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FINAL REPORT
PRODUCTION TEST 234-4
PRODUCTION OF PLUTONIUM (IV) FLUORIDE BY
DIRECT HYDROFLUORINATION OF
PLUTONIUM (III) OXALATE

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BY

F. J. QUINN, JR.
TECHNICAL DIVISIONS

MARCH 30, 1951

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Final Report

Production Test 234-4

PRODUCTION OF PLUTONIUM (IV) FLUORIDE BY DIRECT
HYDROFLUORINATION OF PLUTONIUM (III) OXALATE

by

F. J. Quinn, Jr.
Process Section
Separations Technology Division

March 30, 1951

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Final Report
Production Test 234-4

PRODUCTION OF PLUTONIUM (IV) FLUORIDE BY DIRECT
HYDROFLUORINATION OF PLUTONIUM (III) OXALATE

INTRODUCTION

Plutonium (IV) fluoride, the reducible compound used in the production of metallic plutonium, has been and is at present produced in the 234-5 Building from a plutonium (IV) and (VI) nitrate solution by the following sequence of operations:

- 1) reduction and subsequent precipitation of plutonium (III) oxalate,
- 2) oxidation to plutonium (IV) oxide,
- 3) metathesis of the oxide to plutonium (IV) fluoride with anhydrous HF.

These three operations require about 12 1/2 hours and constitute one of the major restrictions to increased production. A shorter procedure was proposed by the 234-5 Development Group (1). The oxidation of plutonium (III) oxalate to plutonium (IV) oxide is eliminated in this method and the following sequence is substituted:

- 1) reduction to and precipitation of plutonium (III) oxalate,
- 2) hydrofluorination of the oxalate to plutonium (III) fluoride, and conversion of the plutonium (III) fluoride to plutonium (IV) fluoride by direct hydrofluorination.

Production Test 234-4 (2) has been executed in the 234-5 Building on a production scale to endeavor to substantiate with plant equipment, the favorable results obtained from the laboratory work and to permit additional evaluation of the proposed modification.

OBJECTIVES

The objectives of the production test were to:

- 1) Determine the metal yield from plutonium (IV) fluoride produced by the proposed process modification.
- 2) Determine the time cycle resulting from the process change.
- 3) Determine the density of the directly fluorinated plutonium (IV) fluoride and its effect on subsequent processing.

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- 4) Determine the purity of the metal as produced by modified processing vs. current processing.
- 5) Determine the mechanical problems which result from the proposed process.
- 6) Determine a practical accountability method for the new process.

SUMMARY AND CONCLUSIONS

The thirty-seven runs which were processed in 234 Building equipment utilizing the direct hydrofluorination method have substantiated the performance and feasibility demonstrated by the laboratory work. Plutonium (IV) fluoride produced by the new method has been converted to metal with quality and purity comparable to that obtained by the present production process. The following advantages can be realized from this method:

- 1) The time required to produce plutonium (IV) fluoride from the oxalate is reduced from 12 1/2 hours to 9 1/2 hours per run which will allow a 24 per cent increase in production.
- 2) The metal yield from test material was slightly higher than that from present process material based on comparable accountability points. (231 assay and fluoride powder weight.)
- 3) The equipment will operate at a maximum temperature 60°C. lower than the current process. This lowered operating temperature should reduce the corrosion rate of the equipment and result in savings in equipment maintenance and replacement.

The possible disadvantage of the process is the lower bulk density of the plutonium (IV) fluoride powder (ca. 1/2 that of present fluorides). This limits the maximum number of fluoride batches that can be charged into the reduction crucible to 2 instead of 3 batches as is now possible. However, because this latter type of reduction is made so infrequently, the objection is not too important.

RECOMMENDATIONS

In view of the test results, it is recommended that the present dry chemistry operation be replaced by the method of direct hydrofluorination of the plutonium (III) oxalate. Because of the somewhat shortened duration of the test, it is also recommended that the new process be employed as the production process for a period of one month.

At the end of this period the operation shall be reviewed by representatives of the "S" Division and Technical Divisions, and the acceptance or rejection of the method be made.

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Secondly as a result of observations made from the test runs, it is recommended that the purification and recovery equipment be flushed periodically in the interest of nuclear safety. The flush data indicate that ca. 1-1/2 grams of product per run were deposited in the supernate and recovery system.

EXPERIMENTAL

Prior to the test, which was conducted in the 234-5 Building rubber glove line, the equipment in one purification hood and one recovery unit were flushed to remove all product. The system was then used exclusively for the test material. This was necessary to accumulate the data necessary to strike a material balance and to calculate an average reduction yield, since the oxide accountability point was to be by-passed.

Thirty-seven batches were processed normally through the systems which had been flushed. The oxalate precipitates were transferred to the dry chemistry hood where they were processed with the following 9 1/2 hour cycle. All temperatures listed are indicated controller temperatures.

1. Drying

With a gas flow of 75 gm/hr. of dry air passing over the material:

- a. Heat from room temperature to 130°C. in 15 min.
- b. Hold at 130°C. for 1 hour.
- c. Heat from 130°C. to 190°C. in 15 min.
- d. Hold at 190°C. for 2 hours.

2. Hydrofluorinating to PuF_3

With a gas flow of 25 gm/hr. of oxygen and 500 gm/hr. of anhydrous hydrogen fluoride, hold the temperature at 190°C. for 2 hours.

3. Hydrofluorinating to PuF_4

With a gas flow of 80 gm/hr. of oxygen and 200 gm/hr. of hydrogen fluoride:

- a. Heat from 190°C. to 540°C. in 30 min.
- b. Hold at 540°C. for 2 hours.
- c. Cool the furnace to 200°C. (About 70 Min.)

4. Cooling

Cool with air from 200°C. to 140°C. with a gas flow of 17 gm/hr. (About 20 Min.)

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Eighteen reduction runs, each one composed of two production test plutonium (IV) fluoride batches together with recycled metal chips, were made. The bulk density of the test fluoride is about 1.0 g/cc. while that of normal material is about 2.4 g/cc. Thus, where the reduction equipment could accommodate three normal batches of powder and turnings, it can hold only two batches of directly hydrofluorinated powder and turnings. Normal production will not be affected by this limitation as most reductions consist of two fluoride batches plus added recycle metal. Occasionally, when no recycle material is available, three fluoride batches are combined to produce a reduction button of equivalent size. If buttons are made of two fluoride batches and no recycle for an extended period of time, the following would become important objections:

- 1) The combination of buttons so produced is not an optimum weight for melting.
- 2) The number of reduction crucibles used would be increased.

Advantageously, the smaller buttons which will be produced occasionally, will be ideal to combine with a rejected piece for recasting.

The accountability material balance is given in Table I. Subsequent to the test it was reported that the 231 assay figure is low (3). This is supported by the fact that over 100 per cent of the theoretical PuF_4 was produced. The low 231 assay is also responsible for the low loss to reduction slags, which was calculated by difference. As may be seen from Tables I and II, the reduction yield averages 97.9 per cent for the normal runs, whose accountability is based on the oxide weight, as compared to 99.7 per cent for the test runs. Slag losses are about 10 grams per normal run instead of less than one gram as per test run.

Table II compares the operation by the two methods, i. e. direct hydrofluorination vs. present process. The control runs used were the normal dry chemistry runs processed concurrently with the test runs. Based on the 231 assay, the metal yield in reduction was 98.2 per cent for test material and 97.9 per cent for regular material. Based on the fluoride powder weight (assuming it to be 100% PuF_4), the metal yield was 97.6 per cent for test material, 96.9 per cent for regular material. Thus, from both standpoints[⊙], the yield from test material is better.

⊙

Nine of the test buttons produced were sampled and analyzed for purity. Impurities found in buttons made from test material are compared to those in

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standard buttons sampled during February in Table III. These results indicate that lanthanum is the only element present in the test buttons in a greater amount than in the normal product. The high lanthanum (which occurred during the test period) has since been attributed to another process change, and consequently any interpretation assigning this increase to the direct fluorination method is felt to be erroneous.

As a result of by-passing the oxide weight, alteration of accountability procedures is necessary. Two possible methods are suggested. The first uses the 231 assay, fluoride weight, and button weight as accountability points; the second uses the 231 assay and button weights as control points and is made on a group basis. The first method is probably more desirable since Method 2 will ascribe very little loss to reduction fragments.

METHOD 1
INDIVIDUAL RUN BASIS

<u>Material</u>	<u>Debit</u>	<u>Credit</u>
1. 231 Assay	Purification Account	231 Building
2. Supernate and Flush Losses	Recovery Account	Purification Account
3. Fluoride Weight *	Dry Chem. Account	Purification Account
4. Recycle Weight	Reduction Account	Machining Account
5. Button Weight Less Recycle	Reduction Account	Dry Chem. Account
6. Fragment Loss (3)-(5)	Recovery Account	Reduction Account

* Assume 100% PuF_4

METHOD 2
GROUP RUN BASIS

<u>Material</u>	<u>Debit</u>	<u>Credit</u>
1. 231 Assays	Purification Account	231 Building
2. Supernate Losses	Recovery Account	Purification Account
3. Supernate System Flush for Group	Recovery Account	Purification Account
4. Recycle Weights	Reduction Account	Machining Account
5. Button Weights Less Recycle	Reduction Account	Purification Account
6. Fragment Loss 1. -(2. +3. + 5.)	Recovery Account	Reduction Account

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REFERENCES

1. HW-18796; J. F. Facer and W. L. Lyon; 234-5 Development Group-Summary Report, Direct Hydrofluorination of Pu (III) Oxalate; Sept. 11, 1950.
2. HW-19651; F. J. Quinn, Jr.; Production Test 234-4, Direct Hydrofluorination of Plutonium (III) Oxalate; Dec. 7, 1950
3. HW-20330; F. W. Albaugh; A Revised Method for 200 Area Accountability and Material Balance Control; Feb. 19, 1951

F. J. Quinn, Jr.
F. J. Quinn, Jr.

FJQ:lb

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TABLE I
PRODUCTION TEST 234-4
MATERIAL BALANCE
234 BUILDING OPERATION

(All quantities are in grams unless otherwise marked)

231 Assays 5772*

Supernate Loss	23.59
Recovery Flush	53.31
Filter Paper Recovery	1.84
Transfer Flask Recovery	7.50
	86.14

Calculated Weight of Metal Fluorinated 5685.86

Theoretical Fluoride Weight ($5685.86 \times \text{PuF}_4$)
 $\frac{\text{Pu}}{\text{Pu}} = 7493.9$

Actual Fluoride Weight 7653.9

235 BUILDING OPERATION

Calculated Metal in Fluoride 5684.72**

Total Weight of Buttons 7896.80

70-58 and Recycle in Buttons 2229.24

Metal from Fluoride 5667.56

Metal to Reduction Slag. 5667.56
17.16

% Yield = $\frac{5667.56}{5684.72} \times 100 = 99.7\%$

Slag Loss per Run = $\frac{17.16}{18} = 0.95$

* Quantity is a summation of Pu contents of 36 sample cans from Radio assays.

** The difference in metal in fluoride between 234 Building and 235 Building is due to holdup in the transfer equipment.

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TABLE II
PRODUCTION TEST 234-4
REDUCTION YIELD COMPARISONS
231 BASE VS. METAL YIELD

	<u>Test Material (1)</u>	<u>Control Material (2)</u>
1. 231 Assays	5772	6434
2. Metal from Fluoride	5667.559	6298.592
3. % Yield (2) ÷ (1)	98.2%	97.9%

FLUORIDE POWDER WEIGHT VS. METAL YIELD

1. Fluoride Powder Weight	7653.9	8569.9
2. Theoretical metal in powder (100% PuF ₄ assumed)	5807.26	6502.2
3. Metal from Fluoride	5667.5	6298.59
4. % Yield (3) ÷ (2)	97.6%	96.9%

- (1) Observed values for eighteen Production Test buttons.
- (2) Observed values for forty 234 Building runs from X-11-2-101 to X-11-2-176 (excluding test runs and X-11-2-143) and from the twenty buttons made with these runs.

TABLE III
PRODUCTION TEST 234-4
PURITY COMPARISONS
SPECTROGRAPHIC ANALYSIS OF BUTTONS

(ppm based on Pu)

	<u>TEST MATERIAL (1)</u>			<u>CONTROL MATERIAL (2)</u>		
<u>Impurity</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>
Al	19	50	L10	14	50	L10
Be	L0.02	L0.02	L0.02	L0.02	L0.02	L0.02
Ca	17	40	10	21	100	4
Cr	15	20	L4	25	100	L4
Fe	233	500	L200	372	2000	100
La	1044	G2000	40	342	2000	L10
Li	1.1	L2	L1	1.1	L2	L1
Mg	256	500	100	252	500	200
Mn	94	200	50	161	200	100
Na	7	L15	L5	5.4	L15	L5
Ni	92	500	L20	71	200	20
Si	30	100	10	30	50	10

G: Greater than

L: Less than

- (1) Observed values for test buttons, Y-11-2-53, 63, 66, 69, 72, 75, 78, 81, 84.
- (2) Observed values for standard buttons, Month of February, 1951.

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