	Cerium Deposited, grams
Cathode	Anode			
3	0.7	2.2	53	23.7
4	0.7	1.0	82	15.4
5	0.8	2.3	50	30
4-6	0.5-0.6	2.3	16	11
4-6	1.5	1.6	33	15
4.2	1.4	4.5	25	24.9



As in preceding experiments the electrolysis cell consisted of a graphite crucible fitted with a graphite anode and a molybdenum cathode. In the series of seven runs the type and arrangement of the electrodes was varied, and in one run the graphite crucible was replaced by a molybdenum crucible. The conditions and results of the runs are summarized in the following table. The melt initially contained 20.8% LiF - 34.6% BaF<sub>2</sub> - 41.3% PuF<sub>3</sub> - 3.3% PuO<sub>2</sub>. The same melt was used throughout the series of runs; the weight and composition of the melt changed slowly, as the feed and deposition rates were varied. The cell temperature was maintained at 800-825°C in all runs. OCT 1961

The role of oxide in the molten electrolyte was clarified by several of the experiments summarized in the table. In Run 1, PuO<sub>2</sub> was added to the melt as the run progressed, according to the calculated rate of deposition; this procedure produced the best yields of metal in the previous runs with cerium as described in the August report. The cathode current efficiency in this run was 26%, the highest yet attained with plutonium, but the metal did not coalesce. The lack of coalescence was attributed to excess PuO<sub>2</sub> that was present as a sludge in the bottom of the cell. In Run 2 the bath was depleted of this oxide, and the metal was removed from the bath at the end of the run. In Run 3, the oxide-free melt was electrolyzed at 26% current efficiency; about 20 grams of plutonium was deposited as a coalesced button. As in previous runs, it was necessary to maintain the anode current density below 1 amp/cm<sup>2</sup> to avoid erratic current interruptions that are attributed to the formation of a nonconducting film of fluorocarbon at the anode, as described in the August report. The fluoride melt (Run 3) required the use of a somewhat lower anode current density than the oxide melt (Run 1). The anode reactions in the two systems may be represented by the equations: OCT 1961



The PuO<sub>2</sub> system has the advantages of permitting the use of higher anode current densities, of having a lower decomposition potential, and of producing an innocuous anode gas. However, the presence of undissolved oxide in the cell interferes seriously with the coalescence of the plutonium.

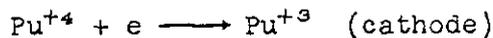
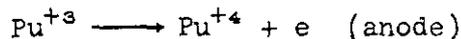
Runs 4 and 5 were similar to Run 3 except that the crucible was used as the anode to provide larger area and thereby allow higher total currents at low current density. This procedure risked the anodic dissolution of some of the plutonium metal, but an attempt was made to minimize this dissolution by limiting the duration of the runs so that most of the metal produced would remain on the cathode. This attempt was not completely successful, as evidenced by the lower yields. OCT 1961

## Electrodeposition of Plutonium

OCT 1961

Run	Conditions	Current Density, amp/cm <sup>2</sup>		Time, hr	Cathode Current Efficiency, %	Pu Metal Deposited, g
		Cathode	Anode			
1	Cathode-3/16" Mo rod Anode-3/8" graphite rod 3.6 volts, 12 amperes PuO <sub>2</sub> added during run	3	1.5	2	26	14.8
2	Cathode-3/16" Mo rod Anode-graphite crucible 3.6 volts, 18-20 amperes	4	0.2	2	15	12
3	Cathode-3/16" Mo rod Anode-3/8" x 1-1/4" graphite block 3.6 volts, 18 amperes	5	0.8	1.5	26	20.6
4	Cathode-1/2" Mo rod Anode-graphite crucible 4-4.5 volts, 40-44 amperes	5	0.8	1.25	12	17.3
5	Cathode-3/16" Mo rod Anode-graphite crucible 3.5 volts, 30-32 amperes	8	0.6	1	11	9.3
6	Cathode-graphite crucible Anode-1" graphite rod 3 volts, 18-19 amperes	0.2	1	2	-	0
7	Cathode - Mo crucible Anode-1" graphite rod 3-3.6 volts, 44-50 amperes	0.4	0.8	2	-	0

The effect of cathode current density was investigated in Runs 6 and 7. The anode current density was maintained near the desired value of 1 amp/cm<sup>2</sup> but the cathode current density was lowered by operating with the crucible as the cathode. No plutonium metal was produced in these runs; this result was apparently not caused by reaction of the molten plutonium with the crucible to form carbide, because the same result was obtained with a molybdenum crucible in Run 7. The results indicated that the low cathode current density favored redox cycling of ionic plutonium between the III and IV states rather than reduction to the metal:



Apparently, cathode current densities in the range of 5 amp/cm<sup>2</sup> must be used to minimize the consumption of current by this mechanism. The required value of current density undoubtedly depends also on the plutonium content of the melt.

Further runs were planned with plutonium to define the optimum current densities more explicitly. A gas chromatograph will be used in the cell system to analyze the anode gases.

ELECTRODEPOSITION OF PLUTONIUM

NOV 1961

In the continuing laboratory study of the electrodeposition of plutonium metal from molten salt, efforts were concentrated on defining the factors that affect the cell efficiency. The electrodeposition of plutonium from fused salt systems has potential advantages over the present process in which batches of plutonium fluoride are reduced with calcium; the electrolytic process could be adapted to continuous operation, and extended use of the same batch of electrolyte for several throughputs of  $\text{PuO}_2$  or  $\text{PuF}_3$  would reduce the amount of plutonium that must be recovered from reduction wastes. Because the size of the equipment is limited by criticality considerations, a reasonably high current efficiency (25-50%) is required to obtain the desired production rate with a small number of units (2 to 4).

The studies described in the October report have shown that current densities at the anode and the cathode have important influences on the cell efficiency in electrodepositing plutonium (or cerium) from fused fluoride baths. Optimum values of the current densities are difficult to define because they depend on a number of variables including the composition of the melt, the temperature, and the electrode materials. For practical purposes, however, the results to date indicate that the current density at a graphite anode must be maintained below 1 amp/cm<sup>2</sup> to avoid interruptions of the current by the formation of a film of fluorocarbon at the anode. The current density at the cathode must be maintained (1) below about 5 amp/cm<sup>2</sup> to avoid the electrodeposition of metals other than plutonium or cerium, and (2) above about 2 amp/cm<sup>2</sup> to avoid loss of current by cyclic reduction and oxidation of the plutonium (or cerium) ions.

The preferred current densities are obtained with the simple cell arrangement that has been used in much of this work, in which a cylindrical crucible of graphite is used as the anode and a small rod of molybdenum or graphite is used as the cathode. This arrangement, however, allows electrodeposited metal to drip to the bottom of the crucible, where it can be dissolved anodically. The extent of this anodic dissolution was studied in a series of tests with cerium, which showed that the average cathode current efficiency can be increased from about 30% to approximately 50% by avoiding the anodic dissolution.

NOV 1961

Two methods were used in the tests to minimize anodic dissolution. In the first method, used in Runs 1, 2, and 3, as summarized in the following table, the temperature of the melt was successively lowered in an attempt to deposit the cerium in solid form on the cathode. In the other method the induction heating coil was raised so that it would heat only the upper part of the crucible, in an attempt to maintain a frozen cake of salt in the bottom of the crucible and thereby insulate the cerium from the crucible. In Runs 1 and 2, solid cerium was not deposited directly on the cathode as planned, but the relatively low temperatures apparently allowed the cerium droplets to solidify rapidly, so that anodic dissolution was decreased. In Run 3, at 765°C, the cerium was deposited as dendritic crystals on the cathode, and the efficiency was sharply reduced because of the large increase in surface area of the cathode and the accompanying decrease in cathode current density that occurred as the crystals were formed. In Runs 4 and 6 a solid salt cake was maintained in the lower portion of the crucible, and the cerium evidently was successfully insulated from the crucible as it dripped from the cathode. In Run 5, at 825°C, the solid phase was not present, and the lowered yield was attributed to anodic dissolution of liquid cerium. Comparison of Runs 1, 2, 4, and 6, in which little dissolution occurred, with Run 5, showed that anodic dissolution can account for a reduction in current efficiency from about 50% to about 30%.

NOV 1961

The Effect of Anodic Dissolution on Efficiency  
in the Electrodeposition of Cerium Metal

NOV 1961

Run	Melt Composition	Current Density, amp/cm <sup>2</sup>		Temp, °C	Duration		Results	
		Anode	Cathode		hr	amp-hr	Metal, g	Efficiency, %
1	19% LiF - 31% BaF <sub>2</sub> - 20% CeF <sub>3</sub> (400 grams)	0.25	2.5	800	1.5	30	25	48
2	As Run 1	0.25	2.5	775	1.5	35	25	42
3	As Run 1	0.25	2.5	765	1.5	35	12	20
4	21% LiF - 36% BaF <sub>2</sub> - 43% CeF <sub>3</sub> (630 grams)	0.30	3	800	1.5	48	45	54
5	As Run 4	0.20	2.5	825	2.0	62	36	33
6	As Run 4	0.30	2.7	800	1.5	35	32	52

New experimental cells were designed and constructed to minimize the anodic dissolution and plans were made to test these cells in future runs. In one of the new designs, the wall of the crucible is shaped as shown in Figure 2.3. With this design, the crucible will serve as the cathode to prevent anodic dissolution of the molten metal. The cathode current density is expected to be high enough to avoid the redox cycling of the ionic plutonium, because the cathodically active area of the crucible is expected to be restricted to the tips of the protruding ridges. NOV 1961

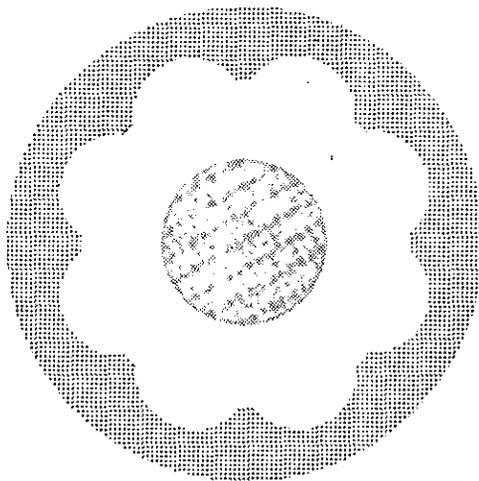


FIG. 2.3 MODIFIED CRUCIBLE-CATHODE , 0.85X  
Anode Rod at Center

NOV 1961

PUREX PROCESS

ELECTRODEPOSITION OF PLUTONIUM

Analysis of Evolved Gas

A gas chromatographic method was developed and tested for the determination of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CF}_4$  in the off-gas from electrolytic cells for experimental deposition of Ce and Pu from molten fluorides. Analysis of the off-gas will aid in defining the electrolytic processes and establishing the optimum conditions of operation.

The gas chromatograph with dual columns, arranged as shown in Figure 2.1, was selected because of low cost, versatility, and ease of operation. A sample of the off-gas is injected manually into the helium carrier gas and is swept successively through a dryer, a partition column containing hexamethylphosphoramide (HMPA), one section of the detector cell, an adsorption column containing molecular sieve 13X, and the second section of the detector cell, from which it is discharged to the atmosphere.

The partition column selectively retards the passage of the  $\text{CO}_2$  but does not resolve the other constituents of the sample. These constituents,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CF}_4$ , are sensed as a composite peak by the first section of the detector, as shown in Figure 2.2, and are then swept into the adsorption column; the  $\text{CO}_2$  peak is then sensed separately, by the first section of the detector. The  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CF}_4$  are resolved in the adsorption column and are sensed as individual peaks by the second section of the detector; the  $\text{CO}_2$  is irreversibly adsorbed in the adsorption column.

Calibration of the chromatograph and determination of the precision of the method were started in preparation for connecting the instrument to the electrodeposition apparatus.

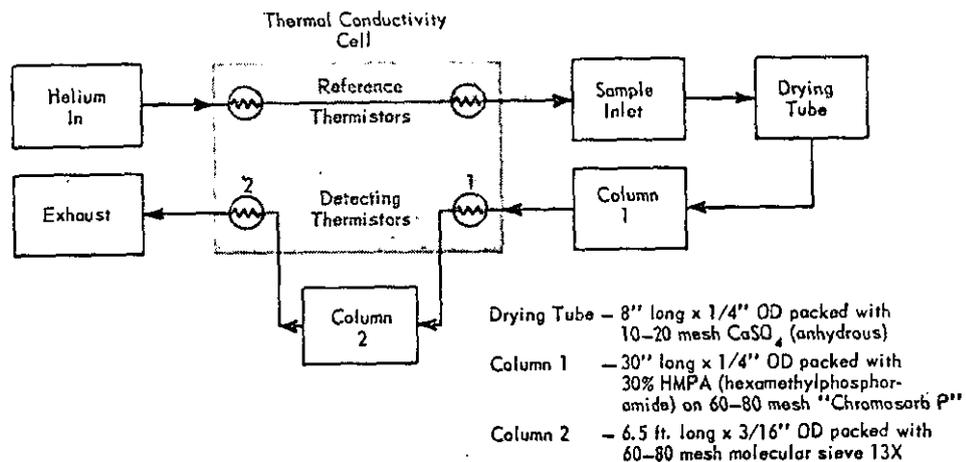


FIG. 2.1 FLOW DIAGRAM FOR FISHER GAS PARTITIONER Model 25, with Dual Columns

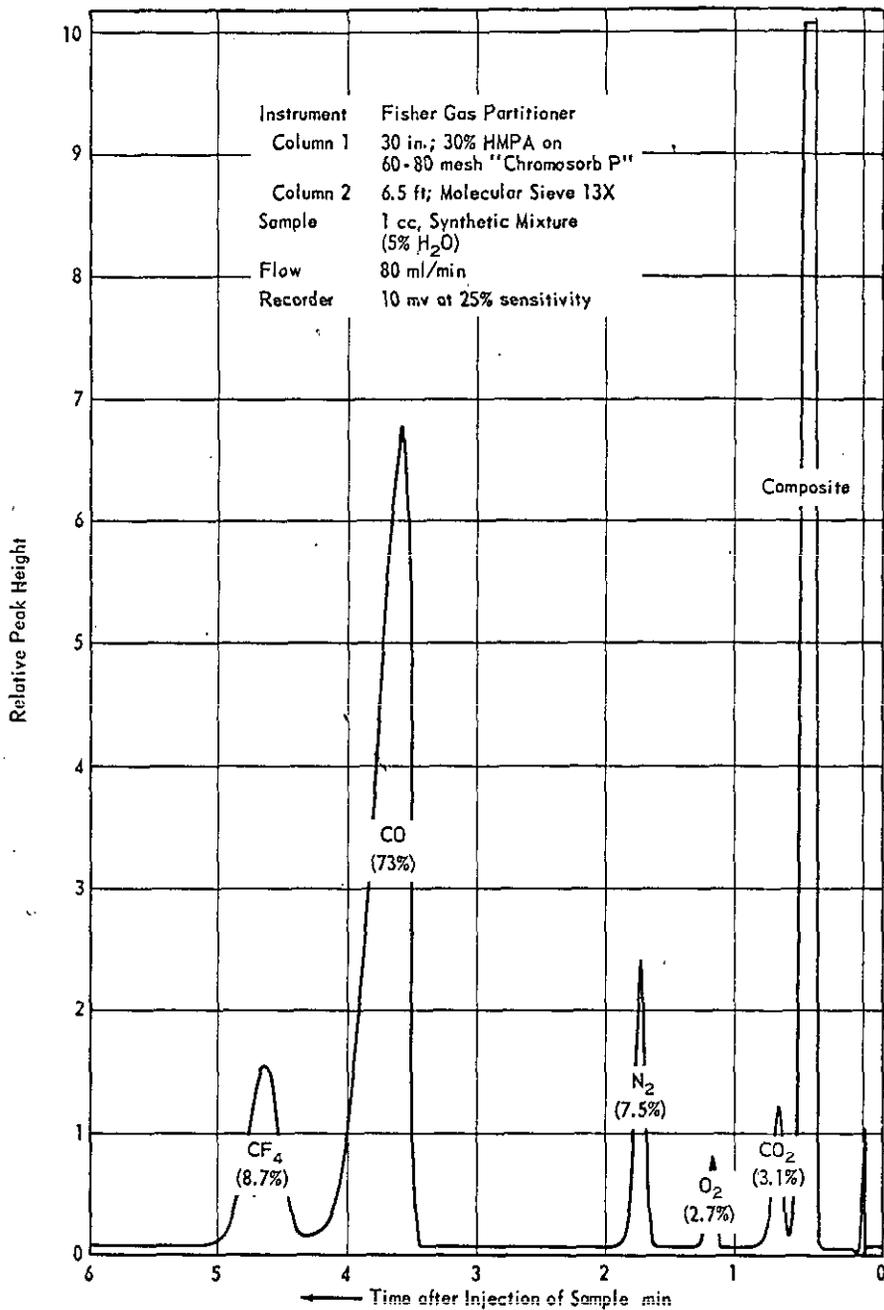


FIG. 2.2 GAS CHROMATOGRAM

ELECTRODEPOSITION OF PLUTONIUM

JAN 1962

In the continuing laboratory study of the electrodeposition of plutonium metal from molten salts, recent runs with cerium as a stand-in for plutonium have broadened the understanding of the major cell reactions that influence the deposition. The important influence that the cathode and anode current densities have on the cell efficiency was explained in the November report, and ways of avoiding loss of electrodeposited metal by anodic dissolution were described. Recent runs were made in a new cell that was designed to provide the desired control of these factors. The graphite crucible was electrically neutral, and a central graphite cathode rod was surrounded by a circular array of graphite anode rods; the melt consisted of  $\text{LiF-BaF}_2\text{-CeF}_3$ . The new cell provided the desired high ratio of anode surface to cathode surface and allowed the cerium metal to drip from the cathode to the bottom of the neutral crucible, so that anodic dissolution of the metal was avoided. Cerium yields that corresponded to current efficiencies of 40-50% were obtained in several runs of about 2 hours duration. These tests demonstrated the most favorable performance to date in oxide-free melts with either plutonium or cerium.

With the provision of the favorable ratio of current densities and the minimization of anodic dissolution, the principal reaction that competes with metal deposition appears to be oxidation of Ce(III) at the anode to produce Ce(IV), which in turn oxidizes Ce metal. The fact that a significant fraction of the Ce(III) was oxidized during the electrolysis was indicated by the color change in the melt, and confirmed by analysis of the melt at the completion of a run. The following qualitative description of the major reactions in the cerium system is consistent with the observations to date. The results of tests with plutonium have likewise indicated that analogous reactions occur in the plutonium fluoride system. The principal electrode reactions are as follows; the gaseous products  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CF}_4$  have been identified in the anode off-gas and are routinely measured with the gas chromatograph.

<u>Anode Reactions</u>	<u>Cathode Reactions</u>
(1a) $\text{O}^= + \text{C} \rightarrow \text{CO} + 2\text{e}$	(5) $\text{Ce}^{3+} + 3\text{e} \rightarrow \text{Ce}$
(1b) $2\text{O}^= + \text{C} \rightarrow \text{CO}_2 + 4\text{e}$	(6) $\text{Ce}^{4+} + \text{e} \rightarrow \text{Ce}^{3+}$
(2) $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + \text{e}$	
(3) $4\text{F}^- + \text{C} \rightarrow \text{CF}_4 + 4\text{e}$	
(4) "Anode effect" (formation of nonconducting fluorocarbon film on anode at current density $>1 \text{ amp/cm}^2$ )	

Although the reactions are written in terms of simple ionic species, complex ions are almost certainly involved. When oxide is present in the molten salt in relatively high concentration, Reactions 1a and 1b predominate; Reaction 1a increases as the temperature increases. When the system is depleted of oxide, Reactions 2, 3, and 4 occur, in this order of diminishing extent. Thus, the use of cerium oxide as the feed can avoid the undesirable Reaction 2, which causes deposited metal to be dissolved by the reaction  $3 \text{Ce}^{3+} + \text{Ce} \rightarrow 4 \text{Ce}^{4+}$ . Reaction 3 is the desired anode reaction, for operation with oxide-free melts, but apparently this reaction is always accompanied by Reaction 2. Reaction 5 is the desired cathode reaction; Reaction 6 combined with Reaction 2 leads to loss of current by cyclic oxidation and reduction.

In the continuing program, the solubilities of cerium and plutonium oxides in the  $\text{LiF-BaF}_2$  melt will be measured. Previous experiments have indicated that cerium oxide is sufficiently soluble to yield a system that behaves as described by Reactions 1a and b, but that plutonium oxide is less soluble, to a sufficient degree that Reactions 2, 3, and 4 occur to a significant extent. In addition, more exact measurements of the ratio of  $\text{Ce(III)}$  to  $\text{Ce(IV)}$  in an electrolyzed melt will be obtained by chemical analyses and by spectrophotometric methods, and silicon carbide and boron nitride will be evaluated as crucible material.

The gas chromatograph that was described in the December report was calibrated to analyze the off-gas from the electrolytic cell described in the foregoing section. The chromatograph is now installed at the electrodeposition apparatus and is used routinely to determine CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, and CF<sub>4</sub>, with satisfactory sensitivity, precision, and speed. DPST-65-432

The chromatograph was calibrated over the range of 0-100 vol % for each of the components. The sensitivity of the chromatograph is shown in the following table. Additional sensitivity can be obtained when desired by increasing the sample size and/or the recorder sensitivity.

Sensitivity of Gas Chromatograph

<u>Component</u>	<u>Detectable Concentration(a), vol %</u>
CO <sub>2</sub>	0.2
O <sub>2</sub>	0.1
N <sub>2</sub>	0.2
CO	0.4
CF <sub>4</sub>	0.4

(a) The concentration that will produce a peak of 0.2 mv (2% of full scale) when a 1-cc sample of off-gas at STP is analyzed.

II-9

The precision of the method was determined by analyses of 1-cc (STP) aliquots of a synthetic mixture. The data from this limited test, shown in the following table, indicate that coefficients of variation of 3% or less may be expected over the range of 3 to 72 vol % of the various components.

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No further development of the chromatograph for the analysis of electrolysis off-gas is planned at present.

Precision of Gas Chromatograph

<u>Component</u>	<u>Concentration, vol %</u>	<u>Number of Determinations</u>	<u>Coefficient of Variation, %</u>
CO <sub>2</sub>	3.8	3	1
O <sub>2</sub>	3.0	4	3
N <sub>2</sub>	11.4	4	3
CO	71.9	4	0.3
CF <sub>4</sub>	9.9	4	1

ELECTRODEPOSITION OF PLUTONIUM    MAR    1962

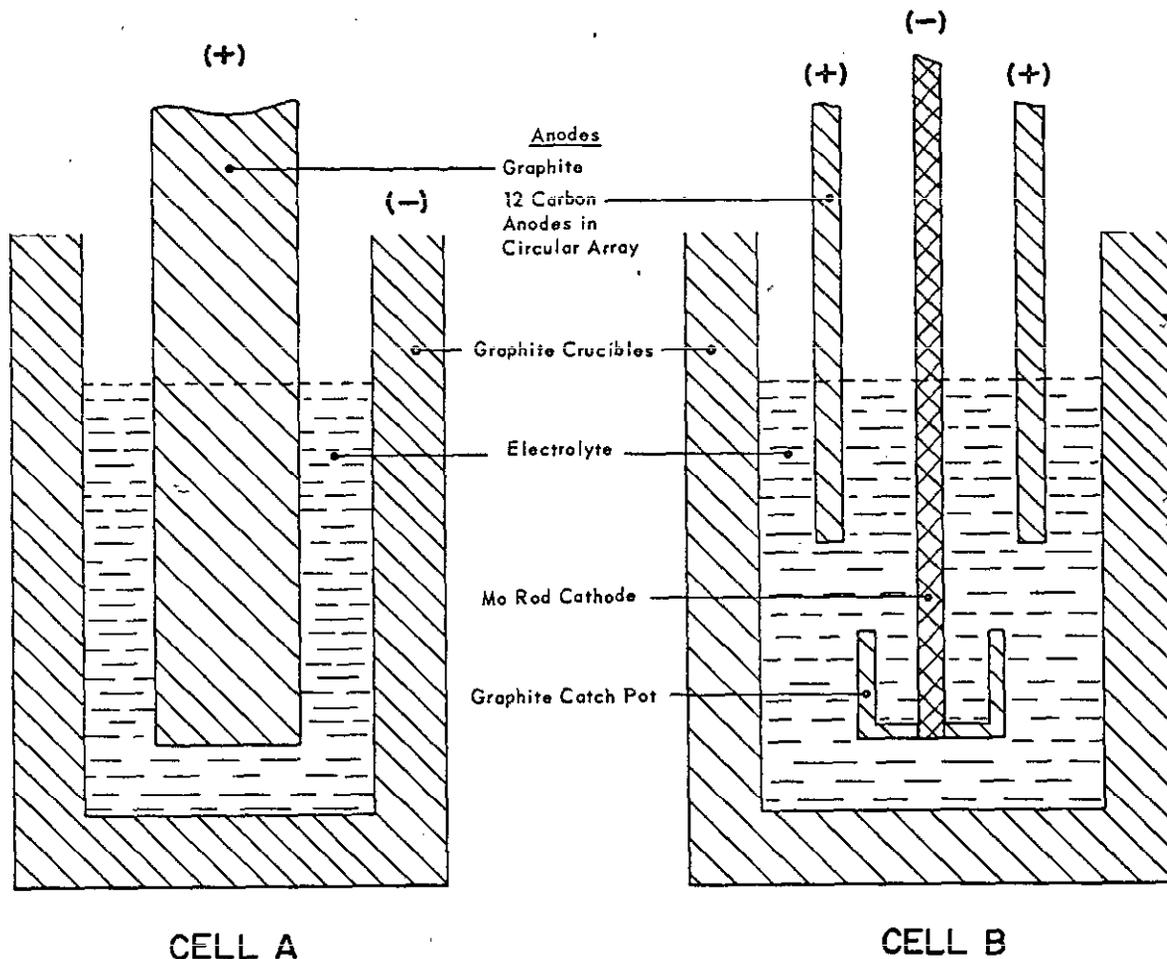
In the continuing laboratory study of the electrodeposition of plutonium metal from molten fluoride salts, additional runs with cerium as a stand-in for plutonium provided further information concerning the design of cells that will suppress competitive side reactions in extended practical operation.

The additional tests with cerium were made with cells of two basic designs. The first type of cell tested is shown schematically as Cell A in Figure 2.2. This arrangement has been used previously in tests with plutonium and cerium, but no metal was ever deposited in the previous tests with this cell. The failure to produce metal was attributed to the consumption of current by a cyclic process involving cathodic reduction of  $Ce^{4+}$  and anodic oxidation of  $Ce^{3+}$ . The most effective method that was previously apparent for overcoming this cyclic redox process was by maintaining a high cathode current density,  $>2$  amp/cm<sup>2</sup>; the high current density was not possible with this cell design because of the large surface area of the cathode. In the recent runs it was found that decreasing the concentration of  $CeF_3$  in the melt from 75 to 25 wt % permitted the production of metal with a current efficiency of about 10%. The more dilute melt apparently allows the formation of concentration gradients of  $Ce^{3+}$  at the cathode and  $Ce^{4+}$  at the anode, and thus promotes the desired production of metal at the cathode and  $CF_4$  at the anode.

The second type of cell used in the recent tests, shown as Cell B in Figure 2.2, is also a modification of a design previously used. The previous design, however, did not include the small graphite catch pot, and the efficiency of metal production was only about 30%; the efficiency was assumed to be limited by the same cyclic redox process and also by the oxidation by  $Ce^{4+}$  of part of the deposited metal after the metal dripped from the cathode. The catch pot was added to keep the deposited metal cathodic in order to prevent its reaction with  $Ce^{4+}$ . In the 2-hour run, about 30 grams of Ce was deposited in the catch pot; the over-all cathode current efficiency was about 30%. The anode current efficiency for the production of  $CF_4$  was also about 30%, as shown by chromatographic analysis of the off-gas. Although the electrodes were arranged to minimize the deposition of cerium on the outside of the catch pot, there was evidence that such deposition had occurred and that some cerium had dripped into the melt where it was oxidized by reaction with  $Ce^{4+}$ . The results of this test are consistent with those of several previous tests in implying that cyclic oxidation-reduction is the most important competitive side reaction that occurs under the conditions that have been studied to date.

The duration of the runs with each of the cells was limited to about 2 hours because of short-circuiting by graphitic deposits that accumulated on the melt surface. In Cell A the crucible wall eroded severely where the cerium was deposited. This erosion appeared to release particles of graphite that floated on the melt. In the case

of Cell B, the floating particles deposited first at the central cathode rod; the deposit then grew until it touched the anodes and short-circuited the cell. In one run the cell was purged with  $\text{CO}_2$  in an attempt to eliminate the problem by oxidizing the graphite to  $\text{CO}$ . Gas chromatographic analyses showed that at  $850^\circ\text{C}$  about 5% of the  $\text{CO}_2$  purge gas was converted to  $\text{CO}$ ; at  $950^\circ\text{C}$  the  $\text{CO}$  production increased tenfold but short-circuiting still occurred. This problem will be studied further in an attempt to extend the duration of the runs. Samples of silicon carbide and boron nitride were obtained and are being tested as crucible materials to replace graphite.



Run Conditions

Melt: 400g 28%  $\text{LiF}$  - 47%  $\text{BaF}_2$  - 25%  $\text{CeF}_3$   
 Temp:  $800-825^\circ\text{C}$   
 Current:  $\sim 25$  amps at 6 volts  
 Current Density: Anode  $0.25\text{a}/\text{cm}^2$   
                           Cathode  $0.15\text{a}/\text{cm}^2$

Run Conditions

Melt: 800g 28%  $\text{LiF}$  - 47%  $\text{BaF}_2$  - 25%  $\text{CeF}_3$   
 Temp:  $850^\circ\text{C}$   
 Current:  $\sim 30$  amps at 6 volts  
 Current Density: Anode  $0.5\text{a}/\text{cm}^2$   
                           Cathode  $3\text{a}/\text{cm}^2$

FIG. 2.2 ELECTRODEPOSITION OF PLUTONIUM

ELECTRODEPOSITION OF PLUTONIUM

MAY 1962

In the continuing laboratory study of the electrodeposition of plutonium metal from molten fluoride salts, additional runs were made with cerium as a stand-in for plutonium. Short-circuiting of the electrolysis cells by scums of graphite particles was nearly eliminated by the substitution of molybdenum or tantalum crucibles for the graphite crucible and by purging with  $\text{CO}_2$  to oxidize the carbon particles. Boron nitride and silicon carbide, as well as molybdenum and tantalum, were found to be fairly stable in the fused fluoride melts.

The additional runs were made with a cell of the simple design shown as "Cell A" in Figure 2.2 in the March report. In this design the crucible is used as the cathode and a graphite rod inserted in the melt is used as the anode.

In previous runs, when the concentration of  $\text{CeF}_3$  was kept below 25 wt % to decrease cyclic oxidation and reduction of cerium, 10-gram quantities of metal were deposited at about 10% current efficiency, but the duration of the runs was limited to about 2 hours by the accumulation of short-circuiting graphite particles that were eroded from the anode and the cathode by the electrode reactions. In one of the recent runs with a molybdenum crucible and a  $\text{CO}_2$  purge, the electrolysis was continued for 5 hours and as much as 55 g of cerium was produced at an average cathode current efficiency of 15%. The runs with the molybdenum crucible are summarized in the following table.

The runs with the metal crucibles were stopped for operating convenience; they could have proceeded considerably longer without short-circuiting. The cerium was deposited as a well-formed button in the bottom of the crucible. The button could not be removed easily because the cerium adhered to the molybdenum, but the cerium appeared to be sound and free from gross inclusions of melt.

Two runs under essentially the same conditions as those described in the table were made with a tantalum crucible, with similar freedom from short-circuiting. The cerium that deposited in these runs, however, did not coalesce, but was distributed through the salt phase so that the yield of metal could not be accurately determined. The only operating condition that was known to be different from the conditions of the runs with the molybdenum crucible was the cell temperature, which exceeded the intended 850°C.

The molybdenum crucible showed evidence of only very slight attack after many hours of use. The tantalum crucible was attacked to a much greater extent, but will be useful for a number of runs. In addition to these materials, boron nitride and silicon carbide were tested for corrosion in a LiF-BaF<sub>2</sub>-CeF<sub>3</sub> melt at 800°C. Two commercial types of silicon carbide were tested, "KT" silicon carbide (Carborundum), and "Crystolon 63" nitride-bonded silicon carbide (Norton). After 4 hours at 800°C, all of the specimens were attacked only slightly as indicated by a small loss in weight and an etched appearance. Crucibles of "Crystolon 63" have been ordered for further evaluation, and specimens of aluminum nitride were ordered for testing.

Because of the favorable results obtained with the metal crucibles, plans were made to resume the series of development tests with plutonium.

#### Electrodeposition of Cerium

Molybdenum crucible; CO<sub>2</sub> purge; 825-850°C  
 Melt 500 g [27% LiF, 46% BaF<sub>2</sub>, 27% CeF<sub>3</sub>]  
 Current Density Anode 0.75 amp/cm<sup>2</sup>; Cathode 0.25 amp/cm<sup>2</sup>

Run	Current, amp	Duration, hr	Cerium Yield, g	Cathode Current Efficiency, %
1	35	4.5	43	17
2	45	5	54	15
3	45	5	55	15
4	55	0.7	20	35

ELECTRODEPOSITION OF PLUTONIUM

JUL 1962

In the continuing laboratory study of the electrodeposition of plutonium metal from molten fluoride salts, additional runs were made with cerium as a stand-in for plutonium. The use of  $\text{CeO}_2$  rather than  $\text{CeF}_3$  as feed material greatly improved the operation. A 445-gram button of cerium was produced at 61% cathode current efficiency, in a run of 11.5 hours.

Previous tests with plutonium and with cerium had indicated that the electrolysis was more efficient with oxide as the feed material than with fluoride. Because the principal anode reactions produce CO and  $\text{CO}_2$  when the electrolyte contains dissolved oxide, both the anodic

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oxidation of  $Ce^{3+}$  to  $Ce^{4+}$  and the consequent loss of current by cyclic oxidation and reduction of the cerium are decreased. A major problem observed during the previous tests with oxide, however, was that the cerium did not coalesce but was dispersed in small nodules in the melt. The lack of coalescence was caused by undissolved oxide, which was difficult to avoid because the solubility of the oxide is only ~1.5 wt %.

In the new series of runs, the excess oxide was avoided by a combination of two techniques: (1) a continuous feed device provided a uniform rate of oxide addition, and (2) current was supplied substantially in excess of that required to reduce all of the oxide to the metal. The excess current was dissipated by cyclic oxidation-reduction of cerium, as evidenced by the fact that essentially no  $CF_4$  was evolved -- thus, the electrolysis of fluoride was negligible.

The new runs were made with a cell similar to that used successfully in previous runs with cerium fluoride. The tantalum crucible was the cathode, and a graphite anode was inserted in the center of the melt. In Run 1 in the following table, the graphite anode was a rod; in the other runs, the graphite anode was a perforated tube through which the  $CeO_2$  was added to the melt. The other conditions are summarized in the table.

The operation of the cell was smooth, and was not sensitive to minor variations in the operating conditions. The current efficiency at the cathode was controlled principally by the rate of feed addition, because a constant but excess current was supplied to the cell. A more meaningful evaluation of the runs is provided by the "feed utilization efficiency", which is the percent of the oxide feed that was reduced to metal. The feed utilization was high; lack of attainment of 100% reduction of the oxide was attributed to the fact that some of the oxide did not enter the melt, but dusted away from the crucible. The dusting was more evident in Run 1 with the anode rod than in the other runs in which the oxide was added through the tubular anode.

The cerium was deposited as a sound button in all of the runs. The button stuck to the tantalum crucible, and was removed either by dissolving or by melting. Analysis of the button from one of the runs showed the major impurities to be 420 ppm C and 320 ppm Fe. Smaller amounts of Mg, Mn, Sr, Al, Ba, Ni, and Cu were detected. The density was 99.4% of the theoretical value, and the cerium was sound and free from gross inclusions of the melt.

The major problem observed was that the anodes were not consumed uniformly but were attacked principally near the surface of the melt. The thin (1/8-inch-walled) tubular anodes fractured after 4 to 5 hours of operation; three anodes were consumed in this manner in the 11.5-hour run. The deterioration of the graphite is largely the result of operating with small cells and with a melt essentially depleted of oxide. Although the oxide has low solubility, it dissolves very rapidly near the surface

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of the melt where it is apparently rapidly electrolyzed under present operating conditions. The most obvious solution to the problem is the use of thicker anodes; the need for stirring is not apparent because the anode gases appear to agitate the melt vigorously. No trouble was experienced with short-circuiting scums of graphite particles, in contrast to (previous) runs with fluoride feed. The  $\text{CO}_2$  produced in the electrolysis of oxide apparently oxidizes the graphite particles that are eroded from the anode.

The runs have demonstrated that operation with oxide feed is smooth and predictable. Both the current efficiency and the rate of metal production were higher than previously obtained with fluoride feed, and further improvement appears to be feasible.

Plans were completed for resuming the series of development tests with plutonium. Metal crucibles will be used in the plutonium tests, and further comparisons will be made of oxide and fluoride feed materials.

#### Electrodeposition of Cerium

825-835°C; 5.3-5.5 volts; 48-52 amperes; helium blanket  
Tantalum crucible cathode; "CS" graphite anode  
Melt: 800-1000 g, 47%  $\text{BaF}_2$ , 28%  $\text{LiF}$ , 25%  $\text{CeF}_3$   
Current density: Cathode 0.2 amp/cm<sup>2</sup>; Anode 0.6 amp/cm<sup>2</sup>

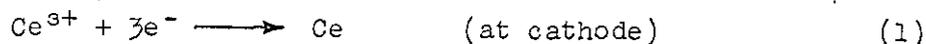
Run	Duration, hr	$\text{CeO}_2$ Feed, g/hr	Cerium Yield, g	Cathode Current Efficiency <sup>(a)</sup> , %	Feed Utilization Efficiency, %
1	5	33	109	35	82
2	4.5	34	109	39	87
3	11.5	51	445	61	93

(a) Calculated on the basis of  $\text{Ce}^{4+} \rightarrow \text{Ce} + 4e^-$

ELECTRODEPOSITION OF PLUTONIUM      OCT    1962

In continuing laboratory study of the electrodeposition of plutonium metal from molten fluoride salts, tests with plutonium were resumed after successful demonstration of the process with cerium as a stand-in for plutonium. In the most satisfactory procedure with cerium, as summarized in the July report, the average rate of production was 40 grams per hour when  $CeO_2$  was fed continuously to a molten mixture of  $LiF$ ,  $BaF_2$ , and  $CeF_3$  in a 2.8-inch-diameter tantalum crucible which was the cathode of the electrolysis cell; a hollow, perforated cylinder of graphite was the anode. In the preliminary tests of the analogous procedure with plutonium, however, the efficiency of the cell appeared to be more sensitive to the properties of the  $PuO_2$  feed than had been the case with  $CeO_2$ .

The major problem with most of the similar cells, with oxide feeds such as  $UO_2$  and  $ThO_2$ , arises from both the low solubility and the slow dissolution of the oxides in the molten salt, so that it is difficult to obtain the desired rates of electrochemical reaction without maintaining excess, undissolved, oxide in the cell; the excess oxide contaminates the molten metal product and interferes with its coalescence. The successful operation of the process with cerium oxide was found in more recent tests to be the result of assimilation of the oxide by a rapid chemical mechanism in addition to the slow mechanism of simple dissolution. When a melt of  $LiF$ - $BaF_2$ - $CeF_3$  is electrolyzed, the following electrode reactions apparently occur with high efficiency:



As the concentration of  $Ce^{4+}$  increases, the following cathode reaction competes with Reaction (1) and reduces the efficiency of metal production:



The cell efficiency (Reaction (1)) is high as long as dissolved oxide can be maintained in the electrolyte, because oxide ion is oxidized to  $CO$  at the anode, in preference to Reaction (2). The supply of dissolved oxide is difficult to maintain in most cases other than the cerium case, because of the slowness of dissolution of the oxide. In the case of the cerium cell, however, the cerium oxide that is added as feed reacts directly with the  $Ce^{4+}$  in the melt:



At temperatures in the region of  $800^\circ C$ , Reaction (4) is so rapid that oxygen is evolved vigorously. The reaction has two favorable effects: it reduces the anodically produced  $Ce^{4+}$ , thus improving the electrical efficiency of the cell, and it maintains an adequate concentration of

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dissolved cerium in the electrolyte (without depending on simple dissolution of the oxide) so that high rates of production are possible. The over-all cell reaction, the sum of Reactions (1), (2), and (4), is the same as if dissolved oxide were electrolyzed; the oxygen produced by Reaction (4) can react with graphite cell components to form  $\text{CO}_2$ .

Further tests were then made with plutonium to determine whether  $\text{PuO}_2$  would react with  $\text{Pu}^{4+}$ . The thermodynamic conditions are highly favorable for Reaction (4) in the case of cerium, but are marginal in the case of plutonium. Samples of plutonium oxide prepared by different methods were tested, because the oxide is known to be quite variable in reactivity. The tests were made with an electrolyte containing approximately 24 wt %  $\text{LiF}$ , 39 wt %  $\text{BaF}_2$ , and 37 wt %  $\text{PuF}_3$ ; the cell arrangement was the same as was used successfully with cerium. The oxide feeds for the three tests were prepared, respectively, by pyrohydrolysis of the fluoride,  $\text{PuF}_3$ , at  $600^\circ\text{C}$ , by decomposition of the oxalate,  $\text{Pu}_2(\text{C}_2\text{O}_4)_3$  hydrate, at  $400^\circ\text{C}$ , and by decomposition of the peroxide,  $\text{PuO}_4$ , at  $300^\circ\text{C}$ . Each test was limited to 45 minutes by the small supply of the oxides. The oxides were added to the cell at a rate equivalent to  $\sim 10$  g Pu per hour during the first 25 minutes, and at a rate equivalent to 20 g Pu per hour for the remainder of each test. The cell performance was evaluated on the basis of the  $\text{CO}$  and  $\text{CO}_2$  content of the off-gas. No significant quantity of  $\text{CF}_4$  was evolved in any test; the absence of  $\text{CF}_4$  indicated that essentially no direct electrolysis of fluoride was occurring.

When the plutonium dioxide prepared by pyrohydrolysis of  $\text{PuF}_3$  was fed to the cell, the off-gas composition indicated that only about 1 g Pu metal per hour was being produced; essentially the same rate of production was obtained at each feed rate. Significantly higher, but still very low, rates of production were obtained with the dioxides formed from peroxide and oxalate; the production rate was 7 g per hour at the slower feed rate and 9 g per hour at the higher feed rate, in contrast to the production rate of 40 g per hour for cerium. The tests demonstrated that the oxalate and peroxide produce dioxides that are more reactive than the dioxide prepared from the fluoride. The failure of the off-gas rate to show a proportionality between the feed rate and the production rate is a preliminary indication that the  $\text{PuO}_2$  is assimilated principally by dissolution rather than by reaction. Longer tests, with higher feed rates, will be made to study this point. The present tests were not long enough to assure steady-state off-gas rates, and the quantity of gas was not sufficient to measure very accurately.

Should further tests show that the plutonium dioxide is assimilated solely by dissolution, highly reactive forms of the dioxide and methods for obtaining fast dissolution of the oxide will be sought. In a parallel approach,  $\text{PuF}_3$  rather than  $\text{PuO}_2$  would be used as the feed compound and additives would be sought for reducing the anodically produced  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$ .

ELECTRODEPOSITION OF PLUTONIUM

L-10 1962

In the continuing laboratory study of the electrodeposition of plutonium metal, the desired rapid assimilation of plutonium dioxide feed by the mixed-fluoride electrolyte was obtained by operating at 950 rather than 835°C.

Slow assimilation of the plutonium dioxide in the electrolyte had been identified as the factor that limited the rate of electrodeposition in the first plutonium tests with the procedure by which cerium dioxide had been demonstrated to be converted rapidly to cerium. In those tests, which were described in the October report, the cathode of the cell was the tantalum crucible that contained the LiF-BaF<sub>2</sub>-PuF<sub>3</sub> electrolyte, the anode was a central graphite rod, and the cell was operated at 835°C, 4 to 5 volts, and 25 to 30 amperes.

The tests in October showed that PuO<sub>2</sub> that was prepared from plutonium oxalate or peroxide was assimilated more readily by the electrolyte than was PuO<sub>2</sub> that was prepared from plutonium fluoride, but none of the types of PuO<sub>2</sub> was assimilated completely. Inadequate assimilation was indicated by low CO and CO<sub>2</sub> content in the cell off-gas, and was substantiated by the presence of undissolved oxide in the cell after electrolysis.

The first of the two possible routes for assimilating the PuO<sub>2</sub> feed in the fluoride electrolyte is by simple dissolution; this assimilation is very slow and is limited by low solubility of the dioxide (~3 wt %). The second route is by the following reaction, which is analogous to the reaction that permits the successful operation of the cerium system.



The thermodynamic conditions for this reaction with plutonium are marginal; the reaction is reversible, and the change in free energy is quite small at the temperatures of interest. However, the change in free energy becomes slightly more negative with rising temperature. The successful assimilation of plutonium dioxide in the recent tests at 950°C could be the result of either increased rate of dissolution or increased rate of reaction, or both. Further tests will be made to define the mechanism.

In the first of the two recent tests at 950°C, a tantalum crucible was used and 30 g of PuO<sub>2</sub> was fed to the cell during a period of 1 hour. In the second test a graphite crucible was used and 105 g of PuO<sub>2</sub> was fed during a period of 3 hours. The cells were operated at 4.5 to 5.0 volts and 40 to 45 amperes. The rates of generation of CO and CO<sub>2</sub> during both tests were consistent with the feed rate, and responded rapidly to changes in the feed rate. The final electrolyte contained no undissolved PuO<sub>2</sub>.

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Plutonium metal was isolated in the first run as a thin film on the tantalum crucible. Because only 30 g of  $\text{PuO}_2$  was used in this test, the plutonium did not coalesce. In the run with the graphite crucible-cathode, the plutonium was deposited not as metal but as a black shell in the melt adjacent to the crucible. This shell formation may have been caused by the production of plutonium carbide, although the rate of formation of the carbide is reportedly quite slow below  $1000^\circ\text{C}$ . More than 50 g of plutonium was recovered from the graphite crucible by leaching with acid.

The two tests show that plutonium dioxide is assimilated rapidly and completely by the fluoride electrolyte at 900 to  $950^\circ\text{C}$ . Continuing tests of the process are being made with crucibles of tantalum or molybdenum, to avoid the possibility of carbide formation and to promote coalescence of the metal.

QUANTITATIVE ELECTRODEPOSITION BY CARRIER TECHNIQUE

JAN 1968

A new rapid technique was developed for electrodepositing actinides in 99.8% yield from aqueous solutions on alpha counting plates. The addition of uranyl nitrate ( $\sim 0.001M$ ) to the aqueous sample provides a carrier for the actinides and insures the quantitative deposit, which permits precise alpha counting (coefficient of variation 0.17% for ten measurements) and high resolution (1.5%) of alpha spectra. The new technique is well suited for precise accountability analyses and is expected to have many applications in radiochemical analysis.

Previously, alpha counting plates have been prepared by evaporating aliquots of solution or by subliming solid materials at high temperature in a vacuum. Evaporation of solutions is rapid and quantitative but the nonuniform deposit of solid material on the plate limits the precision of counting and the resolution of alpha spectra. Vacuum sublimation produces a uniform deposit for high resolution but is not quantitative and fractionation of elements in the sample occurs frequently.

The electrodeposition method of Mitchell<sup>(1)</sup> provides 97  $\pm$  3% yield of actinides in the  $10^{-12}$ -curie quantities typical of health physics analyses. The method has been used in the laboratory to prepare counting plates for high resolution of alpha spectra as described in the March report. Further analysis of Mitchell's data suggested that the rate and yield of deposition are direct functions of the concentration of the actinide being deposited. On the basis of this apparent relationship the addition of uranium as a carrier was evaluated and was found to be the key to quantitative electrodeposition. Uranyl nitrate was added to a plutonium nitrate solution in varying amounts and the treated solution was then electrodeposited on alpha counting plates. Uranium was selected as the carrier because of its low specific activity and its chemical similarity to plutonium. The increase in the deposition of plutonium with added uranium is shown in the following table.

Increased Deposition of Plutonium<sup>(a)</sup>

<u>Uranium Added,</u> <u>μg</u>	<u>Plutonium Deposited,</u> <u>%</u>
0	85
5	93
10	96

(a) Each sample contained 0.3 μg Pu and was electrolyzed 5 minutes with 2-amp current

<sup>(1)</sup> Mitchell, R. F., Anal. Chem. 32, 326 (1960).

JAN 1963

Ten alpha counting plates were prepared by the carrier technique. Each plate was prepared by the electrolysis of  $0.3 \mu\text{g}$  of plutonium contained in a  $1000\text{-}\mu\text{l}$  aliquot of stock solution. The electrolysis was continued (in the cell shown in Figure 2.3) for 20 minutes at 2 amperes. To obtain a maximum yield a total of  $30 \mu\text{g}$  of uranium in three  $10\text{-}\mu\text{g}$  increments was added at 5-minute intervals during the electrolysis. Each plate ( $\sim 25,000 \text{ c/min}$ ) was counted in a  $2\pi$  counter for a total of  $1.3 \times 10^7$  counts to give a counting error of only  $0.03\%$ . The yield was  $99.8 \pm 0.17\%$ , as determined by extraction analysis of the residual electrolyte.

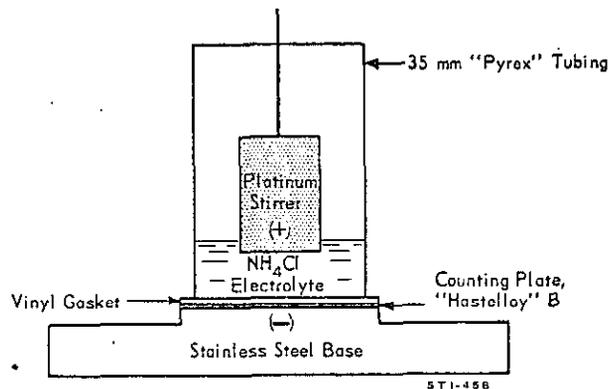


FIG. 2.3 ELECTRODEPOSITION CELL

The carrier technique for quantitative electrodeposition was very useful in the preparation of plates for determining  $\text{Am}^{241}$  and  $\text{Ce}^{144}$  in analyses for the Transplutonium Isotopes Program. Alpha (and even gamma) counting with good precision was not possible by other mounting techniques because of the high salt content ( $11\text{M LiCl}$ ) of the samples.

The improvement in electrodeposition removes a limitation to measurements of specific activity and half-life of various actinides. To exploit this advance, improvement in the precision of primary alpha standards will be attempted. At present the carrier electrodeposition is being evaluated as a highly precise method for accountability analyses for plutonium in unprocessed Purex feed solutions, as well as for  $\text{Pu}^{238}$  and  $\text{Np}^{237}$  in other processes.

ELECTRODEPOSITION OF PLUTONIUM FEB 1963

Continuing laboratory tests confirmed that utilization of the  $\text{PuO}_2$  feed is rapid and essentially complete when plutonium is electrodeposited from  $\text{LiF-BaF}_2\text{-PuF}_3$  electrolytes at  $950^\circ\text{C}$ . In contrast, the  $\text{PuO}_2$  was not assimilated adequately in previous tests at  $835^\circ\text{C}$ .

In all tests to date the utilization of  $\text{PuO}_2$  has been determined principally by analysis of the off-gas. In the two tests at  $950^\circ\text{C}$  that were described in the December report, a 1-hour test with 30 g of  $\text{PuO}_2$  in a tantalum crucible did not involve enough plutonium to produce an accurately recoverable deposit, and a 3-hour test with 105 g of  $\text{PuO}_2$  in a graphite crucible apparently led to the formation of plutonium carbide.

In a recent test at  $950^\circ\text{C}$  in a tantalum crucible, plutonium was produced as a visible film adhering to the crucible but the quantity of plutonium involved in the run ( $\sim 120$  g) formed a film only 10 to 15 mils thick and the quantity of plutonium deposited could not be determined directly by weighing. In this test, the cell was operated as usual at 5 volts and 50 amperes with the crucible as the cathode and a graphite rod as the anode;  $\text{PuO}_2$  was fed to the cell during 3 hours at 40 g Pu/hr. Analyses of the off-gas again indicated essentially complete utilization of the oxide feed. Tests with 300 grams or more of  $\text{PuO}_2$  feed have been planned, to obtain more conclusive data on the yield obtainable with the process.

Electrolytic removal of plutonium from spent fluoride electrolytes was tested briefly. Removal of the plutonium without aqueous processing of the spent electrolyte is desirable in the

FEB 1963

interest of economical operation, and would be particularly helpful in the event that electrodeposition is used for processing  $\text{Pu}^{238}$  or transplutonium elements. In the tests, other oxides such as  $\text{SiO}_2$  or  $\text{MgO}$  were added to spent cerium- or plutonium-containing electrolytes and the electrolysis was continued. Alloys (of  $\text{CeSi}$  or  $\text{PuMg}$ , for example) were deposited from both the cerium- and the plutonium-containing electrolytes. These tests will be continued to define conditions for complete removal of the plutonium and to explore the use of other oxides such as  $\text{Li}_2\text{O}$  or  $\text{BaO}$  with the objective of depositing the plutonium in nonalloyed form.

ELECTRODEPOSITION OF PLUTONIUM

APR 1963

Continuing laboratory tests led to more efficient conditions for electrodepositing plutonium from  $\text{PuO}_2$  in an electrolyte of fused fluorides. In one test 115 grams of plutonium was produced from 161 grams of  $\text{PuO}_2$  that was added continuously to the cell during five hours. The yield of metal represented about 95% conversion of the  $\text{PuO}_2$ . The efficiency of conversion was found to increase markedly with increasing current density at the cathode.

The electrodeposition of plutonium from fused salt systems has potential advantages over the present process, in which batches of plutonium fluoride are reduced with calcium. The electrolytic process could be adapted to continuous operation, and extended use of the same batch of electrolyte for several throughputs of  $\text{PuO}_2$  or  $\text{PuF}_3$  would reduce the amount of plutonium that must be recovered from reduction wastes.

The present tests indicate that the  $\text{PuO}_2$  is assimilated into the electrolyte principally by simple dissolution, without significant dependence on a chemical reaction such as was described in the December report:  $\text{PuO}_2 + 3\text{PuF}_4 = 4\text{PuF}_3 + \text{O}_2$ . In previous studies, the highly successful operation of the model cerium cell was shown to depend on chemical reaction of  $\text{CeO}_2$  with  $\text{CeF}_4$ .

In the recent series of tests the electrolyte contained 41.7 wt %  $\text{BaF}_2$  - 25.0 wt %  $\text{LiF}$  - 33.3 wt %  $\text{PuF}_3$ . The electrolyte was ~4 inches deep (600-700 grams) in all tests. A tantalum or molybdenum cathode crucible, 2 to 2.5 inches in diameter, contained the electrolyte, and a central graphite rod 1 to 1.25 inches in diameter was the anode.

To study the effect of current density at the cathode, the crucible size was decreased from 2.5 to 2 inches and the current was increased from 50 to 100 amperes in the series of tests shown in the following table. In all except the first test, the current density at the anode was near the maximum that was attainable without occurrence of the "anode effect", in which a nonconducting film of fluorocarbon is formed at the anode. The off-gas in all cases was entirely CO and  $\text{CO}_2$ , with no  $\text{CF}_4$ .

The data summarized in the table show that the conversion of the  $\text{PuO}_2$  increased with increased current density at the cathode. The percent of the  $\text{PuO}_2$  that is converted to plutonium is the most important indicator of the cell performance. The cathode current efficiency, which is of less importance,

APR 1963

was limited to a maximum of 15 to 20% by the low rate of addition of  $\text{PuO}_2$  and the operation of the cell under conditions such that only the oxide was electrolyzed. The influence of the current density on the conversion efficiency is explained by the competition between electrolysis of the oxide and the cyclic oxidation and reduction of plutonium between the Pu(III) and Pu(IV) valence states. At low current density, essentially all of the cell current is consumed by the cyclic reactions and no electrolysis products are formed. Higher current density causes increased electrode polarization, which decreases the cyclic reactions and increases the efficiency for electrolyzing the oxide.

The cell efficiency was calculated on the basis of off-gas analyses, and the values are therefore approximate. For a precise measurement of cell efficiency, the yield of plutonium metal must be measured accurately. In the first three tests, conversion of the oxide was low. Because considerable undissolved oxide accumulated in the cell, the plutonium did not coalesce well and only a fraction of it could be isolated. In the fourth test, in which the oxide conversion was quite high, the coalescence of the plutonium was much improved, although not complete, and isolation of the plutonium was greatly facilitated. The problem of coalescence will be studied in more detail in future tests.

The effect of increased temperature was studied in the third test. The only significant effects observed were increased corrosion of the crucible, increased formation of undesirable solids, and probably a slight decrease in cell efficiency.

The dependence of the efficiency of oxide conversion on current density and the generally low rate of assimilation of  $\text{PuO}_2$  indicate that simple dissolution is the principal mechanism of assimilation of the oxide. In addition, the absence of  $\text{O}_2$  in the off-gas indicated that the reaction of  $\text{PuO}_2$  with  $\text{PuF}_4$  is not important.

The large-scale tests with  $\text{PuO}_2$  as feed will be continued in an attempt to develop satisfactory production conditions.

#### Electrodeposition of Plutonium

Test	Temp, °C	Duration,		Current Density, amp/cm <sup>2</sup>		PuO <sub>2</sub> Feed Rate, g Pu/hr	Oxide Conversion, %	Cathode Current Efficiency, %	Pu Isolated, grams
		hr	amp-hr	Cathode	Anode				
1	950	8	400	0.25	0.5	39	30	10	50
2	950	3-1/2	230	0.4	1.0	30	70	14	43
3	1025	5	400	0.4	0.9	27	75	11	52
4	950	4-3/4	460	0.5	1.0	30	95	13	115

## GENERAL STUDIES

JUN 1963

ELECTRODEPOSITION OF PLUTONIUM

The rate of electrodeposition of plutonium was tripled by agitating the slurry of  $\text{PuO}_2$  in fused  $\text{BaF}_2\text{-LiF-PuF}_3$  electrolyte in continuing laboratory tests. Electrodeposition is being studied because it has potential advantages over the present process, in which batches of plutonium fluoride are reduced with calcium. Electrodeposition is expected to be adaptable to continuous operation, with substantial decrease in the over-all quantity of plutonium that must be salvaged from spent reduction residues.

Experiments that were summarized in the April report demonstrated that  $\text{PuO}_2$  can be converted directly to plutonium metal with ~95% efficiency of conversion and with essentially no depletion of the  $\text{PuF}_3$  in the electrolyte. The assimilation of the  $\text{PuO}_2$  in these previous tests was slow, however, and apparently depended on simple dissolution of the oxide in the molten electrolyte. The average rate at which the  $\text{PuO}_2$  could be fed to an unagitated electrolyte was equivalent to ~25 g Pu/hr. In the recent tests, agitation of the electrolyte increased this processing rate to ~85 g Pu/hr. As described in the following paragraphs, mechanical agitation and sparging with the anode gases were similarly beneficial.

The effect of mechanical agitation of the oxide-electrolyte slurry was tested with two stirrer designs; a tantalum crucible was used as the cathode in both tests. In the first design a perforated thick-walled graphite tube was used as the anode, and a molybdenum paddle whose shaft extended through the anode was used to agitate the slurry. Rates of deposition of plutonium, as indicated by off-gas analyses, were as high as 40 g Pu/hr, but the stirrer was dissolved anodically. In the second design a solid rod of graphite was used as the anode and also as the agitator. This test lasted 5 hours, with an average deposition rate of 30 g/hr; somewhat faster deposition (~40 g/hr) occurred during short periods. A portion of the plutonium deposited in this test was coalesced; the remainder was dispersed as very small beads. Because no excess  $\text{PuO}_2$  was found in the cell after the test, the dispersion was attributed to the vigorous agitation.

JUN 1963

Tests were then made without mechanical agitation but with the anode redesigned so that the anode gas would sparge the electrolyte and keep the oxide suspended. The modified anode was a large, perforated tube of graphite, the bottom of which was an inverted funnel that concentrated the flow of anode gas through the axial region of the cylinder. This principle has also been used recently with fused chloride electrolyte at Hanford. The  $\text{PuO}_2$  was added to the electrolyte at the top of the axial region. Thus, unassimilated  $\text{PuO}_2$  was suspended by the upward flow of gas and electrolyte, and was largely contained within the anode. The inner wall surfaces of the tantalum cathode crucible were insulated with a liner of magnesia so that most of the current flow, and generation of anode gas, occurred at the bottom of the cell. Good circulation of the electrolyte and rapid assimilation of the  $\text{PuO}_2$  were obtained. The cell design also provided for a high cathode current density ( $\sim 1 \text{ amp/cm}^2$ ), which has been shown to increase the cell efficiency. The operation during the first hour was quite satisfactory and encouraging; analyses of the off-gas indicated that the rate of deposition of plutonium was as high as 85 g/hr. Operation of the cell was limited to 2 hours by corrosion of the magnesia insulator, which was expected. The 2-hr yield of plutonium was 80 g, at least 93% of which was well coalesced.

These tests have shown that rather rapid assimilation of plutonium dioxide feed into the fluoride electrolyte is possible when good circulation is maintained within the cell. Further tests with new anode designs are in progress.

## GENERAL STUDIES

ELECTRODEPOSITION OF PLUTONIUM

AUG 1963

Continuing laboratory tests confirmed that the rate of electrodeposition of plutonium is increased substantially by directing the flow of anode gas to agitate the slurry of  $\text{PuO}_2$  in the fused fluoride electrolyte. The desired conditions, in which most of the current flow and generation of anode gas occur at the bottom of the cell, were obtained by redesigning the anode to eliminate the need for an insulating liner in the tantalum cathode crucible. In a 4-hour test with the new conditions 160 grams of coalesced plutonium was deposited, with essentially 100% utilization of the  $\text{PuO}_2$  that was fed to the cell.

Electrodeposition of plutonium in fused  $\text{BaF}_2\text{-LiF-PuF}_3$  is being studied because it has potential advantages over the present process, in which batches of plutonium fluoride are reduced with calcium. Electrodeposition is expected to be adaptable to continuous operation, with substantial decrease in the over-all quantity of plutonium that must be salvaged from spent reduction residues. The cells that are being used in the laboratory would be scaled up by a factor of ~5 for plant operation.

In previous operation of the cell with unagitated electrolyte the  $\text{PuO}_2$  was converted to plutonium with satisfactorily little depletion of the  $\text{PuF}_3$  in the electrolyte, but slow assimilation of the  $\text{PuO}_2$  limited its rate of addition to ~25 g/hr. As summarized in the June report, preliminary tests in which the oxide-electrolyte slurry was sparged with the anode gas increased the assimilation of the  $\text{PuO}_2$  and the deposition of plutonium to as much as 85 g/hr, but the duration of these tests was limited by rapid corrosion of the insulating liner that was used to confine the flow of current to the bottom portion of the cell.

The two cell designs studied in the recent tests are shown in Figure 2.6. The cells differ in the design of the graphite anodes and exhibit significantly different operating characteristics. Both of the anodes are cylindrically symmetrical and are so shaped that most of the current flow and generation of anode gas occur at the bottom of the cell. Thus, no insulating liner for the tantalum crucible is needed. Both cells were operated at 95-100 amperes and with a 2.5-inch depth of electrolyte (~750 g) containing 42 wt %  $\text{BaF}_2$  - 25%  $\text{LiF}$  - 33%  $\text{PuF}_3$ .

AUG 1963

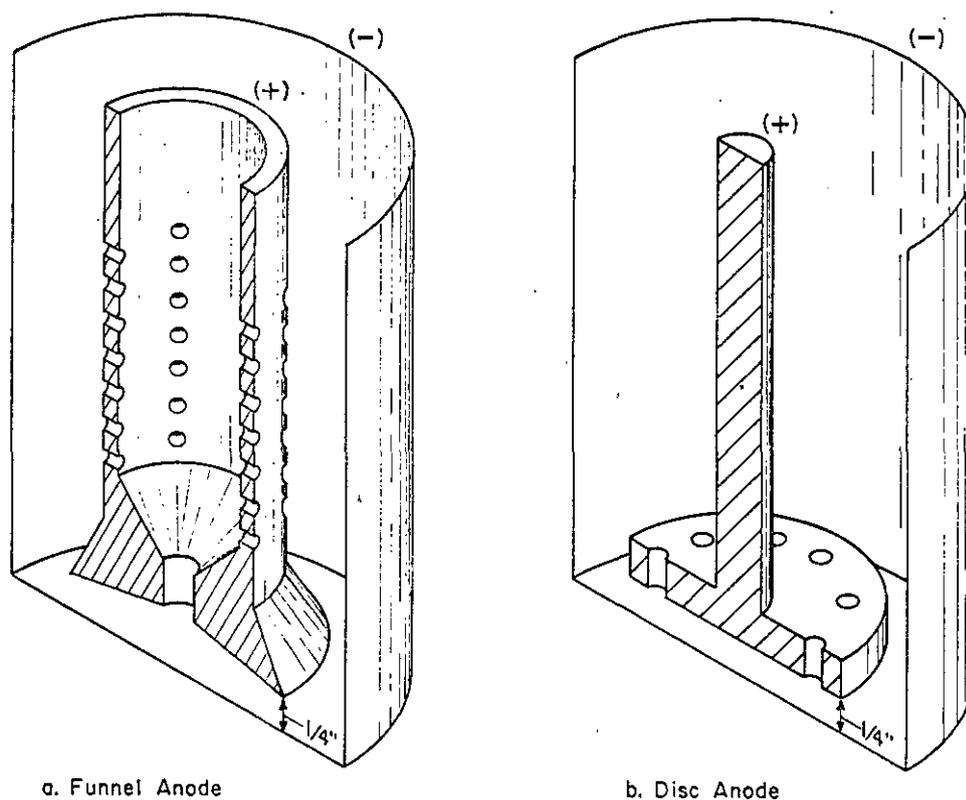


FIG. 2.6 PLUTONIUM ELECTRODEPOSITION CELLS  
Each Cathode is a Tantalum Crucible

The "funnel" anode of the cell shown in Figure 2.6a is a hollow cylinder perforated with holes. The  $\text{PuO}_2$  feed is added to the melt within the anode. The gas generated at the bottom of the anode sparges the melt and keeps the oxide in suspension. Most of the oxide is confined within the space enclosed by the anode until it is assimilated into the electrolyte. The average values of the cathode and anode current densities for this cell are 0.6 and 1.3 amp/cm<sup>2</sup>, respectively; the current densities are highest at the bottom of the cell because of the closer electrode spacing.

The anode of the cell shown in Figure 2.6b is a flat disc with a small-diameter support rod. The gas generated at the bottom of the disc flows up through holes in the disc and agitates the electrolyte quite vigorously. The  $\text{PuO}_2$  is fed at the top of the cell -- although the anode does not confine the  $\text{PuO}_2$ -electrolyte slurry the sparging provides substantial suspension and agitation. The average cathode and anode current densities are both approximately 1.5 amp/cm<sup>2</sup>. The current density is highest at the bottom of the cell.

AUG 1963

The cell with the funnel anode has been operated successfully in tests of 3 to 4 hours that yielded 100 to 125 grams of plutonium. The utilization of the  $\text{PuO}_2$  feed approached 100%, and current efficiencies as high as 20% were attained. The maximum production rate attainable with this cell is rather low, and is a function of temperature as shown in Figure 2.7. While several theories might account for the temperature effect, additional data will be obtained to define the mechanism. In 3-to-4-hour tests with the funnel anode cell at 900-950°, which is the usual operating temperature, deposition rates of 25-30 g Pu/hr have been attained.

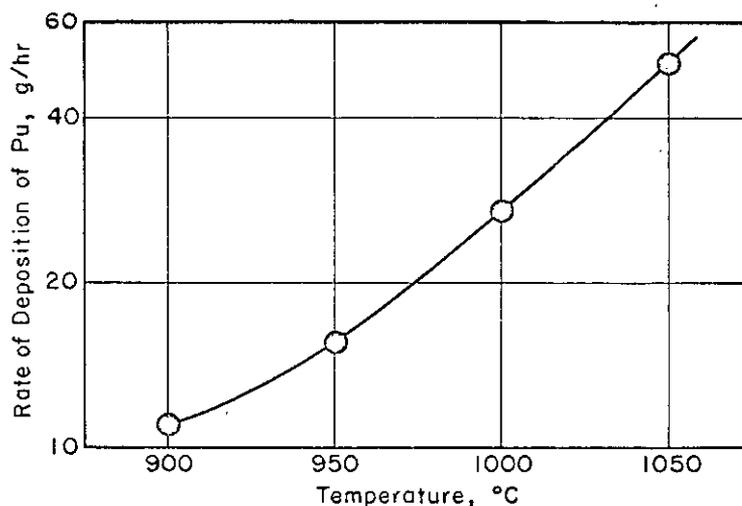


FIG. 2.7 EFFECT OF TEMPERATURE ON DEPOSITION OF Pu IN CELL WITH FUNNEL ANODE

The disc anode has been used in tests of 3 to 4 hours, which yielded as much as 160 grams of plutonium. The utilization of the  $\text{PuO}_2$  feed approached 100%, and current efficiencies were as high as 40%. The maximum production rate attainable with this anode design has not been determined; instantaneous rates of 75 g/hr have been observed. The effect of temperature on the operation with the disc anode has not yet been determined; all tests have been at 900°C.

The degree of metal coalescence has ranged from excellent to poor in these tests. About 95% coalescence has been obtained in the best runs. A small amount of dispersed metal does not seem to be troublesome. Best coalescence has been obtained by operating with the anode about 1/4 inch from the crucible bottom and centered in the cathode. Under these conditions deposition appears to occur almost entirely into the molten metal pool, which is the area of highest cathode current density. If the anode is not positioned correctly, the plutonium is deposited in small drops on the crucible wall.

AUG 1963

A sample of plutonium deposited in a recent test had satisfactory density, 19.1 g/cc, and was analyzed with the following satisfactory results.

Analysis of Deposited Plutonium, ppm

Al	77	Ca	<10
Cr	25	Cd	<10
Cu	40	Ga	<10
Fe	100	Mg	<10
Ni	50	Mn	<10
Pb	20	Sn	<10
Si	20	Zn	<50

The tests have shown the disc anode to be a highly promising design. Studies with this anode are continuing with the objective of defining the maximum rate of deposition, and preliminary design of cells for continuous operation is in progress.

ELECTRODEPOSITION OF PLUTONIUM

NOV 1963

Laboratory study of the electrodeposition of plutonium from fluxes of fused  $\text{BaF}_2\text{-LiF-PuF}_3$  was continued with the objective of increasing the deposition rate in cells with the disc anode described in the August report. In previous tests of 3 to 4 hours with these cells, about 40 g plutonium per hour was deposited with 100% utilization of the  $\text{PuO}_2$  feed; instantaneous rates based on off-gas analyses were as high as 75 g/hr. As much as 100 g/hr has now been deposited in recent short tests. This rate is adequate for a practical plant process.

Electrodeposition of plutonium is being studied because it has potential advantages over the present batch process in which batches of plutonium fluoride are reduced with calcium. Electrodeposition is expected to be adaptable to continuous operation, with substantial decrease in the overall quantity of plutonium that must be salvaged from reduction residues in the plant. The cells that are being used in the laboratory would be scaled up by a factor of ~5 for plant operation. A total of ~2.1 kg of plutonium has been electrodeposited in the tests during 1963.

NOV 1963

The electrodeposition fluxes in previous tests with plutonium contained initially 42 wt %  $\text{BaF}_2$  - 25%  $\text{LiF}$  - 33%  $\text{PuF}_3$ . In the three tests that are summarized in the following table the concentration of  $\text{BaF}_2$  was increased (52 wt %  $\text{BaF}_2$  - 15%  $\text{LiF}$  - 33%  $\text{PuF}_3$ ) and the cell was operated at increasing rates of addition of  $\text{PuO}_2$  to determine its capacity. All tests were made at 95-100 amperes and 6-7 volts, in a tantalum crucible cathode with a graphite disc anode.

In all tests the deposition rate as indicated by the off-gas rate was equal to the feed rate. In the first test the yield of plutonium was quite low; this low yield was probably due to an excessively large (1/2-inch) separation of the electrodes. In the second test the electrode separation was 1/4 inch and an excellent yield of coalesced plutonium was obtained, including a portion of the plutonium that had not coalesced in the first test. In the third test the yield was closely equivalent to the  $\text{PuO}_2$  added, but the plutonium was dispersed as a black solid. Inadequate control of temperature is believed to have been the cause of the lack of coalescence. The short (1- to 3-hr) tests demonstrated encouraging deposition rates of 100 g/hr.

#### Electrodeposition of Plutonium

	$\text{PuO}_2$ Feed, <sup>(a)</sup> g Pu/hr	Deposition, <sup>(b)</sup> g Pu/Hr	Plutonium Yield,		Current Efficiency, %
			g	% <sup>(c)</sup>	
1	35	~40	17	19	~3
2	70	~65	116	132	~49
3	117	~105	87	99	~53

(a) 100 g  $\text{PuO}_2$  (88 g Pu) was fed to each test.

(b) Indicated by off-gas rate.

(c) Based on the 100 g  $\text{PuO}_2$  fed during the test period.

Plutonium dioxide can be assimilated in the fluoride fluxes in two ways: (1) by dissolution, and (2) by a chemical reaction:  $\text{PuO}_2 + 3 \text{PuF}_4 = 4 \text{PuF}_3 + \text{O}_2$ . The solubility of the oxide is known to be low, and in some instances the oxide dissolves slowly. The rather high rates of deposition of plutonium that have been attained recently, however, indicate that the chemical reaction is assisting to some extent in assimilating the  $\text{PuO}_2$  in the flux.

Further evidence for the occurrence of the chemical reaction was obtained in the experiments summarized in the following table. In each experiment, 50 g of the flux was melted in a graphite crucible by heating to 900°C; 25 g of a  $\text{PuO}_2$ - $\text{PuF}_4$ - $\text{PuF}_3$  mixture was then added; and the slurry was

heated 1 hr at 900°C in an inert atmosphere. After cooling, the mixture was examined for residual  $\text{PuO}_2$  and the salt phase was analyzed to determine the total plutonium fluoride content and the Pu(III)-to-Pu(IV) ratio.

Plutonium Oxide Reaction Tests

Initial Flux, mol %	Final Plutonium Content	
	Fluorides, g Pu	Ratio, Pu(III)/Pu(IV)
1 100 LiF	17.8	0.23
2 80 LiF - 20 BaF <sub>2</sub>	17.5	3.3
3 80 LiF - 20 CaF <sub>2</sub>	15.9	2.1
4 50 LiF - 50 KF	19.0	6.7
5 60 LiF - 40 NaF	17.7	2.8
6 40 NaF - 60 KF	18.3	4.3
PuO <sub>2</sub> -PuF <sub>3</sub> -PuF <sub>4</sub> mixture added to each flux	15.1(a)	0.18(a)

(a) Initial value

The approximate composition of the initial plutonium oxide-fluoride mixture was 21 wt %  $\text{PuO}_2$  - 67%  $\text{PuF}_4$  - 12%  $\text{PuF}_3$ . In each experiment both the plutonium fluoride content of the mixture and the Pu(III)-to-Pu(IV) ratio were increased. These results indicate that  $\text{PuO}_2$  reacted with  $\text{PuF}_4$ , but the residue of  $\text{PuO}_2$  that remained after each test showed that the reaction did not proceed to completion. Because the preliminary data represent single determinations for each flux and the experimental error has not been determined, the results are not necessarily indicative of differences in the extent of reaction.

Electrodeposition tests of longer duration are now in progress and a new cell with provisions for continuous withdrawal of liquid plutonium is being evaluated in preliminary tests with cerium.

ELECTRODEPOSITION OF PLUTONIUM      MAR      1964

In the continuing laboratory study of the electrodeposition of plutonium, maximum production rates were determined for a cell that utilizes a carbon disc anode in a tantalum crucible cathode. In the previous tests with this cell that were summarized in the November report ~40 g plutonium per hour was deposited with 100% reduction of the  $\text{PuO}_2$  feed, in tests of 3 to 4 hours duration. This rate is adequate for a reasonable scale-up to plant operation. Production rates of 75 to 100 g plutonium per hour, which would reduce the number of cells needed in a plant installation, were obtained in tests of shorter duration, but these operations were erratic and not reproducible.

In recent tests, no significant improvement was made by varying either the composition of electrolyte or the temperature. Thus, the practical limit of throughput for this laboratory

cell (approximately 20% of a proposed plant-scale cell) was concluded to be about 50 g per hr.

Electrodeposition of plutonium in fused fluoride salt is being studied because of potential advantages over the present process, in which batches of plutonium fluoride are reduced with calcium. Electrodeposition is expected to be adaptable to continuous operation, with substantial decrease in the overall quantity of plutonium that must be salvaged from reduction residues.

The 15 recent electrolysis tests evaluated the effects of electrolyte composition and temperature. The arrangement and size of the cell were described in the August report. The sketch of the cell cross section is reproduced in Figure 9. The anode of the cell is a disc with a small-diameter support rod. The gas generated at the bottom of the disc flows up through holes in the disc and agitates the electrolyte quite vigorously. The  $\text{PuO}_2$  is fed at the top of the cell. The average cathode and anode current densities are both approximately  $1.5 \text{ amp/cm}^2$ . The current density is highest at the bottom of the cell. All tests were made at about 100 amperes and 6 to 7 volts. Data for representative tests are summarized in the following table.

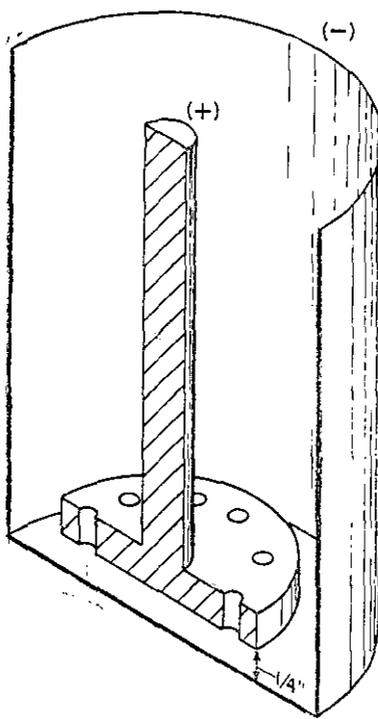


FIG. 9 PLUTONIUM ELECTRODEPOSITION CELL

The cathode is a tantalum crucible

MAR 1964

In the first series of tests, the melt was made richer in  $\text{BaF}_2$  than the previously used  $\text{LiF-BaF}_2$  binary eutectic (20 mol %  $\text{BaF}_2$  before  $\text{PuF}_3$  is added). The increased concentration of  $\text{BaF}_2$  increases the melting temperature and requires an operating temperature above  $900^\circ\text{C}$ . The yield of plutonium in these tests improved somewhat with increasing temperature, but was generally low. Because no beneficial effect of the increase in  $\text{BaF}_2$  was observed, the conclusion was drawn that the  $\text{LiF/BaF}_2$  binary eutectic ratio is the most favorable ratio for cell operation.

In the second series of tests, increased production rates were attempted at higher temperatures with melts containing  $\text{LiF}$  and  $\text{BaF}_2$  in the binary eutectic ratio. Again, increased temperature appeared to increase the yield of plutonium, but the operations were generally not satisfactory. In the last two tests the cell current was increased from 100 to about 125 amperes, and the cell operation deteriorated further.

#### Electrodeposition of Plutonium

Flux, mol %			Temp, °C	$\text{PuO}_2$ Feed, (a) g Pu/hr	Plutonium Yield, %
$\text{BaF}_2$	$\text{LiF}$	$\text{PuF}_3$			
33	57	10	925	35	32
			950	53	90
			975	52	45
			1050	53	90
18	72	10	900	75	55
			1000	75	39
			1000	77	103
			1000	70	18
			1000	96	30

(a) 100 g  $\text{PuO}_2$  (88 g Pu) was fed in each test.

The cell behavior in many respects was similar in these two series of tests. Occasional tests were satisfactory, but could not be reproduced. Good plutonium coalescence occurred only in the tests with high yields. The off-gas rate in nearly all cases indicated essentially 100% reduction of the  $\text{PuO}_2$  feed; excess residual oxide was never observed. In most tests solid phases different from pure plutonium accumulated at the bottom of the crucible and interfered with cell operation. These phases contain dispersed metal, oxyfluorides, double salts, and unidentified compounds, both alone and in combinations. The tantalum crucible was corroded deeply at the surface of the flux in the tests at the higher temperatures, possibly by oxygen produced by the reaction  $\text{PuO}_2 + 3\text{PuF}_4 \rightarrow 4\text{PuF}_3 + \text{O}_2$ . The corrosion was prevented in later tests by a graphite liner in the crucible. The over-all behavior in these tests indicates that the capacity of the cell was exceeded, and that no significant gain can be obtained by operating above  $900^\circ\text{C}$ .

MAR 1964

An additional analysis of electrodeposited plutonium indicates good quality although results are not yet available for tantalum, which is the impurity expected in highest concentration.

Analysis of Electrodeposited Plutonium

Density 19.5 g/cc

Al	22 ppm	Mg	<10 ppm
Ca	<10	Mn	<10
Cd	<10	Ni	<10
Cr	<10	Pb	<10
Cu	< 2	Si	< 5
Fe	60	Sn	<10
Ga	<10	Zn	<50

Further tests are in progress with the objective of reproducing, in extended operations, the highly successful performance that has been obtained in previous tests with lower deposition rates and at lower temperatures.

ELECTRODEPOSITION OF PLUTONIUM

MAY 1964

A series of tests was started with the objective of demonstrating the operating stability of the cell system that has been developed in continuing laboratory study of electrodeposition of plutonium. This cell, which has been chosen as the most promising of several alternatives for potential plant application, comprises a carbon disc anode in a tantalum crucible cathode as sketched in the March report. The electrolyte is molten  $\text{LiF-BaF}_2\text{-PuF}_3$  and the feed is  $\text{PuO}_2$ , which is added to the cell continuously.

Electrodeposition of plutonium in a fused fluoride salt system is being studied because of potential advantages over the current process, in which batches of plutonium trifluoride are reduced with calcium. Electrodeposition is expected to be adaptable to continuous operation, with substantial decrease in the over-all quantity of plutonium that must be salvaged from reduction residues.

One series of seven 50-g  $\text{PuO}_2$  demonstration tests was completed; a series of 100-g tests was started; and a final series of ~400-g tests is planned. The tests will give information on the durability of the cell components, the stability of the molten salt system, and the quality of the plutonium.

In the 9 recent tests the cell was operated at about 100 amperes and 6 to 7 volts; the feed rate was varied between 15 and 45 g Pu/hr; and the temperature was maintained near 1000°C. Optical pyrometry of the surface of the electrolyte provided more reliable control of temperature than was obtained with external thermocouples in contact with the crucible. Control of temperature is important because PuO<sub>2</sub> tends to accumulate in the bottom of the cell and prevent coalescence of the plutonium at temperatures below a critical value of about 925°C.

Data from the recent tests are shown in the following table. The 50-g tests, with the exception of the first and last, showed reproducibly good performance. The low yield in the first test was attributed to the low temperature, and the low yield in the last test was attributed tentatively to the higher rate of feeding PuO<sub>2</sub>, although yields from earlier tests at this feed rate had been satisfactory. Coalescence of the plutonium in Tests 2 through 6 was excellent, and the yields were good; the three yields below 100% are attributable primarily to inability to separate all of the plutonium when the frozen electrolyte is removed from the crucible.

The same sample of electrolyte was reused in the series of 50-g tests; the composition was adjusted slightly with LiF and BaF<sub>2</sub>. Barium fluoride was omitted from the first three tests to demonstrate that the process is not very sensitive to this variable. A small quantity of BaF<sub>2</sub>, however, reduces the volatilization of LiF.

The conditions for the two 100-g tests were essentially the same as those in the shorter tests, but new electrolyte was used. The first test showed a somewhat lower yield of plutonium, which is typical for the first operation with new electrolyte. Coalescence of the plutonium was excellent in both tests. This series of tests will be continued and the products of all tests will be analyzed for purity.

#### Electrodeposition of Plutonium

Flux, mol %			Temp, °C	PuO <sub>2</sub> Feed, g Pu/hr	Plutonium Yield, %
LiF	BaF <sub>2</sub>	PuF <sub>3</sub>			
<u>50 g PuO<sub>2</sub> (44 g Pu) per test</u>					
94.5	-	5.5	925	35	10
			1010	16	100
			1020	20	100
89	5.5	5.5	1010	16	83
91	5.0	4.0	1010	22	82
			1015	32	97
			1010	44	20
<u>100 g PuO<sub>2</sub> (88 g Pu) per test</u>					
88	6	6	1010	25	77
			1015	18	92