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THE PREPARATION OF PLUTONIUM TETRAFLUORIDE
BY DIRECT HYDROFLUORINATION OF
PLUTONIUM OXALATE

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BY

J. F. FACER, W. L. LYON AND B. WEIDENBAUM

TECHNICAL DIVISIONS

FEBRUARY 1, 1951

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DIRECT HYDROFLUORINATION OF PLUTONIUM OXALATE

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THE PREPARATION OF PLUTONIUM TETRAFLUORIDE BY
DIRECT HYDROFLUORINATION OF PLUTONIUM OXALATE

INTRODUCTION

The direct conversion of plutonium(III) oxalate to plutonium tetrafluoride has been investigated to determine the process feasibility, process variables and product quality. This direct hydrofluorination study has been made in order to find a method of reducing the time required for the dry conversion process at Hanford Works.

The dry conversion process now in use at Hanford and Los Alamos consists in drying plutonium(III) oxalate, converting the oxalate to the oxide at 600°C., cooling and weighing the oxide for plutonium accountability, hydrofluorinating the oxide to tetrafluoride at 600°C. and cooling the plutonium tetrafluoride.

While some hydrofluorination of plutonium(III) oxalate has occurred inadvertently during one or more Hanford plant runs and some hydrofluorination of plutonium(III) oxalate may have occurred during two Los Alamos plant conversions⁽¹⁾ in April 1945, the direct hydrofluorination of plutonium(III) oxalate has never been employed routinely, and the temperature cycle in the instances cited makes it seem probable that much of the oxalate was converted to oxide and thence to fluoride. It has been recognized^(1, 2, 3) since 1944 that a direct hydrofluorination should shorten the process cycle, but further information has been lacking. This report describes the results of Hanford laboratory studies of the direct conversion of either plutonium(III) oxalate or plutonium(IV) oxalate to plutonium tetrafluoride.

SUMMARY

A satisfactory process has been developed in the laboratory for the conversion of either plutonium(III) oxalate or plutonium(IV) oxalate directly to plutonium tetrafluoride without intermediate conversion to plutonium oxide. Processing time, power consumption, and hydrogen fluoride usage should be reduced by this process. The variables which affect the process are also considered.

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PROCESS

A. Cycle

The following cycle has given satisfactory results on a five gram scale for the direct hydrofluorination of plutonium(III) oxalate or plutonium(IV) oxalate to plutonium tetrafluoride:

- (a) Pass 200 ml. per minute of dried air across the plutonium oxalate slurry in a platinum boat at 130°C. for 90 minutes.
- (b) Introduce oxygen at 0.7 liters per minute and hydrogen fluoride at 2 1/2 to 3 liters per minute through item (f) below.
- (c) Hold the furnace temperature at 130°C. for one hour.
- (d) Heat the furnace to 500°C. in 30 minutes.
- (e) Hold the furnace temperature at 500°C. for one hour.
- (f) Cool the furnace, maintaining the flow of both oxygen and hydrogen fluoride until the temperature is 300°C.
- (g) Purge the system with oxygen after the hydrogen fluoride flow is stopped.

An appreciable saving of process time, with accompanying savings of power and hydrogen fluoride, should result from the substitution of the direct hydrofluorination process for the oxalate to oxide to fluoride process which is now employed. On a laboratory scale this time saving would be a reduction from 10 hours to 4 1/2 hours, and on a plant scale a process time reduction from the present 12 1/2 hours to about 7 1/2 hours would be expected.

B. Equipment and Handling

The laboratory hydrofluorination and reduction equipment and its use have been described in detail in an earlier report⁽⁴⁾.

The plutonium oxalate was received in the dry chemistry hood as approximately 30 ml. of slurry in a two ounce bottle. The bottle was swirled to restore any settled cake to the slurry, and the slurry was transferred to a 90% platinum, 10% rhodium boat. This boat was placed in a nickel scow which

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was then inserted in a nickel furnace-reaction tube mounted horizontally in a resistance furnace. The furnace was brought to 130°C. with dry air aspirated through the reaction tube. As soon as the plutonium oxalate was dry, a mixture of oxygen and hydrogen fluoride was aspirated through the reaction tube instead of the drying air, and the hydrofluorination reaction proceeded. The gas mixture was controlled by reducing valves on the gas cylinders as well as by line valves at rotameters which indicated the flow of hydrogen fluoride and of oxygen.

After the conversion to plutonium tetrafluoride had been completed the fluoride was weighed. The bulk density of the fluoride was determined from the volume to which it packed when the containing tube was tapped repeatedly.

The plutonium tetrafluoride was reduced to metal by heating the proper mixture of calcium, iodine and plutonium tetrafluoride in a magnesia-lined steel bomb.

C. Drying

On the five gram plutonium scale used for these investigations, drying for ninety minutes at 100° to 130°C. in a dry air stream of approximately 200 ml. per minute was adequate for the complete removal of water from a plutonium oxalate slurry. At higher drying temperatures, spattering of the slurry became objectionable. The drying of a filtered plutonium oxalate cake was not investigated since it was desirable that the process developed should be adaptable to existing plant equipment.

Any hydrofluorination of plutonium oxalate during the drying appears to have been deleterious to the product. When a trace of hydrogen fluoride from a previous run was introduced inadvertently from the pipe lines to the reactor tube, some purple plutonium trifluoride was formed during the drying period. The lots of plutonium tetrafluoride which were prepared from such oxalate-trifluoride cakes had lower bulk densities (average 1.1 gms./cc.) and gave lower metal yields upon reduction (Average 93%) than tetrafluorides prepared from oxalates which were dried in the absence of hydrogen fluoride. (Average 1.3 gms./cc. bulk density and >96% reduction yield) (Table I)

D. Low Temperature Hydrofluorination

The low temperature hydrofluorination is the distinguishing and

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most essential step in any cycle for the direct hydrofluorination of plutonium(III) oxalate. At temperatures of 100 to 180°C. the reaction proceeds according to the following equation: $\text{Pu}_2(\text{C}_2\text{O}_4)_3 + 6 \text{HF} \longrightarrow 2 \text{PuF}_3 + 3 \text{H}_2\text{C}_2\text{O}_4$. A crop of oxalic acid crystals covers the surface of the plutonium trifluoride after the low temperature hydrofluorination. The identity of the crystals has been confirmed by an equivalent weight determination with potassium permanganate. At higher temperatures plutonium oxalate decomposition occurs, and the resulting decomposition products are more difficult to convert to plutonium tetrafluoride than is plutonium trifluoride.

While satisfactory low temperature hydrofluorination was obtained at temperatures from 100° to 180°C., temperatures of 120° to 130°C. were normally used, since the dry oxalate and the furnace were in that temperature range at the completion of the drying. One hour of hydrofluorination at 130°C. was adequate for the conversion of plutonium(III) oxalate to plutonium trifluoride.

When hydrofluorination was begun at 130°C. with simultaneous furnace heating to raise the temperature to 500°C. within one hour, direct hydrofluorination was incomplete, and three hours of hydrofluorination at 500°C. would not complete the conversion to plutonium tetrafluoride. The fluoride product of an incomplete conversion gave very low (90%) metal yields upon reduction, and had a low bulk density (1.1 gms./cc.). The low conversions obtained when low temperature hydrofluorination was omitted are substantiated by data ⁽¹⁾ from two Los Alamos plant scale runs in which the hydrofluorination cycle consisted of 3 and 3.5 hours of HF treatment at 200° to 600°C. Conversions were 96.0 and 94.6%. Reduction yields were excellent and comparable yields would be expected on a laboratory scale if the final temperature were raised to 600°C. These cycles were condensations of the present oxalate to oxide to fluoride process, but the conversion yield and fluoride quality were decidedly inferior to those obtained by the longer existing plant process.

Gas mixtures of 80% HF, 20% O₂ to 98% HF, 2% O₂ by volume, flowing at 2 to 5 liters per minute, gave excellent low temperature hydrofluorinations

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in one hour. No advantage was noted for longer hydrofluorination at 130°C.; and while a shorter hydrofluorination at 130°C. might be used, one hour included a factor of safety to insure complete conversion of plutonium(III) oxalate to plutonium trifluoride.

E. Heating

The temperature of the plutonium trifluoride charge was increased from 130°C. to 500°C. in 30 to 60 minutes. The time required for this temperature rise was governed by the furnace rather than by an optimum condition for hydrofluorination.

F. High Temperature Hydrofluorination

The high temperature hydrofluorination is an oxidation reaction which proceeds according to the equation: $4 \text{PuF}_3 + 4 \text{HF} + \text{O}_2 \longrightarrow 4 \text{PuF}_4 + 2 \text{H}_2\text{O}$. The reaction rate increases with temperature. In laboratory tests some re-action was observed at temperatures as low as 325°C., and a satisfactory product was obtained by 3 hours of hydrofluorination at 400°C. However, the 400°C. product had a blue tint which was normally associated with incomplete conversion of plutonium trifluoride to plutonium tetrafluoride. Under the same conditions, two hours of hydrofluorination at 500°C. sufficed to produce a satisfactory product which was free of blue tint.

The use of a gas mixture containing a ratio of hydrogen fluoride to oxygen, which was stoichiometric (4:1) for the high temperature hydrofluorination reaction, was found to be optimum. Gas compositions for the high temperature hydrofluorination were varied from 98% HF, 2% O₂ to 80% HF, 20% O₂ by volume. On the nominal 5 gram plutonium scale, using a gas flow of 3 to 4 liters per minute, two hours at 500°C. was the minimum time in which the reaction could be completed with 98% HF, 2% O₂, whereas one hour under the same conditions was sufficient with a 80% HF, 20% O₂ mixture. Gas mixtures containing as high as 35% O₂ were used for short periods of time without deleterious effect upon the product, but if a large enough excess of oxygen were employed, undesirable oxidation products, such as plutonium oxide and oxyfluoride, might result. For this same reason hydrogen fluoride flow was maintained during cooling of the plutonium tetrafluoride from 500°C. to below 300°C. When the hydrogen fluoride flow was stopped at temperatures above 300°C., some yellow oxide was

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formed and could not be converted to tetrafluoride without a 600°C. hydrofluorination treatment. This oxidation was most severe when the furnace was opened to the air. In practice, the purging of hydrogen fluoride from the gas lines required sufficient time that hydrogen fluoride flow could be stopped at 400°C., and no oxidation would occur during cooling unless the furnace were opened to the air. However, in laboratory tests, oxidation of plutonium tetrafluoride occurred at least as readily in oxygen at 400°C. as it had in air.

PRODUCT

The plutonium tetrafluoride prepared by direct hydrofluorination of plutonium(III) oxalate was a free-flowing pink powder which had a bulk density of 1.2 to 1.6 grams per cubic centimeter. The theoretical amount of plutonium tetrafluoride was obtained from a known amount of plutonium as (III) oxalate, indicating that the tetrafluoride is as satisfactory as the oxide as a basis for plutonium accountability figures. While the bulk density of fluoride prepared directly from oxalate was low, (1.4 as compared to 2 or more for fluorides prepared from plutonium oxide,) it packed well in reduction crucibles. Reduction yields were as good ($\sim 96\%$) as were obtained on the same laboratory scale with fluorides prepared from plutonium oxide.

PLUTONIUM(IV) OXALATE

Plutonium(IV) oxalate was hydrofluorinated directly by using the same conditions as were used for hydrofluorinating plutonium(III) oxalate. Work has been limited to three laboratory runs (Table II), but these gave theoretical weights of plutonium tetrafluoride, with an average bulk density of 1.1 and yield on reduction of 96.2%.

The hydrofluorination of plutonium(IV) oxalate appears to consist of a more complex series of reactions than occur when plutonium(III) oxalate is hydrofluorinated. Oxalic acid is formed during the 130°C. hydrofluorination, but neither PuF_3 nor PuF_4 has been observed. During the heating cycle (200° to 300°C.) plutonium trifluoride is formed and then plutonium tetrafluoride is obtained during the 500°C. hydrofluorination.

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J. F. Facer
J. F. Facer

W. L. Lyon
W. L. Lyon

B. Weidenbaum
B. Weidenbaum

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TABLE I

DIRECT HYDROFLUORINATION OF PLUTONIUM (III) OXALATE

Run No.	39	40	42	43	44	47	48	49	50	51	52	53	55	57	58	73
Gms. of Pu as $\text{Pu}_2(\text{C}_2\text{O}_4)_3$	5.146	5.400	<5.168	<5.180	5.156	4.972	4.957	4.956	4.952	4.941	4.945	4.912	5.040	4.883	4.952	5.000
Drying Time, Hrs.	2	1	1.5	1.5	1.2	1.5	0.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Drying Temp., °C.	100-180	80-130	80-150	80-130	80-160	110-135	110-135	130	130	130	130	130	130	130	130	130
Color of Material	Gray	Purple and Green	Purple and Green	Purple and Green	Purple	Moist Purple	Wet Purple	Green	Green	Green	Green	Not Examined	Mottled Gray	Green	Green	Green
Hydrofluorination Cycle:																
Time, Hrs.	1		1	2					1	1	1	1	1	1	1	1
Temp., °C.	130		130	130					130	130	250	130	130	130	130	130
O ₂ Flow, ml./min.	60		60	60					60	60	60	60	300	700	700	700
HF Flow, l./min.	3.5		3.5	3.5					3.5	3.5	3.5	3.5	3.0	2.5	2.5	2.5
Product	H ₂ C ₂ O ₄ over Purple Cake		Gray	H ₂ C ₂ O ₄ over Blue-Gray					H ₂ C ₂ O ₄ over Purple Cake	H ₂ C ₂ O ₄ over Purple Cake	Blue	Not Examined	Mottled Gray	Oxalic Acid Crystals over lavender cakes		
Time, Hrs.	1	1	.67	.5	1	1	1	1	1	.5	.5	.33	.5	.5	.5	.5
Temp., °C.	130-500	130-500	130-500	130-500	120-600	130-500	130-500	130-500	130-500	250-500	250-500	130-400	130-500	130-500	130-500	130-500
O ₂ Flow, ml./min.	60	60	60	60	60	60	60	60	60	60	60	60	300	700	700	700
HF Flow, l./min.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	2.5	2.5	2.5
Product	--	--	--	Gray	Pink and Yellow	--	--	--	--	--	--	--	--	--	--	--
Time, Hrs.	2	2	2	2	1	1.67	1.67	3	2	2	2	3	2	1.1	1.1	1.0
Temp., °C.	500	500	500	500	600	500	500	500	500	500	500	400	500	500	500	500
O ₂ Flow, ml./min.	60	60	60	60	60	60	60	60	60	60	60	60	300	700	700	700
HF Flow, l./min.	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.0	2.5	2.5	2.5
Product	Pink	Pink	Pink	Pink	Pink	Pink	Bluish-Pink	2 Hrs. Bluish-Pink 3 Hrs. Pink	Pink	Bluish-Pink	Pink	Bluish-Pink	Pink	Pink	Pink	Pink
Gms. of PuF ₄	6.790	7.110	6.672	6.686	6.571	6.723	6.465	6.555	6.567	6.473	6.555	6.533	6.497	6.570	6.575	6.410
% of Theor. PuF ₄	100.2	99.1	>98.0	>98.2	97.0	100.0	98.7	100	100.5	99.2	100.6	100.9	98.8	100.0	100.7	97.3
Bulk Density of PuF ₄	1.4	0.9	1.1	1.4	1.0	1.1	1.1	1.2	1.6	1.6	1.4	1.2	1.5	1.0	1.1	1.3
% Reduction Yield ¹	95.0	96.8	96.1	91.8	90.6	89.4	89.7	89.7	97.7	96.5	93.2	97.1	87.1	97.3	83.2	98.9
($\frac{\text{Pu obtained}}{\text{PuF}_4 \times 239} \times 100$)																
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TABLE IIDIRECT HYDROFLUORINATION OF PLUTONIUM (IV) OXALATE

Run No.	41	45	54
Gms. of Pu as $\text{Pu}(\text{C}_2\text{O}_4)_2$	<4.548	5.106	5.040
Drying Time, Hrs.	1.5	1.5	1.5
Drying Temp., $^{\circ}\text{C}$.	80-150	80-130	130
Color of Dry Oxalate	Tan	--	Yellow
Hydrofluorination Cycle:			
Time, Hrs.	1	.67	1
Temp., $^{\circ}\text{C}$.	130	130-300	130
O_2 Flow, ml./min.	60	60	250
HF Flow, l./min.	3.5	3.5	2.5
Product	$\text{H}_2\text{C}_2\text{O}_4$ on Yellow- Gray Powder	Purple Powder	Yellow-Gray with some Pink
Time, Hrs.	.67	.33	.5
Temp., $^{\circ}\text{C}$.	130-500	300-500	130-500
O_2 Flow, ml./min.	60	150	250
HF Flow, l./min.	3.5	0	2.5
Product	--	Yellow and Pink Powder	Pink Powder
Time, Hrs.	2	1	
Temp., $^{\circ}\text{C}$.	500	500	
O_2 Flow, ml./min.	60	60	
HF Flow, l./min.	3.5	3.5	
Product	Pink Powder	Pink Powder	
Gms. of PuF_4	5.615	6.723	6.823
% of Theor. PuF_4	>93.7	100	102.7
Bulk Density of PuF_4	0.9	1.1	1.1
% Reduction Yield	96.3	89.4	96.0
$\left(\frac{\text{Pu obtained}}{\text{Pu F}_4 \times 239} \times 100 \right)$			
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