

c.3

LA-3029

CIC-14 REPORT COLLECTION
**REPRODUCTION
COPY**

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

LARGE SCALE ELECTROREFINING OF
PLUTONIUM FROM PLUTONIUM-IRON ALLOYS



LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Price \$ 0.75. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

UNIVERSITY OF CALIFORNIA

LOS ALAMOS SCIENTIFIC LABORATORY
(CONTRACT W-7405-ENG-36)
P. O. Box 1663
LOS ALAMOS, NEW MEXICO

IN REPLY
REFER TO:

August 10, 1964

To: Copyholders of LA-3029

From: Report Library

Subject: ERRATA TO LA-3029

Please make the following corrections in the above report:

Page 10, line 6

Change 67.5 to read 66.7

Page 10, line 7

Change 67.5 to read 66.7



LA-3029
UC-4, CHEMISTRY
TID-4500 (27th Ed.)

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: October 10, 1963

REPORT DISTRIBUTED: April 7, 1964

LARGE SCALE ELECTROREFINING OF
PLUTONIUM FROM PLUTONIUM-IRON ALLOYS

by

L. J. Mullins
J. A. Leary
A. N. Morgan



This report expresses the opinions of the author or authors and does not necessarily reflect the opinions or views of the Los Alamos Scientific Laboratory.

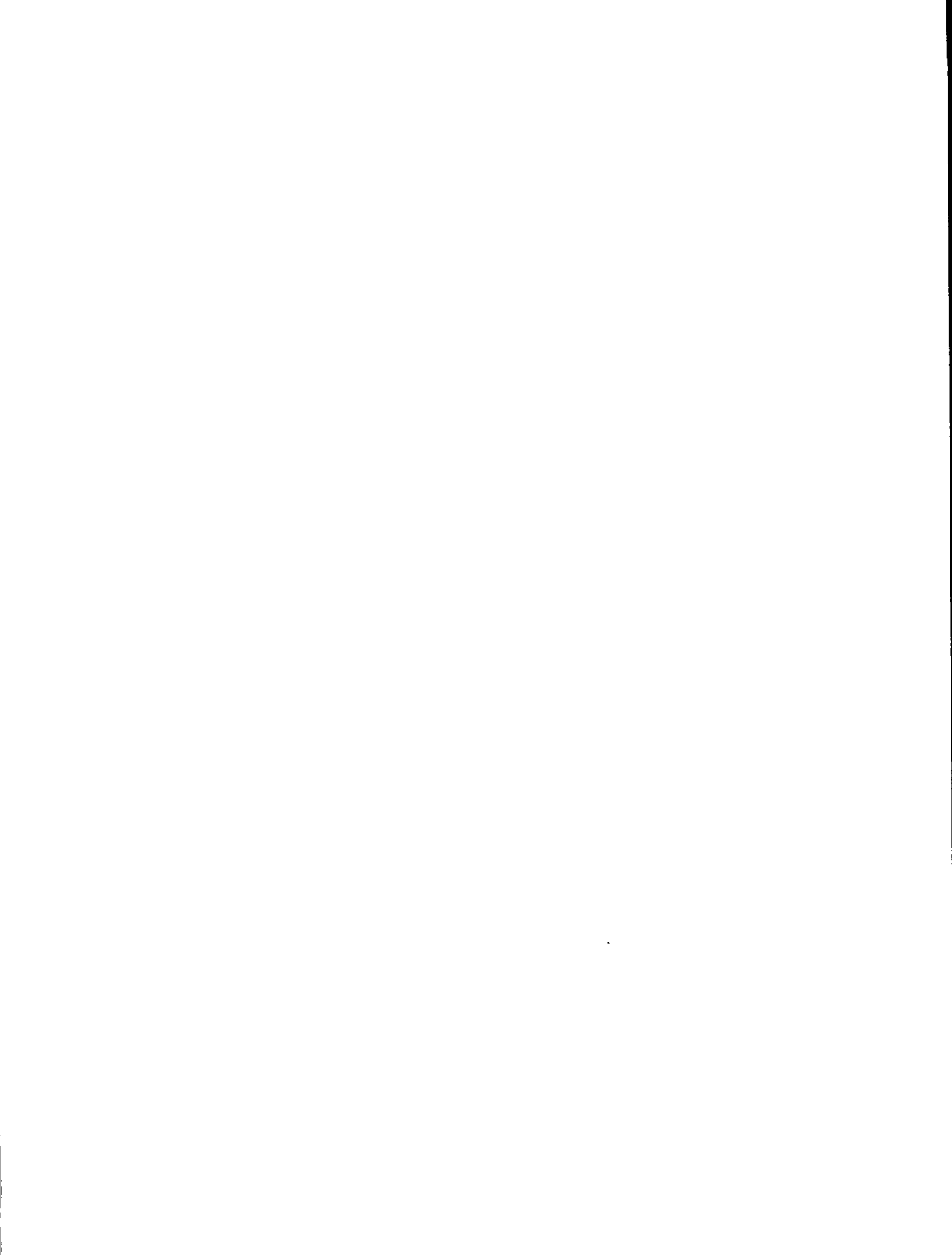
Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission



ABSTRACT

Electrorefining processes have been developed for the recovery of plutonium from plutonium-iron alloys on the 3.5 kg. scale. The process can be controlled to produce plutonium metal containing <35 p.p.m. of iron and a total of <100 p.p.m. of detectable metallic impurities. With an alloy initially containing 2.50 w/o iron, the recovery yield is ~82%.

The theory of plutonium alloy electrorefining is discussed, and a method based on back e.m.f. measurements for controlling the process automatically is presented.



CONTENTS

| | Page |
|---|------|
| Abstract | 3 |
| Introduction | 7 |
| Theory | 7 |
| Experimental | 13 |
| Preparation of Electrolyte | 13 |
| Preparation of Plutonium-Iron Anodes | 13 |
| Fabrication of Ceramics | 14 |
| Equipment | 14 |
| Procedure | 16 |
| Results and Discussion | 16 |
| Back E.M.F. as a Function of R | 16 |
| Product Purity as a Function of R | 19 |
| Permissible Anode Depletions | 22 |
| Product Yield | 24 |
| Product Purity | 25 |
| Comparison of Theory and Experiment | 27 |
| Conclusions | 33 |
| Glossary of Symbols, Terms, and Equations | 34 |
| References | 35 |

TABLES

| | <u>Page</u> |
|---|-------------|
| 1. Product Purity as a Function of R | 22 |
| 2. Summary of Pu-Fe Electrorefining Runs | 23 |
| 3. Plutonium Material Balance, Run 4 | 25 |
| 4. Analyses of Feeds and Products, 3.5 kg. Scale Plutonium-Iron Electrorefining | 26 |
| 5. Am Distribution in Multikilogram Electrorefining Runs | 27 |

FIGURES

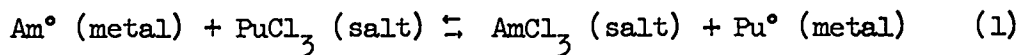
| | |
|---|----|
| 1. Plutonium-iron phase diagram | 11 |
| 2. Electrorefining cell, schematic drawing | 15 |
| 3. Electrorefining cell assembly | 17 |
| 4. Back e.m.f. vs. θ for different anode compositions | 18 |
| 5. Back e.m.f. at $\theta = 0$ vs. R for two typical electrorefining runs (Inset: Back e.m.f. at $\theta = 0$ vs. D for Run 5) | 20 |
| 6. Back e.m.f. at $\theta = 0$ vs. R for large terminal value of R, Run 2. | 21 |
| 7. Back e.m.f. vs. $\log \theta$ for large values of θ | 29 |
| 8. Anode residue, top surface, Run 5 | 30 |
| 9. Anode residue, bottom surface, Run 5 | 31 |
| 10. Anode residue, top surface, Run 6 | 32 |

INTRODUCTION

The Los Alamos molten plutonium electrorefining process (LAMEX process) for preparing high purity plutonium metal in kilogram quantities has been described in earlier reports.¹⁻⁵ These reports were concerned primarily with the development of a method for purifying plutonium metal containing about 0.2 w/o metallic impurities in batches of 500 g. and 3.5 kg. The extension of the LAMEX process to the electrorefining of plutonium-iron alloys is given in this report. (This alloy is of interest because of its use as fuel in the LAMPRE nuclear reactor.)⁶

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

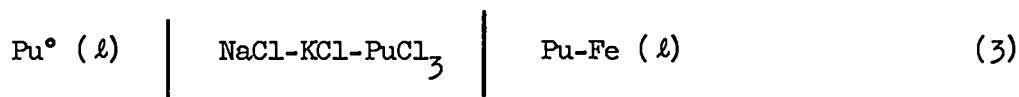


Thus, when current is passed, the concentration of the electropositive impurities in the product will depend upon their concentration, with respect to plutonium, in the salt. If equilibrium conditions existed at the cathode, the following equation applies

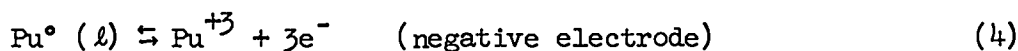
$$\left(\frac{\text{Am}^\circ}{\text{Pu}^\circ} \right) \text{ metal product} = \frac{1}{K} \left(\frac{\text{AmCl}_3}{\text{PuCl}_3} \right) \text{ salt} \quad (2)$$

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.

The behavior of the noble metal impurities can perhaps be understood best by considering the case of a plutonium concentration cell which could be used for determining the activity of plutonium in a plutonium-iron alloy. (The principle and theory of operation of such cells are summarized well in references 7 and 8.) Such a cell would be represented as follows:



The electrode reactions would be





Net cell reaction:

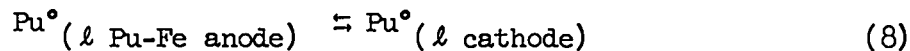


The free energy change and potential for this cell would be

$$-\Delta F = nFE = -RT \ln \left(\frac{\text{Pu}}{\text{Pu-Fe}} \right) \quad (7)$$

where the parentheses refer to activity and the standard electrochemical symbols are used, (see Glossary).

Similar considerations can be applied to hypothetical Pu-Fe electrorefining cells operating under reversible conditions. The net reaction for such a cell would be the reverse of equation (6) or



Since only plutonium would be dissolved at the anode,* the concentration of iron in the anode would therefore increase during the electrorefining.

*To be more accurate, an infinitesimal amount of iron will be dissolved to the extent permitted by the reaction



Since the standard free energy change for this reaction at 727°C is ~96 kcal/mole of PuCl_3 , the equilibrium constant for the above reaction will be ~ 10^{-21} .

For the case of electrorefining a Pu-10 w/o Fe alloy, the increase in iron concentration would eventually result in phase changes in the anode at all temperatures less than 1530°C. From the Pu-Fe phase diagram presented by Schonfeld and Ellinger,^{9,10} shown in Fig. 1, at 727°C (1000°K) the anode will be a single-phase liquid up to ~23 a/o iron, liquid plus solid PuFe₂ up to ~~67.5~~^{66.7} a/o iron, and completely solid at ~~67.5~~^{66.7} a/o iron. For a hypothetical electrorefining cell operating under reversible conditions, the appearance of these phases could be detected by interrupting the infinitesimally small electrolyzing current and observing the open-circuit potential of the electrorefining cell. The open-circuit potential is given by equation (7). Thus, for the electrorefining of a 10 a/o Fe-Pu alloy, an initial open-circuit potential of ~3 millivolts* would be obtained. This potential would gradually increase, until solid PuFe₂ appeared, to a value of ~8 millivolts. The potential would then remain constant as long as any liquid phase remained and would suddenly increase when the anode consisted solely of PuFe₂.

The foregoing discussion assumes that the electrorefining cell is operated in the absence of polarization. Since a finite current must be passed to secure any product, the anode, cathode, and electrolyte of an actual cell will be polarized. This polarization will result in an open-circuit potential with the same sign or direction as that discussed above for the Pu-Fe galvanic cell. For any fixed current density, this

*In all of the calculations which follow, an activity coefficient of unity has been assumed for plutonium in the (Pu-Fe) liquid.

11

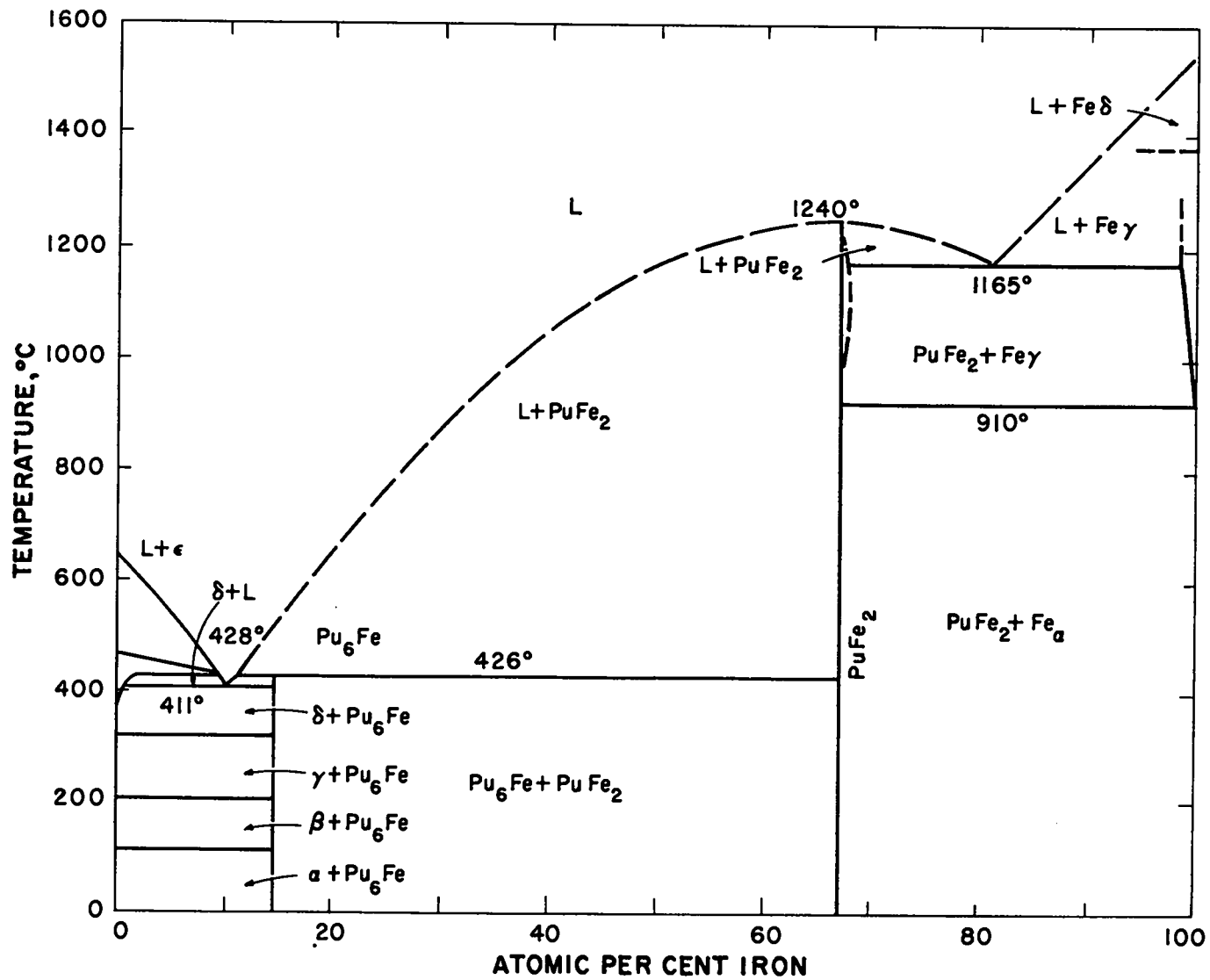


Fig. 1. Plutonium-iron phase diagram.

polarization can be kept to a minimum by stirring the electrolyte and anode phases efficiently. The cathode and electrolyte polarizations under these conditions will remain small and essentially constant as the anode composition changes during the electrorefining. The anode polarization will also be small until the anode becomes solid. Thus, if the anode consists of both liquid and solid phases and both phases are stirred efficiently so that some liquid phase is always present at the metal-salt interface, the anode polarization will be small. When the anode surface is solid, however, the rate of diffusion of Pu through the solid will be slow and polarization will be extensive at any practical current density. Under these conditions, where the plutonium activity at the surface is very low, it becomes possible to dissolve iron into the salt. The plutonium activity at the surface can be estimated by means of equation (7), which can be rewritten as

$$\text{Back e.m.f.}^* = - \frac{RT}{nf} \ln (\text{Pu})_{\text{anode surface}} \quad (9)$$

The essential points in the theory of operation of the LAMEX cell for the electrorefining of a Pu-Fe alloy are:

1. Any iron dissolved at the anode will be reduced to metal at the cathode.
2. No iron will be dissolved at the anode unless it becomes seriously polarized (i.e., deficient in plutonium).

* Open-circuit potentials are commonly called back e.m.f.'s if they are the result of a passage of current. In the present report the two terms are used interchangeably.

3. Open-circuit potential measurements (back e.m.f. measurements) can be used to determine the extent of anode polarization.

4. No polarization will take place at reasonable anode current densities as long as a plutonium-rich liquid phase is present at the anode-salt interface.

5. Polarization will be serious when the anode is completely solid.

6. To fully realize the process advantages offered by points 3 and 4, efficient stirring of both the anode and salt phase is essential.

7. The concentration of PuCl_3 in the electrolyte will remain essentially constant since the only reactions taking place at the electrodes are the oxidation of Pu^0 to Pu^{+3} and the reduction of Pu^{+3} to Pu^0 .

EXPERIMENTAL

Preparation of Electrolyte

A chloride electrolyte consisting of 10 w/o PuCl_3 ,* 50.4 w/o KCl, and 39.6 w/o NaCl was used. Cylinders of NaCl-KCl were prepared by melting the A.R. grade salts in a 90 mm. quartz tube under vacuum.⁵ Vacuum distilled PuCl_3 was added when the salt casting was introduced into the electrorefining cell.

Preparation of Plutonium-Iron Anodes

Plutonium-iron alloys were prepared by two methods:

1. Adding plutonium and iron to the electrorefining cell and

*The use of lower concentrations of PuCl_3 and the substitution of either PuF_3 or PuF_4 for PuCl_3 are discussed in³ref. 5; also see Table 5.

stirring the mixture for 2 hr. prior to the passing of current.

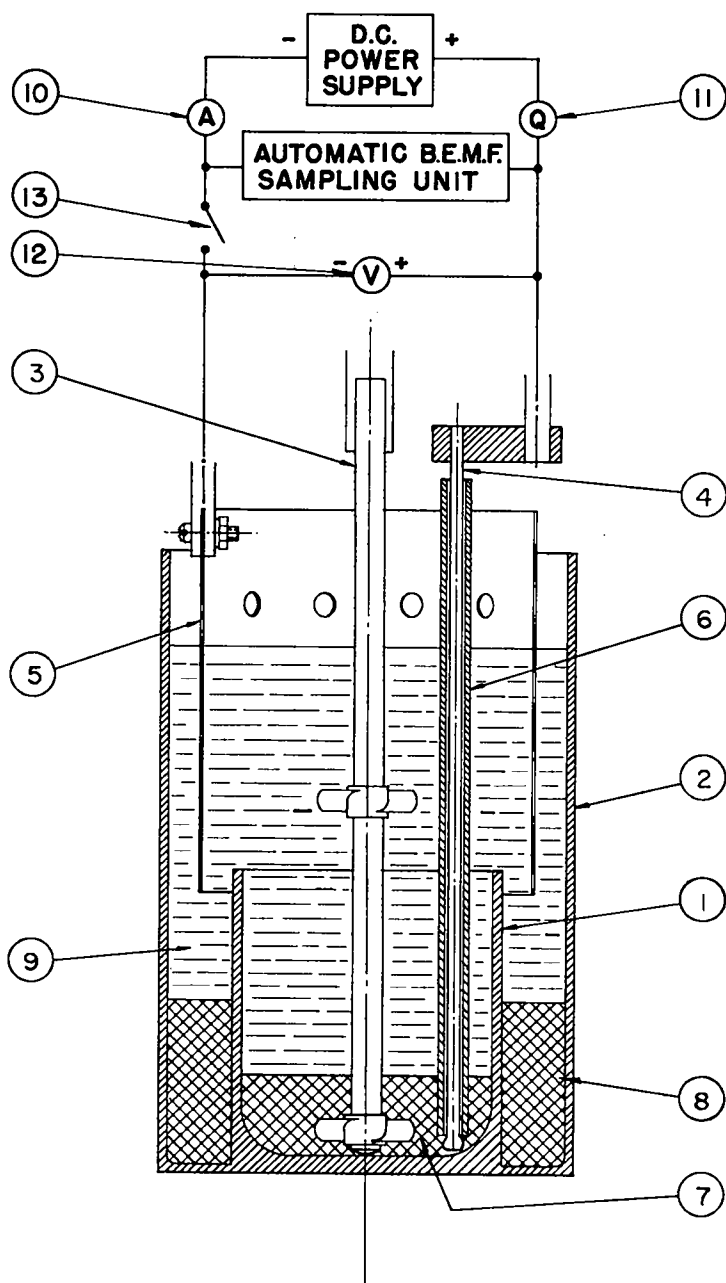
2. Vacuum casting a plutonium-iron alloy.¹¹

Fabrication of Ceramics

Magnesia-3 w/o yttria cells and alumina stirrers were fabricated by Group CMB-6 of the Los Alamos Scientific Laboratory. Morganite, Triangle RR grade, alumina tubes were used for anode protective sheaths.

Equipment

The 3.5 kg. scale electrorefining cell is shown schematically in Fig. 2. The cell consisted of an outside container (2), 4-1/8 in. O.D. by 6-1/8 in. high, which contained the molten salt electrolyte and a concentric inner anode compartment (1). Both containers were made of highly vitrified magnesia-3 w/o yttria and were cemented together. A perforated tungsten tube (5) served as the cathode. A tungsten rod (4) protected by an alumina sheath (6) conducted current to the anode metal (7). An alumina stirrer (3) coupled to a stainless steel shaft and rotated by an electric motor was used to agitate both the anode metal and the electrolyte (9). The entire assembly was 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 was oxidized at the anode, entered the molten salt electrolyte, and was reduced to metal at the cathode. The molten product (8) drained continuously into the annular product collection zone. The D.C. power supply was equipped with an automatic back e.m.f. sampling device.⁵ The back e.m.f. could also be measured manually by opening the switch (13) and observing the



- 1 Anode container,
MgO-3 w/o Y_2O_3
- 2 Electrolyte container,
MgO-3 w/o Y_2O_3
- 3 Ceramic stirrer,
 Al_2O_3 -2 w/o Y_2O_3
- 4 Anode lead,
1/8 in. dia. W rod
- 5 Cathode cylinder, W
- 6 Protective anode
sheath, Al_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. 2. Electrorefining cell, schematic drawing.

open-circuit potential at the meter (12).

The complete cell assembly is shown in Fig. 3.

Procedure

The general procedures were identical to those already described,⁵ with the following exception.

In addition to the automatic interruption of current once each hour, the current was interrupted frequently during the terminal stages of an experiment for the purpose of making back e.m.f. measurements. These measurements were made usually with the stirrer in operation. Most of the measurements were made with a Simpson volt meter. A Rubicon potentiometer was used in special cases, e.g., for e.m.f. measurements which did not change rapidly with time.

RESULTS AND DISCUSSION

Back E.M.F. as a Function of R

Typical plots of the back e.m.f. vs. θ , time after interruption of the electrolysis current, are given in Fig. 4 as a function of R,* the atomic ratio of iron to plutonium in the anode at the instant of current interruption. 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

*R was calculated from the initial anode composition and the amount of plutonium dissolved at the anode. The calculated terminal values of R in most cases were within 4% of those determined by dissolution and analysis of the entire anode residue.

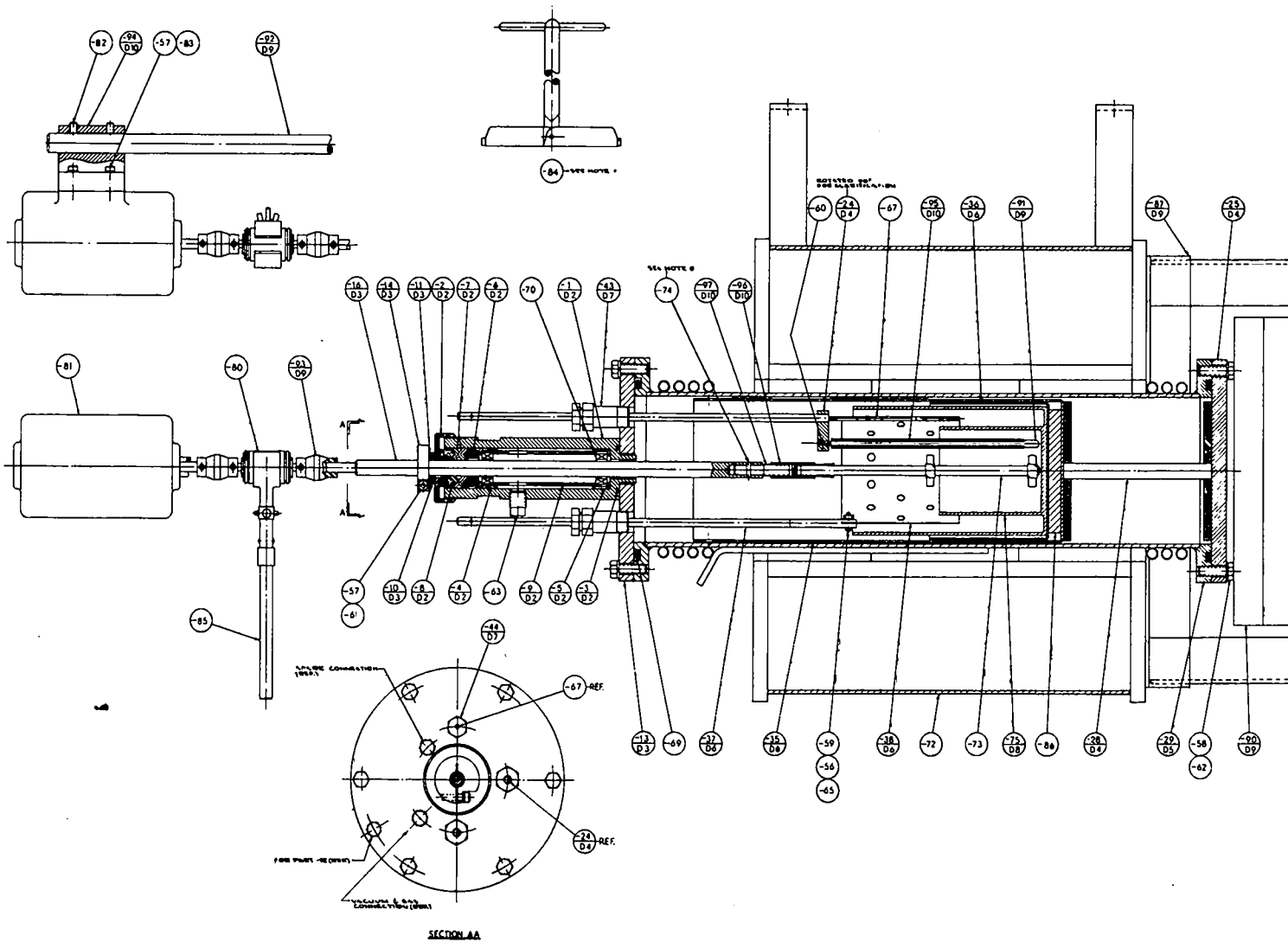


Fig. 3. Electrorefining cell assembly, Drawing No. 26Y-72325.

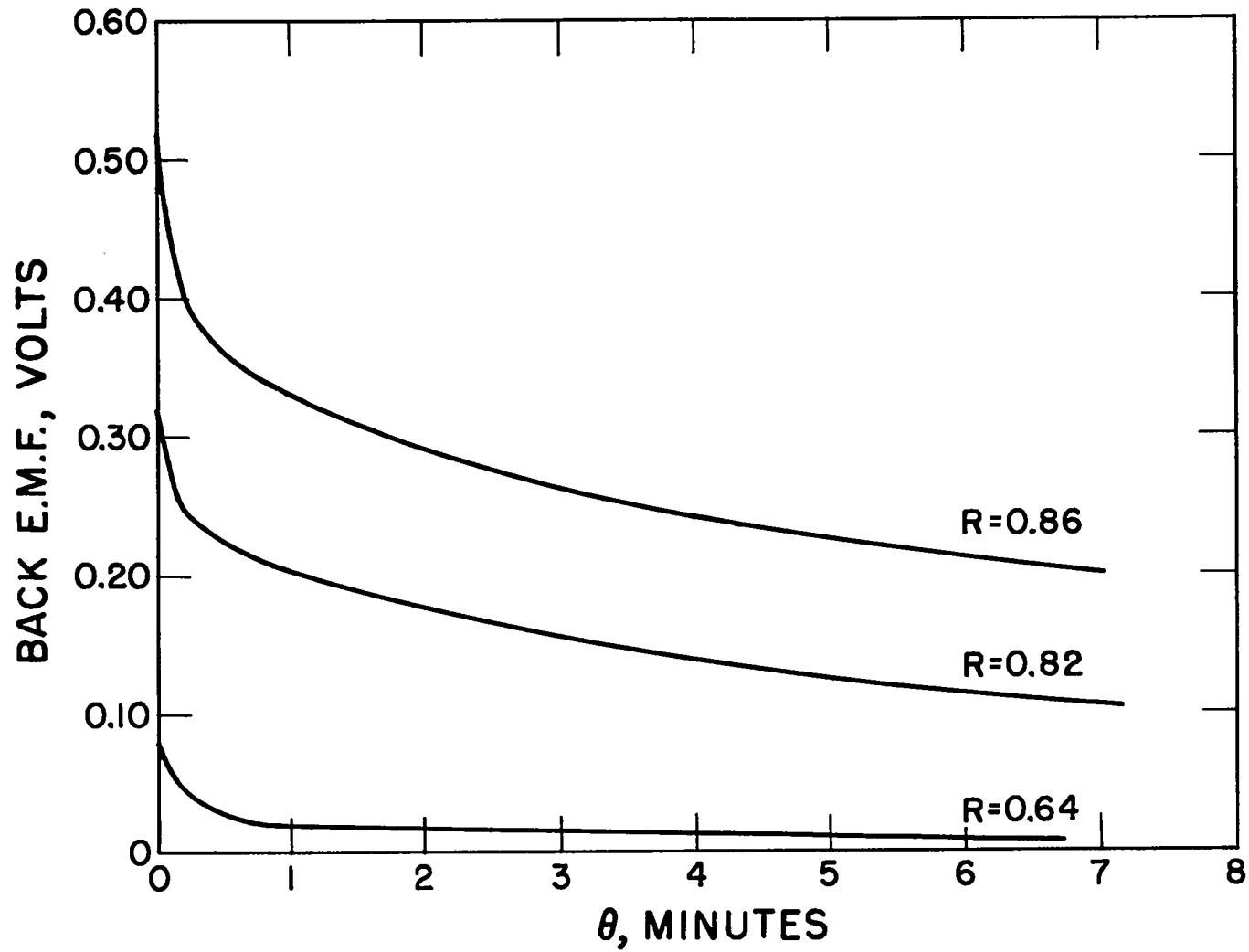


Fig. 4. Back e.m.f. vs. θ for different anode compositions.

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, Runs 5 and 6, are given in Fig. 5. 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. 6. 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.

Product Purity as a Function of R

Analyses of the products and anode residues from runs shown in Fig. 5 and 6 show that no detectable amounts of iron were dissolved in either Run 5 or 6; however, an excessive amount of iron was dissolved in Run 2 as evidenced by both the anode and product compositions shown in Table 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.

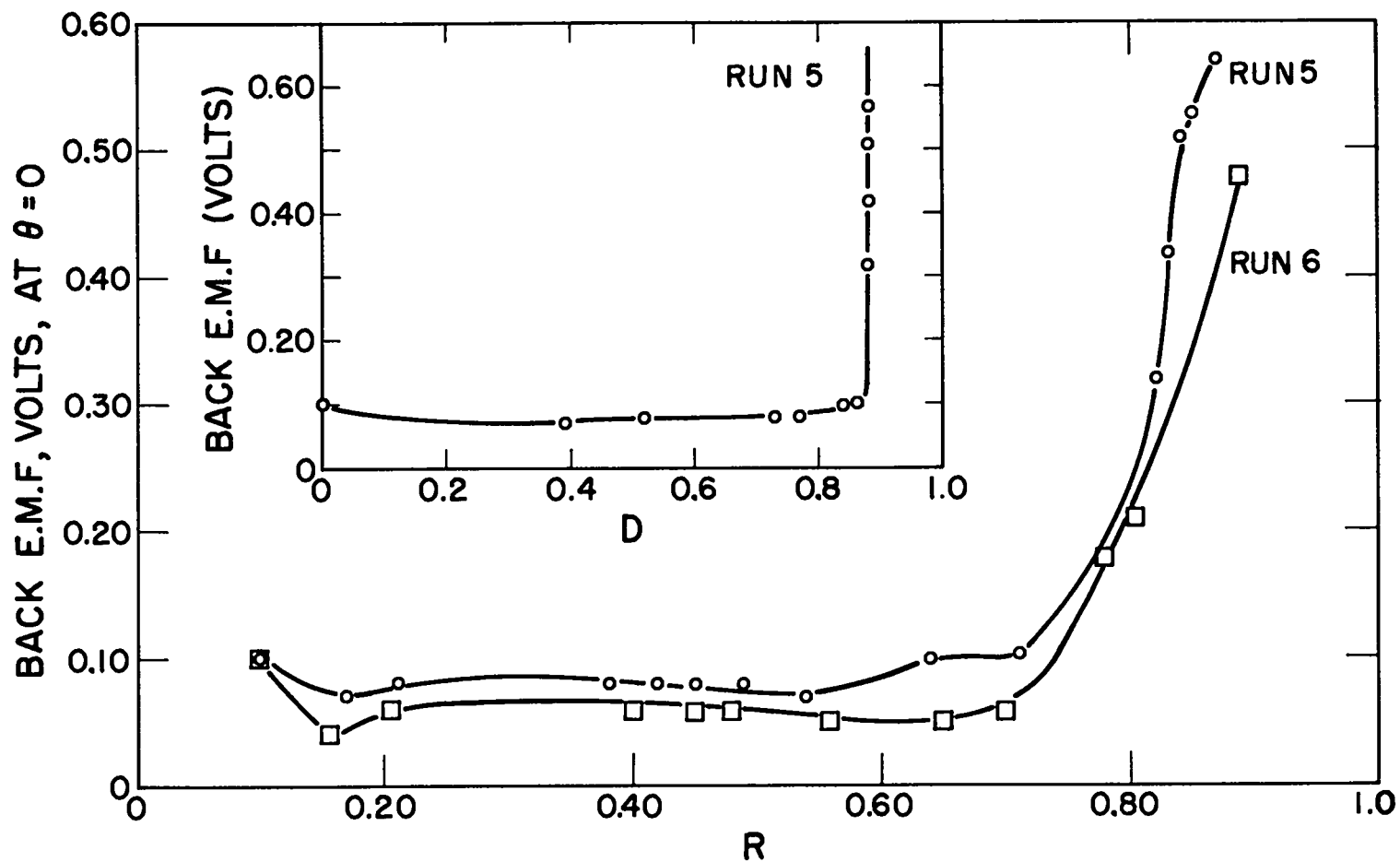


Fig. 5. Back e.m.f. at $\theta = 0$ vs. R for two typical electrorefining runs. (Inset: Back e.m.f. at $\theta = 0$ vs. D for Run 5.)

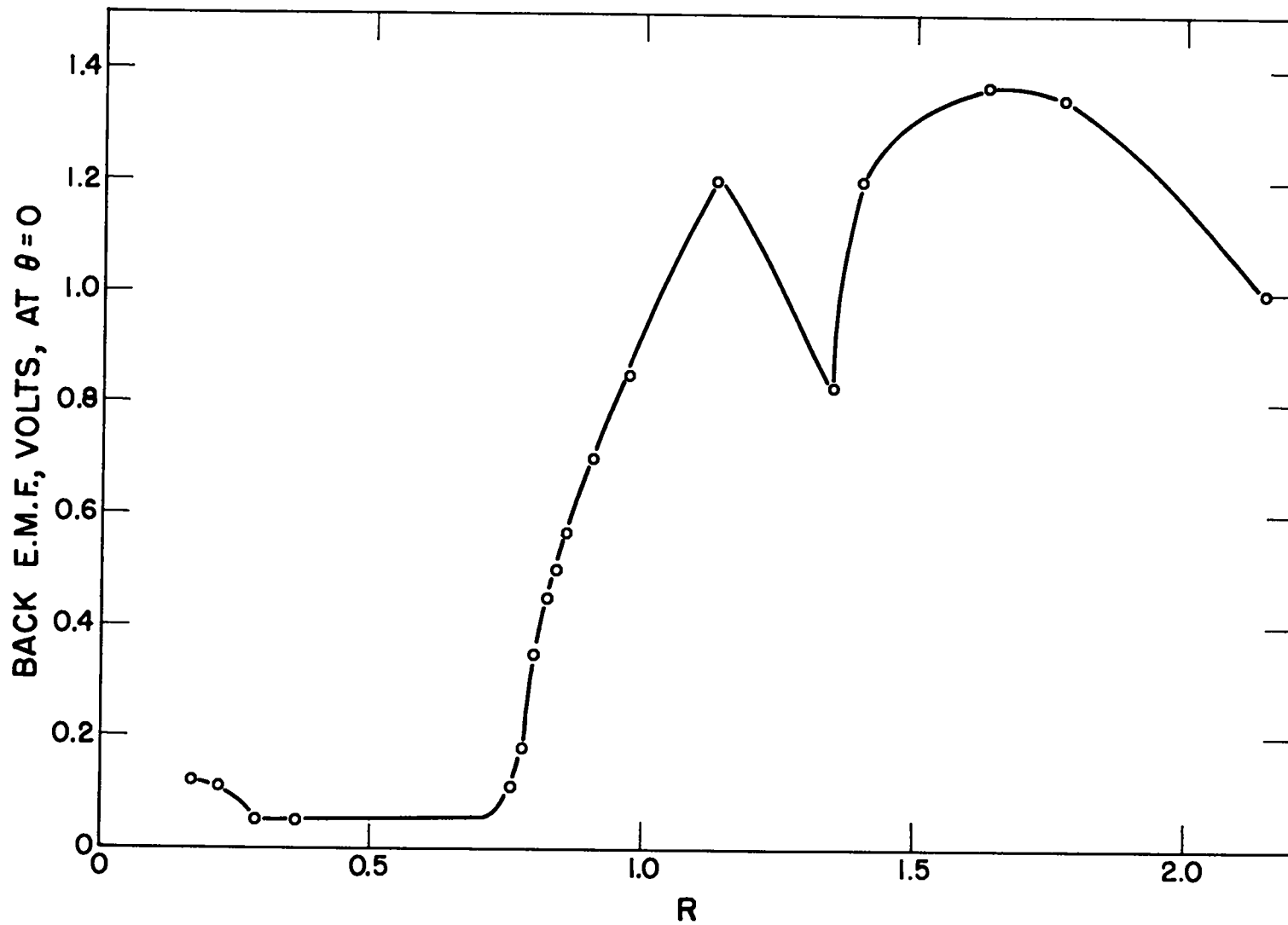


Fig. 6. Back e.m.f. at $\theta = 0$ vs. R for large terminal value of R, Run 2.

Thus, to insure a pure product, the electrorefining should be terminated when serious anode polarization is indicated by the back e.m.f.

Table 1
Product Purity as a Function of R

| Pu-Fe Run | R, Terminal Value | | Metal Feed | Fe Concentration, w/o | | |
|--------------|---------------------|------------------|---------------|-----------------------|-------------------|-----------|
| | Calc'd ^a | Analysis | | Anode Residue | | Product |
| | Calc'd ^a | Analysis | | Calc'd ^a | Analysis | Product |
| 5 | 0.90 | 0.91 | 2.32 | 17.3 | 17.5 | <0.002 |
| 6 | 0.99 | 1.03 | 2.21 | 18.8 | 18.7 | 0.002 |
| 2 | 2.14 | 1.4 ^b | 3.98 | 33.3 | 24.5 ^b | 0.16-0.38 |

^aCalculated on the assumption that only plutonium was dissolved at the anode.

^bThe measured value is questionable because the material balance was poor.

Permissible Anode Depletions

All of the Pu-Fe electrorefining experiments, except Run 2 in which the anode was intentionally "over-depleted" of Pu, are summarized in Table 2. These runs were discontinued when anode polarization was indicated by back e.m.f. measurements. In every case essentially no iron was transported from the anode to the cathode. (Experience has shown that approximately 20-30 p.p.m. of iron is introduced into the product as "tramp" iron.⁴ This iron probably comes from the MgO-Y₂O₃ crucible which contains ~600 p.p.m. of iron.)

Table 2

Summary of Pu-Fe Electrorefining Runs

| <u>Pu-Fe Run</u> | <u>Current, amp.</u> | <u>Terminal Back E.M.F., volts</u> | <u>E.M.F.,</u> | | <u>Fe Concentration, w/o</u> | |
|------------------|--------------------------|--|----------------|----------|------------------------------|----------------|
| | | | <u>D</u> | <u>R</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 |

The terminal values of R listed in Table 2 varied from 0.66 to 1.13; the average value was 0.88 (± 0.15). This latter value corresponds to a plutonium dissolution of 87.5 (± 2.7) % from a 2.50 w/o Fe-Pu alloy.

Product Yield

The yield or recovery of pure plutonium can be considered as the product of the fraction of plutonium dissolved at the anode and the per cent of the dissolved plutonium which is collected, i.e., % Pu recovery = D (% Pu collection). The per cent collection is particularly sensitive to the terminal temperature cycling and agitation or stirring of the product. These steps in the process have not been optimized. However, with the terminal procedure* recommended in reference 5, the collection yields in the runs listed in Table 2 varied from 98.8% in Run 8 to 93.2% in Run 1. An average collection yield of ~94% can be expected with confidence. The per cent Pu recovery will therefore be ~82%. A material balance for a typical run is given in Table 3. The PuCl_3 concentration in the salt phase remains essentially constant during a run, and the loss of Pu to the salt is in the form of metallic shot.

* In brief, this procedure consists of stirring the product metal with the tungsten cathode, heating to 840°C, and holding at this temperature for 2 hr.

Table 3
Plutonium Material Balance, Run 4

| <u>Item</u> | <u>g. Pu°</u> | <u>% of Pu°</u> |
|---|---------------|-----------------|
| Feed Metal | 3134 | 100 |
| Anode Residue | 426 | 13.6 |
| Pu Shot Loss and Crucible Loss ^a | 140 | 4.5 |
| Pu on Cathode | 20 | 0.6 |
| Pu Product Ring | 2548 | 81.3 |

^aThe PuCl₃ concentration remains essentially constant during the electrorefining.

Product Purity

The purification of plutonium from elements other than iron is also of interest. Analyses of the feeds and product metals are therefore given in Table 4. It will be noted that the remaining detectable metallic impurities in the product are Am (9-29 p.p.m.), W (18-63 p.p.m.), and Fe (~20 p.p.m.). Only a few analyses were done for non-metallic impurities in the product. Typical results, e.g., Run 6, were C (<10 p.p.m.), O (20 p.p.m.), N (5 ± 3 p.p.m.), and H (5 ± 5 p.p.m.). This level of impurities is surprisingly low in view of the fact that the cells are unloaded in an air atmosphere.

Since Am grows into the Pu at the rate of ~12 p.p.m. per month, the values shown in Table 4 have been corrected to the date of termination of the electrorefining. As discussed earlier (see Theory) the Am

Table 4

Analyses of Feeds and Products
3.5 Kg. Scale Plutonium-Iron Electrorefining

Concentration of Elements, p.p.m.

| Element | Run 1 | | Run 3 | | Run 4 | | Run 5 | | Run 6 | | Run 7 | | Run 8 | |
|---------|----------------------|---------|----------------------|---------|----------------------|---------|----------------------|---------|----------------------|---------|----------------------|---------|----------------------|---------|
| | Feed | Product | Feed | Product | Feed | Product | Feed | Product | Feed | Product | Feed | Product | Feed | Product |
| Mg | 100 | 5 | < 5 | 10 | < 5 | 10 | 20 | 20 | 20 | < 5 | < 10 | < 10 | 10 | < 10 |
| Al | 15 | < 5 | 20 | < 5 | < 5 | < 5 | 50 | 10 | 15 | < 5 | 35 | < 5 | 30 | < 5 |
| Si | 20 | < 10 | 70 | 15 | < 100 | < 10 | < 100 | < 10 | 220 | < 10 | 190 | < 10 | 160 | < 10 |
| Pb | < 2 | < 2 | < 2 | < 2 | < 200 | < 2 | < 20 | < 2 | < 20 | < 2 | 20 | < 2 | 20 | < 2 |
| Cu | < 2 | < 2 | 5 | 10 | < 20 | < 2 | < 20 | < 2 | < 20 | < 2 | 200 | < 2 | 50 | < 2 |
| Mn | 6 | 2 | 4 | < 2 | < 20 | < 2 | < 20 | < 2 | < 20 | < 2 | 10 | < 2 | 15 | < 2 |
| Ni | < 20 | < 10 | 60 | < 10 | 10 | < 10 | 75 | < 10 | 100 | < 10 | 50 | < 10 | 325 | < 10 |
| Cr | < 20 | < 10 | 15 | < 10 | < 100 | < 10 | < 100 | < 10 | < 100 | < 10 | 30 | < 5 | 90 | < 5 |
| Zn | 20 | < 10 | < 10 | < 10 | < 200 | < 10 | < 200 | < 10 | < 200 | < 10 | < 10 | < 10 | < 10 | < 10 |
| Mo | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | 70 | < 5 | 11 | < 5 |
| Ta | < 30 | < 35 | < 35 | < 35 | < 35 | < 35 | < 35 | < 35 | < 35 | < 35 | < 35 | < 35 | 55 | < 35 |
| Th | < 15 | < 15 | < 15 | < 15 | < 15 | < 15 | 140; 275 | < 15 | 245 | 36 | < 15 | 18 | < 15 | < 15 |
| U | 30 | < 30 | 30 | < 30 | - | < 30 | < 30 | < 30 | < 30 | < 30 | 130 | < 30 | 30 | < 30 |
| W | < 10 | 40 | 40 | 18 | 320 | 34 | < 10 | 55 | < 10 | 47 | 35 | 43 | 51 | 63 |
| Am | 128 | 24 | 130 | 24 | 47 | 9 | 307 | 29 | 101 | 14 | 180 | 29 | 101 | 20 |
| Fe | 5.55x10 ⁴ | 20 | 2.46x10 ⁴ | 30 | 2.49x10 ⁴ | 30 | 2.32x10 ⁴ | < 20 | 2.21x10 ⁴ | 20 | 2.54x10 ⁴ | 20 | 2.58x10 ⁴ | 20 |

contamination is determined to a large extent by the concentration of PuCl_3 in the salt. 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>Init. Conc.,</u> | <u>No. of</u> | <u>K^a</u> |
|------------------|---------------------|-------------------------|-----------------------------|
| Salt | m/o | Electrorefining Runs | |
| PuCl_3 | 2.10 | 19 | $(1.9 \pm 0.2) \times 10^2$ |
| PuCl_3 | 0.49 | 3 | $(2.2 \pm 0.2) \times 10^2$ |
| PuF_3 | 2.10 | 2 | (65 ± 1) |
| PuF_3 | 0.49 | 20 | $(1.1 \pm 0.1) \times 10^2$ |

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

Comparison of Theory and Experiment

The experimental control of product purity and anode depletion was in general agreement with the theory discussed above. The theory predicted serious anode polarization at $R \cong 2.0$ (the anode will be completely

solid at $R = 2.0$). The experiments gave an average value of $R = 0.88$ (± 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" or "solid-like" condition at the termination of the electrorefining. The slow rate of diffusion is shown in Fig. 7, 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. 8, 9, and 10) showed that the metal was solid or paste-like at the termination of the electrorefining. In spite of the fact that 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 (see Fig. 9).

*For complete operational details, see reference 5.

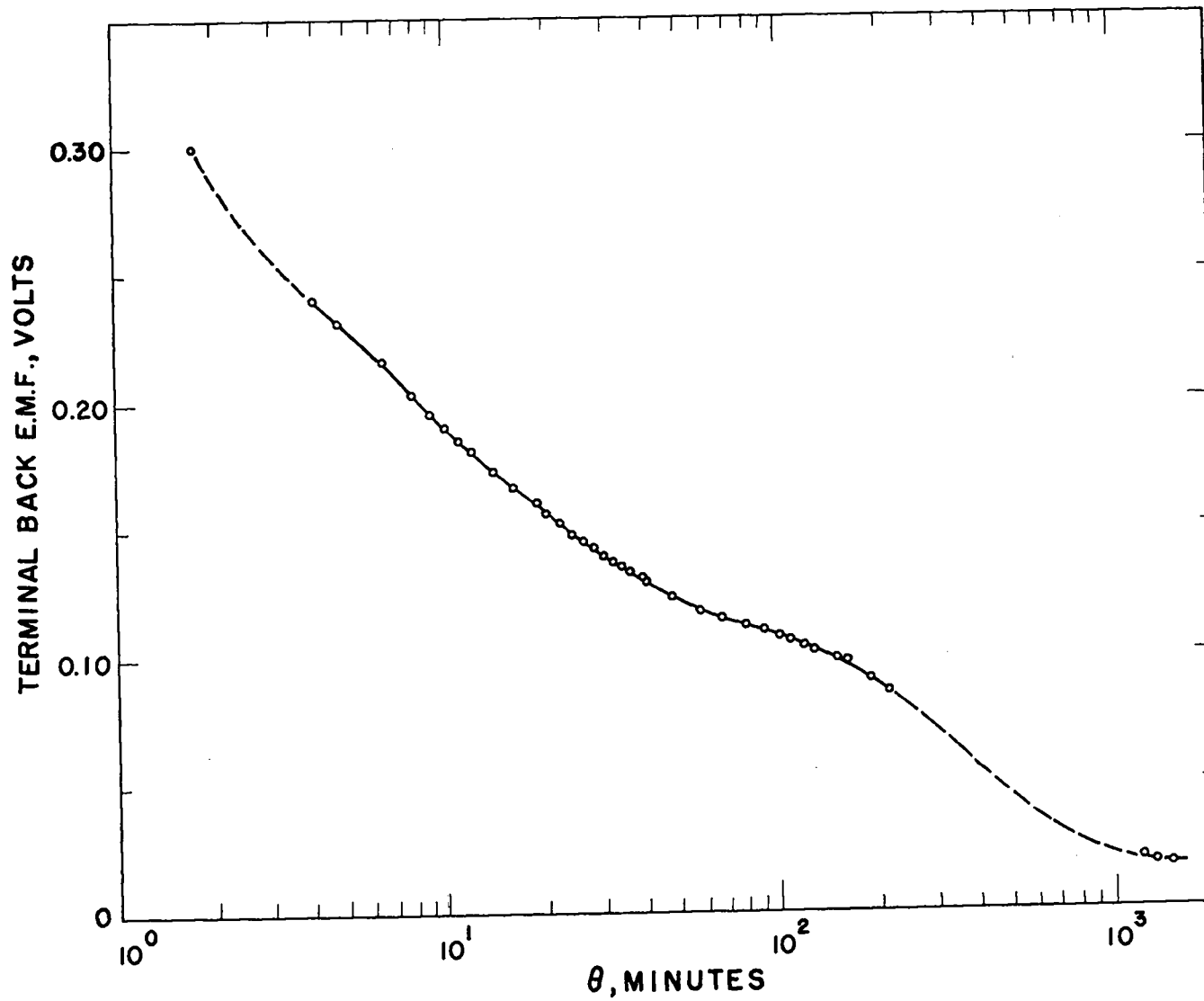


Fig. 7. Back e.m.f. vs. $\log \theta$ for large values of θ .



Fig. 8. Anode residue, top surface, Run 5.

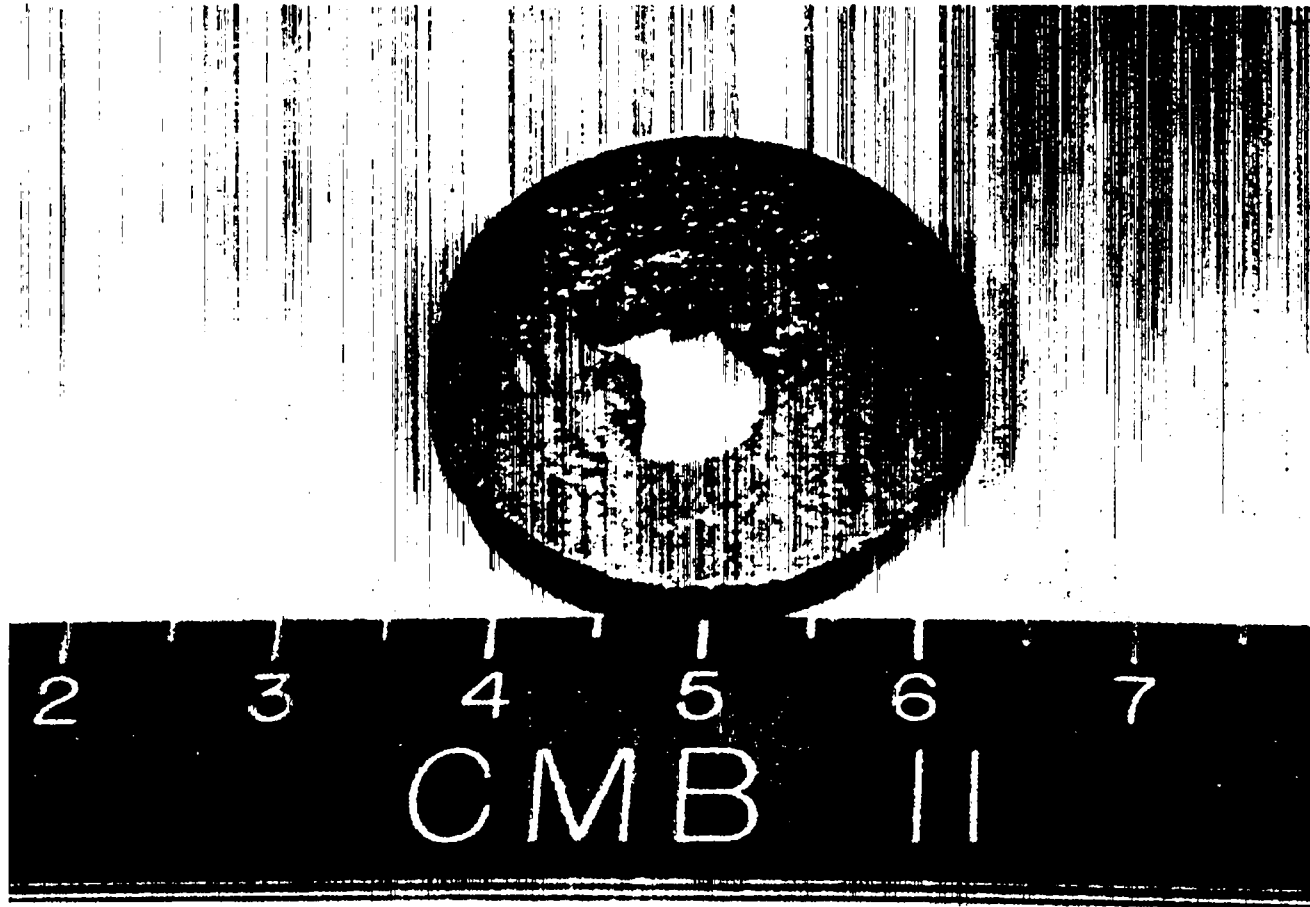


Fig. 9. Anode residue, bottom surface, Run 5.



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

CONCLUSIONS

The following conclusions can be drawn from these experiments:

1. Plutonium containing <35 p.p.m. of iron and a total of <100 p.p.m. of detectable metallic impurities can be produced on the multi-kilogram scale by electrorefining plutonium-iron alloys. At high current densities anodic dissolutions of $\sim 88\%$ of the plutonium are feasible starting with 2.5 w/o iron alloys; over-all yield of electrorefined metal should be $\sim 82\%$.
2. The limitation on the amount of plutonium that is dissolved anodically is imposed by the initial iron concentration and the acceptable limit of iron concentration in the product.
3. Separation of plutonium from iron is quantitative as long as the anode remains unpolarized. Therefore, stirring of the anode is very essential. (This is also desirable when unalloyed, impure plutonium feeds are used, for the same reasons.)
4. Anode polarization can be easily detected by back e.m.f. measurements.
5. The back e.m.f. can be checked automatically during the run, and the run can be terminated automatically when the back e.m.f. indicates either that the run is complete or stirrer operation is faulty. (Inadequate stirring will result in both anode polarization and deposition of sodium at the cathode.)

GLOSSARY OF SYMBOLS, TERMS, AND EQUATIONS

D = fraction of plutonium feed dissolved at anode

$$D = \frac{\text{g. Pu in feed} - \text{g. Pu in anode residue}}{\text{g. Pu in feed}}$$

$$R = \frac{\text{g. atoms Fe}}{\text{g. atoms Pu}}$$

t = time after interruption of electrolysis current

p.p.m. = parts of impurity per million parts of plutonium, weight basis

$$D = 1 - \frac{x}{100-x} \frac{239}{55.85} \frac{1}{R} \quad \text{for a Pu-Fe feed containing } x \text{ w/o Fe}$$

n = no. of electrons in the balanced half-cell reaction (= 3 in this report)

f = the faraday = 23,060 cal. (volt)⁻¹ (g. equiv.)⁻¹

E = galvanic cell potential, volts

m/o = mole per cent

w/o = weight per cent

REFERENCES

1. 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).
2. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Electrorefining," Los Alamos Scientific Laboratory Report LA-2666 (1962).
3. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Electrorefining," Ind. Eng. Chem. Process Design Develop., 2, 20 (1963).
4. 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).
5. 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).
6. R. M. Keihn et al., "LAMPRE: A Molten Plutonium Fueled Reactor Concept," Los Alamos Scientific Laboratory Report LA-2112 (1957).
7. R. A. Oriani, "Electrochemical Techniques in the Thermodynamics of Metallic Systems," J. Electrochem. Soc., 103, No. 3, 194 (1956).
8. Carl Wagner and Alfred Werner, "The Role of Displacement Reactions in the Determination of Activities in Alloys with the Aid of Galvanic Cells," J. Electrochem. Soc., 110, No. 4, 326 (1963).
9. F. W. Schonfeld and F. H. Ellinger, "Binary Alloys of Plutonium," LADC-2656 (1956). (Diagram also appears in Reference 10.)
10. 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).
11. L. J. Mullins, J. A. Leary, and W. J. Maraman, "Removal of Fission Product Elements by Slagging," Ind. Eng. Chem., 52, No. 3, 227 (1960).