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

PLUTONIUM ELECTROREFINING

Printed in USA Price $ 1.75. Available from the

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

LA-2666
CHEMICAL SEPARATIONS PROCESSES
FOR PLUTONIUM AND URANIUM
TID-4500 (17th Ed.)

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

REPORT WRITTEN: February 2, 1962

REPORT DISTRIBUTED: June 22, 1962

PLUTONIUM ELECTROREFINING

by

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

(This report extends LAMS-2441)

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

ABSTRACT

Electrorefining processes have been developed for the preparation of high purity, high density plutonium metal on the 500 g. and 3.5 kg. scales. Equipment, procedures, and results are discussed.

ACKNOWLEDGMENTS

Without doubt, the development of this process would not have been possible without the excellent cooperation and services of S. D. Stoddard, D. E. Nuckolls, and R. E. Cowan of the Ceramics Section, Group CMB-6. We also are indebted to Group CMB-1 under the direction of C. F. Metz for the many chemical analyses required. All of the plutonium(III) chloride was prepared by R. L. Nance of Group CMB-11.

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INTRODUCTION

The electrochemical preparation of milligram quantities of plutonium metal was first reported in 1944 by Kolodney of this Laboratory.[1] The method was never applied to large scale operation because of the success of the bomb reduction method developed at about the same time at Los Alamos.[2]

More recently, plutonium electrorefining on a large scale has been considered for application to the following important problems:

1. preparation of high purity metal for chemical and metallurgical studies;
2. recycle of impure plutonium metal scrap (at the present time this is done by rather expensive methods);
3. recycle of impure plutonium compounds by converting these to impure metal for subsequent electrorefining;
4. reprocessing of plutonium from plutonium-fueled nuclear reactors.

In 1958, the purification of plutonium nuclear fuel by electrorefining was reported by Leary *et al.*[3] These experiments indicated that excellent purification of plutonium was possible, as anticipated from thermodynamic estimates.

Small scale preparation of pure plutonium metal by electrorefining was reported by Blumenthal and Brodsky of Argonne National Laboratory in 1960.[4] Their method consisted of collecting the electrorefined product below the melting point of plutonium, then melting it into a button in a second container. Plutonium electrorefining rates of about 10 g./day were achieved, resulting in buttons weighing up to 55 g.

Large scale preparation of pure plutonium at LASL also was reported in 1960 by Mullins _et al._[5] In this method, the plutonium product was deposited as a liquid at the cathode by operating the cell above the melting point of plutonium. The liquid metal could either be cast into the desired shape _in situ_ or removed from the cell continuously. A maximum of 278 g. of metal was electrorefined in a single run.

It is not possible to compute quantitatively the purification that is attainable when plutonium is electrorefined. However, useful qualitative estimates can be made from standard free energy of formation data. The $-\Delta F^o$ values[6] arranged in Table 1 pertain to electrorefining in chloride electrolytes at 1000°K. One can estimate that impurities having a $-\Delta F^o$ value that is considerably less than 59 kcal./g. atom chlorine should concentrate in the plutonium anode residue, while those having a $-\Delta F^o$ value that is considerably greater than 59 should concentrate in the electrolyte. These estimates are supported by the behavior of impurities in electrorefining[3] and in chloride slagging experiments.[7] Ruthenium, molybdenum, copper, iron, and zirconium concentrated markedly in the metal phase (anode), while lanthanum and cerium concentrated in the salt phase.

The results of 31 plutonium electrorefining experiments are discussed in this report. These experiments were conducted on two scales, 500 g. and 3.5 kg. of plutonium, which are reported in corresponding sections of this report.

Table 1

STANDARD FREE ENERGIES OF FORMATION OF SELECTED CHLORIDES IN ORDER OF INCREASING STABILITY AT 1000°K.[a]

Compound	$-\Delta F^{\circ}$, kcal./g. atom Cl
WCl_4	4
$NbCl_5$	12
$NiCl_2$	18
AgCl	19
CuCl	21
$TaCl_3$	22
$FeCl_2$	27
$CrCl_2$	32
$MnCl_2$	41
$AlCl_3$	46
UCl_3	54
$NpCl_3$	55
$ZrCl_2$	56
$MgCl_2$	58
$PuCl_3$	59
$ThCl_3$	59
$CeCl_3$	66
$LaCl_3$	67
$AmCl_3$	67
NaCl	76
$CaCl_2$	78
LiCl	79
KCl	82

[a] See Ref. 6.

INITIAL DESIGN CONSIDERATIONS

Because of the electropositive nature of plutonium, electrorefining is limited to high temperature systems. The desirability of collecting the electrorefined metal as a liquid in a large scale process has been discussed in previous reports.[5,8] For plutonium, this establishes the lower operating temperature limit at > 640°C.; the upper limit is taken somewhat arbitrarily as 750°C.

Numerous molten salt systems can be used in this temperature range. A chloride system was selected because of less anticipated corrosion of container materials. Specifically, an equimolar solution of NaCl and KCl was selected because these components are less hygroscopic than alternative chlorides. An additional advantage to using the NaCl-KCl solvent is that it freezes (650°) before the expansion that accompanies the transition from epsilon to delta-prime phase plutonium. In a batch electrorefining operation, this metal expansion during cooling could crack the container and permit leakage of the molten salt. Plutonium trichloride was selected because macroscale preparative methods for the pure salt were well-known and already in use at this Laboratory.[9] The concentration of plutonium trichloride was chosen somewhat arbitrarily as 10 w/o of the total chloride electrolyte. It was anticipated that this concentration was low enough to prevent difficulty from the mutual solubility of plutonium metal and plutonium trichloride, but high enough to minimize concentration polarization.

Batch operation was selected over the continuous method for initial experiments. It was anticipated that batch electrorefining would have immediate applications and would provide a sound basis for development of continuous methods if desired.

Figure 1 shows the initial cell design concept. In principle, the operation of such a cell is simple. Plutonium is oxidized at the anode to form trivalent plutonium ions in the molten salt electrolyte. The plutonium ions are transported through the electrolyte to the cathode, where they are reduced to metal. This molten metal drains down into the product reservoir.

The choices of container material for molten salts and molten plutonium are rather limited. Both tantalum and tungsten metals were known to be reasonably compatible with molten plutonium and salt. However, previous experience had indicated that tantalum containers fabricated by fusion welding were unsatisfactory. Generally they failed by corrosion of the heat-affected zone adjacent to the weld. Similarly, tungsten was rejected because fabrication methods were not known.

Ceramic cells made from highly vitrified refractory oxides are suitable. The standard free energies of formation shown in Table 2 indicate that magnesia, yttria, thoria, and calcia probably could be

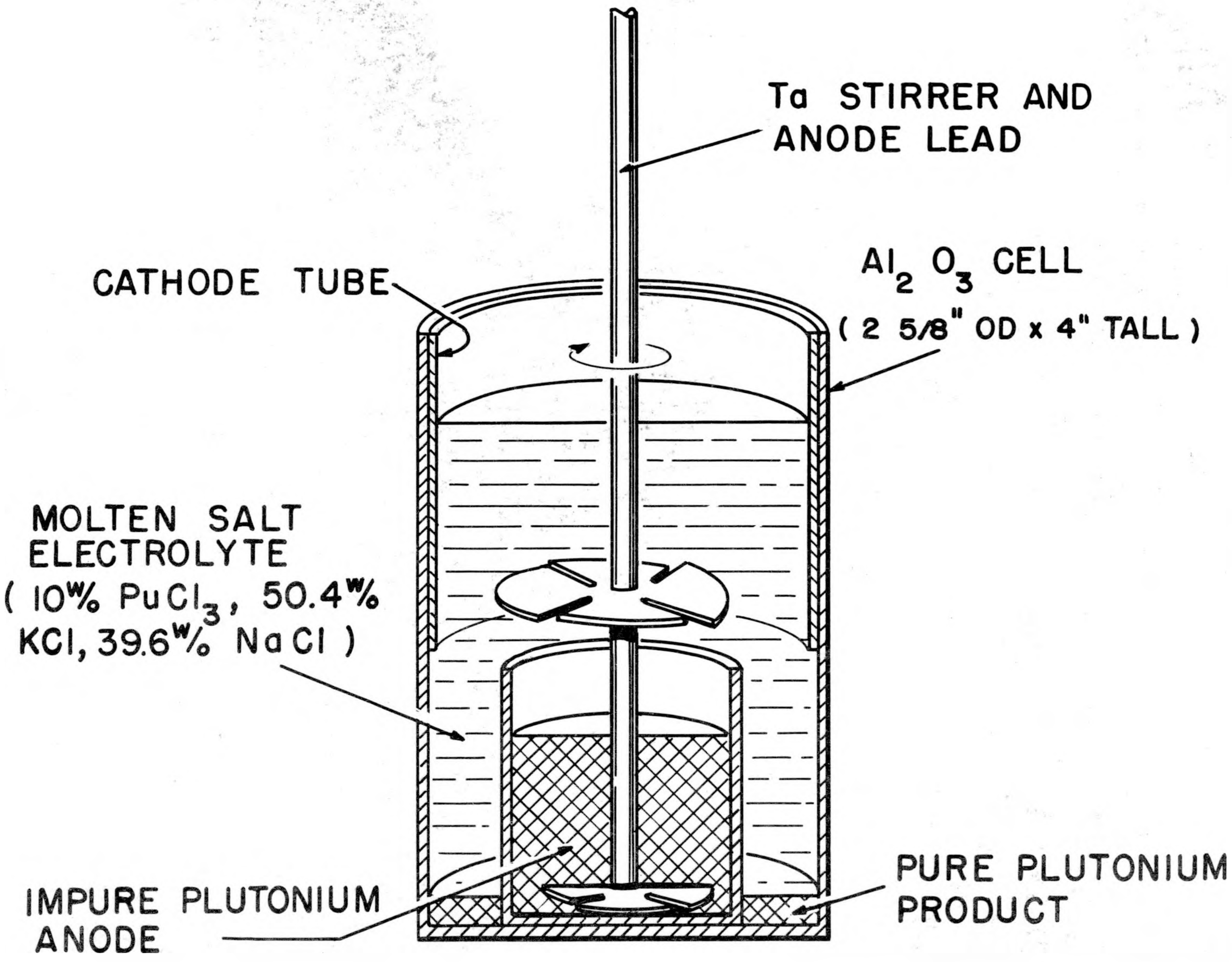

Fig. 1. Initial cell design concept

used without serious chemical attack. Although alumina might be considered to be somewhat unsatisfactory from a chemical stability viewpoint, it was selected as the cell construction material because highly vitrified alumina ware was available at this Laboratory. Recently, highly vitrified magnesia, magnesia-2% yttria, and calcia ware were made available.[10]

Table 2

STANDARD FREE ENERGIES OF FORMATION OF OXIDES IN ORDER OF INCREASING STABILITY AT 1000°K.[a]

Oxide	$-\Delta F^{o}$, kcal./g. atom oxygen
SiO_2	84
Al_2O_3	109
Pu_2O_3	109
MgO	119
Y_2O_3	119
ThO_2	124
CaO	127

[a] See Ref. 6

The molten salt electrolyte was stirred in all experiments to prevent polarization at high current densities required to achieve practical processing times. Tantalum was selected as the material of construction for the stirrer because of its ease of fabrication (no welds are required). When a plutonium alloy is electrorefined on a batch basis, it may be necessary to stir the molten anode pool to prevent insoluble intermetallic compounds from forming a crust on the anode surface. Therefore the initial design provided for both a salt phase stirrer and an anode pool stirrer, mounted on a common shaft.

The cell was operated under an inert atmosphere (helium or argon) rather than vacuum primarily because of salt volatility. An additional disadvantage of vacuum operation is the more difficult seal and bearing requirement for the stirrer shaft.

The scale of the initial experiments was set at 300 g. This represented a reasonably practical first goal for process demonstration without exceeding criticality limitations during aqueous recovery. When the first experiments were successful, this scale was increased to 500 g. plutonium.

500 g. SCALE EXPERIMENTS

EXPERIMENTAL

Preparation of Electrolyte: Chloride and mixed fluoride-chloride electrolytes were used. The chloride electrolyte consisted of 10 w/o plutonium(III) chloride, 50.4 w/o potassium chloride, and 39.6 w/o sodium chloride. Cylinders of this salt were prepared by melting A.R. grades of potassium and sodium chloride with vacuum-distilled plutonium(III) chloride in a 50 mm. quartz tube. The plutonium(III) chloride was prepared by the hydrochlorination of plutonium(III) oxalate, followed by distillation in vacuum. After the alkali halides were thoroughly mixed, the salt charge was held at a pressure of 10^{-5} mm. Hg at room temperature for at least 18 hr. The charge was then heated to 300°C. at a rate of

50°/hr. and then to 700°C. at a rate of about 400°/hr. The molten salt was held at 700°C. under vacuum for 1 hr., and the charge was then allowed to cool to room temperature. The resulting salt cylinder could be easily removed from the quartz tube.

Fluoride-chloride electrolytes consisting of 10 w/o plutonium(III) fluoride, 50.4 w/o potassium chloride, and 39.6 w/o sodium chloride were made in a similar fashion.

An equally satisfactory method for making the electrolyte was to cast a cylinder of sodium and potassium chlorides and to add the plutonium salt when the salt casting was introduced into the electrorefining cell.

Preparation of Plutonium Anodes: Plutonium metal was prepared by the bomb reduction of plutonium(IV) fluoride. This metal was then vacuum cast into a cylindrical shape.

Equipment: The 500 g. scale equipment is shown in Fig. 2. An alumina cell (1) was used to contain the plutonium anode, the electrolyte, and the cathode product. The electrolyte was stirred by a tantalum stirrer shaft (2) and blade. A perforated tungsten tube (3) served as the cathode. Electrical contact was supplied to the anode metal through the stirrer shaft. In addition, a second blade (4) continuously stirred the molten anode pool. Electrical contact to the cathode was provided by a tantalum rod (5), joined to the tungsten above the molten electrolyte level.

1. Alumina-yttria cell,
   2-5/8 in. O.D. x 4 in. tall
2. Tantalum stirrer,
   1/4 in. O.D. x 16 in. long
3. Tungsten cathode,
   2 in. I.D. x 2-1/2 in. tall x 0.030 in. thick
4. Tantalum stirrer blade,
   3/4 in. dia. x 0.030 in. thick
5. Tantalum extension rod,
   1/4 in. dia. x 9 in. long
6. Tantalum safety crucible,
   2-3/4 in. I.D. x 3-1/2 in. tall
7. Stainless steel spacer,
   4-1/4 in. O.D. x 7-1/2 in. long
8. Thermocouple well,
   1/2 in. dia. x 2 in. deep
9. Stainless steel pedestal,
   4 in. tall
10. Stainless steel furnace tube,
    4-1/2 in. I.D. x 4 in. tall x 1/8 in. thick
11. Copper cooling coils,
    3/8 in. O.D.
12. Teflon-lined compression seal,
    1/4 in. I.D.
13. Graphite brushes, grooved for 1/4 in. shaft

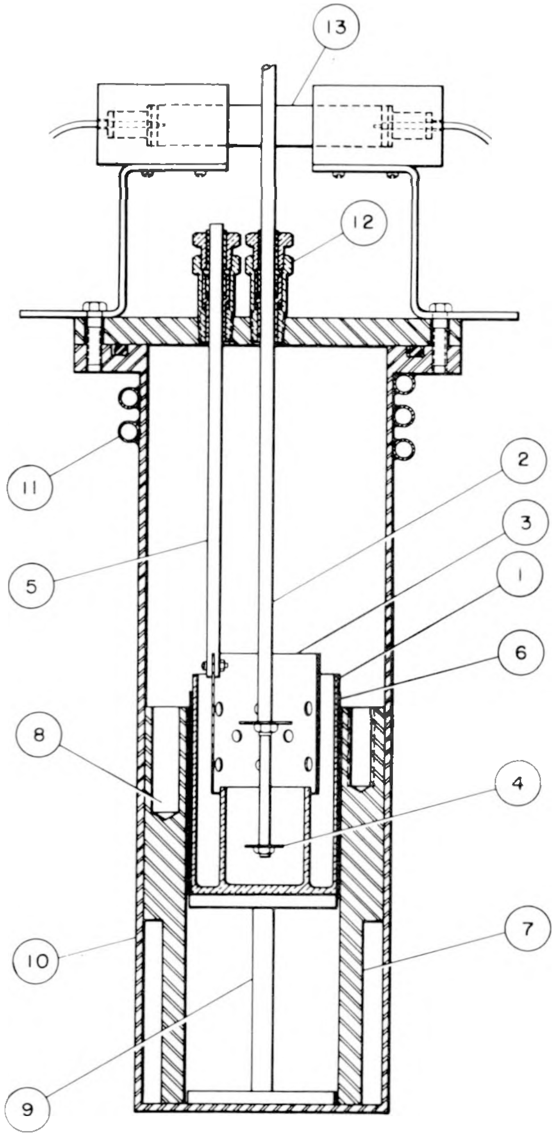

Fig. 2. Electrorefining cell assembly, 500 g. scale

The cell was contained in a tantalum safety crucible (6) which was supported on a stainless steel stand (9) and positioned centrally by a stainless steel insert (7). A thermocouple (not shown) was inserted in the well (8) to indicate the temperature. This entire assembly was enclosed in a 4-3/4 in. O.D. stainless steel tube (10) that was provided with cooling coils (11). Electrical leads through the cover plate were insulated by means of teflon-lined seals (12). Electrical contact to the rotating anode lead was accomplished by carbon brushes (13).

In addition to the seals shown, the cover plate also contained a seal for a 1/8 in. dia. tungsten pre-electrolysis cathode, a seal for the thermocouple tube, and an inert gas line connection. These are not shown in Fig. 2, but can be seen in the photograph, Fig. 3. Also visible in Fig. 3 is a thermocouple mounted on the outside of the 4-3/4 O.D. tube. This thermocouple was used for activation of the furnace controller. A Type M-5012 Hevi Duty Electric Co. 5 in. I.D. tube furnace, used to heat the 4-3/4 in. O.D. tube, is not shown in Fig. 3. A photograph of an unused alumina cell and used cathode, stirrer, and pre-electrolysis rod are shown in Fig. 4.

External to the glove box enclosure were located a Drierite column and uranium chip furnace operated at 600°C. to purify the inert gas. The system also could be evacuated through the inert gas line by means of an external pump and appropriate valving.

A Dressen Barnes Corp. Regulated Power Supply Model 62-121 provided the direct current supply.

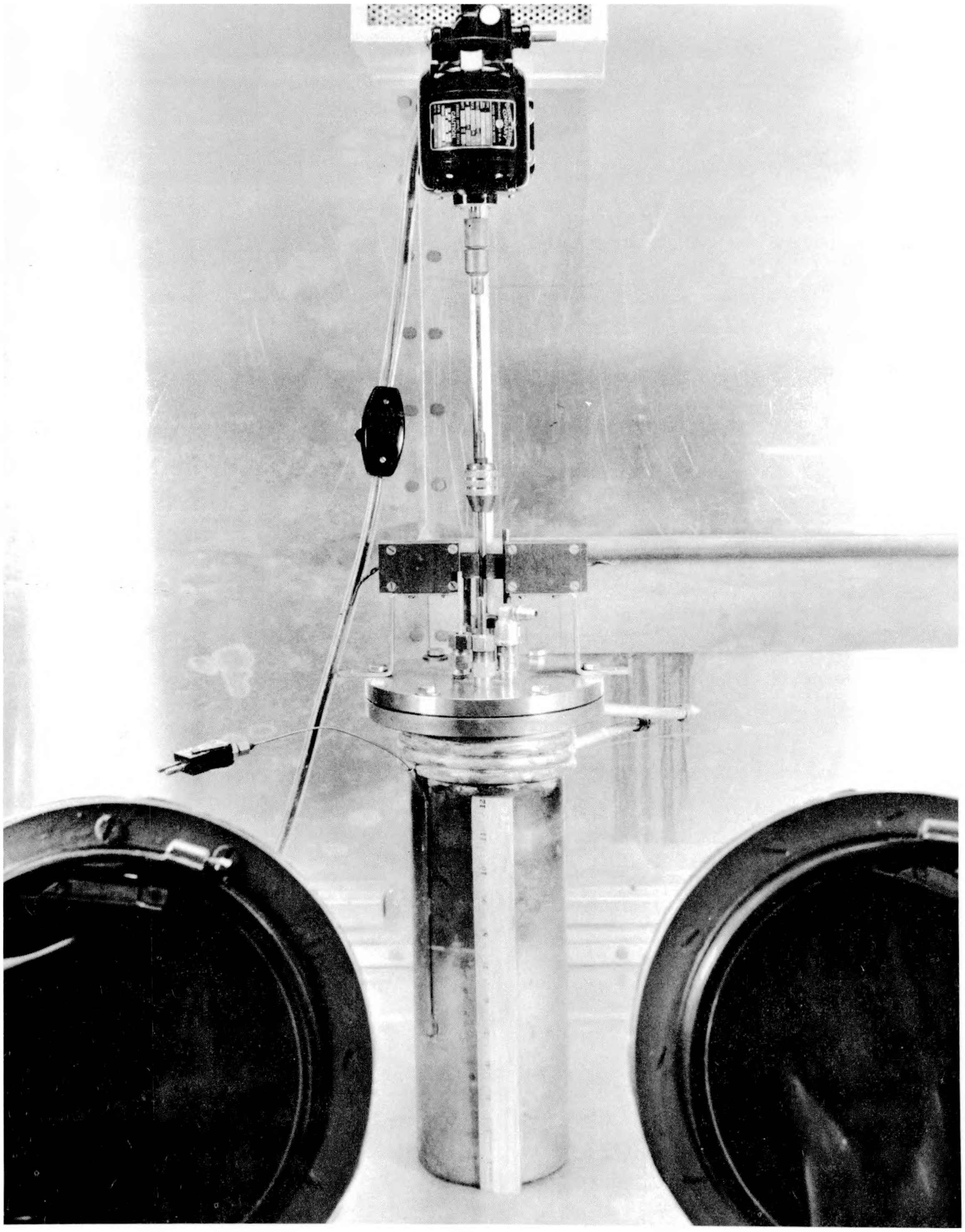

Fig. 3. Photograph of electrorefining cell, 500 g. scale, in glove box enclosure

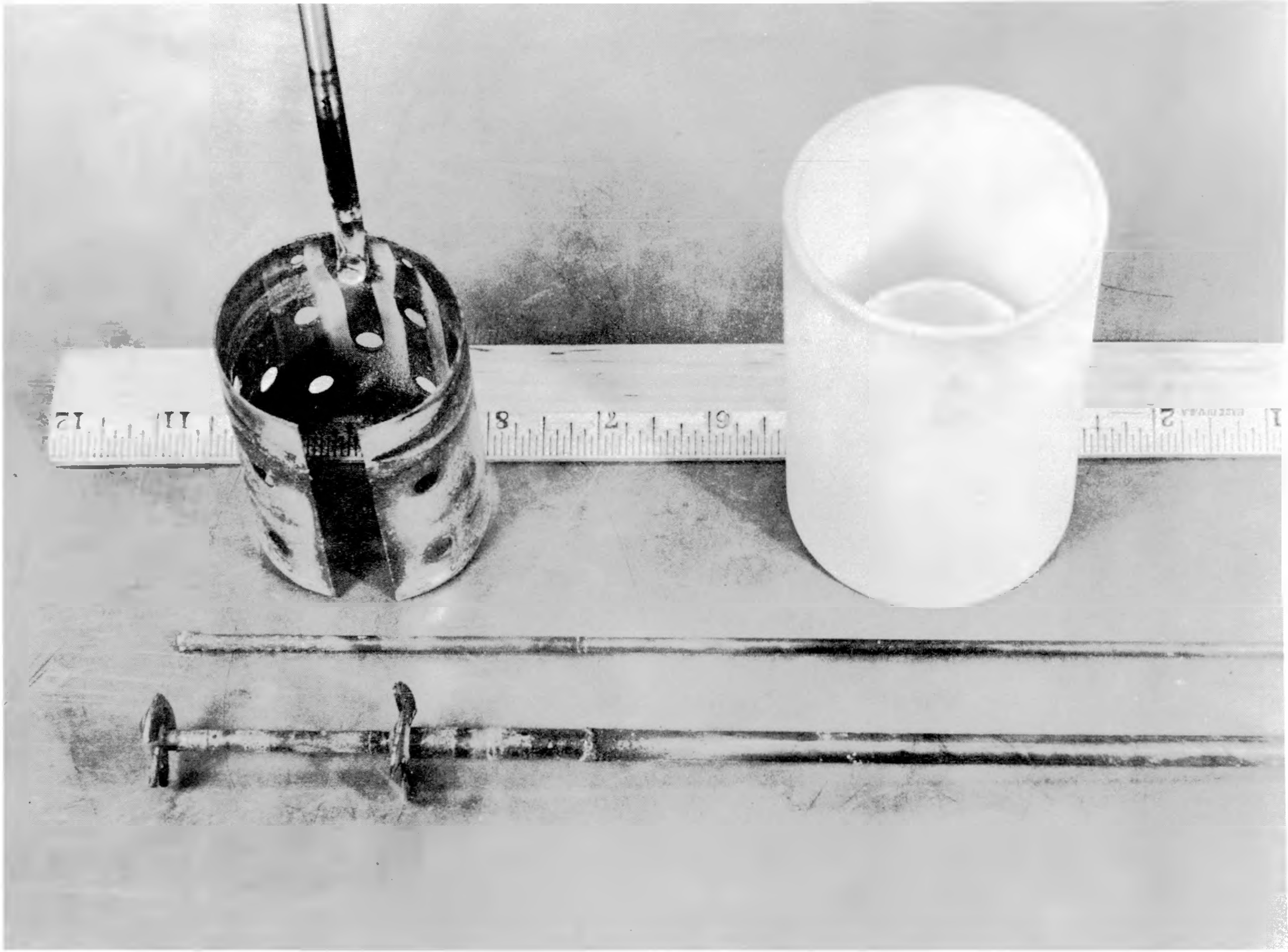

Fig. 4. 500 g. scale cathode, cell, pre-electrolysis rod, and stirrer

The equipment just described was used in small scale experiments subsequent to Run PMR-7. The equipment used in earlier runs has already been reported.[5]

Procedure: Prior to each experiment, the electrorefining cell was outgassed at 800°C. for 1 hr. under vacuum. The general procedure for an experiment consisted of loading the solid plutonium anode and the salt into the electrorefining cell, and then heating the mixture to ~400°C. under vacuum. The system was then filled with helium to a gauge pressure of 3 p.s.i. (The leakage around the stirrer seal was usually < 1 cu. ft./hr. at this pressure.) The cell was then heated to 700°C., and the stirrer and pre-electrolysis cathode were lowered into position.* The stirrer was operated at ~1600 r.p.m. The pre-electrolysis was conducted for 1 hr. at 1 amp. At the conclusion of the pre-electrolysis, the current was interrupted, the 1/8 in. tungsten cathode rod was withdrawn from the melt, and the cylindrical tungsten cathode was lowered into position. The electrolysis was then resumed. Generally the current was held constant at a value between 2 and 10 amp. At the conclusion of the electrorefining period, the stirrer and cathode were withdrawn, and in most cases the cell was heated to 800°C. and held at this temperature for 1 hr. The furnace was then cooled to room temperature. The cell was broken apart and the plutonium product was recovered as an annular metal casting. A typical metal product ring is shown in

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*In some of the runs, the cathode from a previous electrorefining experiment was used instead of the 1/8 in. dia. pre-electrolysis rod. In these cases the "old" cathode was made the anode for the pre-electrolysis period and the feed material was the cathode.

Figs. 5, 6, and 7. The casting was sampled by cutting wedges from the ring. Chemical composition and density of the product were determined.

In these experiments the salt and plutonium metal at room temperature were handled in a dried-air atmosphere (15°F. dew point). The heated salts and metal were never exposed to the air, however.

RESULTS

The experimental results are summarized in Appendix A in Tables A1 and A2. The tables include results of Runs 1-4, which were reported previously.[5] Subsequent experiments have been designated as PMR runs. For the sake of clarity and to emphasize the important points of the electrorefining process, these data have been regrouped in Tables 3 through 8.

The results of electrorefining experiments in alumina-yttria cells with the procedures and equipment described are given in Table 3. Experiments were conducted at 5 and 10 amp. In all cases, products containing less than 167 p.p.m. detectable metallic impurities were obtained from plutonium containing as much as 1715 p.p.m. impurities. In the 5 amp. experiments, the products contained less than 100 p.p.m. metallic impurities. It is shown in Table 7 that the higher impurity level in the products from the 10 amp. runs is due primarily to tantalum.

Obviously the degree of purification achieved will depend upon the specific impurity elements. The detailed behavior of some impurity elements is given in Table 4. In general, the common impurity elements such as iron, nickel, and chromium are easily removed from the plutonium.

Fig. 5. Plutonium product ring from 500 g. scale experiment - top view
(No surface cleaning)

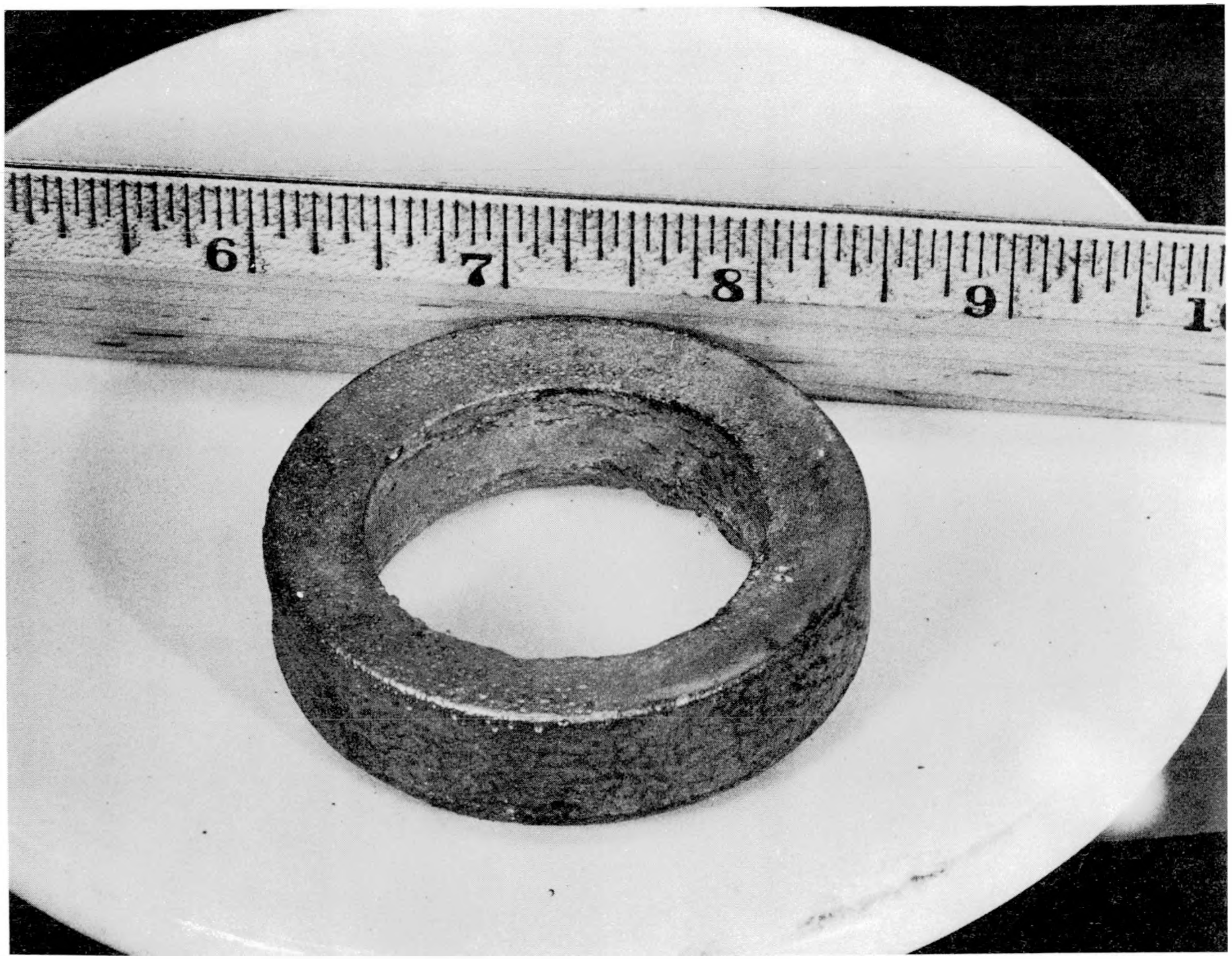

Fig. 6. Plutonium product ring from 500 g. scale experiment - bottom view
(No surface cleaning)

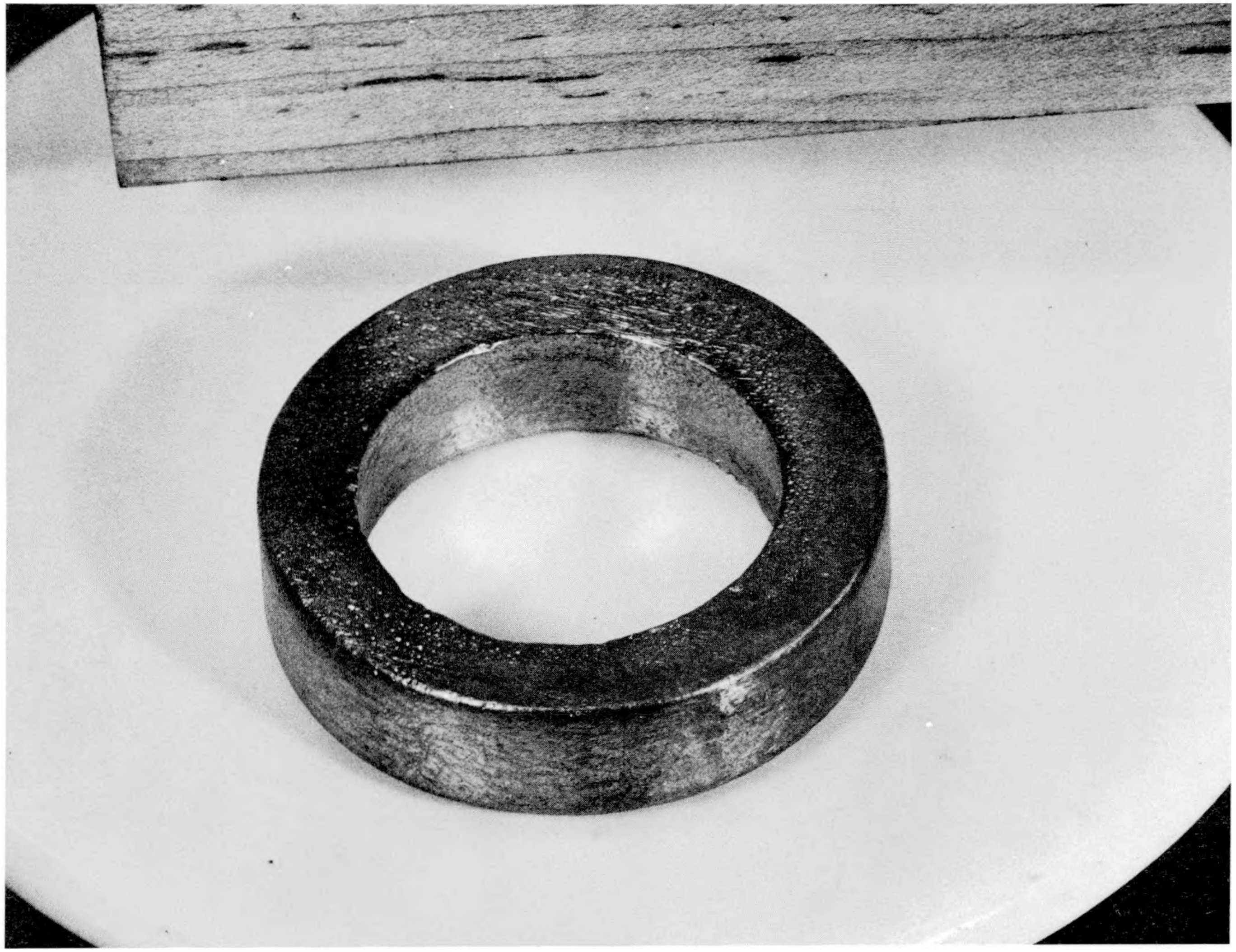

Fig. 7. Plutonium product ring from 500 g. scale experiment - bottom view (After wire brushing for cleanup)

Table 3

SUMMARY OF EXPERIMENTAL RESULTS USING Al_2O_3-Y_2O_3 CELLS AND NaCl-KCl-$PuCl_3$ ELECTROLYTE

Salt:	50.4 w/o KCl-39.6 w/o NaCl-10 w/o $PuCl_3$
Cell:	Al_2O_3-2 w/o Y_2O_3
Electrorefining temp.:	700°C.
Terminal heating:	800°C. for 1 hr. PMR-17 and PMR-24 700°C. for 1 hr. PMR-28

					Efficiencies, %		Metallic Impurities		
Run	Current, amp.	Salt, g.	Feed, g.	Product,[a] g.	Anode[b]	Product Collection[c]	p.p.m. Feed	p.p.m. Product	Product Density
PMR-17	5	271	446	324	95	100	646	90	19.67
PMR-18	10	273	626	497	90	97.3	1715	166	19.59
PMR-19	5	252	619	479	83	98.2	1715	74	19.62
PMR-24	10	246	516	369	87	86.8[d]	476	112	-
PMR-28	10	275	592	404	78	96.9	~ 1100[e]	165	19.62

[a] g. product = g. product ring + g. Pu on cathode.

[b] Calculated on the basis of the reaction $Pu^0 \rightarrow Pu^{+3} + 3e^-$.

[c] Product collection efficiency = $\frac{\text{g. product}}{\text{g. Pu dissolved at anode}} \times 100$.

[d] Helium flow rate for the last 6 hr. of operation was 30 cu. ft./hr.

[e] The thorium and uranium analyses of the feed are in considerable doubt because of segregation in the feed samples.

Table 4

PURIFICATION OF "DIRTY" PLUTONIUM FEEDS

Element	Concentration of Elements, p.p.m. PMR-7 Feed	PMR-7 Product	PMR-19 Feed	PMR-19 Product
Al	175	15	60	40
Si	210	< 10	120	< 10
Pb	< 2	< 2	20	< 2
Cu	100	2	30	2
Ni	750	< 10	320	< 20
Cr	220	10	80	< 20
Mn	70	< 2	35	< 2
Sn	< 1	< 1	10	< 1
Fe	750	30	480	< 20
Zn	< 10	< 10	10	< 10
W	< 10	18	< 10	32
Ta	< 35	80	< 35	< 35
Th	--	< 10	60	< 10
U	275	< 20	490	< 25
Pu, w/o	--	100.00	--	100.04

Elements such as uranium and thorium which form chlorides that have a free energy of formation almost equal to plutonium chloride are also removed to a considerable extent. Other experiments, e.g., PMR-28, Table A2, have shown that americium is perhaps the most difficult metal to separate from plutonium. This result was not predictable from thermodynamic estimates and is considered in more detail in the kg. scale results which follow.

From Table 3 it is evident that product collection efficiencies of 97% or higher were obtained in all runs except PMR-24. In this experiment, the excessive helium leak rate, 30 cu. ft./hr., was probably responsible for the yield of 87%. Presumably, the excessive leak rate results in the introduction of gaseous impurities which interfere with the metal collection process into the cover gas over the cell. These impurities could arise either from diffusion of air through the leaking seal or from impurities in the helium.

During the course of these experiments, the refined metal products were in demand for metallurgical studies. As a result, the emphasis of the program was on preparing metal, rather than on a systematic study of variables involved in the electrorefining process. However, the effects of some of the variables can be derived from comparisons of selected runs.

The reasons for agitating both the anode metal and the electrolyte were discussed earlier in this section. Subsequent experiments have shown that agitation of the salt, particularly in the vicinity of the anode and cathode, is essential. When plutonium was depleted in the vicinity of the cathode, alkali metals were deposited. When the plutonium(III) chloride that formed at the anode was not stirred into the electrolyte, solid salts were formed which seriously decreased the plutonium transport rates. The effect of stirring is shown in Table 5. In one run both the anode and electrolyte were stirred. In the other run no stirring was used. In both runs a current of 2 amp. was passed through the cell. From Table 5 it can be seen that there was no product collection when the salt was unstirred. The principal cathode product was alkali metal, although a small amount of plutonium shot could also be observed.

Table 5

EFFECT OF STIRRING ON ANODE EFFICIENCY AND ON PRODUCT METAL COLLECTION

		Efficiencies, %	
Run	Condition	Anode Current	Product Collection
PMR-2	With stirring	84	88.2
PMR-1	Without stirring	34	0

The superiority of tungsten to tantalum as a cathode material can be seen from Table 6, where products collected from tantalum and tungsten cathodes are compared. As a result of these experiments, tungsten cathodes were used in all runs subsequent to Run 2. (Tantalum stirrers were used in all experiments).

Table 6

COMPARISON OF PURITY OF PLUTONIUM COLLECTED ON TANTALUM AND TUNGSTEN CATHODES

Run	Cathode	Current, amp.	Concentration of Element in Product, p.p.m.	
			Ta	W
1	Ta	4	270	-
2	Ta	3	400	-
4	W	2	< 35	12
PMR-3	W	3	< 35	22

The use of a tantalum stirrer to conduct current to the anode pool appears to impose a limitation on the current, even when a tungsten cathode is used. Tantalum contamination of the product has never been observed for runs with a tungsten cathode in which the current was 6 amp. or less. However for runs in which the current was 9 amp. or higher, tantalum contamination was frequently observed. The tantalum analyses of the products from all the small scale runs with tungsten cathodes (with the exceptions of Run 3 in which a tantalum thermowell failure occurred and Run 5 in which no product was collected) are given in Table 7. It can be seen that in the nine experiments at 6 amp. or less, tantalum was not detectable in the product. Of the eight experiments at 9 amp. or higher, tantalum could be detected in five products. Thus, when the tantalum stirrer is in contact with the anode pool, the electrorefining current should not exceed 5 amp.* if nondetectable concentrations

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*This is equivalent to an anode current density of 0.45 and a cathode current density of 0.05 amp./sq. cm.

Table 7

EFFECT OF CURRENT ON TANTALUM CONCENTRATION IN THE ELECTROREFINED PLUTONIUM

Run	Current, amp.	Pu Salt	Ta Conc. in Product, p.p.m.
PMR-2	2	$PuCl_3$	< 35
4	2	$PuCl_3$	< 35
PMR-4	3	$PuCl_3$	< 35
PMR-5	3	$PuCl_3$	< 25
PMR-3	3	$PuCl_3$	< 35
PMR-15	4	$PuCl_3$	< 35
PMR-19	5	$PuCl_3$	< 35
PMR-17	5	$PuCl_3$	< 35
PMR-14	6	PuF_3	< 35
PMR-11	9	$PuCl_3$	175
PMR-12	9	PuF_3	240
PMR-13	10	PuF_3	100
PMR-6	10	$PuCl_3$	< 25
PMR-7	10	$PuCl_3$	80
PMR-18	10	$PuCl_3$	124
PMR-24	10	$PuCl_3$	< 35
PMR-28	10	$PuCl_3$	< 30

of tantalum in the product are to be insured. In the large scale electrorefining experiments, described in the following section, higher current densities may be used if the current is conducted to the anode pool by a shielded tantalum rod and if the tantalum stirrer does not contact the anode.

The use of plutonium(III) fluoride as a substitute for plutonium(III) chloride in the electrorefining process has been investigated in alumina cells. Analyses of both the metal product and the electrolyte, Table 8, indicate attack of the alumina crucible by the fluoride salt. In all other respects however the fluoride salt was satisfactory. Thus with containers such as magnesia or calcia, plutonium(III) fluoride might be an acceptable substitute for plutonium(III) chloride. If so, this would provide a marked improvement from a practical standpoint, because the fluoride is not hygroscopic and because it generally is available in all laboratories that produce plutonium metal.

Table 8

EFFECT OF FLUORIDE ON CONCENTRATION OF ALUMINUM IN PRODUCT

		Conc. of Al, p.p.m.	
Pu Salt	Run	Electrolyte	Product
PuF_3	PMR-12	1000	400
PuF_3	PMR-13	1000	500
PuF_3	PMR-14	< 200	> 500
$PuCl_3$	PMR-17	< 200	20

The reasons for the selection of alumina as a crucible material have already been discussed (see Initial Design Considerations). In actual experiments with chloride electrolyte, contamination of the plutonium product by aluminum was much less than had been anticipated. This is undoubtedly due to the fact that the product metal is protected from the alumina by a salt phase that is visible in broken cells after a run. Nevertheless it is of interest to compare alumina to oxides that are thermodynamically more stable, such as CaO. In Table 9, a small scale run done in alumina is compared with a large scale run done in calcia. The concentration of calcium in the product was 70 p.p.m., and this concentration was reduced to nondetectable levels by remelting the product under vacuum. Thus, calcia crucibles do offer a potential purity advantage. However, they do not have the mechanical strength of alumina crucibles, and they are hygroscopic.

Table 9

COMPARISON OF PRODUCTS FROM ALUMINA AND CALCIA CELLS

		Conc. of Element, p.p.m.			
		Electrorefined Product		Vacuum Remelt Product	
Cell	Run	Al	Ca	Al	Ca
Al_2O_3	PMR-3	25	< 5	25	< 5
CaO	PMR-9	< 5	70	< 5	< 5

3.5 kg. SCALE EXPERIMENTS

EXPERIMENTAL

Preparation of Electrolyte and Anode Feeds: Procedures identical to those already described for the 500 g. scale were used.

Equipment and Procedure: The first five large scale electrorefining runs were done in equipment very similar to that already described, page 17. In the large scale runs, the stainless steel insert and the pedestal were omitted, the cell being seated in the bottom of the furnace. In PMR-29 and later runs, the equipment shown in Fig. 8 was used. The essential changes in this design were the installation of a double ball bearing stirring gland (15), replacement of the tantalum safety crucible by a stainless steel can (9), replacement of the furnace pot by a furnace tube (11), and provision for conducting the current to the anode pool by a stationary shielded tantalum or tungsten rod (3).

The procedure for a run was as follows: The plutonium cylinder, 2-1/4 in. dia. x 3 in. high, was placed in the anode cup (1). On top of this was placed the NaCl-KCl-$PuCl_3$ salt casting, 3.5 in. dia. The alumina cell was placed in the stainless steel can which was then put in the furnace tube. The top flange complete with stirrer (14), cathode (5), anode rod (2), and pre-electrolysis rod (not shown in figure) was placed

1. Alumina-yttria cell,
   4-1/8 in. O.D. x 6-1/8 in. tall
2. Anode assembly
3. Tungsten anode protected by alumina sheath
4. Tungsten cathode
   3-3/8 in. I.D. x 4 in. tall x 0.030 in. thick
5. Cathode rod
   1/4 in. dia.
6. Tantalum stirrer
7. Tantalum spacer
8. Alumina spacer
9. Stainless steel safety can
10. Stainless steel pedestal
11. Stainless steel furnace tube
    4-3/4 in. I.D. x 20 in. long x 1/8 in. thick
12. Cooling coils
13. Teflon lined compression seal
14. Stainless steel shaft
15. Stirring gland

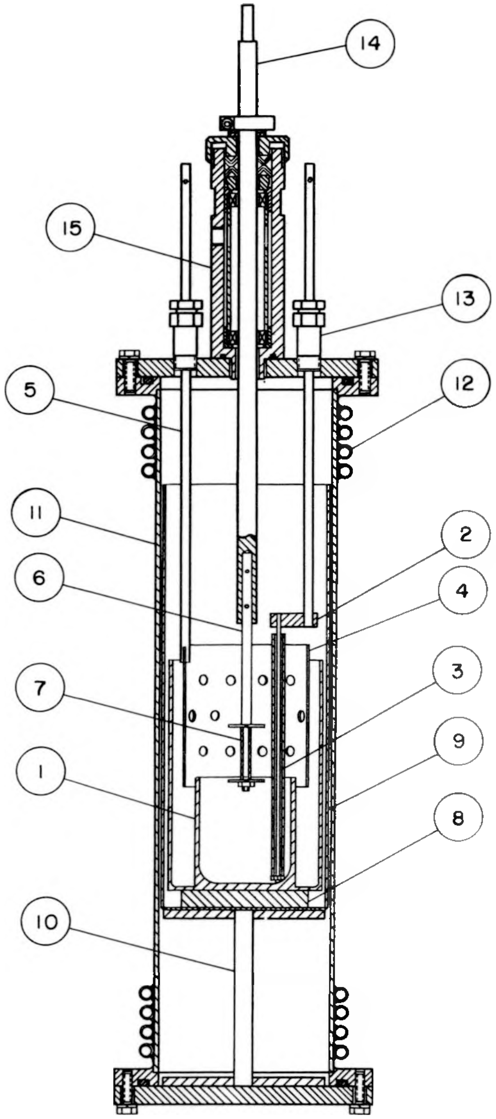

Fig. 8. Electrorefining cell assembly, 3.5 kg. scale

on the furnace tube. The furnace was heated at a rate of 50°C./hr. under vacuum. At 400°C. the furnace was flushed with purified helium or argon and a positive pressure of 3 p.s.i. was maintained on the furnace tube. (The argon leak rate at this pressure was < 1 cu. ft./hr. when the stirrer was in operation.) When the metal and salt had melted, the stirrer, cylindrical cathode, pre-electrolysis rod, and anode were lowered and positioned as shown in Figs. 8 and 9. The stirrer was rotated at about 1400 r.p.m. by a 1/20 h.p. electric motor (Howard Industries Motor 4-58, 6 MFD condenser, 1250 r.p.m.). Direct current was supplied to the anode rod and pre-electrolysis rod. These rods, as well as the cathode and stirrer, were electrically insulated from the furnace tube. The pre-electrolysis was conducted at 2 amp. for 1/2 hr. The power supply (Model CMB-7-PS-52) was designed and built at this Laboratory. When a "clean" tungsten cathode coated with plutonium was available, the preferred procedure for conducting the pre-electrolysis was to make the tungsten cylinder anodic and the plutonium feed material cathodic. Upon completion of the pre-electrolysis period, the pre-electrolysis rod was removed from the melt. The tungsten cylinder was made cathodic and the electrorefining was started. At the conclusion of the electrorefining period, the stirrer, cathode, and anode were raised from the melt and the cell was heated to 800°C. at a rate of 50°/hr. The cell was held at this temperature for 2 hr. and then permitted to cool to room temperature. After it was unloaded, the cell was removed from the furnace and broken apart. The salt was easily

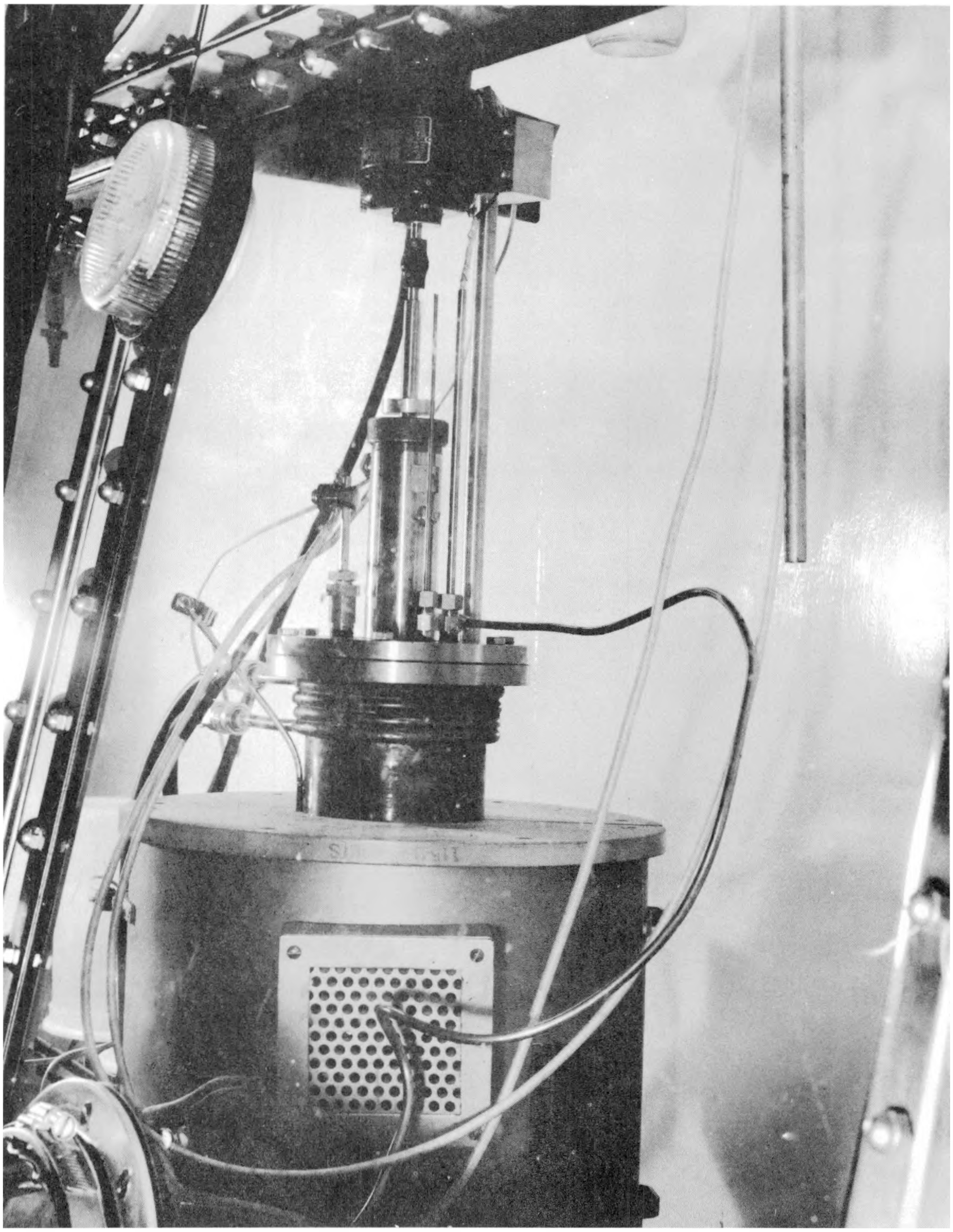

Fig. 9. Photograph of electrorefining cell, 3.5 kg. scale

separated from the metal, and after it was sampled, it was stored for future runs. Wedges were broken from the metal ring for analysis. The cathodes, anode rod, and stirrer were also stored for future runs. These items of equipment, after an electrorefining run, are shown in Fig. 10. Pictures of the electrorefined product and anode residue are shown in Figs. 11 through 14.

RESULTS

The results of all the large scale electrorefining experiments are given in Appendix A in Tables A3 and A4.

The results of the four experiments done in alumina-yttria cells with the equipment shown in Fig. 8 are summarized in Table 10 and in Appendix A in Table A4. Although the cell can accommodate a feed of 4 kg. of plutonium metal, the nominal charge was 3.5 kg. for feed-casting convenience. Experiments were done at 15, 25, and 30 amp., which correspond to production rates of 1.1, 1.8, and 2.1 kg. of metal per day, assuming 100% efficiencies. The cathode and anode current densities at 30 amp. were 0.11 amp./sq. cm. and 0.90 amp./sq. cm. The purification achieved in most of these large scale experiments was excellent and was comparable to the 500 g. scale runs, the principal difference being the greater aluminum and silicon contamination in the kilogram product. The product collection efficiencies listed in Table 10 were less than in small scale experiments (i.e., 93% as compared to 97%). The deleterious effect of impurities in the inert gas on product collection efficiencies was observed in PMR-32 where unpurified argon gas was used unintentionally.

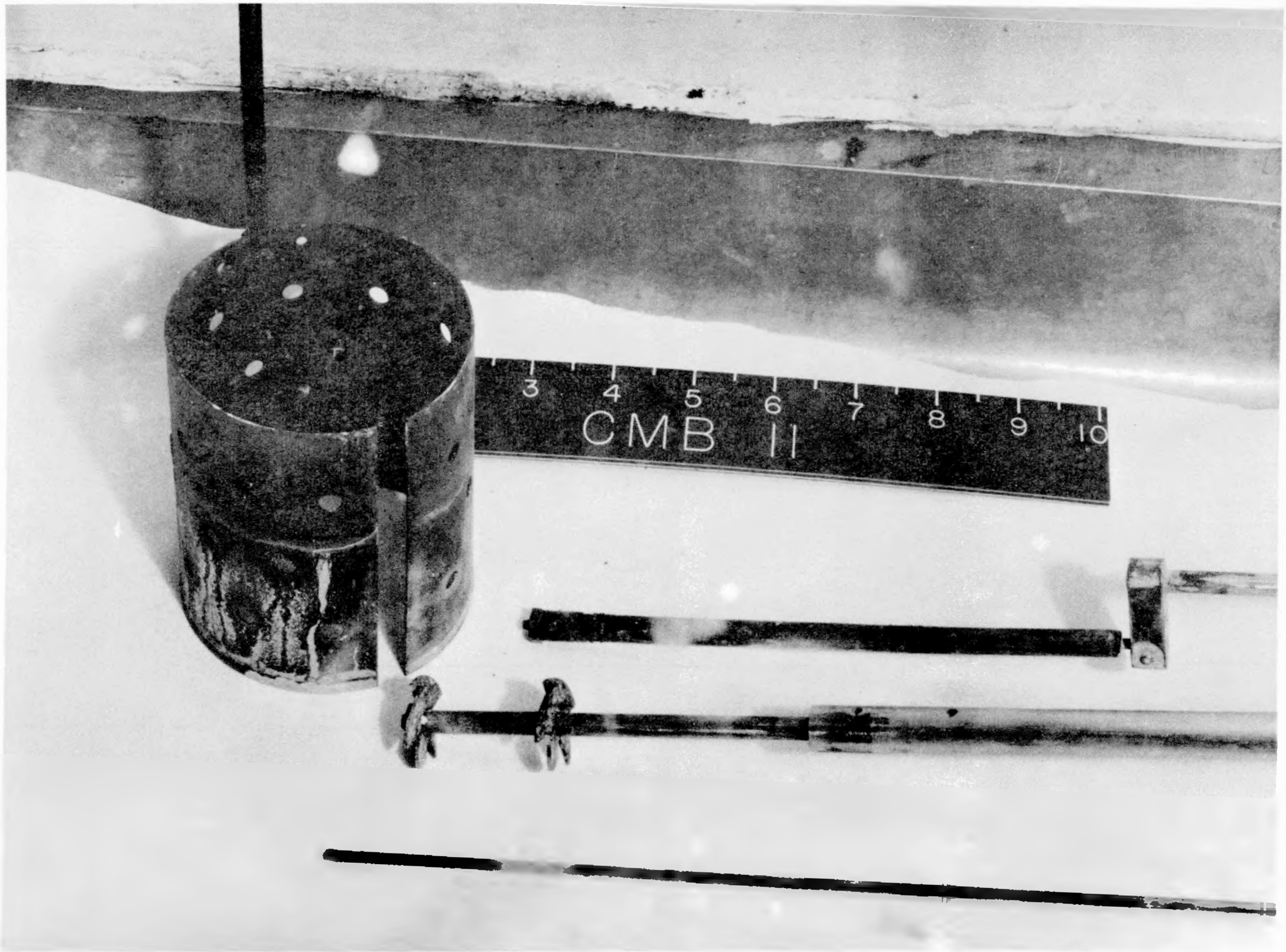

Fig. 10. 3.5 kg. scale cathode, anode rod, stirrer, and pre-electrolysis rod

Fig. 11. Plutonium product ring from 3.5 kg. scale experiment - top view
(No surface cleaning)

Fig. 12. Plutonium product ring from 3.5 kg. scale experiment - bottom view (No surface cleaning)

Fig. 13. Anode residue - top view

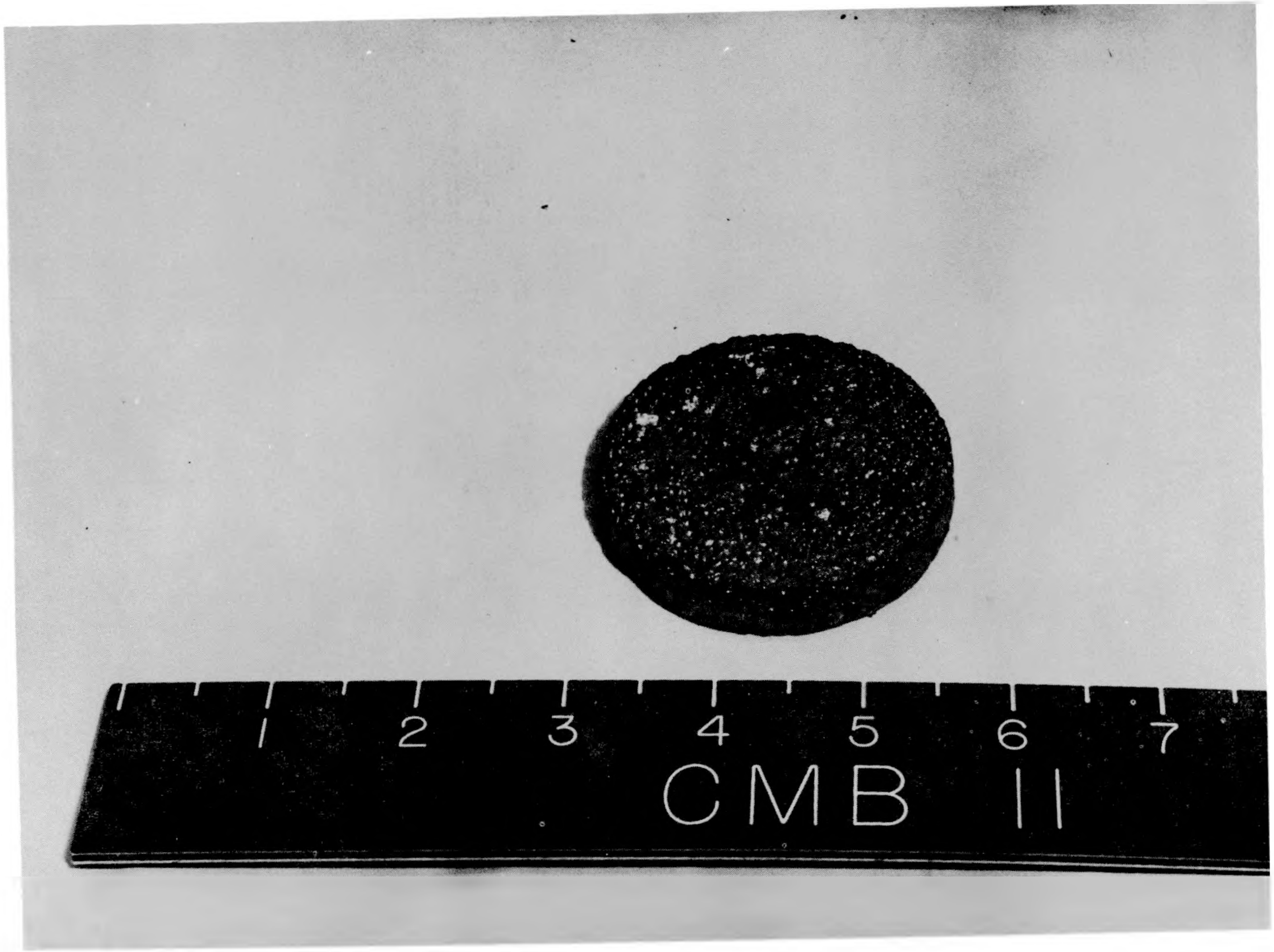

Fig. 14. Anode residue - bottom view

Table 10

SUMMARY OF EXPERIMENTAL RESULTS, 3.5 kg. SCALE, ALUMINA-YTTRIA CELLS

Salt: 50.4 w/o KCl-39.6 w/o NaCl-10 w/o $PuCl_3$

Cell: Al_2O_3-2 w/o Y_2O_3

Feed: Plutonium metal

Run	Current, amp.	Salt, g.	Feed, g.	Product, g.	Metallic Impurities, p.p.m.		Al Conc. in Product, p.p.m.	Product Density	Efficiencies, %	
					Feed	Product			Anode	Product Collection
PMR-29	15	1400	3556	2695	447	124	75	19.64	89	93.5
PMR-30	30	1383	3641	3190	680	193	75	19.56	93	93.5
PMR-32	30	1400[a]	3328	2019	2396	227	50	19.63	67	85.7[b]
PMR-33	25	1378[c]	3544	2466	1125	430	150	19.45	75	96.0

[a] Electrolyte from PMR-29 and PMR-30.

[b] No gas purification; uranium chips completely oxidized.

[c] Electrolyte from PMR-31.

(A leak in the uranium chip furnace resulted in complete oxidation of the turnings.) It is interesting to note the dependence of product density on impurity level. Density measurement thus provides an estimate of product purity.

The poor separation of plutonium and americium in the electrorefining process was mentioned in the discussion of the 500 g. experimental results. From the $-\Delta F^{o}$ values listed in Table 1, one would expect americium to behave similar to cerium. However in Run PMR-32, Table A4, the cerium concentration in the metal was reduced from 527 p.p.m. to < 25 p.p.m., while the americium concentration was only reduced from 65 p.p.m. to 18 p.p.m. The distribution of americium in Runs PMR-29, -30 and -32 is given in Table 11, where the concentration of americium in the metal feed, salt feed, anode residue, metal product, and salt product is tabulated. As expected, americium concentrates in the salt phase. The ratio

$$\frac{\text{p.p.m. Am in salt product}}{\text{p.p.m. Am in metal product}}$$

is approximately constant as one would expect from a consideration of the equilibrium:

$$Am^{o} + PuCl_3 \rightleftarrows AmCl_3 + Pu^{o}.$$

The calculated value of the above ratio, from the relationship $-\Delta F^{o} = RT \ln K$ with the $-\Delta F^{o}$ values of Table 1 and the assumption that all activity coefficients are unity, is 2×10^{5}. This value is greater than those given in Table 11 by a factor of $\sim 10^{3}$. At present the data are inadequate to explain this large difference. It should be obvious that

Table 11

DISTRIBUTION OF AMERICIUM IN ELECTROREFINING RUNS

Run	Am, p.p.m. Metal Feed	Salt Feed	Anode Residue	Metal Product	Salt Product[b]	$k_D \times 10^{-2}$ (ftnt. c)
PMR-29	59	206	33	9	1700	1.9
PMR-30	113	60	58	26	3630	1.4
PMR-32	65	1911	43	18	3580	2.0

[a] Parts of americium per million parts of plutonium.

[b] Salt after electrorefining run.

[c] $k_D = \dfrac{\text{p.p.m. americium in salt product}}{\text{p.p.m. americium in metal product}}$.

the above reaction provides a method for removing americium which has grown into high purity plutonium. The application of this method to the removal of rare earths from plutonium has been reported previously.[7]

The voltage-current relationship for a typical cell after several hours operation is given in Fig. 15. The points can be described by a straight line passing through the origin. This plot indicates the absence of back e.m.f.'s and serious concentration polarization effects.

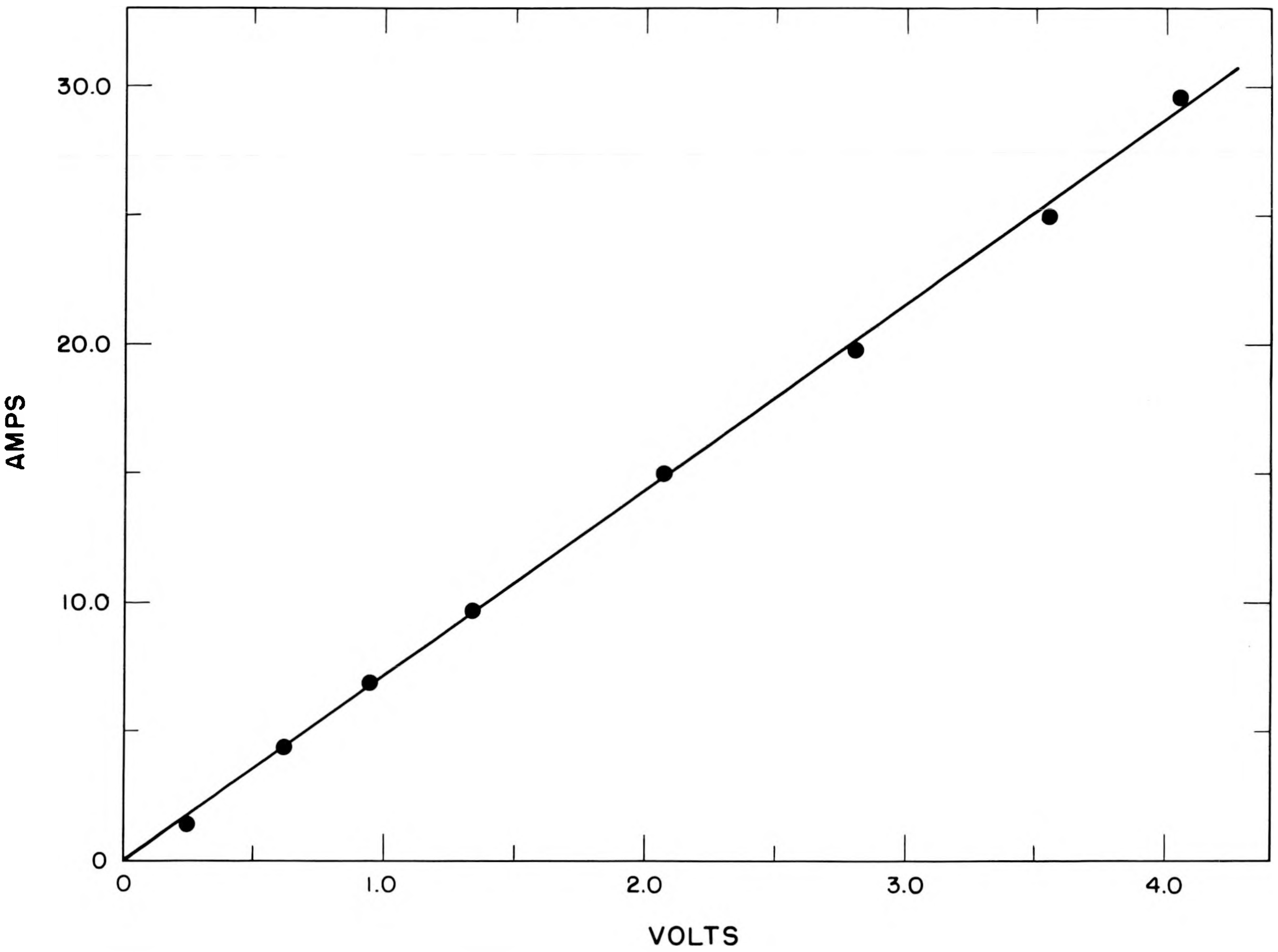

Fig. 15. Current vs. voltage plot for 3.5 kg. scale, Run PMR-32

DISCUSSION

Electrorefining processes have been developed that provide high purity, high density plutonium metal for metallurgical studies on the 500 g. and 3.5 kg. scales. This metal is superior to that produced by high purity bomb reduction techniques.[4,11]

Obviously the 3.5 kg. scale procedure can be used for the processing of plutonium metal scrap. Although this process has not yet been optimized, it is presently capable of competing very favorably with conventional aqueous processing. To demonstrate this fact, the cost of an electrorefining process based on procedures and equipment identical to those already described is outlined in Appendix B. For a reference plant having a capacity of 10 kg./week, the unit cost of electrorefining is $0.32/g. of plutonium. Most of this cost is incurred in the recovery of plutonium waste by conventional aqueous methods.

CONCLUSIONS

1. On a 500 g. scale, plutonium metal containing less than 100 p.p.m. detectable metallic impurities and having a density greater than 19.6 g./cc. can be made from metal containing as much as 1700 p.p.m. impurities.

2. Product collection efficiencies on the 500 g. scale are greater than 97%.

3. On a 3.5 kg. scale, plutonium metal containing less than 200 p.p.m. detectable metallic impurities and having a density greater than 19.6 g./cc. can be made from metal containing as much as 2300 p.p.m. impurities.

4. Product collection efficiencies on the 3.5 kg. scale are greater than 93%.

5. The purity of the product produced by electrorefining is superior to that produced by bomb reduction.

6. A preliminary cost analysis for the recycle of plutonium scrap indicates that electrorefining is considerably cheaper than conventional aqueous methods.

APPENDIX A

RESULTS AND ANALYSES

Results of all the 500 g. and 3.5 kg. scale experiments are summarized in Tables A1 and A3. Analytical data for these experiments are given in Tables A2 and A4. Elements that were not detectable in feeds or products include sodium, lithium, beryllium, lanthanum, boron, bismuth, and cobalt.

Table A1

SUMMARY OF RESULTS, 500 g. SCALE

Salt: 50.4 w/o KCl-39.6 w/o NaCl-10 w/o $PuCl_3$ or 50.4 w/o KCl-39.6 w/o NaCl-10 w/o PuF_3

Cells: Type A - Al_2O_3-0.1 w/o MgO, LASL, CMB-6
B - Al_2O_3-2 w/o Y_2O_3, LASL, CMB-6
C - Al_2O_3-0.1 w/o MgO, U.S. Stoneware
D - Al_2O_3-0.1 w/o MgO, CaO coating, LASL, CMB-6

					Product Thermal Treatment				g. Pu in					Efficiencies, %	
Run	Halide	Cell	Cathode	Temp., °C.	Temp., °C.	Time, hr.	Current, amp.	Salt Charge, g.	Feed	Anode Residue	Cathode		Product Ring	Anode Current	Product Collection[a]
											Initial	Final			
1	$PuCl_3$	A	Ta	700	None	--	4	249	294	23	0	30	192	87	81.9
2	$PuCl_3$	A	Ta	700	None	--	3	250	304	19	0	20	258	92	97.5[b]
3	$PuCl_3$	A	W	700	None	--	3	250	287	--	--	--	128	--	--[c]
4	$PuCl_3$	A	W	690	None	--	2	250	298	107	0	24	146	93	89.0
PMR-1	$PuCl_3$	A	W	700	None	--	2	216	290	246	24	5	15	34	0
PMR-2	$PuCl_3$	D	W	700	None	--	2	250	358	60	0	3	260	84	88.2
PMR-3	$PuCl_3$	A	W	700	None	--	3	235	338	30	0	10	239	91	80.8
PMR-4	$PuCl_3$	A	W	700	None	--	3	235	338	39	10	11	253	90	84.9
PMR-5	$PuCl_3$	A	W	700	None	--	3	280	597	32	0	23	473	--	87.8
PMR-6	$PuCl_3$	A	W	700	800	0.5	10	280	500	272	0	22	196	98	95.6
PMR-7	$PuCl_3$	A	W	700	800	0.5	10	280	545	82	0	19	401	89	90.7
PMR-11	$PuCl_3$	A	W	700	800	1	9	275	481	22	0	13	439	98	98.5
PMR-12	PuF_3	A	W	700	800	1	9	304	491	48	11	15	438	90	99.8
PMR-13	PuF_3	A	W	700	800	1	10	302	487	172	0	7	298	94	96.8
PMR-14	PuF_3	C	W	700	800	1	6	250	483	278	0	15	177	83	93.7
PMR-15	$PuCl_3$	C	W	700	800	1	4	224	481	350	0	10	107	56	89.3
PMR-17	$PuCl_3$	B	W	700	800	1	5	271	446	122	0	16	308	95	100.
PMR-18	$PuCl_3$	B	W	700	800	1	10	273	626	115	0	15	482	90	97.3
PMR-19	$PuCl_3$	B	W	700	800	1	5	252	619	131	0	33	446	83	98.2
PMR-24	$PuCl_3$	B	W	700	800	1	10	246	516	91	0	9	360	87	86.8[d]
PMR-28	$PuCl_3$	B	W	700	700	1	10	275	592	175	0	14	390	78	96.9

[a] Product collection efficiency = $\frac{\text{g. Product ring + (g. Pu final-g. Pu initial) on cathode}}{\text{g. Pu dissolved at anode}}$.

[b] A product remelt was used to consolidate the plutonium shot.

[c] Run terminated after 20 hr. because of a tantalum thermowell failure.

[d] Helium flow rate for the last 6 hr. of operation was 30 cu. ft./hr.

Table A2

ANALYSES OF FEEDS AND PRODUCTS, 500 g. SCALE EXPERIMENTS

Run	1		2		3		4	
Element[a]	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Mg	30	30	15	< 5	80	< 5	80	< 5
Ca	< 5	< 5	20	< 5	25	10	25	15
Al	20	35	90	20	25	250	25	28
Si	<100	<10	20	<10	35	<10	35	<10
Pb	< 20	< 1	< 1	< 1	< 1	< 1	< 1	< 2
Cu	20	1	7	< 1	2	2	2	< 2
Ni	<100	<10	50	<10	35	<10	35	<10
Cr	<100	<10	10	< 5	10	5	10	< 5
Mn	< 20	< 1	15	< 1	5	< 1	5	< 2
Sn	< 20	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Fe	2.54×10^4	178	60	20	80	40	80	<20
Zn	<200	<10	10	<10	<10	<10	<10	<10
W	--[b]	--	--	--	<20	<20	<20	12
Ta	< 50	270	430	400	<50	300	<50	<35
Th	--	--	--	--	--	<10	--	<10
U	--	--	--	--	--	20	--	20
Am	--	--	--	--	--	--	--	--
Y	--	--	--	--	--	--	--	--
C	80	60	140	35	--	--	--	32
O_2	90	--	135	25	--	--	--	25
Cl^-	--	--	--	--	--	--	--	--
Pu, w/o	--	99.98	--	100.02	--	100.00	--	100.02
Density, g./cc.	--	--	--	--	--	--	--	--

[a] The concentrations of all elements except plutonium are given in p.p.m. (i.e., parts of element per million parts of plutonium).

[b] Double dash indicates no analysis made.

Table A2 (Cont'd.)

Run	PMR-2		PMR-3		PMR-4		PMR-5	
Element[a]	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Mg	60	< 5	50	< 5	75	< 5	< 5	< 5
Ca	7	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Al	15	18	40	25	50	15	150	90
Si	30	<10	120	<10	115	<10	260	20
Pb	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Cu	10	< 2	15	< 2	15	< 2	50	3
Ni	<20	<10	360	<10	350	<10	600	55
Cr	<20	< 5	265	< 5	280	<10	140	10
Mn	8	< 2	60	10	60	< 2	35	5
Sn	< 1	< 1	--	--	< 1	< 1	< 1	< 1
Fe	40	<15	155	20	180	20	540	90
Zn	<10	<10	<10	<10	<10	<10	<10	<10
W	<12	32	--	22	--	35	--	20
Ta	<35	<35	<35	<35	<35	<35	--	<25
Th	275	40[c]	<20	< 8	<20	<10	--	<10
U	<25	<25	110	30	100	<20	--	110
Am	--[b]	--	--	--	--	--	--	--
Y	--	--	--	--	--	--	--	--
C	85	<15	--	30	--	10	--	40
O_2	40	15	--	80	--	50	--	80
Cl^-	--	--	--	--	--	--	--	--
Pu, w/o	--	100.00	99.94	100.02	--	--	--	--
Density, g./cc.	--	--	--	--	--	--	--	--

[a] The concentrations of all elements except plutonium are given in p.p.m. (i.e., parts of element per million parts of plutonium).

[b] Double dash indicates no analysis made.

[c] Thorium concentration in the $PuCl_3$ was 440 p.p.m. If all this thorium were plated out in the product, the concentration would be 46 p.p.m.

Table A2 (Cont'd.)

Run	PMR-6		PMR-7		PMR-11		PMR-12	
Element[a]	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Mg	< 5	< 5	< 5	< 5	< 5	< 5	5	< 5
Ca	< 5	< 5	< 5	< 5	<10	<10	<10	<10
Al	175	150	175	15	30	20	20	400
Si	210	<10	210	<10	170	<10	50	20
Pb	< 2	< 2	< 2	< 2	< 2	< 2	3	< 2
Cu	100	1	100	2	2	< 2	10	5
Ni	750	15	750	<10	180	<20	<20	<20
Cr	220	<10	220	10	50	<20	20	<20
Mn	70	2	70	< 2	15	< 2	8	< 2
Sn	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Fe	750	20	750	30	170	20	430	30
Zn	<10	<10	<10	<10	15	<10	<10	<10
W	<10	20	<10	18	--	<10	<10	<10
Ta	<35	<25	<35	80	--	175	<35	240
Th	--[b]	<10	--	<10	<10	<10	30	<10
U	275	60	275	<20	40	<30	70	<20
Am	--	--	--	--	--	--	--	--
Y	--	--	--	--	--	--	--	--
C	--	30	--	55	--	35	--	60
O_2	--	80	--	--	--	175	--	45
Cl^-	--	--	--	--	--	--	--	--
Pu, w/o	--	99.96	--	100.00	100.0	100.0	99.89	99.92
Density g./cc.	--	19.52	--	19.65	--	19.61	--	19.3

[a] The concentrations of all elements except plutonium are given in p.p.m. (i.e., parts of element per million parts of plutonium).

[b] Double dash indicates no analysis made.

Table A2 (Cont'd.)

Run	PMR-13		PMR-14		PMR-15		PMR-17	
Element[a]	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Mg	5	< 5	5	< 5	5	< 5	5	< 5
Ca	<10	<10	<10	<10	<10	<10	<10	<10
Al	20	500	20	>500	20	200	20	20
Si	50	<10	50	20	50	<10	50	<10
Pb	3	< 2	3	< 2	3	< 2	3	< 2
Cu	10	3	10	< 2	10	3	10	< 2
Ni	<20	<20	<20	<20	<20	<20	<20	<20
Cr	20	<20	20	<10	20	<20	20	<20
Mn	8	< 2	8	< 2	8	< 2	8	15
Sn	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Fe	430	30	430	<10	430	20	430	20
Zn	<10	<10	<10	<10	<10	<10	<10	<10
W	<10	<10	<10	24	<10	33	<10	35
Ta	<35	100	<35	<35	<35	<35	<35	<35
Th	30	<10	30	<10	30	<10	30	<10
U	70	35	70	30	70	50	70	<25
Am	--[b]	--	--	--	--	--	--	--
Y	--	--	--	--	--	--	--	--
C	--	20	--	10	--	5	--	5
O_2	--	115	--	35	--	30	--	90
Cl^-	--	--	--	--	--	--	--	--
Pu, w/o	99.89	100.02	99.89	100.01	99.89	100.02	99.89	99.99
Density, g./cc.	--	19.32	--	17.80	--	19.71	--	19.67

[a] The concentrations of all elements except plutonium are given in p.p.m. (i.e., parts of element per million parts of plutonium).

[b] Double dash indicates no analysis made.

Table A2 (Cont'd.)

Run	PMR-18		PMR-19		PMR-24		PMR-28	
Element[a]	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Mg	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Ca	<10	<10	<10	<10	<10	<10	<10	<10
Al	60	40	60	40	20	< 5	15	15
Si	120	<10	120	<10	75	<10	120	<10
Pb	20	< 2	20	< 2	20	< 2	2	< 2
Cu	30	2	30	2	25	< 2	2	< 2
Ni	320	<20	320	<20	50	<20	55	<20
Cr	80	<20	80	<20	<10	<20	<10	<20
Mn	35	< 2	35	< 2	5	< 2	2	< 2
Sn	10	< 1	10	< 1	1	< 1	< 1	< 1
Fe	480	<20	480	<20	90	50	70	40
Zn	10	<10	10	<10	<10	<10	<10	<10
W	<10	<10	<10	32	<10	25	--	20
Ta	<35	124	<35	<35	<35	<35	--	<30
Th	60	<10	60	<10	160	<10	~450[c]	43
U	490	<25	490	<25	30	30	~300[c]	40
Am	--[b]	--	--	--	--	7	77	7
Y	--	< 7	--	< 7	--	--	--	< 5
C	90	15	90	30	--	20	--	25
O_2	80	50	80	60	--	50	--	35
Cl^-	--	--	--	--	--	--	--	<10
Pu, w/o	--	99.97	--	100.04	--	99.96	--	--
Density g./cc.	--	19.59	--	19.62	--	--	--	19.62

[a] The concentrations of all elements except plutonium are given in p.p.m. (i.e., parts of element per million parts of plutonium).

[b] Double dash indicates no analysis made.

[c] Both thorium and uranium were severely segregated in the feed samples. These values are based on analyses of the anode residue.

Table A3

SUMMARY OF RESULTS, 3.5 kg. SCALE

Salt: 50.4 w/o KCl-39.6 w/o NaCl-10 w/o $PuCl_3$

Cells: Type E - CaO container for plutonium metal, Morganite salt container
F - Al_2O_3-0.1 w/o MgO container for plutonium metal, Morganite salt container
G - Al_2O_3-2 w/o Y_2O_3, LASL, CMB-6

Cathode: Tungsten

Anode Contact: A - Tantalum stirrer
B - Tantalum stirrer coated with Al_2O_3
C - 1/8 in. tantalum rod
D - 1/8 in. tungsten rod

			Product Thermal Treatment					g. Pu in					Efficiencies, %	
										Cathode				
Run	Cell	Temp., °C.	Temp., °C.	Time, hr.	Current, amp.	Anode Contact	Salt Charge, g.	Feed	Anode Residue	Initial	Final	Product Ring	Anode Current	Product Collection
PMR-9	E	700	810	4.5	14	A	1642	3183	1318	0	17	1530[a]	58	82.9
PMR-16	F	700	800	1.2	10	B	1630	1690	427	0	30	1189	90	96.5
PMR-20	G	700	800	1.0	10	C	1417	3127	2073[b]	0	48	751	99	75.8
PMR-22	G	700	800	0.5	10	C	1241	4162	2772	0	11	1204	100	87.4
PMR-23	G	700	800	3.0	10	C	1400	4032	--[c]	10	33	--	--	92.8
PMR-29	G	715	820	2.2	15	C	1400	3556	673	0	21	2674	89	93.5
PMR-30	G	715	820	2.0	30	C	1383	3641	253	21	20	3170	93	93.5
PMR-31	G	725	820	3.0	30	C,B	1400	2990	1188	20	38	1419	89	79.7
PMR-32	G	750	820	2.0	30	C	1400	3328	973	0	94	1925	67	85.7[d]
PMR-33	G	720	820	2.0	25	D	1378	3544	976	0	75	2391	75	96.0

[a] Metal ring poorly compacted, honeycomb of metal and salt.

[b] Run terminated because of anode rod breakage.

[c] Anode cup fractured, permitting mixing of anode metal and plutonium product.

[d] No gas purification; leak was present in uranium chip furnace; uranium chips were completely oxidized. Similar situation suspected in PMR-31.

Table A4

ANALYSES OF FEEDS AND PRODUCTS, 3.5 kg. SCALE

Run	PMR-9		PMR-16		PMR-20	
Element[a]	Feed	Product	Feed	Product	Feed	Product
Mg	75	< 5	< 5	< 5	<30	< 5
Ca	15	70[c]	<10	<10	<10	<10
Al	25	< 5	300	15	20	10
Si	35	<10	30	<10	280	<10
Pb	< 2	< 2	< 2	< 2	5	< 2
Cu	< 2	< 2	5	< 2	2	< 2
Ni	60	<20	30	<20	40	<20
Cr	<20	<10	<20	<20	20	<20
Mn	5	< 2	5	5	5	< 2
Sn	< 1	< 1	< 1	< 1	< 1	< 1
Fe	100	30	200	70	200	60
Zn	15	<10	<10	<10	<10	<10
W	--[b]	16	<10	31	<10	57
Ta	<35	<35	<35	<35	<35	<35
Th	130	<10	24	<10	41	<10
U	20	20	40	30	90	30
Am	--	--	--	--	--	--
Y	--	--	--	--	--	< 5
C	90	30	95	15	125	20
O_2	40	~250[c]	80	45	95	30
Cl^-	--	--	--	--	--	--
Ce	--	--	--	--	--	--
Pu, w/o	99.95	100.0	99.92	99.95	--	100.02
Density, g./cc.	--	--	--	19.61	--	19.71

[a] The concentrations of all elements except plutonium are given in p.p.m.

[b] Double dash indicates no analysis made.

[c] Recasting of PMR-9 product under vacuum reduced calcium to < 10 p.p.m. and O_2 to 40 p.p.m.

Table A4 (Cont'd.)

Run	PMR-22		PMR-29		PMR-30	
Element[a]	Feed	Product	Feed	Product	Feed	Product
Mg	15	< 5	20	< 5	< 5	< 5
Ca	10	<10	<10	<10	<10	<10
Al	15	25	25	75	25	75
Si	20	<10	130	15	65	20
Pb	< 2	< 2	< 2	< 2	2	< 2
Cu	3	< 2	5	< 2	75	2
Ni	60	<20	60	<20	90	<20
Cr	20	<10	20	<20	<20	<20
Mn	5	< 1	3	< 2	10	< 2
Sn	< 1	< 1	< 1	< 1	< 1	< 1
Fe	70	40	60	<20	260	30
Zn	<10	<10	10	<10	10	<10
W	<10	40	<10	25	<10	40
Ta	<35	<35	<30	<30	<30	<35
Th	180	<10	55	<15	<10	<10
U	40	<25	<30	<30	30	<30
Am	--[b]	9	59	9	113	26
Y	--	--	--	< 5	--	< 5
C	95	40	80	15	--	--
O_2	145	60	--	50	--	--
Cl^-	--	--	--	<10	--	<10
Ce	--	--	--	--	--	--
Pu, w/o	99.9	99.99	99.92	--	--	--
Density, g./cc.	--	19.75	--	19.64	--	19.56

[a] The concentrations of all elements except plutonium are given in p.p.m.

[b] Double dash indicates no analysis made.

Table A4 (Cont'd.)

Run	PMR-31		PMR-32		PMR-33	
Element[a]	Feed	Product	Feed	Product	Feed	Product
Mg	75	< 5	5	< 5	< 5	< 5
Ca	10	<10	75	<10	<10	<10
Al	75	50	400	50	125	150
Si	110	<10	240	<10	105	45
Pb	5	< 2	3	< 2	15	3
Cu	15	< 2	150	3	35	10
Ni	150	<20	200	<20	85	<20
Cr	40	30	70	<10	55	<20
Mn	10	< 2	15	4	10	3
Sn	< 1	< 1	1	< 1	5	< 1
Fe	170	15	380	40	485	120[c]
Zn	10	<10	15	<10	<10	<10
W	<10	<10	<10	34	--	30
Ta	<30	115	<30	<30	<30	<30
Th	1200	40	180	48	<15	<15
U	350	<30	70	30	90	30
Am	221	40	65	18	115	39
Y	--[b]	--	--	<10	--	< 5
C	--	90	--	--	--	--
O_2	--	45	--	--	--	--
Cl^-	--	--	--	<10	--	<10
Ce	--	--	527	<25	--	--
Pu, w/o	--	99.99	99.90	--	99.89	99.97
Density, g./cc.	--	19.62	--	19.63	--	19.45

[a] The concentrations of all elements except plutonium are given in p.p.m.

[b] Double dash indicates no analysis made.

[c] High iron concentration was due to faulty handling of salt.

APPENDIX B

PRELIMINARY COST ANALYSES

In general, cost analyses are very sensitive to the initial assumptions and to the economic environment of the organization in which the analyses are made. This Appendix was prepared to show that electrorefining may offer a marked economic advantage over aqueous processing methods.

The reference plant for this analysis is a facility capable of producing 10 kg. of pure plutonium metal per week. The plant consists of three separate electrorefining cells, each operated simultaneously on an 8 hour day, 5 day week, 50 weeks a year. The cells are contained in a compartmented glove box enclosure with a floor area of approximately 24 sq. ft., enclosed by a building of 400 sq. ft. This building is assumed to be attached to an existing plutonium plant, such as the Los Alamos facility.[12]

Time Cycles

The time cycles for each cell are shown in Fig. B1. These times were based on experience with the 3.5 kg. scale experiments, which resulted in the following requirements:

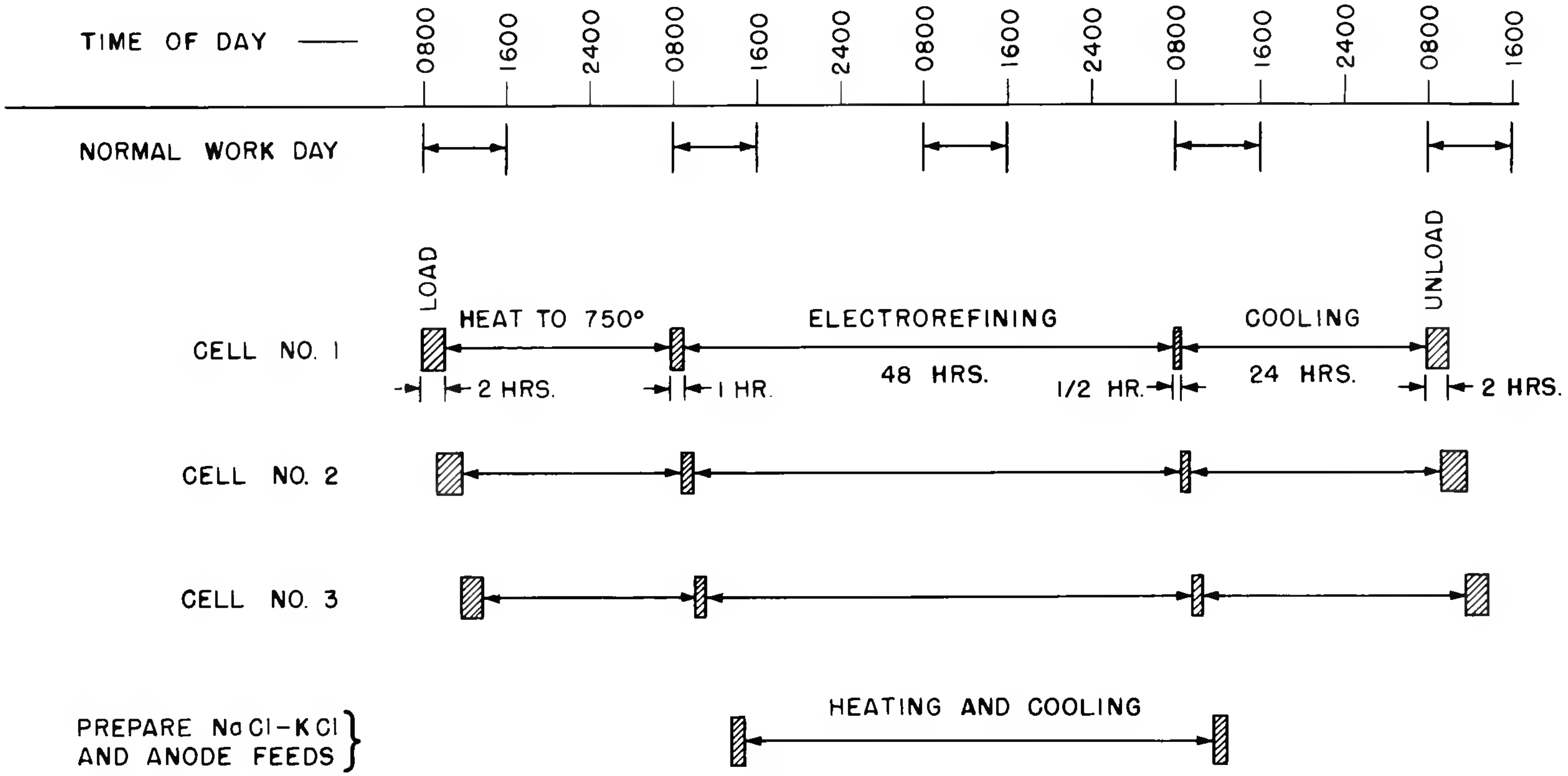

Fig. B1. Time cycles - 10 kg. per week reference plant

	Operation	Hours Required per Run	Man Hours per Run
1.	Load cell	2	3
2.	Heat to 750°C	16	0
3.	Start electrorefining	1	1
4.	Electrorefine*	48	1
5.	Terminate electrorefining	0.5	0.5
6.	Cool	24	0
7.	Unload and cleanup	2	3
	Total	93.5	8.5

Plutonium Balance

	Grams per Run
Feed to anode	3903
Product ring	3333
Anode residue	370
Crucible residue	200

In addition, 100 g. of plutonium is contained in the electrolyte as $PuCl_3$.

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*Although 3.33 kg. of plutonium can be electrorefined in about 37 hr. at 30 amp., for this reference plant 48 hr. at 23 amp. offers a better time cycle.

Capital Costs	Dollars per Year
Building, 400 sq. ft. @ $50 (5 year life)	4,000
Glove box enclosures plus airlock @ $10,000 (5 year life)	2,000
Electric furnaces for cells, 3 @ $350	1,050
Furnace tubes, 3 @ $800	2,400
Tungsten cathodes, 12 @ $500	6,000
D.C. power supplies, 3 @ $1,000 (2 year life)	1,500
Recorder controllers, 3 @ $1,000 (5 year life)	600
Stirrer motors, 9 @ $100	900
Inert gas purification system	1,000
Tantalum catch crucible, 3 @ $800	2,400
Miscellaneous hardware	2,000
Total	23,850

(Based on 500 kg./year, unit cost is $0.048/g. electrorefined plutonium.)

Manpower Costs, Direct Operations

8.5 man hr./run x $25/man hr. = $212.50/run

$$\text{Unit cost} = \frac{\$212.50}{3333\text{ g.}} = \$0.064/\text{g.}$$

Power and Materials Costs	Dollars per Run
Furnace power 270 kw.-hr. @ $0.03/kw.-hr.	8.10
140 g. $PuCl_3$/3 runs @ $1.00/g. (reuse salt 3 times)	47.00
1260 g. NaCl-KCl/3 runs @ $0.01/g.	4.20
1 ceramic cell per run	100.00
Miscellaneous bearings, seals	10.00
Total	169.30

$$\text{Unit cost} = \frac{\$169.30}{3333\ \text{g.}} = \$0.051/\text{g.}$$

Auxiliary Costs

Drying and Precasting of NaCl-KCl (1260 g./week):

Furnace, furnace tube, and controllers @ $1500/year

Unit cost = $0.003/g. plutonium

Manpower = 3 hr. @ $25 = $75

Unit cost = $0.0075/g. plutonium

Precast Plutonium Anode Feed (three 3903 g. batches/week):

Vacuum furnace and enclosure, 4 kg. scale = $12,000
(5 year life) = $2,400/year

Unit cost = $0.0048/g.

Manpower = 2 man hr./4 kg. @ $25/man hr.

Unit cost = $0.013/g.

Total unit cost for auxiliary services = $0.028/g.

Cost of Recovery of Plutonium from Waste

	Grams per Run
Plutonium in crucible residue	200
Plutonium in salt	33
Plutonium in anode residues	37
	270

Assume that this will be recovered by conventional aqueous processes now in use at Los Alamos. Of this 270 g., 100 g. may be purified and converted to $PuCl_3$ for electrolyte at $1.00/g., and the remaining 170 g. will be purified and converted to plutonium metal at $2.00/g. Cost of recovery = $100 + $340 = $440/run.

Unit cost = $0.132/g.

Recapitulation of Costs		Dollars per Gram Plutonium
Capital plant		0.048
Manpower		0.064
Power and materials		0.051
Auxiliary		0.028
Aqueous recovery of wastes		0.132
	Total	0.323

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