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MASTER

FUSED SALT ELECTROREFINING OF MOLTEN PLUTONIUM AND ITS ALLOYS

BY

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ABSTRACT

Results of an extensive development program that culminated in construction of a 40 kg. per month capacity electrorefining plant are reviewed. High purity plutonium is produced in good yield on the 0.2 to 3.5 kg. scale. Impure plutonium metal, plutonium-10 atom percent iron alloy, and plutonium-3.25 atom percent gallium alloy have been refined routinely to plutonium that contained less than 100 p.p.m. by wt. of metallic impurities. In addition to serving as a means of preparing high purity plutonium metal, the large scale process is used to recycle plutonium metal scrap economically.

The theory of plutonium alloy electrorefining is developed. In particular the behavior of elements that are commonly present in impure plutonium metal, such as uranium, thorium, iron and gallium, is reviewed. The special case of americium-241, which results from the decay of plutonium-241 is considered in detail. The distribution coefficients for americium between the molten salt electrolyte and the refined plutonium are reported. Results are correlated with thermodynamic properties and phase diagrams of plutonium alloy systems.

The effects of process variables such as refining temperature, current density, molten salt electrolyte composition, and stirring on the

process are discussed. In addition, various ceramics and refractory metals have been evaluated as container materials for molten salts and molten plutonium.

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INTRODUCTION

Commercial electrorefining processes have been generally limited to the relatively noble metals, i.e., copper, silver, gold, lead, and tin. Aluminum is a notable exception.

Recent developments in electrochemical processing of plutonium have been reported by Hanford Atomic Products Operations, Argonne National Laboratory. All of these processes have been conducted in fused salt systems because of the electropositive nature of plutonium. In spite of this common feature, the HAPO, ANL, and LASL processes differ markedly in purpose and in method.

The HAPO work has been oriented towards developing a large scale process to electrowin plutonium metal from plutonium(III) chloride.⁽¹⁾ The Argonne electrorefining method is directed towards producing relatively small quantities of very pure metal for metallurgical research.⁽²⁾

The Los Alamos process (LAMEX) has been directed towards producing relatively large amounts of metal of high purity by electrofining impure plutonium or its alloys. For example the early experiments were done to evaluate the potentiality of electrorefining plutonium-10 atom percent iron alloy fuel from the LAMPRE reactor.⁽³⁾

This paper summarizes the development of the LAMEX process for preparing plutonium metal of at least 99.98 percent purity from impure plutonium,⁽⁴⁻⁷⁾ plutonium-iron alloys,⁽⁸⁾ and plutonium-gallium alloys⁽⁹⁾. Based on these results, a plant having a 250 g. Pu/hr. capacity is now in operation at Los Alamos.

DESCRIPTION OF THE PROCESS

The preliminary design considerations are discussed in reference.⁽⁴⁾ The final design adopted, as the result of numerous experiments is shown schematically in Fig. 1. The cell consists of an outside container (2), 4-1/8 in. O.D. by 6-1/8 in. high, which contains the molten salt electrolyte and a concentric inner anode compartment (1) which contains 3.5 kg. of plutonium metal feed. Both containers are made of highly vitrified magnesia-3 w/o yttria and are cemented together. A perforated tungsten tube (5) serves as the cathode. A tungsten rod (4) protected by a magnesia sheath (6) conducts current to the anode metal (7). A magnesia stirrer (3) coupled to a stainless steel shaft and rotated by an electric motor is used to agitate both the anode metal and the electrolyte (9). The entire assembly is contained in a 5 in. O.D. stainless steel tube mounted in a commercial tube furnace, Hevi-Duty Electric Co. Model 5012. During operation, plutonium is oxidized at the anode, enters the molten salt electrolyte, and is reduced to metal at the cathode. The molten product (8) drains continuously into the annular product collection zone. The D. C. power supply is equipped with an automatic back e.m.f. sampling device (10).

- 1 Anode Container,
MgO-3 w/o Y_2O_3
- 2 Electrolyte container,
MgO-3 w/o Y_2O_3
- 3 Ceramic stirrer,
MgO-2 w/o Y_2O_3
- 4 Anode lead,
1/8 in. dia. W rod
- 5 Cathode cylinder, W
- 6 Protective anode sheath,
MgO-3 w/o Y_2O_3
- 7 Impure plutonium anode
- 8 Pure plutonium product
- 9 Molten salt electrolyte
- 10 Ammeter
- 11 Ampere-hour meter
- 12 Volt meter, manual
back e.m.f. indicator
- 13 Switch for interrupting
D. C. current

Fig. 1. Electrorefining cell, schematic drawing.

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The complete cell assembly is shown in Fig. 2.

The electrolyte consists of an equimolar mixture of NaCl and KCl and contains 2 mole per cent PuCl_3 , PuF_3 or PuF_4 . Smaller amounts of plutonium salts, 0.5 mole per cent, may be used in routine processing of plutonium metal scrap⁽¹⁰⁾ when a high purity product is not required.

The cell is operated at 740°C in an argon atmosphere. The general procedure consists of loading the cell with a plutonium anode feed cylinder and NaCl-KCl- PuCl_3 and heating to 740°C in an argon atmosphere. After the furnace components are positioned as shown in Fig. 2 the anode and salt phases are agitated by the ceramic stirrer. After a short pre-electrolysis period, 2 amps. for 1 hr., electrorefining with the large cylindrical cathode is started. The electrorefining is continued until it is terminated automatically by the back E.M.F. sampling unit. The cathode, stirrer and anode are then withdrawn from the melt and the cell is heated to 840°C to insure product coalescence. Upon cooling the furnace to room temperature the ceramic cell is broken apart and the plutonium product is recovered as an annular ring shown in Fig. 3.

THEORY

Metallic impurities associated with plutonium metal can be divided into two classes, those metals which are more electropositive than plutonium and those which are less electropositive (i.e., more noble) than plutonium. In the LAMEX process, where a stirred molten anode is used, the electropositive elements can be expected to concentrate in the salt

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Fig. 3. Plutonium Product.

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phase before any current is passed by virtue of a reaction such as

where all phases are liquid phases. Thus, when current is passed, the concentration of the electropositive impurities in the product will depend upon their concentration, with respect to plutonium, in the salt. If equilibrium conditions exist at the cathode, the following equation applies.

$$\left(\frac{\text{Am}^\circ}{\text{Pu}^\circ} \right) \text{ metal product} = \frac{1}{K} \left(\frac{\text{AmCl}_3}{\text{PuCl}_3} \right) \text{ salt} \quad (2)$$

where the parentheses refer to activities, and K is the equilibrium constant for equation (1). Even in the absence of equilibrium, equation (2) can be used to provide useful correlations of the behavior of electropositive elements.

Similar considerations can be applied to the behavior of the noble metal impurities. Again, the entry of impurity elements into the salt phase will be governed by an equation similar to (1) above. For example in the case of iron, an infinitesimal amount of iron will be dissolved to the extent permitted by the reaction

Since the standard free energy change⁽¹¹⁾ for the reaction is ~ 96 k cal/mole of PuCl_3^* , at 1000°K, any iron present in the salt phase will be

* This free energy value is equivalent to an equilibrium constant of 10^{-21} .

reduced to metal when current is passed.

Since the composition of the electrolyte does not change during the LAMEX electrorefining, the cathode processes can be assumed to be constant at the low cathode current densities which are used, 0.1 amps/cm^2 . The composition of the anode however changes continuously but uniformly during the process. This can be best understood by considering the electrorefining of a 10 a/o Fe-Pu alloy. Since only plutonium will be dissolved at the anode, the iron concentration will increase continuously during the electrorefining. From the phase diagram of Schonfeld et al.⁽¹²⁾, shown in Fig. 4, this increase will result in phase changes in the anode at all temperatures less than 1530°C . For example, at 740°C , the anode will be a single phase liquid up to ~ 25 a/o iron, liquid plus solid PuFe_2 up to 66.7 a/o iron and completely solid at 66.7 a/o iron.

As long as the iron concentration is less than 25 a/o, there should be essentially no polarization of a well-stirred anode. Because of the large differences in oxidation potentials between plutonium and iron, essentially no iron is dissolved anodically under these ideal conditions.

At this stage of the electrorefining process the net reaction is

and the free energy change for reaction (4) is

$$\Delta F = RT \ln \frac{(\text{Pu})_{\text{cathode}}}{(\text{Pu})_{\text{anode}}} = RT \ln \frac{1}{(\text{Pu})_{\text{anode}}} = -RT \ln (\text{Pu})_{\text{anode}} \quad (5)$$

Fig. 4. Pu-Fe phase diagram.

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where the parentheses refer to activities. Since the initial plutonium anode atom fraction is 0.9, the free energy change is small. The chemical potential,

$$E = \frac{RT}{nF} \ln (Pu)_{\text{anode}} = 0.0291 \ln (Pu)_{\text{anode}} \quad (6)$$

also is small at this stage.

When the iron concentration reaches 25 a/o, a $PuFe_2$ solid phase appears. Unless the anode is stirred well, this solid phase will float in the anode surface, thereby producing a polarized anode. However, if the anode is well stirred, polarization can be eliminated as long as some liquid phase remains. As the limit of this phase region is approached, i.e., as 66.7 a/o iron is approached, it becomes less possible to maintain a well-stirred anode, and serious anode polarization begins to occur. When the anode is seriously polarized, the net electrorefining reaction is

which corresponds to a potential

$$E = 0.0291 \ln (Pu)_{\text{solid anode surface}} \quad (8)$$

Generally the activity of the plutonium in the polarized anode surface will be considerably less than unity, which results in a measurable EMF for the cell. For example, when $(Pu)_{\text{solid anode surface}}$ is 10^{-3} , E is -0.20 volt.

During the initial stages of electrorefining, while there is a stirred liquid plutonium anode, the cell can be operated at high anode current densities that are required for reasonable processing times. However, after the anode solidifies, the same high anode current densities can be maintained only by dissolving iron at the anode. (The diffusion of plutonium in the solid anode is much too slow to meet the high current density requirements.) Therefore the electrorefining must be terminated before a significant amount of iron is dissolved anodically, if a pure plutonium product is to be achieved. As will be seen in the experimental part of this report, this condition is indicated by a rapid rise in the back e.m.f. of the cell, corresponding to equation 8, or

$$\text{Back e.m.f.} = -.0291 \ln (\text{Pu})_{\text{solid anode surface}}. \quad (9)$$

Similar considerations apply to the electrorefining of Pu-Ga alloys. According to Ellinger's phase diagram,⁽⁴³⁾ Fig. 5, at 750°C the anode will be a single phase liquid up to 16.8 a/o gallium, liquid plus solid up to 25 a/o gallium and completely solid at 25 a/o gallium. This latter value should be the limiting anode composition for LAMEX electrorefining at 750°C. Because the composition of the solidus changes with temperature, it is interesting to examine the effect of temperature on this limit. The fraction of Pu that can be dissolved anodically from a Pu-1 w/o Ga feed is given as a function of temperature in Fig. 6. (This curve was calculated from the phase diagram with the assumption that the electro-

Fig. 5. Pu-Ga phase diagram.

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Fig. 6. $D_{calc'd}$ vs. temperature for a Pu-1 w/o Ga alloys.

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refining would be terminated when the anode solidified completely.) It is apparent from this curve that the electrorefining cell should be operated at temperatures above 720°C.

PURITY AND YIELD OF TYPICAL PRODUCTS

Purity of Product

Generally, the product contains less than 100 p.p.m. of detectable metallic impurities.* Two of the principal impurities, W and Fe are introduced during the electrorefining process by attack of container materials. The other main impurity, Am, will be considered in detail later. Typical analyses of feeds and products for runs in which bomb reduced plutonium metal, plutonium-iron alloy, and plutonium-gallium alloy were used as feed are given in Table 1. The product densities in all cases were greater than 19.6 g./cc.

As discussed earlier, the behavior of impurity elements can be predicted qualitatively from the standard free energy of formation of the corresponding chlorides. This behavior is demonstrated in Table 2 where the elements are listed in order of increasing stability of their chlorides. Elements whose chlorides have a $-\Delta F^\circ$ greater than PuCl_3 concentrated in the electrolyte. The concentration values given in Table 2 are from ~ 50 electrorefining runs. Since the degree of purification obtained at any temperature will depend upon both the number of product throughputs (g product metal per g plutonium in salt) and the extent of anode depletion, only those runs for which the number of product throughputs exceeded 20 and the anode depletion exceeded 80 per cent are listed.

* Typical analyses for non-metallic impurities are 5 (± 3) p.p.m. N, 20 p.p.m. O, < 10 p.p.m. C and 5 (± 5) p.p.m. H.

TABLE 1

PURIFICATION OF PLUTONIUM, 10 w/o PuCl_3 -50.4 w/o KCl -39.6 w/o NaCl

ELECTROLYTE

Concentration of Element^b

Element ^a	Bomb-Reduced Metal		Pu-Fe Alloy		Pu-Ga Alloy	
	Feed	Product ^c	Feed	Product ^c	Feed	Product ^c
Al	75	< 5	15	< 5	75	< 5
Mg	75	< 5	90	5	75	< 5
Si	50	<10	20	<10	50	<10
Cu	10	< 2	< 2	< 2	50	< 2
Mn	7	< 2	7	< 2	7	< 2
Cr	40	<20	<20	<10	40	<20
Ni	110	<20	<20	<10	110	<20
U	30	<30	30	<30	90	<30
Th	124	<15	<15	<15	124	<15
W	<10	30	<10	40	410	28
Am	143	20	128	24	143	20
Fe	280	30	2.5×10^4	20	410	<20
Ga	<25	<25	<25	<25	1.02×10^4	<25

^aElements not detected in feeds or products include Na, Li, Be, La, Bi, B, Co, Cl, Y, Ca, Pb, Sn, Zn, and Ta.

^bParts of impurity per million parts of plutonium, weight basis.

^cProduct density was >19.6 g./cc..

TABLE 2

BEHAVIOR OF IMPURITY ELEMENTS IN ELECTROREFINING^a

Element	$-\Delta F^\circ$ ^b (kcal./g. atom Cl)	Concentration (p.p.m.)		Element Concentrated in
		Feed	Product	
Ni	18	750	<10	Anode
Cu	21	100	2	Anode
Ta	22	5000	80	Anode
Fe	27	25000	20	Anode
Cr	32	280	<10	Anode
Ga	32	10000	<25	Anode
Mn	41	70	< 2	Anode
Al	46	2700	< 5	Anode
U	54	275	<20	Anode
Th	59	160	<10	Anode
Pu	59	-	-	-
Ce	66	527	<25.	Salt
Am	67	850	82	Salt

^a $-\Delta F^\circ$ at 1000°K is tabulated. For elements having a multiplicity of oxidation states, the $-\Delta F^\circ$ for the most stable form of the chloride is given.

Since the concentrations of the elements in the product in most cases were either undetectable or at values close to the limits of the analyses, the values in Table 2 cannot be interpreted as defining the limits of the electrorefining process but merely suggest the capabilities of the method. Further, this table does not imply that a pure product would be obtained in good yield if all impurities were present in the same feed at the indicated concentrations.

Yields

The overall yield of plutonium metal can be considered as two separable yields, (1) the fraction of plutonium that is dissolved at the anode, and (2) the fraction of plutonium deposited on the cathode that is collected as a massive ingot. The fraction of plutonium that can be dissolved at the anode depends on the nature and amount of impurities that are present in the anode feed metal. Generally, electrorefining of the plutonium can be continued as long as the anode remains free from serious polarization. Bomb reduced metal, typical of that shown in Table 1 may be refined until 95 percent of the plutonium has been dissolved anodically.* The Pu-Fe and Pu-Ga alloys shown in Table 1 may be refined until ~88 and ~91 percent, respectively, of the plutonium has been dissolved anodically. In systems that are relatively free from reactive gases (oxygen, nitrogen, water) experience has shown that ~ 95 percent of the plutonium that is reduced at the cathode is collected in the massive ingot.

Plutonium Alloy Electrorefining

Experimental Results

The results reported thus far pertain to systems in which the anodes are essentially free of polarization. In both the Pu-Fe and Pu-Ga systems however serious polarization occurs when the anode is depleted excessively of plutonium. This polarization for the Pu-Fe alloy

* In this case, the geometry of the anode container imposes the 95% limit. The anode residue is recycled as feed material. Obviously the 95% depletion could be extended by tapering the bottom of the anode cup.

is shown in Fig. 7, where the back e.m.f. is plotted as a function of R, the atomic ratio of iron to plutonium in the anode. As anticipated, the back e.m.f. increases as the anode is depleted of plutonium. The back e.m.f. decays rapidly in the first 30 seconds after current interruption. However, the back e.m.f. always increases as R is increased, for any given time, θ .

Plots of back e.m.f. at $\theta = 0$ vs. R for two typical electrorefining runs are given in Fig. 8. In both cases there is a sudden rise in the back e.m.f. when $R = \sim 0.7$; both experiments were terminated at back e.m.f. values less than 0.6 volt. The small inset figure, back e.m.f. vs. D,* where D = fraction of the plutonium feed metal dissolved at the anode, shows how rapidly the back e.m.f. is actually changing during the terminal stages of the electrorefining process. Thus in Run 5, the back e.m.f. changed from a value of 0.10 volt at 86% plutonium dissolution to values of 0.32, 0.42, 0.51 and 0.57 volt at 88% dissolution. (The latter values are all for 88% dissolution.) A plot of back e.m.f. vs. R for an experiment in which the anode was depleted to $R = 2$, Run 2, is given in Fig. 9. As in the previous figure, the back e.m.f. rises rapidly at $R = \sim 0.7$; however, the back e.m.f. behavior is erratic at values of R above 1.1.

*D is related to R by the following equation

$$D = 1 - \left(\frac{x}{100-x} \right) \left(\frac{239}{55.85} \right) \left(\frac{1}{R} \right)$$

where x = w/o Fe in Pu-Fe alloy feed.

Fig. 7. Back e.m.f. vs. θ for different anode compositions, Pu-Fe alloy.

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Fig. 8. Back e.m.f. at $\theta = 0$ vs. R for two typical Pu-Fe electrorefining runs.
(Inset: Back e.m.f. at $\theta = 0$ vs. D for Run 5.)

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Fig. 9. Back e.m.f. at $\theta = 0$ vs. R for large terminal value of R, Run 2, Pu-Fe alloy.

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Continuation of the electrorefining process beyond the point at which serious polarization is indicated results in contamination of the product. For example in the experiment described above in which the anode was depleted to $R = 2$, the product contained 1600 - 3800 p.p.m. of Fe. If the process is terminated when polarization is indicated, essentially no iron is transported from the anode to the cathode, see Table 3.

The results of the Pu-Ga electrorefining experiments were quite similar to the Pu-Fe runs. A plot of back e.m.f. vs. θ for different anode compositions is given in Fig. 10. The results of 4 experiments are given in Table 4. Termination of the process at back e.m.f. values of ~ 0.5 volt resulted in products containing less than 30 p.p.m. of Ga. Continuation for 2 hrs. after the back e.m.f. was 0.5 volt, run 2 Table 4, resulted in a product containing ~ 700 p.p.m. Ga.

Comparison of Theory and Experiment

The experimental control of product purity and anode depletion was in general agreement with the theory discussed above. For the case of the Pu-Ga alloy, the phase diagram predicts serious anode polarization at $R \leq 0.32$ (the anode will be completely solid at 740°C at $R = 0.32$). Three experiments gave an average value of $R = 0.37 (\pm 0.05)$. The agreement with the theory is therefore reasonable.

TABLE 3

SUMMARY OF 3.5 kg Pu-Fe ELECTROREFINING RUNS

<u>Pu-Fe Run</u>	<u>Current, amp.</u>	<u>Terminal Back E.M.F., volts</u>	<u>D</u>	<u>R</u>	<u>Fe Concentration, w/o</u>	
					<u>Metal Feed</u>	<u>Product</u>
1	19	0.60	0.74	0.96	5.55	0.002
3	25	0.58	0.84	0.66	2.46	0.003
4	25	0.70	0.86	0.78	2.49	0.003
5	25	0.60	0.89	0.91	2.32	<0.002
6	25	0.50	0.91	1.03	2.21	0.002
7	40	0.54	0.84	0.68	2.54	0.002
8	25	0.52	0.90	1.13	2.58	0.002

Fig. 10. Anode residue, top surface, Run 6.

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TABLE 4

SEPARATION OF PLUTONIUM AND GALLIUM IN 3.5 KG. SCALE

ELECTROREFINING EXPERIMENTS

10 w/o PuCl_3 Electrolyte

Run	Current amp.	D	Terminal Anode Comp., ^a	Product Density, g./c.c.	p.p.m. Ga in	
			R		Feed	Product
1	15	0.916	0.42	19.67	1.02×10^4	<25
2	25	0.944	0.63	18.75	1.02×10^4	700 ^b
3	25	0.885	0.30	19.62	1.01×10^4	<30
4	25	0.916	0.39	19.69	0.94×10^4	<30

^a $R = \frac{\text{atoms Ga}}{\text{atoms Pu}}$ (R is calculated from the initial and final anode weights because the anode residue is so badly segregated that representative samples for chemical analysis are unobtainable.)

^bAnalyses of top, middle, and bottom samples of ring were 1400, 310, and 270 p.p.m., respectively.

For the case of the Pu-Fe alloy, the theory predicted serious anode polarization at $R \leq 2.0$ (the anode will be completely solid at $R = 2.0$ at temperatures below 1220°C). The experiments gave an average value of $R = 0.88 (\pm 0.15)$. Although this value is smaller than expected, the extremely slow rate of diffusion of Pu in the anode at the end of a run and the physical appearance of the anode residue show that the anode is actually in a "paste-like" condition at the termination of the electrorefining. The slow rate of diffusion is shown in Fig. 11, where the terminal back e.m.f. as a function of time is given for Run 8. After a period of 24 hr., the back e.m.f. decayed from an initial value of ~ 0.5 volt to 0.018 volt; the calculated value for the back e.m.f. assuming no polarization and an activity coefficient of unity for plutonium in the liquid metal phase is 0.008 volt from the liquidus curve of Fig. 1. The physical appearance of many of the anodes (for examples, see Fig. 12) showed that the metal was solid or paste-like at the termination of the electrorefining. Although the cell was heated to 840°C after the stirrer and anode rod were withdrawn from the cell,* the anode residues still retained the voids created by the stirrer and anode rod.

* For complete operational details, see reference⁽¹⁰⁾.

Fig. 11. Back e.m.f. vs. $\log \theta$ for large values of θ .

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Fig. 12. Anode residue, bottom surface, Pu-Fe Run 5.

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Americium Distribution

241 Americium grows into plutonium metal, as the result of the β decay of Pu^{241} , at the rate of ~ 15 p.p.m. per month. It is therefore always present as an impurity in plutonium. As indicated earlier in the theory the separation of plutonium from americium is determined principally by the concentration of PuCl_3 in the electrolyte, equation (2). A summary of the Am distribution data for 44 multikilogram electrorefining runs is given in Table 5. (The Am and Pu concentrations were determined by analyzing samples of the solidified salts and metal product rings.) Table 5 indicates that fluoride has a deleterious effect on the Am separation. This effect can be offset, however, by increasing the PuF_3 concentration.

TABLE 5

Am DISTRIBUTION IN MULTIKILOGRAM ELECTROREFINING RUNS

<u>Pu Halide</u>		<u>No. of Electrorefining Runs</u>	<u>K^a</u>
<u>Salt</u>	<u>Init. Conc., m/o</u>		
PuCl_3	2.10	19	190 ± 20
PuCl_3	0.49	3	220 ± 20
PuF_3	2.10	2	65 ± 1
PuF_3	0.49	20	110 ± 10

$$a_K = \frac{\text{parts Am/million parts Pu (salt phase after run)}}{\text{parts Am/million parts Pu (metal product)}}$$

It is interesting to compare the value of K reported in Table 5 with those obtained by simply equilibrating (Pu)Am metal with (2.10 m/o PuCl_3 -NaCl-KCl) salt. According to the theory already discussed if equilibrium conditions exist at the cathode, the values of K should be identical. The equilibration of 262 g. of Pu° containing 362 p.p.m. of Am with 110 g. of salt (2.10 m/o PuCl_3) gives a value of $K = 227$ at 740°C .

EFFECT OF MATERIALS OF CONSTRUCTION ON PURITY OF PRODUCT

During the development phase of the process, the following modifications were introduced, primarily to improve the product purity:

- (1). Electrorefined metal was not allowed to contact tantalum cell components. Instead, tungsten parts were used. This resulted in a decrease in refractory metal content of from about 500 p.p.m. tantalum to about 30 p.p.m. tungsten.
- (2). The stirrer was changed from tantalum to ceramic. Although magnesia is more desirable from the compatibility viewpoint, alumina is satisfactory in chloride electrolytes.
- (3). Alumina was replaced by magnesia as the principal material of construction of the cell. This altered the impurity content in the product metal from about 40 p.p.m. aluminum to less than 5 p.p.m. magnesium.
- (4). When magnesia was the principal material of construction for the cell, plutonium fluoride could be used in place of the plutonium chloride electrolyte. (Generally, plutonium fluoride is more readily available than the chloride.) The use of mixed fluoride-chloride

was very unsatisfactory when alumina cells were used. The aluminum concentration was increased from 40 to 450 p.p.m.

1. Martin H. Curtis, "Continuous Electrowinning of Plutonium from Chlorides Melts", presented at Electrodeposition Division Symposium, Electrochemical Society Meeting October 1, 1963.
2. B. Blumenthal and M. B. Brodsky, "The Preparation of High Purity Plutonium" Plutonium 1960, pg. 171, Cleaver-Hume Press Ltd., London.
3. J. A. Leary, et. al., "Pyrometallurgical Purification of Plutonium Fuels", Peaceful Uses of Atomic Energy Volume 17 376 (1958).
4. L. J. Mullins, J. A. Leary, and C. W. Bjorklund, "Large Scale Preparation of High Purity Plutonium Metal by Electrorefining," Los Alamos Scientific Laboratory Report LAMS-2441 (1960).
5. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Electrorefining," Los Alamos Scientific Laboratory Report LA-2666 (1962).
6. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Electrorefining," Ind. Eng. Chem. Process Design Develop., 2, 20 (1963).
7. L. J. Mullins and J. A. Leary, "Multikilogram Electrorefining of Plutonium Metal," First Australian Conference on Electrochemistry, February 1963, Paper No. 73, Pergamon Press, Oxford, England, (in press).
8. L. J. Mullins, J. A. Leary, and A. N. Morgan, "Large-Scale Electrorefining of Plutonium from Plutonium-Iron Alloys", Los Alamos Scientific Laboratory Report LA-3029 (1964).
9. L. J. Mullins, J. A. Leary, and A. N. Morgan, "Large-Scale Electrorefining of Plutonium from Gallium Alloys", Los Alamos Scientific Laboratory Report LA-2758 (1962).
10. L. J. Mullins, J. A. Leary, and A. N. Morgan, "Operating Instructions, Procedures, and Equipment for the Los Alamos Plutonium Electrorefining Plant", Los Alamos Scientific Laboratory Report LA-2981 (1963).
11. Glassner, A., "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K," Argonne National Laboratory Report ANL-5750 (1957).
12. F. W. Schonfeld, E. M. Cramer, W. N. Miner, F. H. Ellinger, and A. S. Coffinberry, "Plutonium Constitutional Diagrams," Progr. Nucl. Energy, Ser. V., Vol. 2, Metallurgy and Fuels, 585 (1959).
13. Ellinger, F. H., Land, C. C. and Streubing, V.O., "The Plutonium-Gallium System", J. Nuclear Materials, (in press).