

A Review of Operating Experience at the Los Alamos Plutonium Electrorefining Facility, 1963-1977

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A REVIEW OF OPERATING EXPERIENCE AT THE LOS ALAMOS PLUTONIUM ELECTROREFINING FACILITY, 1963-1977

by

L. J. Mullins and A. N. Morgan

ABSTRACT

This report reviews the operation of the Los Alamos Plutonium Electrorefining Plant at Technical Area 21 for the period 1964 through 1977. During that period, approximately 1568 kg of plutonium metal, >99.95% pure, was produced in 653 runs from 1930 kg of metal fabrication scrap, 95% pure. General considerations of the electrorefining process and facility operation and recommendations for further improvement of the process are discussed.

I. BACKGROUND

A. History

Plutonium electrorefining procedures developed at the Los Alamos National Laboratory in the early 1960s¹⁻¹² resulted in the construction in 1963 of an electrorefining plant⁵ operated at Technical Area (TA)-21 from 1964 through 1977. In 1978, the electrorefining line was moved from TA-21 to the new Los Alamos Plutonium Facility at TA-55. This report reviews the operating experience gained during the 14 years of operation at TA-21.

B. Why Electrorefine?

Electrorefining is a very attractive operation for applications in which the feed materials are impure metals or alloys and the desired product is pure metal. In this process, impure metal is dissolved at the anode and pure metal is deposited at the cathode. This simple electrolytic conversion of impure-to-pure metal eliminates the many processing

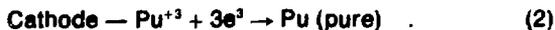
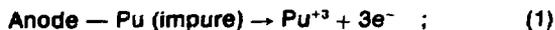
steps in plutonium recovery through chemical processing. In addition, electrorefined metal is purer than that produced by chemical conversion of compounds to metal.

Electrorefining has been used extensively for commercial purification of metals in aqueous solutions. For example, many major refineries use aqueous electrolytes for purifying copper, nickel, cobalt, lead, tin, silver and gold.¹³ Active metals, such as alkalis, alkaline earths, lanthanides, and actinides, however, cannot be deposited in aqueous solution. These metals require molten salt electrolytes. Molten salt electrorefining processes have been studied extensively for aluminum, lead, plutonium, beryllium, niobium, titanium, vanadium, zirconium, tungsten, molybdenum, uranium, tin, and antimony.¹⁴ In spite of these numerous studies and the potential advantages of electrorefining, aluminum refining is the only process that has found extensive industrial use.¹⁴ Molten salt electrorefining, however, is an ideal processing tool for active metals that have reasonably low melting points, such as aluminum (660°C), plutonium (640°C), and neptunium (637°C).

C. Plutonium Electrorefining, Principles of Operation

In the Los Alamos refining cell (Fig. 1), the magnesia crucible consists of two concentric cylindrical containers. The inner cup contains the impure molten plutonium anode and the outer cup contains the electrolyte. During operation, plutonium is oxidized at the anode and reduced back to metal at the cathode. Therefore, the height of metal in the anode decreases during a run as the

height of the product ring or doughnut increases. The cell reactions are simply



Therefore, the net cell reaction is

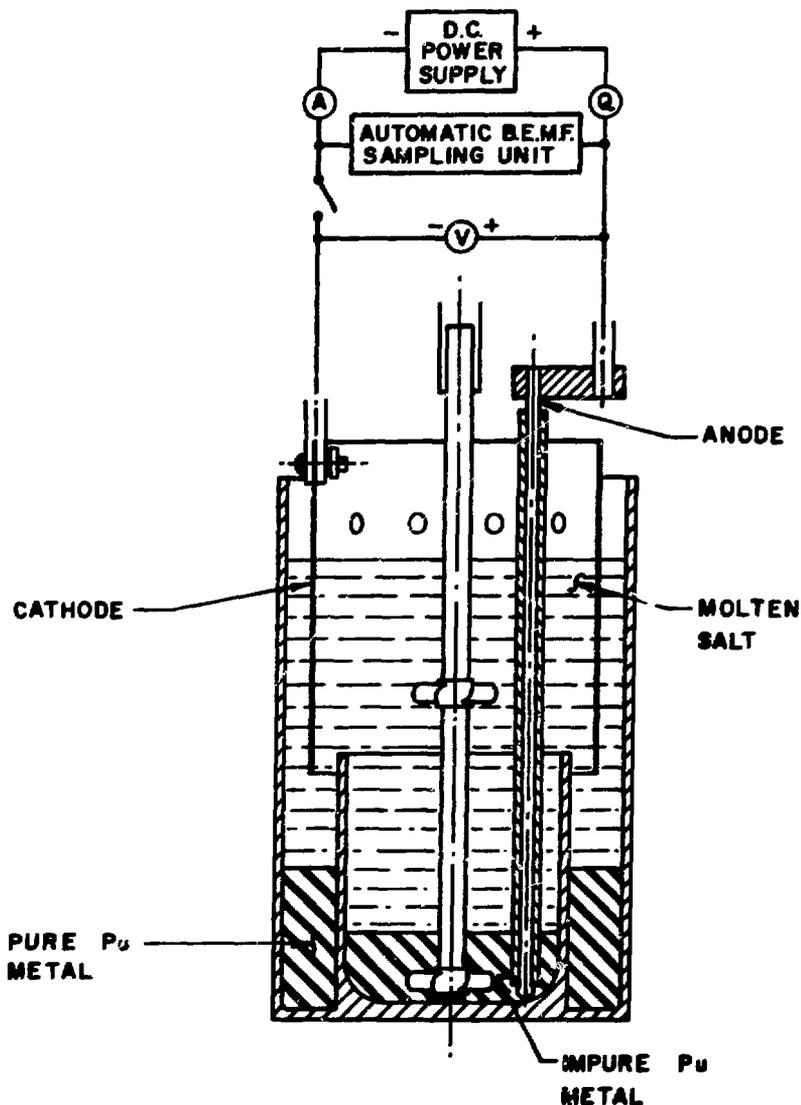


Fig. 1. Los Alamos electrorefining cell.

Because plutonium is a very active or electropositive metal, most of the impurities remain in the anode. Elements such as americium and cerium, which are more electropositive than plutonium, concentrate in the electrolyte. To achieve these separations, however, the electrorefining cell must operate close to equilibrium. Thus, metal and salt phases must be molten and must be stirred effectively. Under these conditions, we can use standard free energy of formation values to estimate purification factors.¹⁵ To ensure that the cell is indeed operating under equilibrium, the electrolyzing current is interrupted periodically during a run, and the polarization potential or instantaneous back-emf is measured. Electrorefining is terminated automatically when the back-emf exceeds a preset value (See Ref. 8 for a discussion of the theory and operation of plutonium electrorefining cells). Electrorefining will continue as long as a plutonium-rich liquid phase is present at the anode metal-electrolyte interface. The back-emf process control ensures product purity while permitting high anode-dissolution yields. However, efficient stirring of both the anode metal and electrolyte are required to achieve conditions that permit effective use of back-emf process control.

D. Electrorefining Cell Components

1. **Solvent System.** An equimolar mixture of NaCl-KCl was selected as the solvent system for the initial development studies¹ and is still used. The advantages of this system are

- its thermodynamic stability,
- its ease of handling (neither component is hygroscopic),
- its ready availability in a pure form, and
- its 650°C melting point, well suited to molten plutonium operations.²

2. **Plutonium Electrolyte.** The importance of the Pu⁺³ concentration in the electrolyte to the purification of plutonium metal is discussed in Ref. 8. The following options are available for achieving the desired plutonium concentration.

(1) Addition of a plutonium halide salt such as PuCl₃, PuF₃, or PuF₄.⁵

(2) *In situ* electrolytic generation of PuCl₃.¹⁶

(3) Addition of MgCl₂.^{17,18}

We have used all three halides listed in option (1). We used PuCl₃ in the early work with vitrified alumina crucibles. Because PuF₃ is readily available from our metal preparation facility, we have used it in virtually all of our kilogram-scale electrorefining runs. It has the advantage of being stable, nonhygroscopic, and readily prepared in a pure anhydrous condition. Before electrorefining, PuF₄ is reduced to PuF₃ by the plutonium metal anode.



Option (2) is ideally suited to purifying small amounts of ²³⁸Pu, ²⁴⁰Pu, ²⁴²Pu, and ²³⁹Pu of unusual isotopic composition.* In the *in situ* generation, dc current is passed through an electrorefining cell with no stirring of metal or electrolyte. Under these conditions, the following reaction takes place.^{16,19}



The reduction of Pu⁺³ to metal competes with the reduction of Na⁺. About 50% of the current results in Na⁺ reduction. After PuCl₃ generation, the sodium is permitted to volatilize from the cathode and collect on the top furnace lid. This method has been used to purify 25, 100 and 200 g of ²³⁸Pu.²⁰ For kilogram amounts of special isotopes, option (3) is recommended. In this case, the following reaction takes place.



This option has been used by workers at Rocky Flats** in electrorefining¹⁸ and has been studied extensively in molten salt extraction studies.²¹ The magnesium metal produced is volatilized slowly from the melt. The magnesium must be volatilized to avoid forming two immiscible liquid metallic

*We have also used this option in preparing high-purity ²³⁷Np metal by electrorefining (L. J. Muffins, unpublished data).

**Rockwell International, Energy Systems Group, P. O. Box 464, Golden, CO 80401.

phases. (At 750°C, the plutonium-magnesium system forms two immiscible liquid phases at 0.12% magnesium.²²)

3. Crucible. Los Alamos electrorefining crucibles have been limited to Al₂O₃, MgO, and MgO-Y₂O₃. For a discussion of both ceramic and metal containers, see Ref. 2. The latter body, fabricated by Los Alamos, was used in our development studies. However, the commercial bodies used in our facility are MgO. (Al₂O₃ can be substituted for MgO if fluoride is not present in the electrolyte.²)

4. Cathode. Tungsten cathodes are used in all routine electrorefining operations. Their use contributes ~50-80 ppm** of tungsten to the product metal.²³ For special preparations, such as those for the National Bureau of Standards, TaC cathodes that eliminate tungsten as an impurity and introduce <20 ppm tantalum and <10 ppm carbon are used.⁹

5. Stirrer. MgO stirrers are used to mix metals and salts in all routine operations. Tantalum stirrers have been used successfully at low dc currents, <5 A, but their use at ≤9 A has resulted in tantalum contamination of the product and dissolution of the stirrer.²

E. OPERATING CONDITIONS

1. Atmosphere. Because of the chemical reactivity of plutonium, tantalum, and tungsten metals at elevated temperatures, electrorefining takes place in an argon atmosphere. Loading operations are done in gloveboxes having a dry-air atmosphere.

2. Temperature. Because most electrorefining feeds have been plutonium - 1% gallium alloys, we chose the electrorefining temperature to optimize yields with this alloy. The plutonium-gallium phase diagram shows that the operating temperature should be above 720°C.⁹ To minimize container-corrosion problems and achieve acceptable yield, we set the electrorefining temperature at 740°C.⁵

3. dc Current. The Los Alamos plutonium electrorefining cells were wired for a maximum current of 30 A. The actual current used for any particular

run was calculated to permit termination of the run at a convenient time because the units were manned only 9 hours per day, 5 days a week.⁵ Thus, for a 3-kg electrorefining operation starting at 10 a.m. on a Friday, the desired termination time would be about 8 a.m. the following Monday. The current used is calculated as follows.

$$\begin{aligned} \text{Current} &= \left(\frac{3000 \text{ g Pu}}{2.97 \text{ g Pu/Ah}} \right) \left(\frac{1}{70 \text{ h}} \right) \\ &= 14.4 \text{ A} \end{aligned}$$

Thus, electrorefining 3 kg of plutonium in 46 hours requires 22 A. Runs that could be completed during the normal work week were usually electrolyzed for 2 days.

The upper limit on the electrorefining current for the Los Alamos refining cell has never been established. Currents as high as 40 A were used in the development studies;²⁴ however, most experiments were done at 25 A. The maximum capability of the equipment for these studies was 50 A. Back-erm measurements at 50 A indicate that polarization is not a problem at these currents. However, the effect, if any, of 50-A currents on yield and product purity was never established.

4. Equilibration and Pre-electrolysis of Electrolyte. Before passing electrorefining current, we equilibrate the anode metal with the electrolyte by stirring at ~800 rpm. As discussed in Sec. I. D, this equilibration results in the reduction of PuF₄ to PuF₃. More important, however, this equilibration also transfers metallic ionic impurities from the salt melt to the anode pool, where they will remain during electrorefining. For example, assume Fe⁺³ is a contaminant in the electrolyte. The following oxidation-reduction will take place upon equilibration.

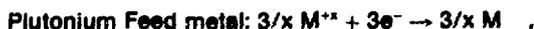


In most runs, the cathode cylinder is coated with plutonium metal from an earlier run. To provide an additional driving force for the salt purification and

*All percentage values in this report are wt%.

**g of tantalum/10⁶ g plutonium

to electropolish the cathode, a pre-electrolysis of the melt is done during equilibration. In this case, the tungsten cylinder is made anodic, and the plutonium feed metal is made cathodic (that is, the electrorefining current is reversed). The following reactions take place during this process.



where M^{x+} is any metallic impurity less electropositive than plutonium, such as iron, nickel, chromium, etc.

F. Feed Limitations

Product purity is relatively independent of purity of the anode feed metal. Excellent separations from most metallic and nonmetallic elements are achieved even at impurity levels of a few per cent.⁸ The poorest separations have resulted with neptunium and americium. For example, in ^{239}Pu electrorefining runs with a ratio of 1 g plutonium as PuCl_3 to 24 g plutonium as metal, the neptunium concentration was reduced from 4180 ppm in the feed metal to 537 ppm in the product.¹⁶ In ^{239}Pu electrorefining runs having a ratio of 1 g plutonium as PuCl_3 to 33 g plutonium as metal, the americium was reduced from 143 ppm in the feed metal to 20 ppm in the product.

Product yields are sensitive to the purity of the anode feed metal because molten plutonium must be present at the anode-salt interface to prevent serious polarization. For example, an anode will go completely solid at 740°C at a gallium/plutonium atom ratio of 0.32. Thus, electrorefining automatically will be terminated when gallium/plutonium ≤ 0.32 .⁸ Plutonium-metal phase diagrams can be used to calculate plutonium-anode dissolution values.⁸

We prepare our anode-feed ingots by vacuum melting the metal, then pouring it into molds of the desired geometry. Vacuum melting removes volatile impurity metals such as calcium and magnesium.

G. Factors Affecting Product Yields

The yield of pure plutonium metal in electrorefining can be considered as two separate yields: (1) the fraction of plutonium dissolved at the anode, and (2) the fraction of plutonium deposited on the cathode and collected as a massive ingot.

As discussed in Sec. I. F, the fraction of plutonium dissolved at the anode depends on the nature and amounts of impurities present in the anode-feed metal. For unalloyed plutonium having a few thousand ppm impurities, ~98% of the plutonium can be dissolved anodically. (In this case, the geometry of the anode container imposes the 98% limit). For plutonium alloyed with 1% gallium, ~90% of the plutonium can be dissolved anodically.

The amount of plutonium deposited on the cathode and collected as a massive ingot depends on many factors. A small amount, ~30 g, of plutonium adheres to the cathode cylinder. However, because the cathode is usually reused in a subsequent run, this plutonium is not lost. The principal metal-collection losses result from metal adhering to the crucible walls and from plutonium shot that does not coalesce in the product ring. Loss to the crucible walls should be essentially constant. Loss as plutonium shot, however, can vary widely and depends on many factors.

In electrorefining, small plutonium droplets are deposited on the cathode. These droplets coalesce into larger drops that fall off the bottom of the cathode. Clean metal surfaces are essential to plutonium metal coalescence on the cathode. Thus, cathodes should be cleaned before use to ensure the absence of oxide films. Used cathodes containing plutonium are stored under argon when not in use. In addition, these cathodes are cleaned anodically during pre-electrolysis (see Appendix). Obviously, maintaining a pure argon atmosphere and using pure electrolyte are essential to ensuring the absence of reactive gases such as oxygen, nitrogen, and water vapor. The anode-metal feed should also be oxide-free. By taking these precautions, we can get collection yields of >95%.

II. DESCRIPTION OF THE LOS ALAMOS ELECTROREFINING FACILITY, EQUIPMENT, AND PROCEDURES

Kilogram scale electrorefining operations were done in gloveboxes ER-1, 2, and 3 (Fig. 2). The fourth glovebox, ER-4, was equipped with a 20-ton hydraulic press to break product rings into pieces suitable for casting operations. This box was also equipped with an electrorefining furnace for special or unique runs on the 0.1- to 0.5-kg scale. The fifth glovebox on the east side of the tunnel was inert and contained equipment for casting ultra-high-purity plutonium metal. The west side of the tunnel contained the introductory hood and glovebox, a weighing box, a pickling box, and a bag-out box. NaCl-KCl salt castings were done in a salt-casting furnace located in the southeast corner. All of the electrical control equipment for operating the electrorefining and casting units was contained in the control panels on the east wall.

Electrorefining equipment and procedures are given in Los Alamos Group CMB-11 Procedure 430-MPP-R01 (see Appendix).

III. RESULTS

A. Product Purity

A general discussion of product purity is given in Sec. I. F. The electrorefined metal produced at TA-21 usually contained <200 ppm metallic impurities. Tungsten at an average value of ~65 ppm was the principal impurity.²³ The tungsten results from attack of the tungsten-cathode cylinder by molten plutonium metal. For ultra-high-purity metal, <100 ppm impurities, we use a TaC cathode.⁸ Analysis of an impure metal feed and product using a tungsten cathode is given in Table I. This feed was less pure than the usual metal feed. However, results demonstrate the effectiveness of electrorefining in converting quite impure metal to high-purity metal. An impure plutonium-1% gallium alloy containing 97.0% plutonium was electrorefined to yield a product containing 99.98% plutonium. Results for a more typical feed are given in Table II. In this case, the plutonium metal feed value was 96.8% and the product value was 99.98%. The average purity for

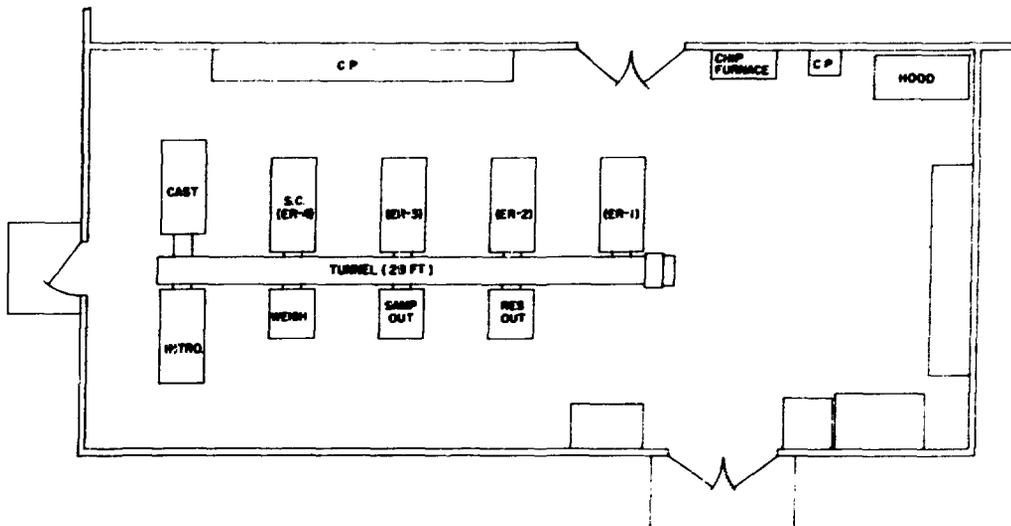


Fig. 2. Electrorefining room layout, TA-21.

TABLE I. Purification of Plutonium, Results With An Impure Feed

Element	Concentration of Element, (g Element/10 ³ g Pu)	
	Feed	Product
Mg	100	2
Al	200	1
Si	50	5
Ca	100	<3
Cr	1000	<0.5
Mn	100	<0.1
Fe	5000	5
Ni	200	2
Cu	100	1
Zn	1000	<0.5
Mo	1000	<0.5
Cd	2000	<0.5
Sn	2000	<0.5
Pb	2000	<0.5
W	<10	60
Th	140	4
U	80	14
Am	140	20
Ga	1.04 x 10 ⁴	<25
Pu%	97.0	99.98

all the feeds processed was ~99.3% (Sec. III. B). This average purity value was obtained by dividing the total plutonium processed, 1916.6 kg, by the total metal weight. In most cases, these plutonium values were "book" or by-difference values. Product metal purities were always >99.9%²³ and were determined directly by chemical analysis.

As discussed earlier, the behavior of impurities can be predicted qualitatively from the standard free energy of formation of corresponding chlorides. Elements whose chlorides have a standard free energy of formation (ΔF°) less negative than that of PuCl₃ concentrate in the anode; those which are more negative concentrate in the electrolyte. The concentrations in Table III are from ~650 electrorefining runs. Because the degree of purification at any temperature depends on both the number of product throughputs (grams of product metal per grams of plutonium in salt) and the extent of anode depletion, only those runs for

TABLE II. Purification of Plutonium, Typical Results

Element	Concentration of Element, (g Element/10 ³ g Pu)	
	Feed	Product
Mg	75	<5
Al	75	<5
Si	200	5
Ca	20	<3
Cr	100	<2
Mn	30	<0.5
Fe	500	<20
Ni	200	<20
Cu	50	<2
W	<10	65
Th	200	2
U	100	<10
Am	140	20
Ga	1.0 x 10 ⁴	<20
Pu%	98.8	99.98

which the number of product throughputs exceed 20, and the anode depletion exceeds 80% are listed. In most cases, the concentrations of the elements in the product were either undetectable or at values close to the limits of the analyses, so the values in Table III do not define the limits of the electrorefining process but merely suggest its capabilities. Further, this table does not imply that a pure product would necessarily be obtained in good yield if all impurities were present in the same feed at the indicated concentrations.

After the first few years of operation, we did not usually analyze product metal and feeds. However, product purity after casting continued to be measured, and these results are reported in Ref. 23.

B. Plutonium Material Balances

A summary of the plutonium flow through the TA-21 electrorefining facility from 1964 through 1977 is given in Table IV. During this period, 1930 kg of impure metal containing 1917 kg of plutonium was processed, yielding 1568 kg of high-purity product. All of these results are averaged in Table V. A further breakdown of the

TABLE III. Behavior of Impurity Elements in Electrorefining

Element*	-ΔF°, KCal per Gram Atom Cl ⁺	Concentration, g Element/ 10 ⁶ g Pu		Element Concentrated In
		Feed	Product	
Ir	2	4 500	110	---
Ni	18	1 000	<0.5	Anode
Cu	21	500	<1.5	Anode
Ta	27	5 000	80	Anode
Pb	27	2 000	<0	---
Fe	27	25 000	20	Anode
Si	28	320	<5	Anode
Cr	32	340	<5	Anode
Ga	32	10 000	<25	Anode
Mn	41	70	<2	---
Ti	43	15 000	10	---
Al	46	2 700	<5	Anode
U	54	330	<20	Anode
Zr	56	10 000	14	---
Th	59	1 300	10	Anode
Pu	59	---	---	---
Ce	66	527	<25	Electrolyte
Am	67	850	82	Electrolyte

*Listed in order of increasing stability of their chlorides.

⁺-ΔF° at 1000 K is tabulated. For elements having a multiplicity of oxidation states, the -ΔF° for the most stable form of the chloride is given. Values are from Ref. 25.

Table IV data is given in Table VI, where the runs are averaged for each calendar year.

C. Product Yields and Plutonium Utilization

Yields for an electrorefining operation can be expressed in several ways. From a plant manager's viewpoint, the most useful number is product yield (PY), which is defined as

$$PY = 100 \times \frac{Pu_{pr}}{Pu_{in}}$$

where

Pu_{pr} = the weight of plutonium in the product ring,
and

Pu_{in} = the weight of plutonium in the anode feed.

This yield gives the per cent conversion of impure-to-pure metal.

Plutonium utilization (PU) is defined as

$$PU = 100 \times \frac{Pu_{pr} + Pu_{cf}}{Pu_{in} + Pu_a + Pu_{cf}}$$

where

Pu_{cf} = weight of plutonium on the cathode cylinder after the run,

Pu_a = weight of plutonium added to the salt as PuF₆, and

Pu_{in} = weight of plutonium on the cathode cylinder before the run.

TABLE IV. Flow of Materials, Electrorefining Summary

CY	No. of Runs	Materials Into Run (kg)			
		Anode Feed		PuF, Pu	Cathode, Pu
		Metal	Pu		
1964	38	115.391	113.747	2.865	0.457
1965	41	123.449	122.583	4.018	0.779
1966	25	74.897	74.620	2.751	0.578
1967	47	133.147	132.226	4.658	0.941
1968	44	125.180	124.288	4.384	1.119
1969	45	130.607	130.158	4.451	1.151
1970	56	164.323	163.185	5.588	1.591
1971	63	182.631	181.565	6.100	1.698
1972	89	263.948	262.284	8.719	2.657
1973	33	100.789	99.906	3.234	0.957
1974	54	163.579	162.288	5.175	1.079
1975	33	95.598	94.967	1.724	0.707
1976	46	146.003	145.304	1.482	1.459
1977	39	110.522	109.500	1.170	0.995
Sums	653	1930.064	1916.621	56.310	16.168

Mat'l Total Pu In = 1989.099
Bal

CY	No. of Runs	Materials Out of Run (kg)			
		Anode, Pu	Salt and Cruc, Pu	Cathode, Pu	Product Ring, Pu
1964	38	17.181	13.370	0.951	85.567
1965	41	10.007	12.121	1.381	103.871
1966	25	7.567	8.379	0.953	81.050
1967	47	14.862	16.131	1.649	105.183
1968	44	10.542	14.092	1.552	103.605
1969	45	10.256	13.777	1.552	110.175
1970	56	14.369	17.535	1.862	136.598
1971	63	20.581	19.243	2.703	146.836
1972	89	26.494	26.522	3.534	215.101
1973	33	8.577	12.755	1.567	81.198
1974	54	14.439	22.439	2.036	129.608
1975	33	7.764	10.402	1.195	78.057
1976	46	11.789	12.970	2.028	121.457
1977	39	8.728	11.291	1.630	90.016
Sums	653	183.157	213.027	24.593	1588.322

Total Pu Out = 1989.099

TABLE V. Average of 653 Runs, 1964-1977

Plutonium Into Run (g)		
Metal Feed		
Wt (g)	2956	
Pu (g)	2935	
Purity, %	99.29	
PuF ₄		
Pu (g)	86.2	
Cathode		
Pu (g)	24.8	
Total Pu in, (g)		3046
Plutonium Out of Run (g)		
Anode, g Pu	280	
Salt and Crucibles	326	
Cathode	38	
Product Ring	2402	
Total Pu Out (g)		3046

Thus, in the above equation, the denominator is the sum of all plutonium species put into the run, and the numerator is the sum of pure plutonium metal products that come out of the run. Because plutonium utilization contains the variable term Pu_{in} , it is not as useful a number as product yield in evaluating electrorefining operations.

Product yields and plutonium utilizations are summarized in Table VII. The average product yield for the first year of operation was 75% but the average was 80% or higher for the following years. Large anode residues were the primary cause of lower yields the first year. Plutonium utilizations were about 2% lower than process yields reflecting the 100 g of plutonium added as PuF₄ during the first 11 years of operation. Product yields and plutonium utilizations were virtually the same during the last 2 years of operation because only 30 g of plutonium was added as PuF₄ (Table VI). Lower requirements for americium removal permitted using less PuF₄ in the last 2 years (Sec. III. E).

D. Anode Depletion, Collection Efficiency, and Process Efficiency

The two principal factors affecting product yield and plutonium utilization are anode depletion (D) and metal collection efficiency (CE).

$$D = \frac{Pu_{in} - Pu_{af}}{Pu_{in}}$$

where

Pu_{af} = weight of plutonium in the anode residue after run;

$$CE = 100 \times \frac{Pu_{pr} + \Delta Pu_c}{Pu_{in} - Pu_{af}}$$

where

$$\Delta Pu_c = Pu_{cr} - Pu_{ci}$$

The value of anode depletion depends primarily on the purity of the feed metal (Sec. I. G). Because virtually all the feeds were Pu-1% Ga alloys, the calculated value for D is 0.89.⁸ The average value of D for CY 1964-1977 (Table VIII) was 0.905, good evidence that electrorefining equipment such as stirrers, back-emf control equipment, and furnace control equipment operated satisfactorily.

Values for metal-collection efficiency depend primarily on cathode design, operating techniques, and operational procedures (Sec. I. G). The average value of collection efficiency obtained in the research and development (R&D) electrorefining studies was 95%.⁹ Collection efficiencies for the production facility are given in Table VIII. The average value over 14 years of operation was 90.87%. Although the value is lower than the 95% value experienced in the R&D work, we consider it to be a reasonable production value.

Process efficiency is defined as the product of (D × CE) and is therefore a measure of electrorefining efficiency, or

$$PE = D \times CE = \frac{Pu_{pr} + \Delta Pu_c}{Pu_{in}}$$

TABLE VI. Electrorefining, Yearly Average

CY	No. of Runs	Average of Materials Into Run (kg)			
		Anode Feed Metal	Pu	PuF ₆ Pu	Cathode, Pu
1964	38	3.037	2.993	0.075	0.012
1965	41	3.011	2.990	0.098	0.019
1966	25	2.966	2.965	0.110	0.023
1967	47	2.833	2.813	0.099	0.020
1968	44	2.845	2.825	0.100	0.025
1969	45	2.902	2.892	0.099	0.028
1970	56	2.934	2.914	0.100	0.028
1971	63	2.869	2.862	0.097	0.027
1972	89	2.966	2.947	0.096	0.030
1973	33	3.054	3.027	0.096	0.029
1974	54	3.029	3.005	0.096	0.029
1975	33	2.997	2.878	0.052	0.021
1976	46	3.174	3.159	0.032	0.032
1977	39	2.634	2.608	0.030	0.026

CY	No. of Runs	Average of Materials Out of Run (kg)			
		Anode, Pu	Salt and Cruc, Pu	Cathode, Pu	Product Ring, Pu
1964	38	0.452	0.352	0.025	2.262
1965	41	0.244	0.296	0.034	2.533
1966	25	0.363	0.335	0.038	2.442
1967	47	0.316	0.343	0.035	2.236
1968	44	0.249	0.320	0.035	2.365
1969	45	0.228	0.306	0.034	2.448
1970	56	0.257	0.313	0.033	2.439
1971	63	0.327	0.365	0.043	2.331
1972	89	0.299	0.329	0.040	2.417
1973	33	0.299	0.386	0.047	2.461
1974	54	0.267	0.416	0.038	2.499
1975	33	0.235	0.315	0.036	2.396
1976	46	0.256	0.282	0.044	2.640
1977	39	0.224	0.299	0.042	2.399

E. Plutonium Tetrafluoride Addition

The amount of plutonium added to the electrolyte depends primarily upon the requirements for americium removal. During the first 11 years of operation, 0.10 kg of plutonium as PuF₆ was added

to remove the americium from 3.00 kg of plutonium feed. The americium decontamination factor (DF) for this case is ~10, where

$$DF = \frac{\text{ppm americium in anode feed}}{\text{ppm americium in cathode product}}$$

TABLE VII. Yearly Average of Product Yields and Process Efficiencies

	Yearly Average	
	Product Yield (%)	Plutonium Utilization (%)
1964	75.24	73.93
1965	84.72	82.62
1966	81.81	79.54
1967	79.56	77.52
1968	83.36	81.02
1969	84.65	82.27
1970	83.70	81.26
1971	80.88	78.98
1972	82.02	79.90
1973	81.30	79.52
1974	79.87	78.12
1975	82.18	81.36
1976	83.57	83.28
1977	82.19	82.05

TABLE VIII. Yearly Averages of Anode Depletion (D), Collection Efficiency (CE) and Process Efficiency (PE)

CY	Yearly Average		
	D	CE (%)	PE (%)
1964	0.8490	99.14	75.68
1965	0.9184	92.79	85.22
1966	0.8985	91.81	82.31
1967	0.8877	98.23	80.10
1968	0.9150	91.49	83.71
1969	0.9212	92.19	84.33
1970	0.9118	91.98	83.87
1971	0.8865	91.86	81.43
1972	0.8889	91.82	82.36
1973	0.9141	88.58	81.88
1974	0.9111	88.31	88.46
1975	0.9183	98.85	82.88
1976	0.9198	81.36	83.96
1977	0.9282	88.94	82.78

Requirements for americium removal during the last 2 to 3 years of operation relaxed, and 0.030 kg of plutonium as PuF₃ was sufficient to achieve the desired DF of 3.

F. Equipment Failures

Premature terminations of electrorefining runs have resulted from the following causes.

1. Broken ceramic stirrer
2. Broken cathode cylinder
3. Broken anode rod
4. Broken crucible
5. Operator's inability to position hardware
6. Furnace failure

The failure rate from all causes amounted to 12% of all runs. Of these failures, 33% were due to broken stirrers, 29% to broken cathodes, 9% to 2 broken anode rods, 11% to crucibles, 7% to hardware positioning problems, and 11% to furnace failures.

The fragile anode stirrer is the weakest component of the electrorefining equipment. Breakage, when it occurs, usually takes place during the lowering of the stirrer into the crucible. The fracture plane is usually at the junction of the magnesia stirrer and the stainless steel collet.

When the tungsten cylinder breaks, the break occurs in the area where the slotted tantalum rod is joined to the tungsten cylinder. Strict adherence to drawing specifications is required to minimize mechanical stresses. Tighter fabrication specifications would likely eliminate this problem.

G. Casting of Electrorefined Metal

The casting of electrorefined metal is outlined in Ref. 23, which provides an excellent summary of foundry practices and analytical results. The metal is melted under vacuum in an oxidized tantalum crucible and is bottom-poured into a variety of molds. Oxidized tantalum, graphite coated with calcium fluoride, aluminum, and copper are used routinely as molds with virtually no contamination of the plutonium metal.

H. Recycle of Electrefining Residues

Depleted anodes, salts, and crucibles are the principal residues created in the electrefining operation. To recover depleted anodes, we burn the metal to oxide, dissolve the oxide in HNO_3 -HF, and purify the plutonium by anion exchange.²⁶ Most of the crucible pieces are separated from salt or chloride melt and are leached with 10 M HNO_3 -- 0.05 M HF. The chloride melt and the magnesia pieces from the anode cup are leached with 2 M NaOH. This treatment dissolves the NaCl-KCl salt and precipitates plutonium as the hydroxide that is subsequently dissolved in nitric acid and purified by anion exchange.

IV. SUMMARY AND RECOMMENDATIONS

It is very surprising that virtually no changes were made to electrefining equipment or procedures during the 14 years of operation at TA-21. This was due to the successful operation of the facility. A part-time staff of three produced more than 1700 kg of high-purity metal in a relatively small, inexpensive facility. The facility's output was limited by the availability of metal feed rather than by its capacity, which was 10 kg plutonium per week. Equipment failure, other than that discussed in Sec. III. F, was rare, and product quality was always high. Indeed, after the first few years of operation, chemical analysis of the product metal was discontinued, and the metal went directly to the foundry. Subsequent analysis of finished parts has continued to show the same high chemical purity. The small labor requirements and elimination of the need for chemical analysis of both metal feeds and products have resulted in low unit costs for high-purity plutonium metal. Though the facility has been very successful, we recommend further study to improve

- process efficiencies,
- operational efficiencies, and
- recycling of process residues.

A. Improve Process Efficiency

Process efficiency could be increased by improving collection efficiency and anode depletion (Sec.

III. D). A better understanding of the mechanisms of cathode deposition and product coalescence could optimize collection efficiency. An alternative to mechanistic studies is an in-depth study of the variables involved in collection.

Efficient anode stirring is essential to high anode depletion. The present ceramic stirrer is adequate for good anode depletion with relatively pure Pu-1% Ga alloys. In this case, the anode contains only a liquid phase at the beginning of a run. The appearance of a solid Pu_3Ga phase does not interfere with the progress of the run so long as some liquid phase is present. Satisfactory anode depletion has been difficult for anodes that split into two immiscible liquid phases during the run. Our present ceramic stirrer does not mix or turn over these phases adequately so electrefining terminates prematurely. Therefore, we need a better stirrer.

B. Improve Operational Efficiency

- The operational efficiency could be improved by
- increasing the plutonium anode loading,
 - decreasing the time of a run, and
 - decreasing the failure rate.

Material specifications for the anode-feed metal were established by specifying 2 1/4 in.-diam by 3-in.-tall dimensions for the cast cylinder.⁵ Thus, an alpha-phase ingot of these dimensions would weigh ~3.7 kg and a delta-phase ingot would weigh ~3.0 kg. Both these weights can be increased to 4 kg of plutonium by specifying that the plutonium be cast into a 2.5-in. diam die.

Improvements in critical mass measurements²⁷ have resulted in higher mass units for foundry operations at Los Alamos. Present foundry limits are 6 kg plutonium for delta phase and 4.5 kg for alpha phase. These limits should be examined for electrefining operations.

Time of a run can be decreased by increasing dc current and increasing heating and cooling rates. As discussed in Sec. I. E, the electrolyzing current has never been optimized. The use of ceramic components precludes very rapid heating and cooling rates. The present very slow heating rate was selected for operational convenience but never optimized. Cooling rates could be increased by equipment modification.

The 12% failure rate probably could be reduced to <5% by redesigning some of the electrorefining hardware (Sec. III. F).

C. Nonaqueous Recycle of Process Residues

The recovery of electrorefining residues by aqueous methods requires more labor than electrorefining and casting operations. This effort might be reduced by using pyrochemical techniques. Anode heels and salt residues are prime candidates for pyrochemical processing.

The chemical composition of a depleted anode depends upon the purity of the electrorefining feed metal because virtually all of the impurities remain in the anode. Thus, for a feed containing 98% plutonium, 1% gallium, and 1% other impurities, we expect a depleted anode containing 83.3% plutonium, 8.3% gallium, and 8.4% other impurities. This anode is still a rich source of plutonium metal from which plutonium could be isolated either by the $ZnCl_2$ pyrochemical method^{28,29} or by further electrolytic refining (a solid anode process or metal solvent process). The plutonium from these processes need not be of high purity. The metal could serve as feed to the existing electrorefining process.

Electrorefining salts are also prime candidates for pyrochemical processing. These salts consist primarily of ~1200 g NaCl-KCl, ~300 g plutonium, and ~3 g americium. The plutonium is present as both salt and metallic shot.

Recovery of plutonium from the crucible surfaces is now done by leaching or washing the crucible fragments in acid. This method is quite efficient and is probably superior to alternate pyrochemical techniques.

D. Summary

This report discusses how the Los Alamos Electrorefining Facility has performed admirably in recycling metallic plutonium scrap. Large amounts of high-purity metal were produced with minimal labor. However, the report also indicates that an update is overdue. A modest investment in process development could increase dramatically the effectiveness of this recycling tool.

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APPENDIX

**OPERATING PROCEDURES FOR
ELECTROREFINING OF PLUTONIUM METAL**

The operating procedures described here summarize and revise those given in Ref. 5. The purpose of the electrorefining operation is to convert impure plutonium metal and alloys to high-purity metal.

The maximum permissible plutonium content of one electrorefining glovebox is 4 kg.

I. MATERIAL SPECIFICATIONS

- A. Ceramic Cell - vitrified magnesium oxide crucibles specified in Los Alamos Drawing 26Y-72325, Rev. A, and specification CMB-11-76-8.
- B. Ceramic Stirrer - vitrified magnesia as specified in Los Alamos Drawing 26Y-72500, C-1, and specification CMB-11-76-8.
- C. Anode Feed Metal - cylinder with maximum dimensions of 2-1/4-in.-diam by 3 in. tall.
- D. Electrolyte - NaCl-KCl cylinder, 3-1/2 in. diam, weighing 1.4 kg; hole, 1-in.-diam by 3 in. deep, drilled in the curved end of the cylinder. The amount of PuF₃ or PuF₄ used depends on the quality of anode feed (see Ref. 5, pp. 14 and 26). For most routine runs, 39.5 g of PuF₄ is used. The alkali halides are analytical grade reagents, and the fluoride should contain <1000 ppm of metallic impurities.

II. EQUIPMENT SPECIFICATIONS

- A. Electrorefining Furnace Assembly - The furnace assembly is shown in Fig. A-1. The construction materials for various components are given below.

Item	Part No. (Fig. A-1)	Material
Furnace tube	9	Inconel 600
Cathode	13	Tungsten
Anode	36	Tungsten
Stirrer	14	MgO
Safety can	12	Tantalum
Thermal insulator	37	MgO
Loading can	32	Stainless steel, type 316
Crucible	11	MgO
Pre-electrolysis rod	Not shown	Tungsten

- B. Instrumentation - The instrument stacks contain the following equipment.
 1. Automatic back-emf sampler.
 2. Ampere-hour meter.
 3. dc power supply, ammeter, volt-meter.
 4. Furnace programmer.
 5. Temperature recorder.
 6. Current, voltage recorder.
 7. Timer for starting program.

C. **Resistance Furnace** - The electrorefining cell is heated by a 6-in.-id resistance furnace, Lindberg Type 6015S. The furnace is thermally interlocked to negative pressure cooling water. The maximum attainable temperature is established by setting the Variac at 80%. Two Platinell II thermocouples are installed in the center of the furnace. One of these thermocouples goes to the furnace programmer, and the other goes to the temperature recorder.

D. **Safety Features** - The electrorefining equipment has these safety features to permit full-time unattended operation.

1. Automatic back-emf sampler.
2. Heat sensor interlock, furnace-cooling water-return line.
3. Tantalum safety can.
4. Water-cooled bottom plate on glovebox furnace can.
5. Thermocouple burn-out protection on controller thermocouple.
6. Variac control of maximum furnace temperature.

III. OPERATING PROCEDURE

A. Inspection of Equipment

The stirrer, cathode, and anode should be inspected visually for mechanical defects. Use a resistance meter to check the integrity of the cathode and anode insulators.

B. Loading of Furnace (Fig. A-1)

1. Place MgO plate (37) in stainless steel can (32).
2. Place tantalum safety crucible (12) in stainless steel can.
3. Place magnesia cell (11) *carefully* in tantalum safety crucible.
4. Place metal feed cylinder *carefully* in anode cup.
5. Place stainless steel can in furnace tube (9).
6. Place head flange (24) on furnace tube and lower cathode (13) to bottom of crucible to assure proper

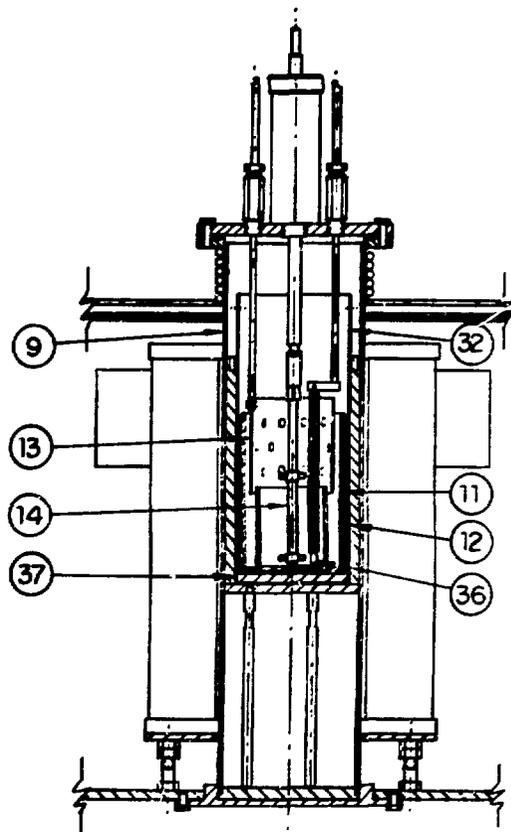


Fig. A-1. Assembly, Electrorefining Furnace, Los Alamos Drawing 26Y-79819.

alignment. If cathode cannot be lowered to this point, consult supervisor.

7. Raise cathode and remove head flange.
8. Place NaCl-KCl casting in magnesia cell.
9. Place PuF_6 in cavity of NaCl-KCl casting.
10. Seal furnace tube by placing head flange provided with stirrer, anode rod, cathode, and pre-electrolysis rod on furnace tube.
11. Bolt down flange and connect gas fitting to inert gas line.
12. Apply vacuum to furnace tube and check for vacuum tightness by closing vacuum valve and observing the

leak rate shown by vacuum gauge. If any evidence of leakage is seen, consult supervisor.

13. Flush system three times with argon and leave system under argon. (Note, the argon gas is purified by the uranium chip furnace.)

C. Furnace Heating Cycle

1. Check furnace tube cooling water; negative pressure circulating water is used.
2. Check positive pressure cooling water on glovebox furnace can.
3. Turn on resistance furnace or set timer to do so. The cam provided on the controller provides a heating rate of 50°C/hour and a hold at ~880°C. (Note, the furnace hold temperature keeps the electrolyte temperature at 740°C. Calibrations are made at the direction of and under the supervision of the responsible staff member.)
4. When furnace controller has reached a temperature of 880°C, turn off controller cam drive.
5. Lower cathode cylinder to bottom of crucible.
6. Lower anode rod to bottom of anode cup with anode rod near center of anode cup; rotate anode rod to side of anode cup; tighten packing nut.
7. Lower pre-electrolysis rod if required; position end below rim of anode cup.
8. Raise cathode to position shown in Fig. A-1. (Bottom rim of cathode is positioned 1/4 in. below rim of anode cup).
9. Lower stirrer to bottom of anode cup; position it ~1/32 in. off bottom.

D. Pre-Electrolysis Using Pre-Electrolysis Rod

1. Connect pre-electrolysis rod to negative terminal of dc power supply.
2. Connect anode rod (27) to positive terminal of dc power supply.
3. Turn on stirrer. It should rotate at ~800 rpm.

4. Stir 1 hour.
5. Turn on current-voltage recorder.
6. Turn on dc power supply and adjust current to 2 A. This should require a potential* of between 0.2 and 0.4 V.
7. After passing current for a few minutes, check and record the back-emf (back-emf should be 0.0 - 0.1 V).
8. Pass 2 A for 1 hour; shut off current; shut off stirrer.
9. Disconnect and raise the pre-electrolysis rod.
10. Connect negative terminal of dc power supply to cathode rod.

E. Pre-Electrolysis Using Cathode from Previous Run

1. Connect negative terminal to cathode rod (29).
2. Switch handle on dc power supply to reverse electrorefining position (REV) before pre-electrolysis.
3. Same as steps 3-8 in Sec. D.
4. Upon completion of pre-electrolysis, switch handle to normal position.

F. Electrorefining

1. Turn on stirrer.
2. Pass current at a value that will permit termination of the electrorefining at a convenient time.** Resistance (V/A) should be ~0.15 Ω.
3. Turn on automatic back-emf sampler. Set sampler dial at 0.3 V.
4. After several minutes operation, measure back-emf (back-emf should be 0.0-0.2 V).
5. Equipment should be checked for proper operation periodically (at

*The potentials are measured across the lead wires carrying current from the dc power supply to the electrorefining cell.

**Example of current calculations:

Assume: charge of 3.2 kg Pu electrolysis to terminate 46 hours later;

$$\text{Current} = \left(\frac{3200 \text{ g Pu}}{2.97 \text{ g Pu/A hour}} \right) \frac{1}{46 \text{ hour}}$$
$$= 23.4 \text{ A}$$

least twice) during the normal 8-hour working day. The check should include

- a. observation of the argon-gas-flow meter. (If more than 0.5 ft³ of gas is being used per hour, the stirrer packing gland should be tightened.)
- b. Check cell resistance.
- c. Inspect stirrer operation visually; stirrer should rotate at ~800 rpm. Electrorefining is terminated automatically by the back-emf sampler.

G. Symptoms of Electrorefining Failure

1. *Back-emf* ≤ 0.00 V and resistance $< 0.08 \Omega$. This condition can be caused by either a broken anode cup or a short-out of anode and cathode. Observance of the operating instructions will eliminate the latter possibility. If the anode cup is broken, stop the run as directed in Sec. H.
2. *Back-emf* > 0.2 V and resistance $> 0.3 \Omega$. This condition is caused by improper positioning of the anode rod, not positioning it in the anode metal. Following the operating instructions will eliminate this failure.
3. *Back-emf* > 0.2 V and resistance $< 0.08 \Omega$. This condition is caused by improper positioning of the anode rod, not placing it in the anode metal and shorting it out against the cathode. Following the operating instructions will eliminate this failure.

H. Terminal Cycle

1. Stop the stirrer when electrorefining ends.
2. Disconnect anode and cathode leads.
3. Raise anode rod and stirrer* out of crucible.

*D on stirrer—1.5 in. (D is the distance from flange (24) to end of stirrer shaft).

4. Agitate the product metal by gently lowering cylindrical cathode to bottom of cell then raising its electrolysis position. Repeat operation ~100 times, exercising care not to rotate the cathode rod or to hit the bottom of the cell.
5. Reposition cathode as shown in Fig. A-1.
6. After ~2 hours, raise cathode.*
7. Approximately 4 hours after electrorefining ends, cut off furnace power.

I. Unloading

1. Do not unload until cell temperature is $< 50^{\circ}\text{C}$.
2. Carefully unbolt and remove furnace head.
3. Remove stainless steel can from furnace tube with handle.
4. Remove cell from tantalum safety can.
5. Break crucible and salt away from product ring and anode residue.
6. Record weights of product, anode residue, and cathode.
7. Sample ring if required.
8. Transfer materials as in DYMAC Operating Procedure 421-MPP.

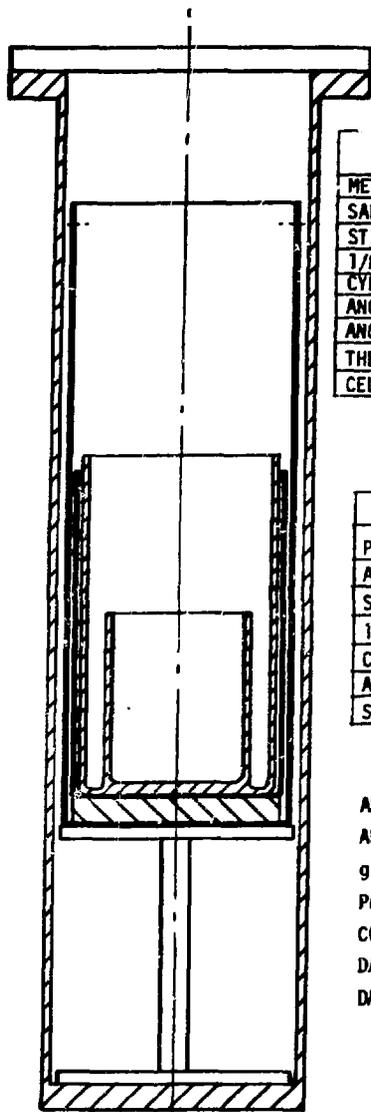
J. Storage and Care of Equipment

1. Store the ceramic stirrer in an inert, dry atmosphere immediately after unloading the furnace.
2. When not in use, keep furnace tube under argon.
3. If cathode is to be used for next run, store in inert, dry atmosphere.

K. Pickle cathode in 6N HCl when directed to do so by supervisor.

L. Record data on data sheet (Fig. A-2).

*D on cathode—9-1/2 in.



SCALE: 1 CM = 1 IN.

BEFORE RUN

	WT, g	LOT OR LENGTH, IN.	D (EL), IN.	Pu, g
METAL				
SALT				
STIRRER				
1/8" CATHODE				
CYL. CATH.				
ANODE ROD				
ANODE SLEEVE				
THERMOCOUPLE				
CELL				

AFTER RUN

	WT, g	Pu, g
PRODUCT RING		
ANODE RES.		
STIRRER		
1/8" CATHODE		
CYL. CATH.		
ANODE ROD		
SALT RECOV.		

METER READINGS

AMP. HR. (END OF RUN) _____
 AMP. HR. (START OF RUN) _____
 g Pu = DIFFERENCE _____ X 2.97
 Pu DISSOLVED _____
 COLLECTION _____
 DATE STARTED _____
 DATE FINISHED _____

Fig. A-2. Electrorefining data sheet.