Recovery of Plutonium
by Pyroredox Processing

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by

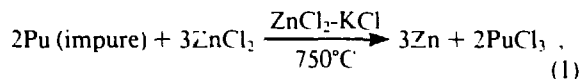James A. McNeese, David F. Bowersox,
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ABSTRACT

Using pyrochemical oxidation and reduction, we have developed a process to recover the plutonium in impure scrap with less than 95% plutonium. This plutonium metal was further purified by pyrochemical electrorefining. During development of the procedures, depleted electrorefining anodes were processed, and over 80% of the plutonium was recovered as high-purity metal in one electrorefining cycle. Over 40 kg of plutonium has been recovered from 55 kg of impure anodes with our procedures.
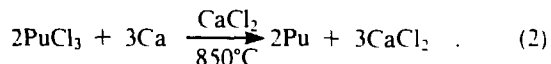
I. INTRODUCTION

The purpose of pyrochemical research and development programs is to examine new techniques for producing high-purity plutonium metal from impure oxides, metals, and scrap. Los Alamos has demonstrated pyrochemical processes by taking plutonium scrap, converting it to oxide, and then, through a series of operations, producing high-purity plutonium metal.[1] The last purification step, electrorefining, is most effective when the metal feed exceeds 95% plutonium. We developed the pyroredox process to upgrade the scrap of low plutonium content to meet the feed requirements for effective electrorefining.

The two basic steps for the pyroredox process are oxidation,

$$2Pu \text{ (impure)} + 3ZnCl_2 \xrightarrow[750°C]{ZnCl_2\text{-}KCl} 3Zn + 2PuCl_3 \,, \tag{1}$$

and reduction,

$$2PuCl_3 + 3Ca \xrightarrow[850°C]{CaCl_2} 2Pu + 3CaCl_2 \,. \tag{2}$$

The plutonium product can be separated mechanically from the salt and cycled into our primary pyroprocessing facility. This oxidation-reduction scheme was initially proposed and studied by J. G. Reavis* for reprocessing plutonium reactor fuels. In his research, zinc chloride in molten sodium chloride oxidized plutonium metal to the trichloride salt, and, in a second step, calcium was added to reduce the plutonium to metal. J. B. Knighton and coworkers at the Rocky Flats Plant[3] have also studied these reactions.

The pyroredox process upgrades lower-purity plutonium metal scrap for electrorefining. However, our principal application has been for spent anodes containing plutonium, gallium, and other less electropositive elements. The major impurity is usually gallium, which is added in casting to ensure a critically safe anode during electrorefining.[4,5] As electrorefining takes place, plutonium is oxidized from the anode pool into the molten eutectic salt and migrates to the cathode. There it is reduced to high-purity metal and drips into the annular chamber of the cell. Under the conditions of the process, elements less electropositive than plutonium

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remain in the anode pool. The run is automatically terminated when this pool solidifies (at about 90% plutonium depletion). Although the plutonium remaining in these anodes can be recovered by aqueous reprocessing,[6] we believe that pyroredox is far more compact, rapid, and efficient. Most of the experiments described in this report were conducted with spent anodes. Additional work with plutonium and simulated scrap, however, indicates that our conclusions are valid for other low-grade mixtures of plutonium.

II. EXPERIMENTAL PROGRAM

A. Equipment

The description of equipment used in this program has been published previously.[1] A typical experimental setup is shown in Fig. 1. Reactions take place in an inner crucible, usually constructed of tantalum or magnesia to minimize reagent attack. The crucible is centered in the heat zone of a 15-cm-diameter clam-shell furnace. Safety containers of stainless steel or tantalum are placed around the reaction crucible to catch any leakage.
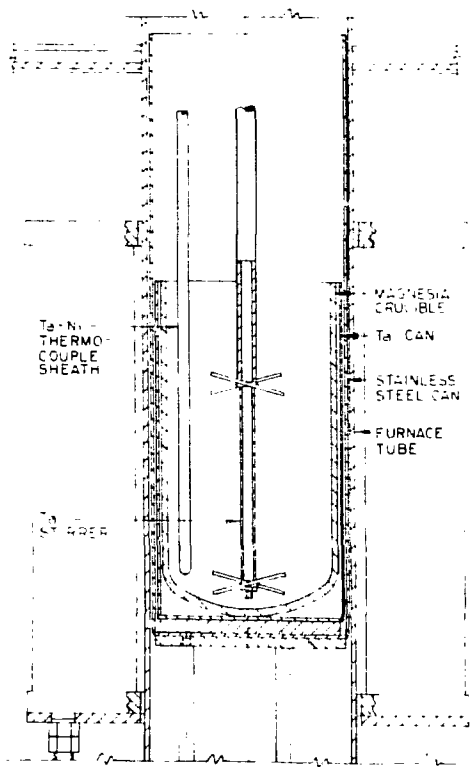

Fig. 1. Experimental apparatus.

In addition, the stainless steel furnace tube is extended below the furnace to provide a cool area in which to collect and freeze any molten products in case of a catastrophic leak at higher temperatures. Type K thermocouples, enclosed in a double-walled tantalum-nickel thermocouple well, measure temperature in the melt. Small microprocessor units program and monitor temperature profiles.

B. Reagents

In the oxidation process, dried Baker's analytical reagent grade zinc chloride and potassium chloride are mixed at a 31-mol% zinc chloride ratio, placed in a large pyrex reaction tube, and melted. The melt is sparged with anhydrous hydrogen chloride for 1 h, flushed with dry argon, and, finally, filtered (in an argon atmosphere) through a coarse pyrex frit and a heated quartz transfer tube into a pyrex crucible. The white eutectic is sealed in a plastic bag in an argon atmosphere and stored in argon until needed. This salt, which melts at 462°C, met purity requirements and was sufficiently moisture-free to prevent foaming during oxidation reactions.

For the reduction process, Malinckrodt food grade calcium chloride was vacuum-dried at 225°C for a minimum of 5 days and placed in a platinum crucible for purification. The salt and crucible were placed in a stainless steel furnace tube; the equipment was assembled and the system heated to 800°C. Anhydrous hydrogen chloride was passed through the melt for 2 h. An argon purge followed. The melt was then transferred through a heated tantalum tube into an erbia-coated, split mold of stainless steel. The resulting salt cast was sealed into a plastic bag and stored in argon until needed.

Pfitzer triple-distilled calcium was pressed into an ingot of ~80% theoretical density to reduce the surface area and, consequently, the rate of reaction in the reduction sequence.

C. Procedures

For the oxidation step, depleted anodes were placed in a tantalum crucible, and 10% excess zinc chloride (calculated) was added as a 31-mol% $ZnCl_2$-KCl eutectic. The system was assembled, evacuated, backfilled with argon, and heated to the salt melt at 462°C. The stirrer and thermocouple well were lowered into the molten salt. The melt was stirred while heating to 750°C. After 1 h at temperature, the mixture was heated and kept at 850°C for 1 h to promote phase separation. The stirrer and thermocouple well were then raised from the melt. After another 4 h at temperature, the system was cooled at a 200°C/h rate to ambient temperature. The two-phase product was removed, and the lighter salt phase was mechanically separated from the zinc button.

For the reduction step, the salt from the oxidation reaction was crushed and mixed with 1 kg of dried calcium chloride. The calculated amount of calcium was added as a pressed ingot; the mixture was placed in a magnesia crucible and the vessel assembled. The vessel was evacuated, backfilled with argon, and heated to salt melt at about 700°C. The thermocouple well and the stirrer were then lowered into the liquid, and the mixture was stirred. During the reaction, the temperature rose gradually to 850°C; after 20 min, the stirrer and thermocouple well were raised above the melt. The system was maintained at 850°C for 15 min, then cooled without power to ambient temperature. The product was broken out of the crucible for liquation or mechanical separation of the phases.

III. RESULTS AND CONCLUSIONS

A. Oxidation

As shown in Eq. (1), the main reactions in oxidation are forming plutonium trichloride in the salt phase while reducing zinc chloride to zinc metal. The free energies of formation of selected chlorides are listed in Table I. All chlorides with energies higher than zinc should be oxidized with the plutonium into the salt phase. Those impurities with lower energies concentrate in the zinc phase. If equilibrium conditions are met, aluminum, americium, uranium, and the rare earths would transfer into the salt phase with plutonium. Iron, tantalum, and gallium would concentrate in the zinc-rich metal phase.

In our experiments, the oxidation was exothermic. The rate and temperature were controlled by slowing the stirring rate. As a result, foaming and overflow from the crucible were eliminated. After the postreaction heat cycle (5 h at 850°C), good phase separation occurred (Fig. 2). The relatively slow cooling rate promoted shrinkage of the product from the crucible walls so that the tantalum crucible could be reused. With simulated anodes containing more than 95% plutonium as feed, a green salt, most likely K_3PuCl_6 in a potassium chloride matrix, and a bottom metal phase of zinc formed. After these phases were mechanically separated, the zinc phase could be discarded (Fig. 3). The green salt was then reduced to plutonium metal.

B. Reduction

The main reactions in reduction of the green salt are the reduction of tripositive plutonium to the metal and oxidation of calcium to calcium chloride (Eq. 2). However, the excess zinc chloride added for the oxidation step is also reduced

$$ZnCl_2 + Ca \longrightarrow CaCl_2 + Zn \quad . \qquad (3)$$
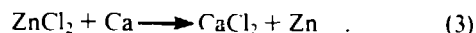
Table I. Behavior of Impurity Elements.

Element	-ΔF° Atom Cl (kcal/g)
Ir	2
W	5
Ni	18
Cu	21
Ta	27
Pb	27
Fe	27
Si	28
Cd	30
Cr	32
Ga	32
Zn	34
Mn	41
Ti	43
Al	46
U	54
Np	55
Zr	56
Mg	58
Th	59
Pu	59
Ce	66
Am	67
Na	76
Ca	77
Li	78
K	82

Fig. 2. Oxidation product and residue.

Fig. 3. Zinc metal residue containing gallium and other metallic impurities.

The reduction is slowed by adding 1000 g of dried calcium chloride to the green salt prior to heating, using pressed calcium, and stirring slowly at a rate lower than 200 rpm. The calcium chloride addition adsorbs calcium oxide formed in reactions and also minimizes formation of black salts. Yields are usually greater than 98% and, under optimum conditions, have reached calculated values of 99.5%. Results showing the purification attained by the two-step process are given in Table II. The high zinc and aluminum concentrations do not interfere with further purification by electrorefining.

In most cases, the reduction product was a salt phase over a two-phase button (Fig. 4). The salt phase was discarded. The bottom, denser phase was mainly plutonium and contained small amounts of calcium and zinc. The upper metal phase was typically 50-60% plutonium, 10-25% zinc, and 4% calcium. Several buttons were collected and coalesced to consolidate phase separation into a less time-consuming procedure. This step, liquation, is discussed below.

C. Additional Processing Steps

To recover spent anodes containing gallium and the impurities that collect in the anode during electrorefining, additional processing steps were necessary.

1. Processing

When we processed spent anodes rather than plutonium-gallium mixtures, three phases formed during oxidation. The upper phase (a green salt) and the bottom phases (metallic zinc) were similar to phases obtained with the simulated anodes. The third (intermediate)

Fig. 4. Two-phase metal product.

phase was a grey salt that we attributed to impurities in the anode. It consisted mainly of a fog of uncoalesced zinc in the salt matrix with some evidence of plutonium oxychloride formation. This third phase was minimized by a polishing step prior to the oxidation of the anode. The spent anode, 300 g of calcium, and 3000 g of calcium chloride were placed in a magnesia reaction crucible. The reaction system was assembled, evacuated, and backfilled with argon. The system was heated to 800°C, and stirring was begun and increased from 200 to 600 rpm as the temperature rose to 850°C.

As shown in Fig. 5, the product was homogeneous. Plutonium losses during polishing were quite low (less than 5 g), and the metal button could be transferred for the oxidation step. Polishing markedly reduced grey salt formation, probably by reducing any partially oxidized species in the spent anode. Additional zinc chloride was now needed, however, to oxidize both the plutonium and the excess calcium contained in the button. Yields in the oxidation step increased to greater than 80% after polishing.

2. Liquation

Liquation removes zinc and calcium from the reduction product while preparing most of the plutonium for further purification. The liquation step is a gravity separation of the two-phase button formed in the reduction. Several of these buttons, totaling 4.5 kg, were placed in a long, narrow magnesia crucible. The reaction system was assembled, evacuated, and backfilled with argon. The vessel was heated and maintained at 850°C for 6 h. The resulting ingot consisted of a lighter upper phase and a more dense plutonium-rich lower phase (Fig. 6). Results of several liquations are summarized in Table III. The bottom phase containing most of the plutonium could be electrorefined without further treatment. The upper phase was recycled to the oxidation step for removal of calcium and zinc.

D. The Electrorefined Product

Even though electrorefining is a mature process, we demonstrated the liquated buttons could be further processed to high-purity metal. Table IV summarizes data from experiments in which the denser phase from the liquation step was electrorefined. Yields were satisfactory; purity of the product ring was excellent (see Table V).

Fig. 6 Lower phase from liquation.

Table III. Composition of Liquation Phase.

Experiment No.	Plutonium		Calcium		Zinc		Density (g/cm³)	
	Top (%)	Bottom (%)	Top (%)	Bottom	Top (%)	Bottom	Top	Bottom
1	42	89	5	130 ppm	8	600 ppm	5.7	15.6
2	0.7	93	20	700 ppm	30	0.4%	2.5	15.0
3	55	95	51	---	12.5	---	---	---
4	47	90	24	1.8%	15.5	3.5%	---	---

Table IV. Results of Liquation Experiments.

| | Ingot | Phase | |
		Top	Bottom
Pu, g	4340	1220	3120
Total Pu, %	99.3	28.1	71.9
Density, g/cm^3	---	7.5	15

Table V. Product of Electrorefining Pyroredox Metal.

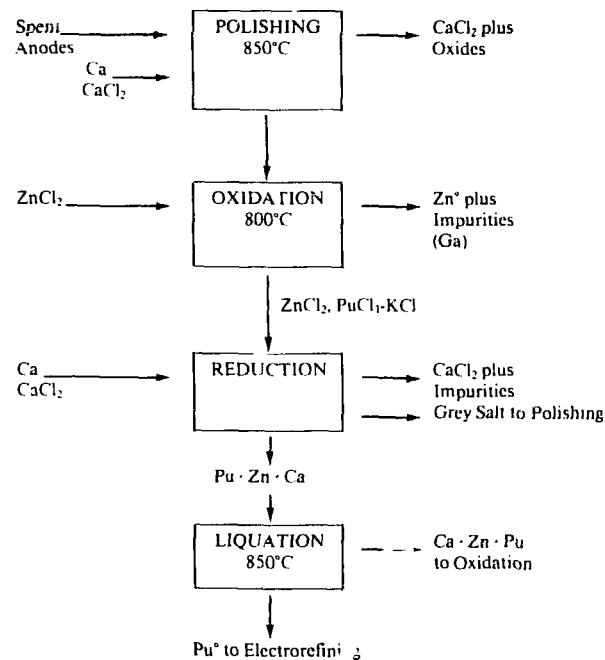| | Plutonium Content | |
Component	(g)	(%)
Product Ring	4081	78.4
Shot	26	0.5
Cathode	9	0.2
Crucible	83	1.6
Salt	671	12.9
Anode	334	6.4
Yield[a]	---	80.1

[a]Yield = 100X(Pu ring + shot)/Pu feed.

Fig. 7. Pyroredox process for recovery of plutonium from impure scrap.

IV. SUMMARY

We have developed a method for removing impurities from plutonium scrap that contains less than 95% plutonium so that it meets the 95%-purity criterion for effective electrorefining. The process consists of oxidation of plutonium to the trichloride followed by reduction to metal. The flow diagram (Fig. 7) shows the process, as modified for recovering plutonium from spent anodes in our production demonstration facility. The liquated product has been purified by electrorefining. Yields from pyroredox processing in our demonstration facility are greater than 80%. We believe that the process is ready for transfer to production facilities.

The 31 mol% ZnCl$_2$-KCl eutectic was successfully prepared in 5-kg batches by drying, heating to a melt, filtering through a coarse pyrex frit, and transferring the melt into a warm quartz crucible. The moisture-free salt did not froth or overflow during the oxidation step.

Prepolishing and liquation were effective steps for treating the impure spent anodes to adapt the general, generic process to our specific requirements.

We are studying methods for minimizing or eliminating the grey salt phase that forms during oxidation. We recycle this phase when necessary.

REFERENCES

1. D. C. Christensen and L. J. Mullins, "Plutonium Metal Production and Purification at Los Alamos," in *Plutonium Chemistry*, W. T. Cornall and G. R. Chopkin, Eds. (ACS Symposium Series, American Chemical Society, New York, 1983), pp. 409-432.

2. J. G. Reavis and J. A. Leary, "Nonaqueous Dissolution of Massive Plutonium," US Patent No. 2,886,410, May 12, 1959.

3. J. B. Knighton, R. G. Auge, and J. C. Brown, "Purification of Plutonium by Oxidation-Reduction Process," RFP-1691-A, in "Research and Development Annual Progress Report, November 1, 1980 to September 30, 1981," Frend John Minor, Ed., Rockwell International, Rocky Flats Plant, Golden, Colorado (August 11, 1982).

4. L. J. Mullins and J. A. Leary, "Fused Salt Electrorefining of Molten Plutonium and Its Alloys," Los Alamos Scientific Laboratory report LA-3118 (November 1964).

5. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Electrorefining," *Ind. Eng. Chem. Process Des. Develop.* **2**, 20 (1963).

6. C. E. Baldwin and J. D. Navratil, "Plutonium Process Chemistry and Rocky Flats," in *Plutonium Chemistry*, W. T. Carnall and G. R. Choppin, Eds. (ACS Symposium Series, American Chemical Society, New York, 1983), pp. 369-380.