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PREPARATION OF ISOTOPICALLY PURE
PLUTONIUM-241 METAL

241 Pu

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U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

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**PREPARATION OF ISOTOPICALLY PURE
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C. R. Forrey of the Analytical Development Group performed the analyses for ^{241}Pu in the process solutions.

Preparation of Isotopically Pure Plutonium-241 Metal

W. V. Conner

Abstract. Procedures are described for the production of two batches of isotopically pure ^{241}Pu metal from plutonium oxide, and for the recovery of plutonium from reduction residues. The conversion of the oxide to plutonium tetrafluoride was accomplished with fluorine gas. The plutonium tetrafluoride was reduced to metal using calcium as the reductant, with an iodine booster. The plutonium recovery was performed by nitric acid dissolution, anion exchange, and oxalate precipitation.

INTRODUCTION

Two batches of ^{241}Pu were received as oxide from Oak Ridge National Laboratory for conversion to metal. The metal was returned to ORNL where it was made into foils for cross section experiments in the materials testing reactor at the National Reactor Testing Station in Idaho.

The ^{241}Pu is a beta emitter with a 13 year half-life. The beta particles have a maximum energy of 20 kev and are easily stopped with a minimum of shielding, but the radiation at the surface of the material is quite intense due to the relatively short half-life. The ^{241}Am produced by the beta decay of ^{241}Pu emits 60-kev gamma rays. The combined beta-gamma radiation required special precautions when handling the material.

The growth of ^{241}Am required that the ^{241}Pu be processed as rapidly as possible. The two batches of ^{241}Pu were received 2 weeks apart. The americium was removed by ORNL before each batch was shipped. The first metal was shipped 10 days after the oxide was received, and the metal from the second batch of oxide was shipped 8 days after receipt of the oxide.

SUMMARY

Isotopically pure ^{241}Pu metal was prepared successfully on a 4- to 18-gram scale. Two batches of plutonium were received as oxide from ORNL. The first batch of plutonium was 99.82% ^{241}Pu and the second batch was 83.8% ^{241}Pu . The oxide was prepared at ORNL by hydroxide precipitation followed by calcination at 600°C.

Conversion of the oxide to plutonium tetrafluoride was attempted at 100°C using fluorine gas. This method usually will give conversions of 85 to 90%. However, the oxide received from ORNL was quite unreactive and the conversion of the first batch of PuO_2 to PuF_4 was only 60% complete. The PuF_4 - PuO_2 mixture was reduced with calcium, using an iodine booster to supply additional heat and form a more fluid slag. The reduction yield was 64.5%. The reduction residues were processed by nitric acid dissolution, anion exchange and oxalate precipitation. The calcined oxalate was contacted with F_2 at a starting temperature of 200°C. The conversion to PuF_4 was 92% complete. The reduction yield was 86%.

The second batch of oxide was converted to plutonium tetrafluoride by a two-step process. The first step was a low-temperature fluorination using a starting temperature of 200°C. This step was followed by a high-temperature fluorination with a 450°C starting temperature. The conversion through both steps was 87.6% complete. The reduction yield was 87.5%.

The reduction of the three batches of PuF_4 to metal was accomplished using a 30% excess of Ca and 0.9 mole of I_2 per mole of Pu. The reduction yields were lower than expected due to the difficulty in converting the PuO_2 to PuF_4 .

The residues from the first reduction were dissolved in HNO_3 with $\text{Al}(\text{NO}_3)_3$ added to complex the fluoride. The solutions were adjusted to 7.5N HNO_3 and the plutonium loaded on anion exchange resin. After washing, the plutonium was stripped with 0.35N HNO_3 -0.1M ascorbic acid, precipitated as oxalate, and calcined to the oxide. The overall plutonium recovery was 96.9%.

EXPERIMENTAL

The work described in this report was performed in a standard alpha containment glovebox (see Figure 1). Radiation protection was provided by attaching 1/8-inch lead sheet and 1/4-inch lead glass to the exterior of the box. The gloves were standard 30-mil leaded

FIGURE 1. Glovebox Used for Processing ^{241}Pu .

type Neoprene. In-line beta-gamma shielding was provided by lead bricks which were drilled to accept the plutonium containers. The ^{241}Pu was held with tongs or forceps to eliminate as much close-contact work as possible. The time spent handling the ^{241}Pu with the gloves was kept at a minimum.

The PuO_2 was converted to PuF_4 with F_2 gas. The fluorination reactor (see Figure 2) consisted of a flanged nickel-tube and a nickel lid. A copper gasket was used to obtain a seal between the tube, flange and lid. The penetrations for thermocouples and gas lines were made through the reactor lid. A horizontal tube furnace enclosed the reactor assembly.

The material to be fluorinated was placed in a nickel fluorination boat. The boat was placed in a support attached to the reactor lid, and the lid was bolted to the reactor. The reactor was purged with argon and checked for leaks. When the system had reached the desired temperature, fluorine gas was introduced. The argon flow was slowly reduced to zero while the fluorine flow rate was increased to 400 cc/min. A short time after the F_2 was introduced into the system, the temperature usually began to increase. The increase in temperature was caused by the exothermic reaction between PuO_2 and F_2 . The occurrence of this heat-spike was an indication that the reaction was occurring. The extent of the heat-spike was an indication to how well the reaction was proceeding.

FIGURE 2. Small Scale Fluorination Reactor and Furnace.

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After a predetermined length of time, the fluorine flow was turned off and the system allowed to cool.

The PuF_4 was reduced to metal using Ca as the reductant and with an I_2 booster. The reduction vessel consisted of a MgO crucible which was placed within a stainless steel pressure vessel (see Figure 3). The annulus between the crucible and pressure vessel was filled with MgO sand. A copper gasket was used to obtain a seal between the pressure vessel and pressure-vessel lid.

The reduction charges were prepared by mixing the PuF_4 with most of the Ca and I_2 . The remaining Ca and I_2 (20% of the I_2) was mixed and one-half the mixture was placed in the bottom of the crucible. The main charge was split into two portions, and the first portion added to the crucible. Enough reagent grade Al wire to give a 1-weight % alloy in the button was then added to the crucible. The remaining portions of the charge and the Ca and I_2 mixture were added and the lid was bolted on the vessel. The reaction vessel was checked for leaks, purged with argon, and placed in a vertical crucible furnace which had been heated to 1000°C . After the charge reacted, the vessel was removed from the furnace and allowed to cool.

The metal button from the reduction step was homogenized at 500°C for 24 hours in a vacuum furnace. The button was then rolled to a thickness of ~100 mils. The rolling was required to reduce the button thickness so that the button could be handled in the rolling mill at ORNL.

RESULTS AND DISCUSSION

Fluorination: The first batch of plutonium was 99.82% ^{241}Pu (see Table I). The oxide was prepared at ORNL by hydroxide precipitation, followed by calcination at 600°C . This material was chunky and greenish-black, and proved to be quite unreactive. The oxide weighed 15.29 g and contained 13.49-g of Pu.* This batch was split into two portions to ensure good contact between the PuO_2 and F_2 . The first portion, 8.80 g of PuO_2 , was placed in the fluorination furnace and contacted with F_2 gas for 30 minutes. The starting temperature was 100°C . After 2 minutes the temperature began increasing, indicating that the reaction had started. The F_2 was turned off after 30 minutes and the furnace

*This Pu weight was obtained from ORNL. The oxide was not analyzed at Rocky Flats in order to conserve the material.

FIGURE 3. 15-Gram Scale Reduction Vessel.

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allowed to cool. Visual observations indicated a poor version. This observation was confirmed by the weight-gain which indicated 61% conversion to PuF_4 .

TABLE I. Isotopic Analysis for First Batch of ^{241}Pu .*

Isotope	Weight %
^{238}Pu	< 0.0006
^{239}Pu	0.013
^{240}Pu	0.103
^{241}Pu	99.82
^{242}Pu	0.061
^{244}Pu	0.002

* Analysis supplied by ORNL.

The second portion, 6.50 g, was fluorinated using the same procedure and the conversion to PuF_4 was only 52% complete. This material was returned to the fluorination furnace and refluorinated at a starting temperature of 200°C . When the heat-spike failed to occur after 6 minutes, the temperature was increased. The temperature had reached 250°C when the F_2 was turned off after 40 minutes of heating. The conversion to PuF_4 was still only 55% complete. When the two portions were combined, the total weight-gain indicated a total conversion of 60%. A summary of the fluorination conditions for both batches is given in Table II.

This method will give conversions of $\geq 85\%$ with normally reactive oxides. Using oxide prepared by burning plutonium metal, the conversion to PuF_4 is usually 85 to 90% with a starting temperature of 100°C , 90 to 95% with a starting temperature of 200°C , and 95 to 100% with a starting temperature of 300°C (1).

An attempt was made to reduce the PuF_4 - PuO_2 mixture. The reduction yield was 64.5%. The reduction residues were processed, and the recovered plutonium precipitated with oxalic acid (see Residues Recovery discussion).

The calcined oxalate was fluorinated using a starting temperature of 200°C and a contact time of 30 minutes. The oxide was quite reactive and the conversion to PuF_4 was 92% complete.

The second batch of plutonium was 83.8% ^{241}Pu . The oxide was prepared at ORNL by hydroxide precipitation, followed by calcination at 600°C . This oxide was a free-flowing powder and almost black. The oxide weighed 21.18 g and contained 18.62-g of Pu.*

* This plutonium weight was obtained from ORNL. The oxide was not analyzed at Rocky Flats in order to conserve material.

TABLE II. Operating Conditions for the Conversion of ^{241}Pu Oxide to PuF_4 .

	Starting PuO_2 Weight (g)	Final Weight (g)	% Conversion to PuF_4	Starting Temp. ($^\circ\text{C}$)	Max. Temp. of Heat- Spike ($^\circ\text{C}$)	Elapsed Time at Start of Spike (min.)	Elapsed Time when F_2 was Turned off (min.)
1. Batch No. 1							
a. Portion No. 1	8.80	9.66	61.0	100	198	2	30
b. Portion No. 2	6.94	7.52	52.0	100	183	2	30
c. Refluorination of Portion 2	7.53	7.55	55.0	200	No Spike	-	40
d. Material Recovered from Reduction Residues	4.68	5.36	92.0	200	280	2	30
2. Batch No. 2							
a. Portion No. 1	13.94	15.06	53.1	200	292	2	38
b. Portion No. 2	7.28	7.90	54.3	200	265	2	45
c. High Temp. Fluorination of Batch 2	23.04	23.56	87.6	450	510	1	25

Assuming that this PuO_2 would be as unreactive as the first batch, two possible methods of processing were considered. The first method would involve dissolution of the PuO_2 and precipitation of the plutonium with oxalic acid. However, previous work (2) had shown that PuO_2 produced from calcined hydroxide was difficult to dissolve.

The second method would involve a low-temperature fluorination similar to the method used for the first batch. If, as was expected, the low-temperature fluorination produced a poor conversion, it would be followed by a high-temperature (450°C) fluorination. This would involve some material-loss due to PuF_6 formation, but it was believed to be the better method.

The batch was split into two portions, and each portion was contacted with F_2 gas using a starting temperature of 200°C . The first portion was fluorinated for 38 minutes and the second portion for 45 minutes. The conversion to PuF_4 was 53.1% for the first portion, and 54.3% for the second portion, for an average of 53.5% for the total batch.

The entire PuF_4 - PuO_2 mixture was returned to the fluorination furnace where it was contacted with F_2 for 25 minutes. The starting temperature was 450°C , and it increased to a maximum of 510°C 7 minutes after the F_2 was introduced to the system. The PuF_6 formed was collected in nickel traps immersed in liquid argon. The weight gained by the "cold" traps indicated there was a 0.4 g plutonium loss. The weight gained by the remaining material indicated a total conversion of 87.6%.

Reduction to Metal: The conversion of the first batch of PuO_2 to PuF_4 was only 60% complete. The possibility existed that an attempt to reduce this material would result in the formation of metal beads which would not agglomerate due to the high oxide content. Since the residues from such a reduction could probably be recycled as easily as the mixture of PuF_4 and unreactive oxide, the charge was prepared for the reduction.

An iodine booster ratio of 0.9 moles of I_2 /mole of Pu and a 30% excess of calcium was used for this reduction. The slag contained several beads that appeared to be plutonium metal. The top of the button had a slag coating that was difficult to remove, but the button was well formed. The button weighed 8.70 g after pickling in 2.0N HNO_3 and rinsing in H_2O .

This gave a reduction yield of 64.5%. After homogenization, the button was rolled to a 0.120-in. thick

The oxide recovered from the reduction residues contained 4.0 g of plutonium (see Residues Recovery discussion). The fluorination produced a 92% conversion to PuF_4 . The reduction charge was prepared with the same Ca and I_2 ratios used for the first reduction. The button was well-formed and the small amount of slag adhering to it was easily removed by pickling in 2N HNO_3 . After pickling and rinsing in water, the button weighed 3.44 g and this gave a reduction yield of 86%. The two buttons represented 90% of the plutonium originally received. The small button was homogenized and rolled to 0.120 inch. The two buttons were packaged in an argon purged container containing a package of BaO desiccant and shipped to ORNL.

The second batch of material contained 18.2 g of plutonium after the conversion to PuF_4 , and the conversion was 87.6% complete. Using the 30% excess of Ca and 0.9 moles I_2 per mole Pu, the reduction produced a 15.92 g button. This gave a reduction yield of 87.5%. The button was well-formed and had very little slag adhering to it (see Figure 4). After the button was homogenized, it was rolled to a 0.080-in. thickness and packaged for shipment to ORNL.

FIGURE 4. 16-Gram Plutonium Button — 83.8% ^{241}Pu .

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charge- and yield-data for the three reductions given in Table III.

TABLE III. Reduction Data.

Reduction No.	Pu wt. (g)	Button Wt. (g)	Metal Yield (%)	Al Wt. (g)	% Excess Ca	Moles I_2 Mole Pu
1	13.49	8.70	64.5	0.12	30	0.9
2	4.0	3.44	86.	0.04	30	0.9
3	18.2	15.92	87.5	0.17	30	0.9

The metal scrap from the rolling operation at ORNL was analyzed for impurities. The results obtained by ORNL are given in Table IV.

TABLE IV. Results of Spectrographic Analysis of ^{241}Pu Metal.

Material Analyzed	Wt. %	Al	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Si	Sn	Ti	V
Batch No. 1 (Buttons 1 and 2)	0.53	100	20	800	10	10	110	+	+	+	+	+	+
Batch No. 2 (Button 3)	0.39	20	30	300	2	2	40	+	+	+	+	+	+

+ Sought but not found.

The Al content was much lower than anticipated. However, the low Al content did not seem to affect the rolling operation, since the second batch (Button No. 3) rolled better than the first batch (Buttons No. 1 and 2) (3).

Residues Recovery: The residues from the first reduction (sand, slag and crucible) weighed 166 g and contained an estimated 4 to 5 g of plutonium. The low metal-yield from the first reduction required immediate recovery of this plutonium to supply the required amount of metal to ORNL. The metal yields from the second and third reduction were sufficiently high and the residues from these reductions were stored for future processing. Recovery of the residues from the first reduction was accomplished by HNO_3 dissolution followed by anion exchange and oxalate precipitation.

The residues from the first reduction were slowly added to 750-ml of concentrated HNO_3 . The reaction was violent, and 30 minutes was required to complete addition. The solution was mixed for 70 minutes at 110°C on a hot-plate equipped with a magnetic stirrer. At the end of this period the solution was

diluted with 650-ml of H_2O to prevent salt formation when the solution cooled, and 100-ml of 60% $\text{Al}(\text{NO}_3)_3$ was added to dissolve any PuF_4 which may have been present. The solution was mixed for another 30 minutes at 100°C . The solution was allowed to cool and was then filtered.

The insoluble residues appeared to be mostly PuO_2 . These were contacted with 200-ml of 8N HNO_3 -0.2M HF at 100°C for one hour. Twenty ml of 60% $\text{Al}(\text{NO}_3)_3$ were added during the last 10 minutes of dissolution to complex the fluoride ions. The insoluble residues from this dissolution were contacted with 200-ml of 8N HNO_3 -0.3M HF for one hour at 110°C . The residues remaining after the third contact weighed 2.0 g after calcination and contained 0.128 g Pu (see Table V).

TABLE V. Summary of Dissolution Data.

Starting Weight (g)		Final Weight (g)		% Solids Dissolved	% Pu Dissolved
Total Solids	Pu	Total Solids	Pu		
166	4.128	2.0	0.128	98.8	96.9

The normality of the combined filtrates from the three acid contacts was adjusted to 7.5N H^+ and 10-ml of ferrous sulfamate was added to reduce any Pu(VI) present to Pu(IV) . The $\text{Al}(\text{NO}_3)_3$ added during the dissolution was sufficient to complex all the fluoride present. The adjusted feed was passed through a bed of Dowex* 1-X4 anion exchange resin. The feed was followed by four column volumes of 7.5N HNO_3 wash solution. The plutonium was eluted with $2\frac{1}{2}$ column volumes of 0.35N HNO_3 -0.1M ascorbic acid. The column was stripped very clean; essentially all the plutonium loaded on the resin was removed in the eluate (see Table VI).

TABLE VI. Summary of Ion Exchange Data.

Item	Volume (l)	Pu Concentration (g/l)	Total Pu (g)
Feed	1.65	2.42	4.0
Effluent and Wash	3.3	9.12×10^{-5}	0.0003
Eluate	0.49	8.16	4.0

* Trademark of The Dow Chemical Company, Midland, Michigan.

In Table VI, the concentration of ^{241}Pu in solution was determined radiometrically. The ^{241}Pu was separated from ^{241}Am by anion exchange. The rate of ^{241}Am growth in the solutions was measured, and the ^{241}Pu concentration was determined from the ^{241}Am growth rate. The analytical method was developed by C. R. Forrey of the Analytical Development Group of The Dow Chemical Company, Rocky Flats Division.

The eluate was heated to 50°C , and 50-ml of 1M ascorbic acid was added to reduce the Pu(IV) to Pu(III). The plutonium was precipitated with 300-ml of 1M oxalic acid. The solution was digested for 30 minutes at 50°C and then allowed to cool. The solution was filtered and the precipitate calcined at 550°C for 10 hours. The filtrate losses were quite low (see Table VII) and the calcined precipitate contained 96.9% of the plutonium originally present in the reduction residues.

TABLE VII. Summary of Precipitation Data.

Item	Volume or Weight	Pu Concentration	Total (g)
Feed	490 ml	8.16 g/l	4.0
Filtrate	920 ml	8.98×10^{-5} g/l	81 μg
Calcined Precipitate	4.68 g	85.47 g/g	4.0

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