

129-88
11-22-88

LA-9464-MS

D
I-6548

Dr. 1001

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

DOE-1001
Los Alamos National Laboratory

*Salt Stripping,
A Pyrochemical Approach to the Recovery of
Plutonium Electrorefining Salt Residues*

MASTER

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DO NOT FILE
COVER

This work was supported by the US Department of Energy, Office of Nuclear Materials Production.

Copyedited by Samantha Forrest

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

LA-9464-MS

UC-10

Issued: October 1982

LA--9464-MS

DE83 002914

**Salt Stripping;
A Pyrochemical Approach to the Recovery of
Plutonium Electrorefining Salt Residues**

D. C. Christensen
L. J. Mullins

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

809

CONTENTS

	PAGE
ABSTRACT	1
I. BACKGROUND	2
II. CHLORIDE MELT BY AQUEOUS RECOVERY	5
III. SALT STRIPPING OF CHLORIDE MELT	8
A. Objectives	8
B. Basic Principles	8
C. Equipment and Materials	9
D. Operating Procedure	9
IV. EXPERIMENTAL RESULTS	11
V. IDENTIFICATION OF BLACK SOLIDS	21
VI. CONCLUSIONS	21
VII. FUTURE WORK	24
REFERENCES	24

SALT STRIPPING[®]
A PYROCHEMICAL APPROACH TO THE RECOVERY OF
PLUTONIUM ELECTROREFINING SALT RESIDUES

by

D. C. Christensen and L. J. Mullins

ABSTRACT

A pyrochemical process has been developed to take the salt residue from the plutonium electrorefining process and strip the plutonium from it. The process, called salt stripping, uses calcium as a reducing/coalescing agent. In a one-day operation, greater than 95% of the plutonium can be recovered as a metallic button. As much as 88% of the residue is either reused as metal or discarded as a clean salt. A thin layer of black salts, which makes up the bulk of the unrecovered Pu, is a by-product of the initial reductions. A number of black salts can be collected together and re-reduced in a second step. Greater than 88% of this plutonium can be successfully recovered in this second stage with the resulting residues being discardable.

The processing time, number of processor hours, and the volume of secondary residues are greatly reduced over the classical aqueous recovery methods. In addition, the product metal is of sufficient quality to be fed directly to the electrorefining process for purification.

I. BACKGROUND

Since 1964, electrorefining has been the principle process for purifying plutonium metal scrap for Los Alamos programs. The scale of production was 200 kg of purified metal per year. In producing this metal, three forms of residues occurred.

1. A metallic anode residue.
2. A salt cake made up of sodium chloride, potassium chloride, and a plutonium mixture.
3. An MgO ceramic crucible.

In all three cases the residual plutonium was recovered by aqueous processing means. The anode residue was burned to oxide and dissolved in acid for further processing. The salt cake and crucible were sent directly for aqueous dissolution.¹ Because there were only a small number of electrorefining runs made each year, the holdup of plutonium in the residues was not significant. Therefore, rapid processing of these residues was not of great concern.

In May 1980, the Los Alamos National Laboratory embarked on a program of both increasing the capacity of the electrorefining operation and in increasing the number of electrorefining cells. The capacity increased from a 3.2-kg plutonium charge up to a 6-kg plutonium charge.²⁻⁴ Along with the increase in plutonium came a commensurate increase in the quantity of salt and anode and likewise an increase of plutonium in the residues. The quantity of salt increased from 1.4 kg/run containing 200 g of Pu up to 2.5 kg/run containing 500 g of Pu.

The depleted anode increased from 400 g Pu to 600 g Pu.

The number of electrorefining cells systematically increased from 2 cells in May 1980 up to 8 cells in April 1981. By the time the scale-up operation was completed the volume of residues had increased 8 fold but the capacity to handle these residues had remained the same.

The quantity of plutonium being held up in these residues dictated that a more timely turnaround of this material was needed. The pyrochemical recovery of plutonium from the salt residue is the subject of the present report.

Three parameters were evaluated in examining a method for recovering the Pu in the salt residues.

1. Form of the Pu in the recovered product.
2. Time involved in recovery, including shelf time awaiting processing.

3. Volume of secondary residues generated in recovery.

The impetus for the entire scale-up operation was to increase the output of pure plutonium metal. Therefore, the most desirable form of recovered product is metal. (The plutonium may exist in different forms during intermediate stages of processing.)

In understanding the process problems, it is important to understand the characteristics of the materials being processed. In the electrorefining operation, the refining cell consists of two concentric, cylindrical, magnesia containers (Fig. 1). The small inner cup contains the impure molten plutonium anode and the outer cup contains an equimolar NaCl-KCl salt electrolyte. In addition, PuF_4 or MgCl_2 is added to the molten mixture to provide Pu^{+3} ions. (The Pu^{+3} concentration determines the purification factors for impurity elements.⁵) The following reactions take place when stirring is initiated before to the actual electrorefining process.



These reactions provide the first mechanism whereby plutonium is put into the salt.

During the refining operation a dc current is passed causing the plutonium to oxidize at the anode and reduce back to metal at the cathode.

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



Because plutonium is a very active, or electropositive, metal, most of the impurities remain in the anode. Elements such as americium and cerium, which

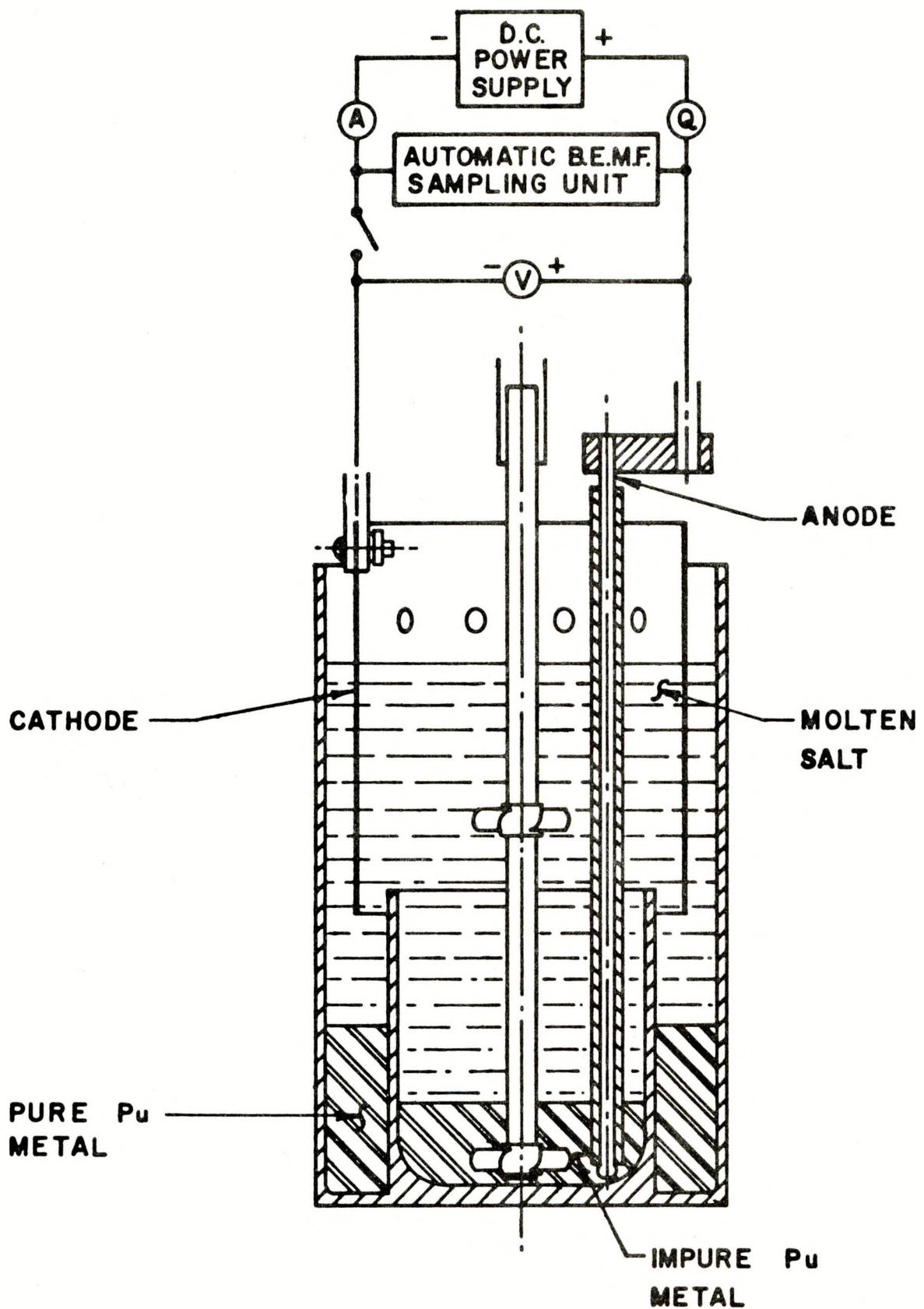


Fig. 1. Los Alamos electrorefining cell.

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.⁵ 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 limit. 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. It also permits unattended operation of the electrorefining cell and terminates the operation automatically.

Because of the design of the cathode, a plutonium-rich surface (inner surface) and a plutonium-poor surface (outer surface) exist. The current density on all surfaces of the cathode is constant. This leads to the second mechanism whereby plutonium is put into the salt. When the density of plutonium ions around the cathode shield becomes too small, sodium begins to reduce at the cathode. Plutonium is still being oxidized at the anode thus putting additional Pu^{+3} into the salt.

The third and final source of plutonium in the salt is from uncoalesced pure metal in the metal collection zone. At the termination of the run a large number of small beads of plutonium exist on top of the product ring. There are many explanations for this; the most plausible is the existence of high surface tension on the small bead that will not allow the bead to coalesce into the product ring. This phenomenon accounts for 50-500 g of Pu metal in the salt.

Therefore, plutonium exists in the salt residue in both the metallic and the ionic forms. The amount of plutonium ranges anywhere from 100 g up to 1.0 kg, with the average being 500 g for the 6-kg electrorefining process.

II. CHLORIDE MELT BY AQUEOUS RECOVERY

The classical method for the recovery of plutonium from chloride-based salt residues has been through a series of aqueous processing steps. Fig. 2 shows the series of steps taken to get the recovered material back to a metal form. In this form it can be either shipped as a product or further purified by electrorefining.

Chloride Salt and Crucible

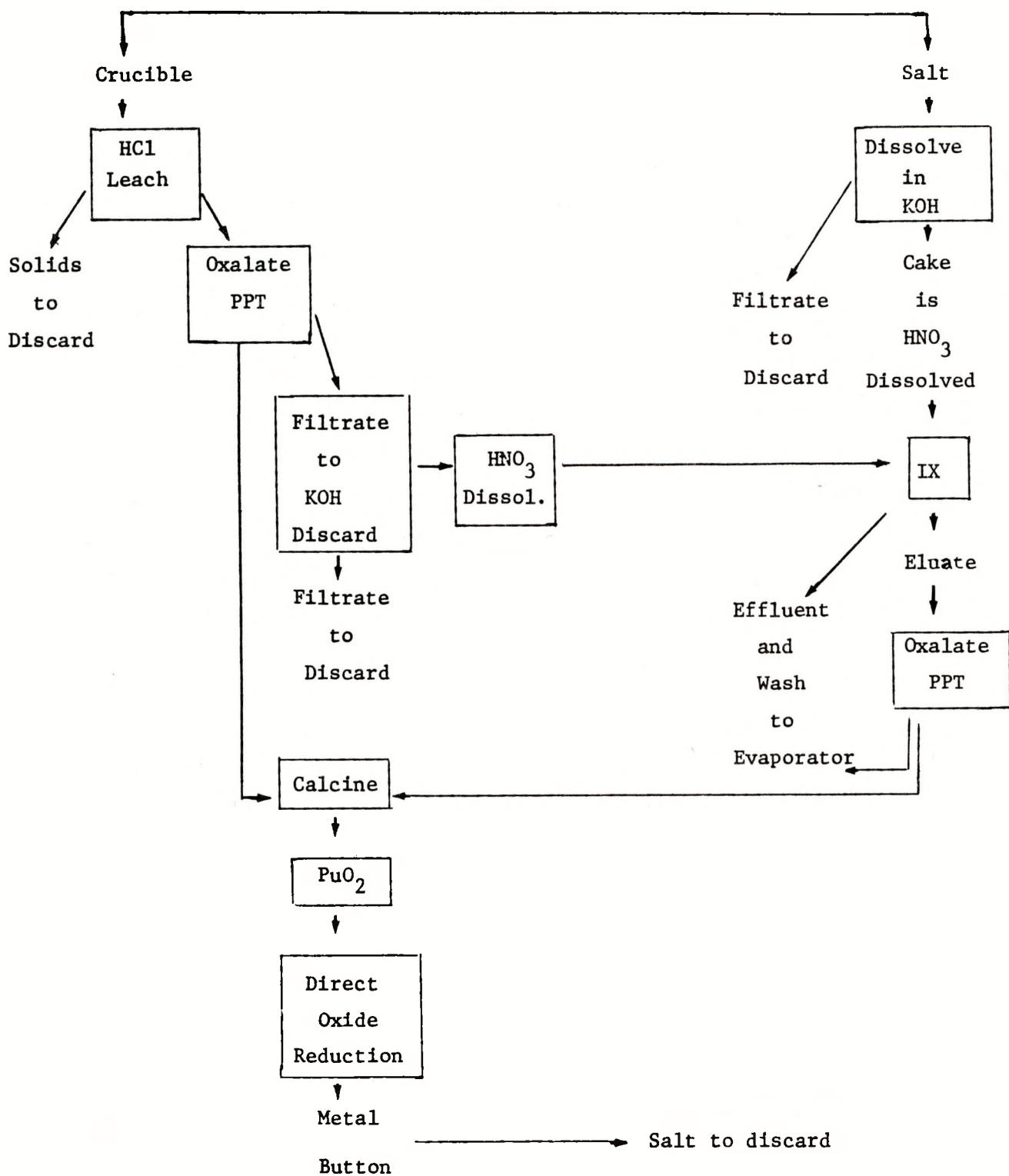


Fig. 2. Aqueous processing steps for chloride metal recovery.

As seen in Fig. 2 the residues are separated into two streams, the crucible pieces and the salt. The crucible is leached with HCl. The crucible pieces are then discarded and the leachate is oxalate precipitated. The oxalate cake is calcined to PuO₂ whereas the filtrate goes through the ion exchange route for concentration/purification.

The salt cake is first dissolved in KOH. The filtrate goes to discard and the cake goes to nitric acid dissolution and on to ion exchange. All effluents off of the ion exchange columns go to the evaporator. The eluate off of ion exchange goes to oxalate precipitation. The filtrate from this step goes to the evaporator. The oxalate cake goes to calcination. The plutonia generated from both branches is then fed to direct oxide reduction. The salt residues out of direct oxide reduction are discardable.

The processing time as well as interim storage is of major concern in the plutonium facility. The time to process material through the aqueous route to the metal product button is approximately 7 days for a one-batch iteration. (Note this does not include evaporation time required for ultimate residue disposal.) Approximately 94% of the material is recovered in this iteration. Subsequent cycles for further recovery add processing time.

In addition to the processing time a large volume of secondary residues are generated in the aqueous route.

The residues for a single batch (one salt and crucible residue) are summarized below.

<u>Item</u>	<u>Residue</u>
Bulk Solids	500 grams
Liquid for discard	28 liters
Liquid for evaporator	65 liters
Reduction salt and crucible	3500 grams

The electrorefining process makes eight runs per week. For the present system to be viable, the residue handling as well as the processing time must be multiplied by 8. This level of effort and the glovebox processing space simply were not available if we were to expect to keep residue recovery up to date with salt generations. Consequently a new method for salt recovery was considered. The process arrived at was a pyrochemical process similar in design to the direct oxide reduction process. The process is called the Salt Stripping Process.

III. SALT STRIPPING OF CHLORIDE MELT

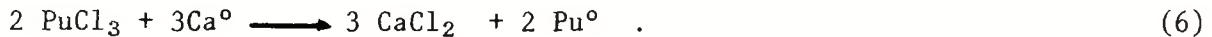
A. Objectives

The objectives of the Salt Stripping Process were as follows.

- Decrease the turnaround time of plutonium in residues.
- Decrease the volume of secondary residues.
- Decrease the cost of processing.
- Render the product directly reusable in the Metal Preparation Facility.

B. Basic Principles

The plutonium in the salt feed exists in two forms, PuCl_3 and Pu metal shot. The reduction procedure for the recovery of the PuCl_3 is the same as the Direct Oxide Reduction procedure.⁶ The chemical reaction is as follows.



In recovering the metal beads, the goal is to break the surface tension of the beads thus allowing them to coalesce into a single metal button. Calcium metal is used to attack the surface of the beads. As a result, both the reduction of PuCl_3 to metal and the coalescence of the metal beads result in a single product button.

Since the salt matrix of the feed salt is $\text{NaCl}\cdot\text{KCl}$, any calcium that encounters NaCl will reduce the NaCl to sodium metal. This sodium metal can either further reduce PuCl_3 to Pu metal or vaporize off. Since the operating temperature is below the boiling point of sodium, the vaporization is not immediate and some secondary reaction with PuCl_3 is certainly occurring.

In estimating the amount of calcium metal needed to provide a complete recovery of the plutonium, an excess must be provided to allow for sodium lost through vaporization.

As discussed earlier, the plutonium in the salt that is as PuCl_3 is derived from two different sources: reaction with MgCl_2 , or PuF_4 and cathodic reduction of Na^+ . It is not easy to calculate the stoichiometric amount of calcium needed based on these two mechanisms because the extent of cathode reaction is not known. Therefore, in designing experiments for evaluating the Salt Stripping operations, a variety of calcium-to-salt ratios were used.

C. Equipment and Materials

The Salt Stripping equipment is shown in Fig. 3. The reduction/coalescence is done in a magnesia crucible contained in a stainless steel loading can. The loading can is contained in a sealed furnace tube having an argon atmosphere and is heated by a resistance furnace, Lindberg Model 6015S. The reaction mixture is stirred by a tantalum stirrer fitted with two sets of oppositely pitched impellers. As the stirrer is rotated clockwise, the bottom impeller lifts the salt residue and the top impeller pulls the calcium metal down into the molten salt. Temperature is measured by a Chromel-Alumel thermocouple immersed in the melt and protected by a tantalum/nickel sheath. The outer tube is tantalum and the inner tube is nickel. The tantalum is resistant to the components of the reaction mixture and the nickel protects the tantalum from air oxidation and provides mechanical strength. The upper ends of the tantalum and nickel tubes are welded together.

The magnesia crucibles are highly vitrified bodies and are fabricated commercially.

The calcium metal is Pfizer's Redistilled-Grade, 6-mesh nodules.

D. Operating Procedure

A salt cake from an entire electrorefining run is loaded into a magnesia crucible. Calcium metal is then poured on top of the salt cake. The crucible is then loaded into the stainless steel loading can. This assembly is then placed in the furnace tube and the cover plate is bolted in place. A vacuum is pulled on the furnace tube, and the assembly is checked for gas tightness. The furnace tube is then filled with argon gas to 4 psig.

The crucible is heated at a maximum rate of 200°C/h up to 800°C. The thermocouple sheath and stirrer are then lowered into the melt to the position shown in Fig. 3. Stirring is initiated and slowly increased to 600 rpm over about a 1-min period. A small increase in temperature may or may not be detected depending on the amount of PuCl_3 present in the salt. If the salt contains a large amount of PuCl_3 an immediate increase in temperature will be seen as a result of the reactions of calcium with the PuCl_3 . The reaction is usually complete in less than 5 min, however; stirring is continued for a total time of 15 minutes to allow for coalescence. Upon completion of stirring the stirrer and thermocouple sheath are raised from the melt and the furnace is shut off.

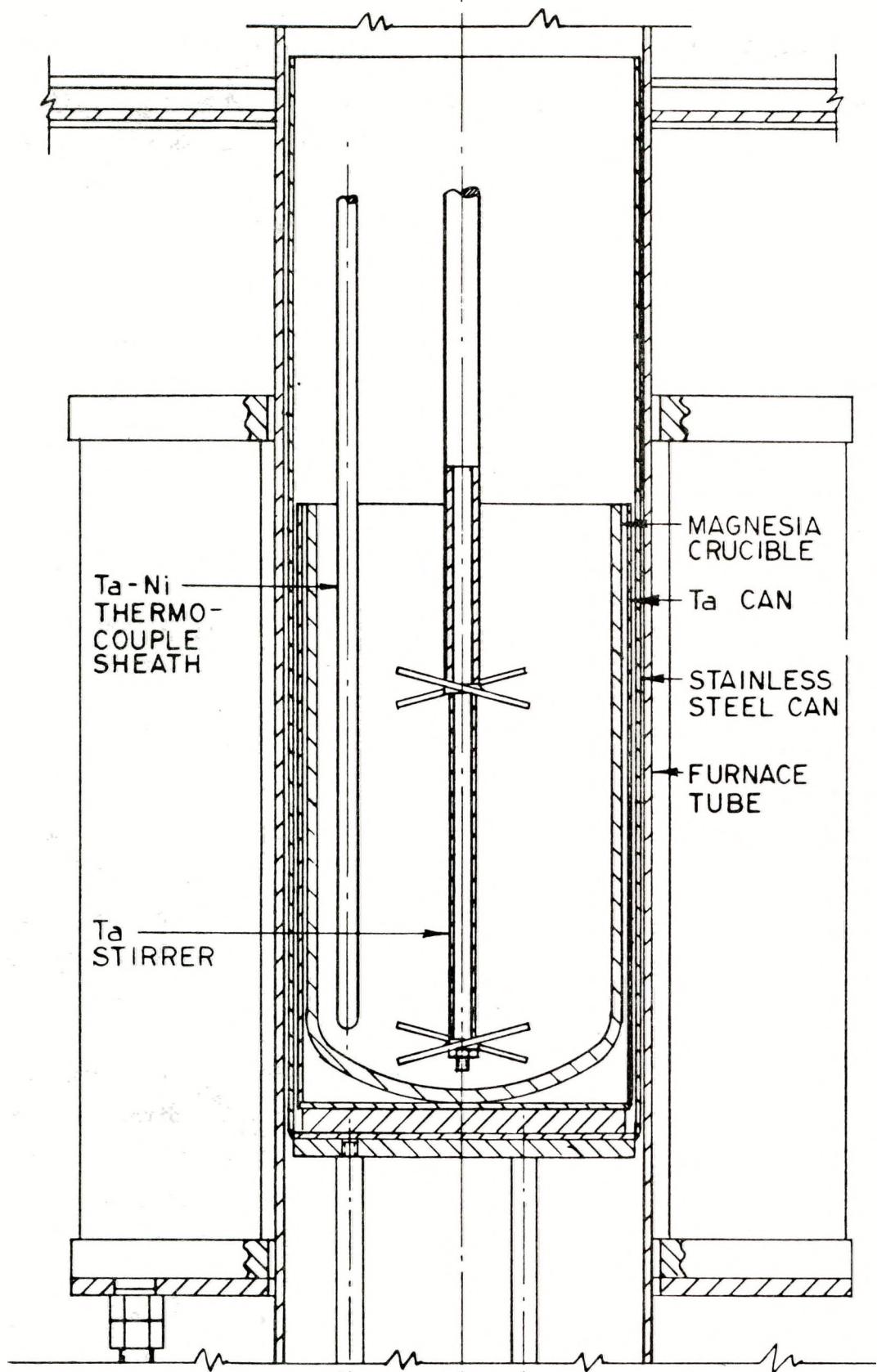


Fig. 3. Salt stripping equipment.

The furnace is allowed to cool for at least 4 hr before unloading. The stainless loading can is removed from the furnace and inverted to remove its contents. The metal button is removed from the magnesia crucible by breaking away the bottom of the crucible.

IV. EXPERIMENTAL RESULTS

Initially, one calcium metal concentration was used in evaluating the applicability of the process. This concentration was selected to be 45 g Ca/ electrorefining salt residue. This amount of calcium is stoichiometrically equivalent to 179 g Pu as Pu^{+3} or 134 g Pu as Pu^{+4} . Fig. 4 shows a typical salt residue that is used as feed for the salt stripping step. It is essentially a purple-to-olive-green salt with small bits of broken MgO crucible.

A number of test reductions were made with the 45-g level of calcium. In all cases a product button was produced. The average yield from these reductions was 95.6%. In all cases a thin layer of black salt occurred lying on top of the product buttons. The product of one of the reductions can be seen in Fig. 5. As seen in the figure the product button is lying on the bottom of the salt residue. The thin layer of black salt is sandwiched between the button and a large section of white salt. In one of the six cases the black salt separated very cleanly from both the button and the white salt. In all other cases the interfaces appeared to be very clean but phase disengagement was difficult.

Each salt residue as well as the crucible were separately assayed nondestructively using a thermal neutron counter. The results of this evaluation are seen in Table I. The white salt contained no Pu residue and was discarded. The crucible contained an average of 0.7 g Pu (<0.1%) and was also discarded. The black salt averaged 38.5 g Pu or 4.3% of the feed. This material was saved for further processing. The average Pu metal button weighed 863 g or 95.6% of the feed.

Also seen in Table I is the distribution of bulk weight of the residues. As seen, the discardable white salt made up 61% of the starting material. The Pu product button made up an additional 27% of the starting material. This means that together, 88% of the starting material is either discardable or reusable in the metal feed without further processing. A summary of the data on these runs can be found in Appendix A.

These results were particularly encouraging in view of the fact that in a one-day operation >95% of the residue plutonium could be recovered. In addition, the product was in the metal form, which was very suitable for use as

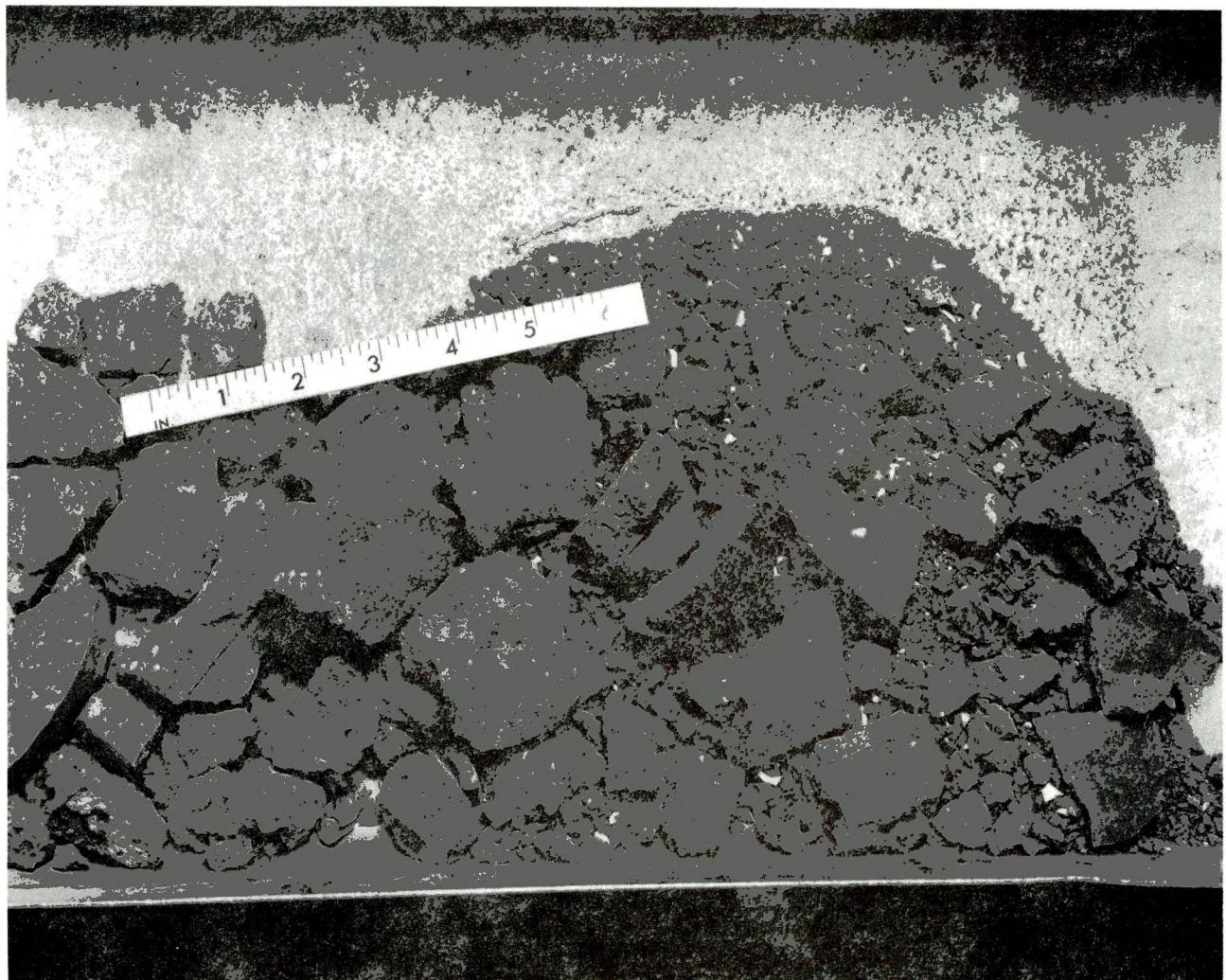


Fig. 4. Electrorefining salt residue. Salt feed to the first-stage salt stripping.

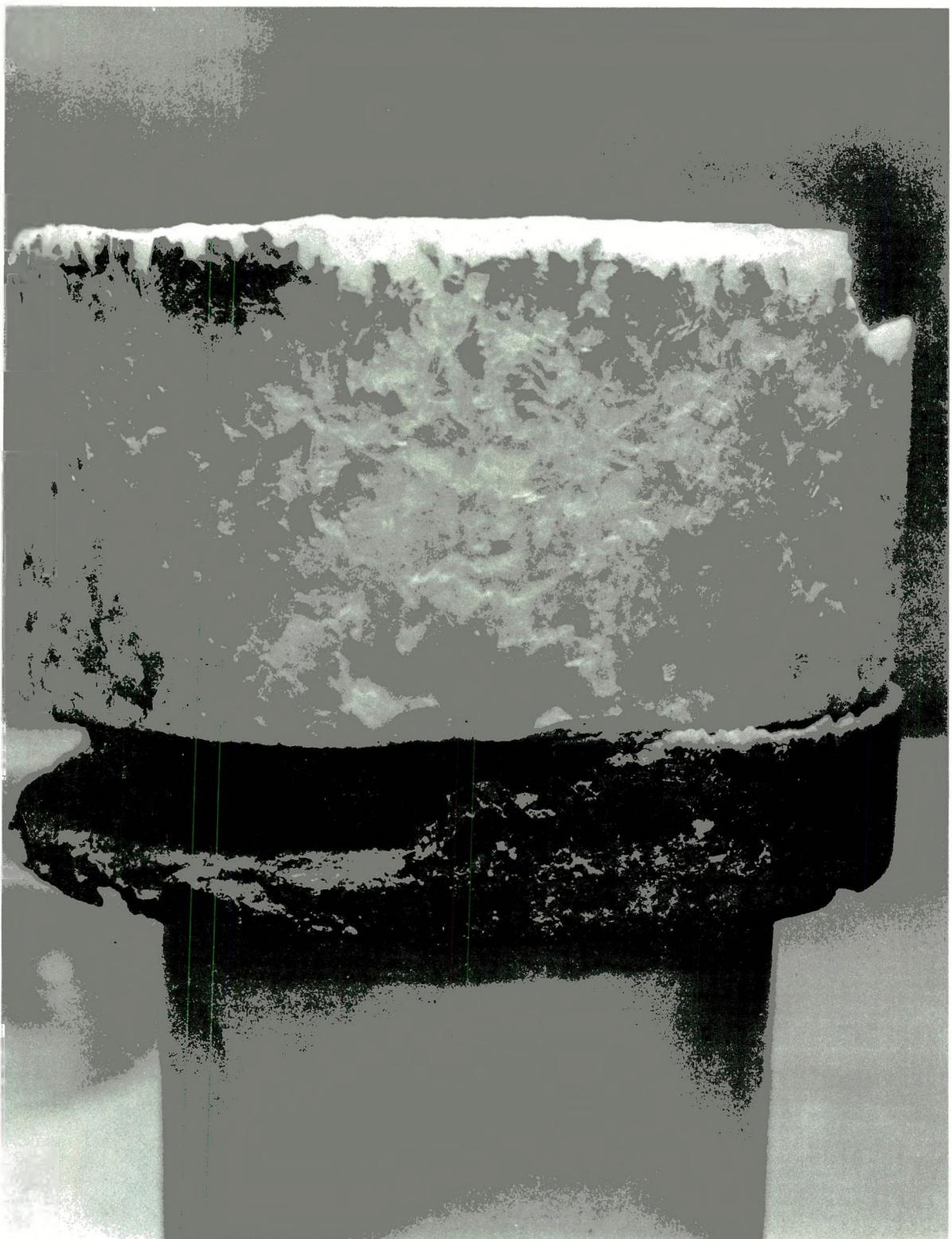


Fig. 5. Reaction products from Run 1. (First-stage reductions.)

TABLE I
 DISTRIBUTION OF BULK WEIGHTS AND Pu IN RESIDUES
 FROM FIRST-STAGE REDUCTION

	<u>Bulk Wt (% of Bulk)</u>	<u>Pu Content (%Pu)</u>
<u>Feed</u>		
Salt	3215 (g)	903 (g)
Calcium	45	0

<u>Product</u>		
White Salt	1980 (61%)	0 (0%)
Black Salt	385 (12%)	38.5 (4.3%)
Crucible		0.7 (0.1%)
Pu Button	895 (27%)	863 (95.6 %)

electrorefining feed. Finally, the bulk of the salt residue was rendered discardable without further processing.

In an effort to both reduce the volume of black salt and recover the plutonium held up in the black salt, two sets of additional experiments were run. In the first set, the calcium level was increased to 100 g per charge and in the second set, the calcium level was increased to 175 g per charge. All other operating conditions remained the same. Surprisingly, increasing the weight of calcium metal resulted in a decreased percentage of plutonium recovered.

Table II shows a compilation of Pu distribution data for all three levels of calcium charge. In the 100- and 175-g cases, there is a marked decrease in the percentage of plutonium recovered over the 45-g case. In the 45-g case, the yield is 95.6% while in the 100- and 175-g cases, the yield is 89% and 90%, respectively. The decrease in yield in the higher calcium cases is followed by an increase in black salt content. In the 45-g case the black salt averaged 4.3% of the Pu while in the 100- and 175-g case the black salt averaged 9% of the Pu. A summary of the data on both the 100 g Ca and 175-g Ca cases can be found in Appendixes B and C, respectively.

The preliminary indication is that the lower calcium level gave better product yields.

A final set of experiments was run using only the black salt residues as feed. The black salt was collected from a number of salt stripping runs (an average of eight runs). The same procedure as before was used except that a 3.5-kg CaCl_2 salt cake was added to the run to act as a solvent for any contaminants in the black salt.

Fig. 6 shows the results of a typical second-stage stage stripping run. The figure shows an inverted salt cake with the product button on top. The product button broke away very cleanly from the salt residue. Fig. 7 shows the surface of the salt after the button was removed. (The black portions of the salt are small bits of crucible that were carried over in the black salts.)

Table III shows the distribution of Pu in the feed and resulting residues from the second-stage reduction. The average Pu in the feed was 570 g. The average product yield was 503 g or 88%. The salt and crucible contained the remaining 12% of the Pu.

The overall results can be summarized as follows. In the present system the first-stage reduction can yield approximately 95.6% of the feed Pu. The bulk of the plutonium residue exists in a thin layer of black salt. By compiling up to

TABLE II
PLUTONIUM DISTRIBUTION FOR VARIOUS LEVELS
OF CALCIUM CHANGE IN FIRST-STAGE PRODUCTION

Ca (g)	45	100	175
Av. Pu Feed			
in Salt (g)	903	727	676
<hr/>			
Av. Pu Prod			
Button (g)	863	648	605
% Pu Recovered	95.6	89	90
% Pu in Crucible	<0.1	1.0	1.0
% Pu in White			
Salt	0.0	0.0	0
% Pu in Black			
Salt	4.3	9	9

TABLE III
DISTRIBUTION OF Pu IN RESIDUES FROM SECOND-STAGE REDUCTION

<u>Feed</u>	<u>Pu Content (g)</u>	<u>% Pu</u>
Black Salts	570	100
Calcium	175	
<hr/>		
<u>Product</u>		
Pu Button	503	88
Salt and Crucible	67	12

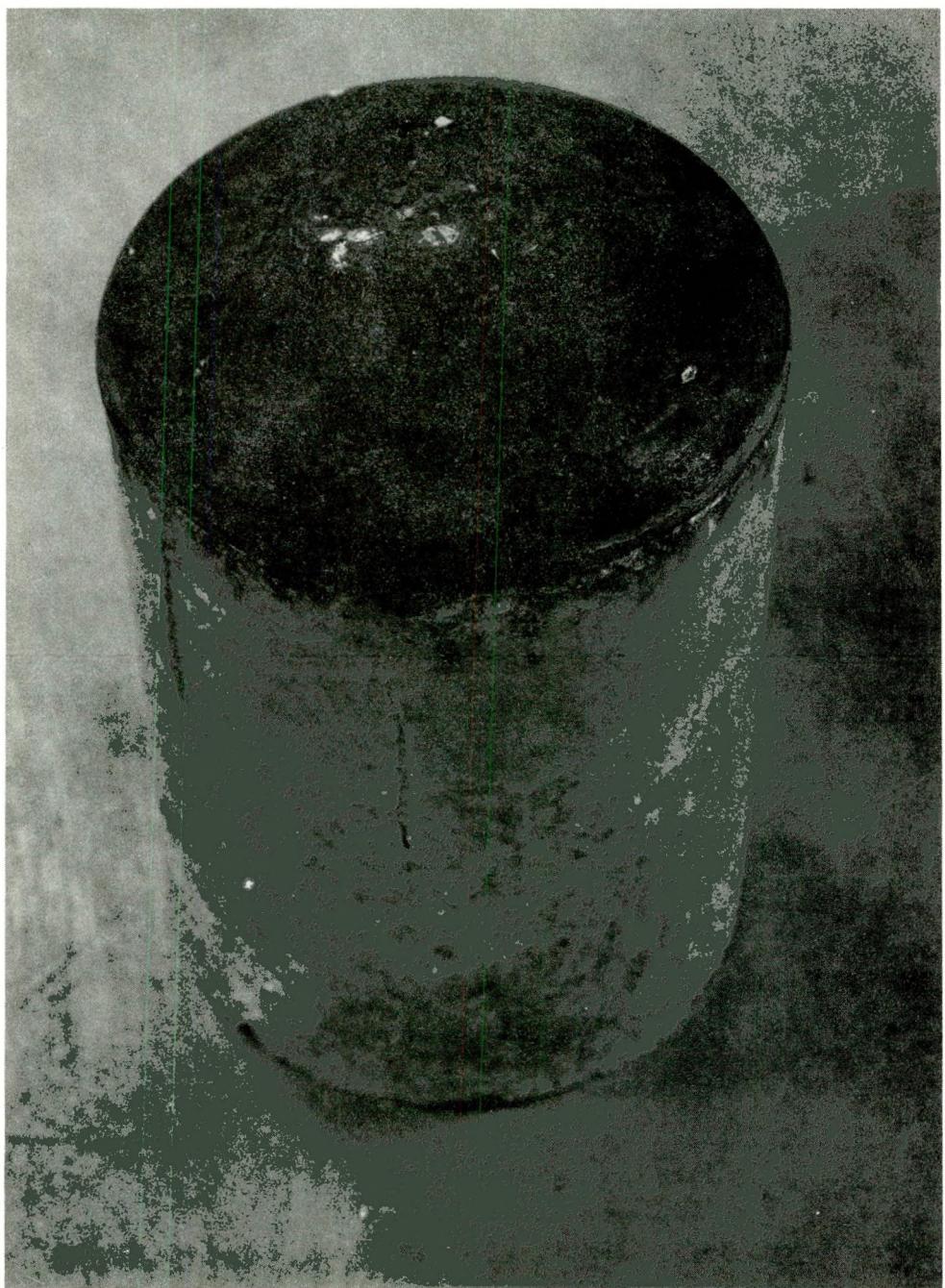


Fig. 6. Reaction product from reduction of black salt.



Fig. 7. Salt cake after button removal.

eight batches of black salt and doing a second-stage reduction an additional 88% of the residue can be recovered. This means that $[(95.6\% + 88\%)(4.4)]$ or 99.5% of the Pu can be recovered.

In comparing the amount of residues generated in processing we must refer back to Fig. 2 on aqueous processing. The electrorefining crucible still follows the aqueous route. But the entire right branch, which involves the salt processing steps, is eliminated. The volume of secondary residues is drastically cut. The following is a summary of these residues.

Secondary Residues		
<u>Item</u>	<u>Aqueous Route</u>	<u>Pyrochemical Route</u>
Bulk Solids	500 grams	500 grams
Liquid for discard	18 liters	9 liters
Liquid for evaporation	65 liters	9 liters
Reduction Salt and Crucible	3500 grams	2500 grams

The processing time has also been greatly affected. In the aqueous case the processing time required was 7 d. This did not include time in the evaporator for final residue disposal. In the pyrochemical case the time is cut to 4 days (3 days for electrorefining crucible leaching and 1 day for the metal reduction from the salt). The quality of the product metal was also of great interest in evaluating the applicability of the process.

The only impurities that concentrate in the salt during the electrorefining process are the alkalis, the alkaline earths, the rare earths, and americium. Of these, only americium is a usual metallic impurity in the electrorefining feed metal. Thus, in principle, plutonium metal derived from the stripping of electrorefining salts should be fairly pure, containing only americium and calcium as impurities. In practice, however, small pieces of both depleted anode and magnesia crucible accompany the salt in the stripping process. Thus, magnesium and anode impurities are also present in the metal product.

The analysis of four lots of metal from salt stripping experiments is given in Table IV. This metal was subsequently cast into an anode and was electrorefined to produce high-purity plutonium metal.

TABLE IV
PURITY OF PLUTONIUM METAL FROM SALT STRIPPING EXPERIMENTS

<u>Element</u>	g Element/ 10^6 g Pu			
	<u>Run 6A</u>	<u>Run 14A</u>	<u>Run 18A</u>	<u>Run 21</u>
B	100	250	<1	50
Na	350	100	2	20
Mg	15	25	300	1000
Al	400	15	<5	400
Si	690	50	<5	150
K	400	200	5	40
Ca	1500	3	5	25
Cr	170	20	<5	95
Mn	20	5	1	10
Fe	3000	250	5	240
Ni	200	100	30	310
Cu	50	5	3	2
U	105	-	160	35
Th	145	-	20	80
Ga	70	3.8%	330	70
C	1400	-	110	-
O	1300	-	-	-
Am	322	1400	1930	8420
Pu	97.47%	95.5%	97.78%	98.07%

V. IDENTIFICATION OF BLACK SOLIDS

Most of the identification work has been done with the solids from Run 208-5A (See Appendix A for details on this run). These solids resulted from the stripping of an electrorefining run in which 143 g Pu as PuF_4 was added to the NaCl-KCl salt. A photomicrograph of a section of this black salt is shown in Fig. 8. The components of the salt were examined by electron microprobe analysis. The matrix material is NaCl-KCl . The major component of the crystals is calcium. The metallic inclusions, the bright spots in Fig. 8, contain magnesium and plutonium together and separately. X-ray diffraction analysis of the same black material identified the solids as a three-phase mixture of NaCl , KCl , and CaF_2 . No plutonium metal or compounds were detected, i.e. no plutonium halides or oxy-halides, no plutonium oxides or suboxides. Chemical analysis showed that the solids contained 6.6% plutonium and consisted primarily of Na, K, Ca, and Cl.

From the above data, we think that the black solids consist primarily of a NaCl-KCl salt matrix containing crystals of CaF_2 , CaCl_2 , and small amounts of CaO . Further, the plutonium is apparently present as small metallic particles.

VI. CONCLUSIONS

The turnaround time for the plutonium in the electrorefining salt residues has been significantly reduced. Up to 95.6% of the Pu can be recovered in 1 day as opposed to the 4-day turnaround of the salt in aqueous recovery. In either case the crucible residues from electrorefining are being processed by aqueous leaching.

The volume of secondary residues has been significantly reduced. The greatest impact lies in the volume of liquid residues where 83 l are generated in the aqueous route and only 18 l are generated in the pyrochemical route.

The level of effort required to process these residues is decreased. With both the decrease in processing time and a reduction in the volume of secondary residues there is a lower level of effort required for salt residue processing.

The product from the salt stripping operation is in the metal form. This is most desirable for further processing. The product out of the aqueous processing route is PuO_2 and must go through the direct oxide reduction step before it is put in the metal form.

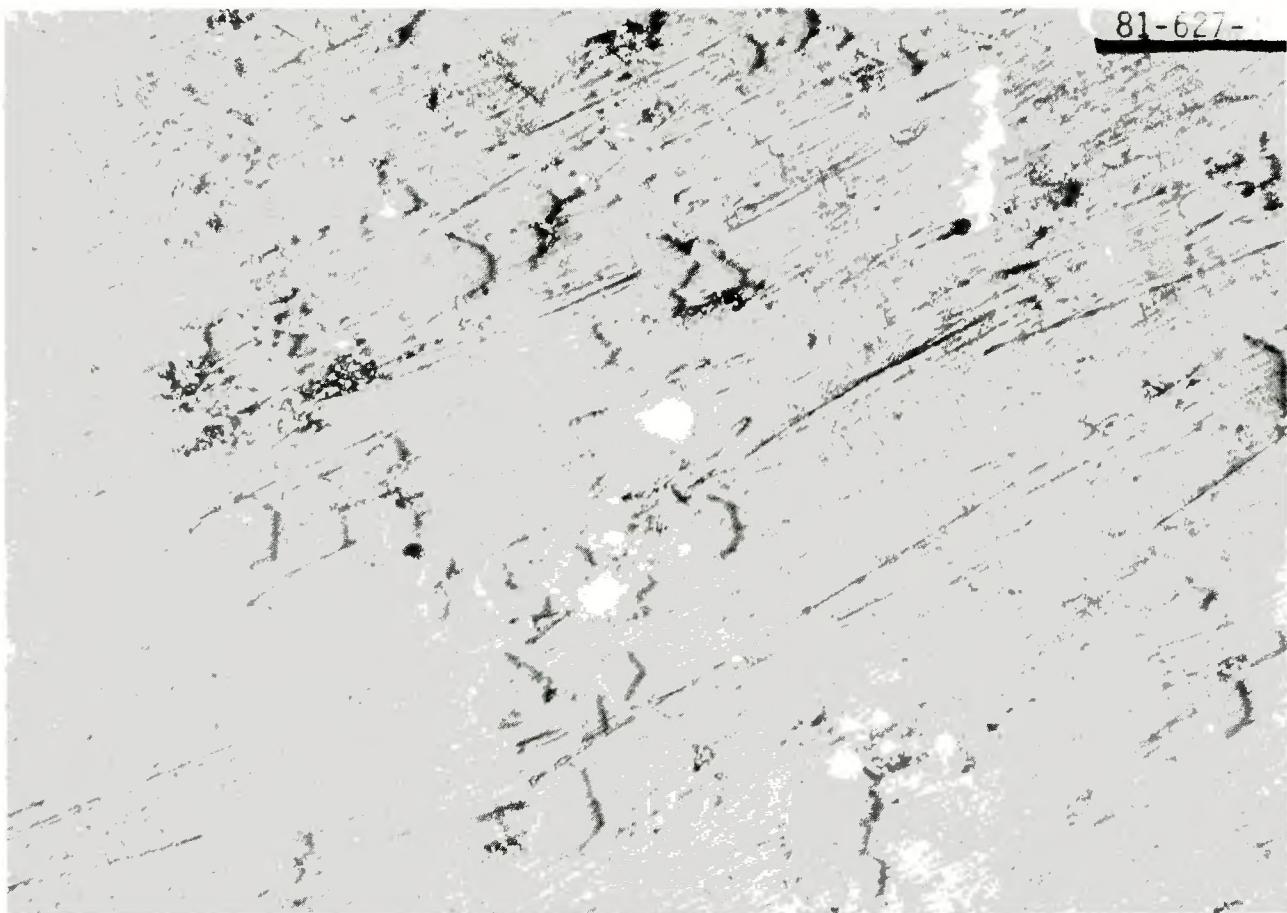


Fig. 8. Photomicrograph of black solid residues from first-stage salt stripping.

The product metal is of sufficient quality to be immediately used as metal feed for the electrorefining operation.

VII. FUTURE WORK

Efforts will be made to isolate the specific Pu composition in the feed salt.

Efforts will continue to identify the composition of the black salt residue.

The calcium metal reducing agent will be optimized.

Different operating conditions and reagents will be evaluated in an effort to eliminate the formations of the black salt and facilitate an increased yield in the salt stripping operation.

REFERENCES

1. E. L. Christensen and W. J. Maraman, "Plutonium Processing at the Los Alamos Scientific Laboratory," Los Alamos Scientific Laboratory report LA-3542 (1969).
2. L. J. Mullins and A. N. Morgan, "A Review of Operating Experience at the Los Alamos Plutonium Electrorefining Facility, 1963-1977," Los Alamos National Laboratory report LA-8943 (1982).
3. L. J. Mullins, D. C. Christensen, and B. R. Babcock, "Fused Salt Processing of Impure Plutonium Dioxide to High-Purity Plutonium Metal," Los Alamos National Laboratory report LA-9154-MS (1982).
4. L. J. Mullins, A. N. Morgan, S. A. Apgar, III, and D. C. Christensen, "Six-Kilogram Scale Electrorefining of Plutonium Metal," Los Alamos National Laboratory internal document LA-UR-82-559.
5. J. A. Leary and L. J. Mullins, "Practical Application of Thermodynamics to Plutonium Process Reactions at High Temperatures," in Thermodynamics, Vol. 1 (International Atomic Energy Agency, Vienna, 1966), pp. 459-471.
6. L. J. Mullins and C. L. Fox, "Direct Reduction of $^{238}\text{PuO}_2$ and $^{239}\text{PuO}_2$ to Metal," Los Alamos National Laboratory report LA-9073 (February 1982).

APPENDIX A

FIRST-STAGE STRIPPING OF ELECTROREFINING SALT RESIDUE WITH 45 g CALCIUM METAL

Run #	Ca in	Pu in	Pu Button	% Rec.	Cruc	%	White Salt	%	Black Salt	%
9	51	1075	1072	100					3	0
25	45	1055	880	83					175	17
208-5A	45	1653	1640	99	1	0	0	0	12	1
208-12B	45	431	426	99	0	0	0.2	0	4.9	1
208-14A	45	787	771	98	1.7	0	0	0	13.3	2
208-18A	45	411	387	94	1.2	0	0	0	23	6
		5412	5176	95.6	3.9	0	0.2	0	231.2	4.3

APPENDIX B

FIRST-STAGE STRIPPING OF ELECTROREFINING SALT RESIDUE WITH 100 g CALCIUM METAL

Run #	Ca in	Pu in	Pu Button	% Rec.	XBRC	%	White Salt	%	Black Salt	%
1072	100	690	542	79	10.2	1	1.6	<1	136	20
3047	100	775	745	96	1.3	<1	9.5	1	18	2
9040	100	801	688	86	1.3	<1	.12	0	113	14
1074	100	787	745	95	2.4	<1	0	0	39.2	5
138	100	722	627	87	19	3	1.5	<1	74.6	10
139	100	589	546	93	7	1	1	<1	31	5
		4364	3893	89	41.2	1	13.7	<1	411.8	9

APPENDIX C

FIRST-STAGE STRIPPING OF ELECTROREFINING SALT RESIDUES WITH 175 g CALCIUM METAL

Run #	Ca in	Pu in	Pu Button	%	Cruc	%	White Salt	%	Black Salt	%
3	175	316	300	95					16	5
43	175	512	478	93	3	1	0	0	31	6
45	175	630	543	86	2	<1	0	0	85	14
46	175	1060	949	90	2	<1	0	0	109	10
48	175	733	575	78	26	4	3	<1	129	18
55	175	824	672	82	10	1	0	0	142	17
56	175	786	746	95	5	<1	3	<1	32	4
58	175	530	376	71	10	2	2	<1	142	27
59	175	678	610	90	2	<1	0	0	66	10
60	175	586	559	95	1	<1	10	2	16	3
61	175	350	330	94	2	<1	8	2	10	3
63	175	948	678	72	2	<1	7	<1	261	28
64	175	941	918	98	1	<1	1	<1	21	2
67	175	686	604	88	5	<1	0	0	77	11
70	175	595	509	86	61	10	0	0	25	4
72	175	696	673	97	1	<1	8	1	14	2
73	175	660	460	70	7	1	0	1	193	29
74	175	441	413	94	0	0	5	1	23	5
76	175	1309	1257	96	1	<1	0	0	51	4
77	175	431	412	96	0	0	0	0	19	4
79	175	1398	1374	6	6	0	0	0	18	1
80	175	466	440	94	7	1	0	0	19	4
81	175	1154	1141	99	0	0	1	<1	12	1
82	175	333	290	87	4	1	0	0	39	12
83	175	412	392	95	0	0	3	1	17	4
85	175	736	641	87	0	0	21	3	74	10
86	175	718	666	93	0	0	0	0	52	7
87	175	606	476	79	0	0	0	0	130	21
88	175	610	590	97	2	<1	0	0	18	3
89	175	133	122	92	1	<1	0	0	10	8
91	175	691	684	99	0	0	0	0	7	1
92	175	488	451	92	2	0	0	0	35	7
93	175	508	489	96	1	<1	4	<1	14	3
94	175	548	530	97	1	<1	7	1	10	3
95	175	628	597	95	7	<1	0	0	24	4
98	175	606	565	93	3	<1	0	0	38	6
130	175	760	584	77					62	23
131	175	1228	1104	90					124	10
133	175	776	624	80					152	20
134	175	<u>511</u>	<u>402</u>	<u>79</u>	<u>175</u>	<u>1</u>	<u>83</u>	<u>0.3</u>	<u>109</u>	<u>21</u>
		27022	24224	90					2426	9

APPENDIX D

SECOND-STAGE STRIPPING OF BLACK SALT RESIDUE FROM FIRST-STAGE
STRIPPING OF ELECTROREFINING SALT RESIDUES

2nd Run DOR Proc.

Run #	Ca in	Pu in	Pu Button	%	Salt + Cruc.	%
208-19	013	451	431	96	20	4
54	175	992	820	83	172	17
127	175	290	236	81	54	19
128	175	400	396	99	4	1
129	175	454	383	84	71	16
132	175	<u>836</u>	<u>752</u>	<u>90</u>	<u>84</u>	<u>10</u>
		3423	3018	88	405	12

DO NOT MICROFILM
COVER

Printed in the United States of America
Available from
National Technical Information Service
US Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Microfiche (A01)

Page Range	NTIS Price Code						
001-025	A02	151-175	A08	301-325	A14	451-475	A20
026-050	A03	176-200	A09	326-350	A15	476-500	A21
051-075	A04	201-225	A10	351-375	A16	501-525	A22
076-100	A05	226-250	A11	376-400	A17	526-550	A23
101-125	A06	251-275	A12	401-425	A18	551-575	A24
126-150	A07	276-300	A13	426-450	A19	576-600	A25
						601-up*	A99

*Contact NTIS for a price quote.

