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LABORATORY EVALUATION OF ONE AND TWO CYCLE PEROXIDE PROCESSING OF F-10-P SOLUTIONS ON THE BASIS OF METAL PURITIES OBTAINED

I. INTRODUCTION

Decontaminated plutonium from the Concentration Process (Building 224) is currently isolated and purified by the following process scheme.

1. Isolation (Building 231) The plutonium accompanied by the lanthanum carrier in nitric acid solution is isolated from the carrier by a two-cycle peroxide process. The resulting product solution containing minor amounts of elemental impurities is concentrated by evaporation to approximately 1.5 molar plutonium nitrate.

2. Purification (Building 234) The nitric acid solution of plutonium nitrate following dilution is purified (primarily the removal of iron, chromium and nickel) by a single precipitation of plutonium (III) oxalate. This product is converted to plutonium (IV) fluoride by treatment with an oxygen-hydrogen fluoride mixture.

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EW-21691

An improved and simplified flowsheet has been proposed wherein the volume concentration step (evaporation) and the oxalate precipitation step would be eliminated. This possibility was premised on the elimination of the products of corrosion by omitting the concentration step and the modification of the peroxide precipitation with respect to composition and manipulation to yield a plutonium peroxide precipitate susceptible to hydrofluorination to plutonium (IV) fluoride with the desired physical properties and chemical purity.

II. OBJECTIVES

The objectives of this laboratory investigation were to examine the feasibility of employing a one or two cycle peroxide precipitation process to produce feed for the hydrofluorination process, based on the following listed criteria.

- a. The purity of the plutonium nitrate solution following dissolution of the peroxide precipitate.
- b. The purity and yield of metallic plutonium obtained by a one or two cycle peroxide process followed by direct hydrofluorination and reduction.

III. SUMMARY AND CONCLUSIONS

A series of five laboratory runs (nominal five-gram scale) starting with F-10-P solutions (Concentration Building product) was carried out employing both one and two peroxide precipitation cycles to produce peroxide cakes which were subsequently directly hydrofluorinated and reduced to metallic plutonium.

a. Single peroxide cycle isolation.

The single peroxide cycle precipitates from two runs were separated by decantation, washed, dried and hydrofluorinated in platinum boats to form plutonium (IV) fluorides with bulk densities of 1.42 to 1.57 g./cc., and reduced to metal with yields of 62.2 and 42.8 per cent. The button purities were comparable between the two runs and both considered unacceptable on the basis that total impurities exceeded 3,300 ppm. Lanthanum values alone were 4,000 and 5,000 ppm.

b. Two peroxide cycle isolation.

Using a two-peroxide-cycle process in which the final peroxide precipitates were separated both as a slurry (one run) and as a filtered cake (two runs) and directly hydrofluorinated in platinum boats, fluoride bulk densities of 1.68 to 1.94 g./cc. and yields upon reduction of 87.4 to 96.3 per cent were obtained. Although four elements, bismuth, iron, nickel and chromium, were present in significantly higher amounts in the laboratory buttons than in buttons produced in the plant (a total of 1113 ppm. as compared to 470 ppm), their amounts were not excessive.

c. Conclusions

From the foregoing results, it may be concluded that a two cycle peroxide isolation process followed by direct hydrofluorination of the peroxide precipitate and reduction of plutonium (IV) fluoride to metal should permit the production of metal of satisfactory purity. Final evaluation of the proposed process should be based upon a production plant test because certain inherent factors tend to make a direct extrapolation of laboratory data to plant conditions of

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HW-21691

-3-

uncertain precision.

IV. EXPERIMENTAL

A. Materials

Samples of filtered P-10-P solution taken from the P-1 tank in the Isolation Building were the starting solutions for the series of five-gram-scale runs for the purpose of testing one and two peroxide cycles for isolation and purification of plutonium. The final peroxide in each case was directly hydrofluorinated to plutonium (IV) fluoride and reduced to the metal button.

B. Equipment and Manipulations

A platinum boat was used for the hydrofluorinations although the peroxide precipitate was introduced either as a slurry (separated by decantation) or as a damp cake (obtained by filtration and washing on a medium porosity glass filter).

In two runs using only a single peroxide precipitation the standard first cycle Isolation Flowsheet (See Hanford Works Technical Manual, HW-10475, Section "C", p. 809) was used except that 50 per cent hydrogen peroxide was used and the slurries were washed four times, the last two washes being five per cent hydrogen peroxide. Wash volumes were proportional to those used in the plant (approximately equal to the settled precipitate volumes).

Three runs were made using the two-peroxide-cycle process. The first precipitations were carried out according to the standard Isolation Flowsheet; the second precipitations were made with 50 per cent hydrogen peroxide from solutions adjusted (by careful dissolution of the first precipitates) to 40 g/l Pu, 1.5 M HNO_3 , and 0.15 M H_2SO_4 . Washing of the second cycle slurry (or filter cakes) was accomplished with portions of five per cent hydrogen peroxide proportional to plant wash volumes.

C. Hydrofluorination

The peroxides transferred as slurries were first dried in the platinum boat with air at 130°C and then directly hydrofluorinated for one hour at 130°C and for three hours at 500°C. When the peroxide had been separated on a filter and transferred to the boat, hydrofluorination was begun when the furnace reached 130°C, and two hours at 500°C were then used to complete the reaction.

D. Reduction

The fluorides were reduced to metal by using the standard reduction technique for the five-gram scale as given in document number HW-14148, "Small Scale Preparation of Plutonium Metal", D. W. Haught, et al, August 12, 1949.

V. DISCUSSION AND RESULTS

A. Reduction Yields

While this series of runs was made primarily for an evaluation of the product on a purity basis, an observation of reduction yields as a function of number of peroxide cycles (or purity) is significant.

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HW-21691

As indicated by the laboratory data presented in Table I, both bulk densities of the fluoride and reduction yields were higher when two peroxide cycles were used as compared to when a single peroxide precipitation was used. It should be noted from Table II that of those impurities reported to be in the buttons, chromium, iron, indium, lanthanum, manganese, and phosphorus appear in significantly higher concentrations in the buttons from a single peroxide process than in those from a two-cycle process. The above observations are consistent with previous studies in which it was shown that a high concentration of certain impurities in the starting solution would, by carrying with the precipitate, cause a deleterious effect on hydrofluorination and reduction.

Reduction yields were somewhat higher for the two runs with the peroxides prepared as filter cakes than for the run with the second precipitate transferred to dry chemistry as a slurry. While some increase in peroxide purity is evidenced when washes are separated on the filter rather than by decantation, the increase in metal yield is more likely a result of the shortened furnace cycle permitted when hydrofluorinating a filtered cake, as compared to the longer time required when drying and hydrofluorinating a slurry. Partial decomposition of the peroxide during drying and consequently poorer conversion to plutonium (IV) fluoride may have thus occurred.

B. Purity Obtainable by a Two-Cycle-Peroxide Process

In the existing plant process (Table III) nine elements (bismuth, calcium, chromium, iron, potassium, lanthanum, sodium, phosphorus, and lead) are appreciably higher in the second cycle peroxide cake than in the button. All of these, together with the increased amounts of iron, chromium, and nickel added during the still operation, are presently reduced to satisfactory levels in plant metal by oxalate precipitation, hydrofluorination, and reduction.

If second cycle peroxide cake is to be transferred directly to dry chemistry, those elements which are present at high concentrations at this point must then be removed only by hydrofluorination and/or reduction. An indication of the extent to which this purification can be accomplished has been obtained from the comparison of laboratory button purity (two-cycle peroxide process) and plant button purity (existing isolation and purification process).

With the exception of the four elements (bismuth, iron, chromium, and nickel) which are present at slightly higher concentrations in laboratory two-cycle-process metal than in plant metal, other impurities are equivalent. Plant metal produced by using two peroxide precipitations followed by hydrofluorination and reduction could be expected, therefore, to be of acceptable purity.

C. Purity Obtainable by a Single Peroxide Process

The metal purity obtained using only one peroxide precipitation would not be satisfactory due to objectionable amounts of lanthanum, iron, chromium, nickel and manganese, with lanthanum alone contributing 4000 to 5000 ppm to the total impurity. (A purity specification for the basic alloy allows 0.33 per cent by weight or 3300 ppm maximum impurity).

VI. FUTURE WORK

Laboratory work aimed at the improvement of a process employing only one plutonium peroxide precipitation might be justified. Such measures as altering the precipitation conditions or increasing the efficiency of washing by use of larger wash volumes or washing on a filter would offer possibilities.

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WH-21691

Table I - Laboratory Data for Five Oxide Peroxide Runs

Run No.	Starting Solution	Number of Peroxide Cycles	Peroxide transferred as	Half Density of PuF_4 (g./cc.)	% Reduction Yield*
81	B-11-01-D-51	1	slurry	1.42	62.2
83	B-11-01-D-51	1	slurry	2.77	42.8
82	B-11-01-D-51	2	slurry	2.75	87.4
87	T-11-04-H-6	2	filter cake	2.04	96.3
88	T-11-04-H-6	2	filter cake	1.68	90.1

*Based on weight of fluoride charged, assuming 100% PuF_4

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NW-21691

Table II -- Spectrochemical Analysis of Laboratory 5 Green Eggs

Single Cycle Process				Two Cycle Process				Two Cycle Process			
①	F-10-F (typical)	Run 81	Run 83	Ave.	Run 87	Run 88	Ave.	Run 82	Run 87	Run 88	Ave.
Ag	*	<1	<1	<1	50	50	50	2	<1	<1	<1
Al		20	20	20	50	100	75	20	<20	20	20
As		<50	<50	<50	<20	<20	<20	<50	<50	<50	<50
B		2	2	2	200	50	125	2	<2	<2	<2
Ba		<20	<20	<20	<20	--	<20	<20	<20	<20	<20
Ba	<2	<0.02	<0.02	<0.02	<0.02	<2	<2	<0.02	<0.02	<0.02	<0.02
Bi	**	10	5	7.5	61000	500	1000	10	20	10	13
Ca	2 x 10 ⁵	40	10	25	61000	1000	1000	40	20	20	27
Ca		<20	<20	<20	100	100	100	20	<20	<20	<20
Ce		<200	<200	<200	<200	--	<200	<200	<200	<200	<200
Ce		20	<20	20	20	20	20	<20	20	10	<20
Cr	4 x 10 ³	500	500	500	20	10	15	100	100	200	133
Cu	*	50	20	35	<10	10	<10	50	10	50	37
Fe	1 x 10 ⁵	1000	1000	1000	500	500	500	1000	500	500	667
In	*	10	20	15	<2	<2	<2	2	2	<2	<2
K	**	<5	<5	<5	1000	50	225	<5	<5	<5	<5
La	2 x 10 ⁶	4000	5000	4500	4000	--	4000	400	200	200	266
La		<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mg		500	50	275	50	50	50	500	500	200	400
Mn	1 x 10 ⁴	500	1000	750	200	20	110	500	200	200	300
Mn	1 x 10 ⁴	25	15	20	150	250	200	25	10	10	15
Ni	2 x 10 ³	500	200	350	20	50	35	500	200	200	300
P		200	100	150	61000	1000	61000	100	<100	<100	<100
Pb	*	<20	<20	<20	50	20	35	<20	<20	<20	<20
Sb		<50	<50	<50	<20	<20	<20	<50	<50	<20	<50
Si		50	<20	35	50	20	35	50	20	20	30
Sn		<5	<5	<5	10	20	15	<5	<5	<5	<5
Sn	4 x 10 ³	<4	<4	<4	24	<4	<4	<4	<4	<4	<4
V		<200	<200	<200	<200	<200	<200	<200	<200	<200	<200
Zn		<50	<50	<50	<50	<50	<50	50	<50	<50	<50
Zn		<100	<100	<100	<100	--	<100	<100	<100	<100	<100

* Positive results

** Very strong

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EE-21691

Table III - Spectrochemical Analysis of Plant Run

	Second Cycle Cakes			P-4 (2)	Fluoride (2)	Bottoms (3)		
	Min.	Max.	Avg.			Min.	Max.	Avg.
Ag	< 1	1	1					< 10
Al	20	100	30	100		< 10	30	14
As	< 20	< 20	< 20					< 50
B	1	2	< 2			0.1	1.6	0.3
Ba	< 200	< 200	< 200					< 20
Be	< 0.1	< 0.1	< 0.1	< 2	< 0.1	< 0.02	< 0.02	< 0.02
Bi	1000	1000	1000					< 2
Ca	500	2000	1200	600	80	4	100	21
Cd								< 10
Ce	< 1	< 1000	< 1000					< 200
Co	< 20	< 20	< 20					< 20
Cr	100	200	170	2400	10	< 4	100	25
Cu	< 10	20	< 15					20
Fe	500	1000	750	610,000		100	2000	372
Hg	2000	2000	2000					< 200
In	< 2	5	< 4					< 2
K	200	61000	1000	1300				< 10
La	2000	10,000	5700	62000	62000	< 10	2000	342
Li	< 1	< 5	< 1		< 2	< 1	< 2	< 2
Mg	100	200	190	50	5	200	500	252
Mn	100	200	180	200	10	100	200	161
Na	250	500	300	500	10	< 5	15	5.4
Ni	20	200	46	1500	50	20	200	71
P	1000	61000	1000	1700				< 100
Pb	20	200	61	50	50			3
Sb	< 20	< 20	< 20					< 50
Si	< 20	20	< 20		< 20	10	50	30
Sn	2	10	5	15				< 2
Sr	< 20	< 20	< 20	< 4	< 4			< 4
Zn	< 50	< 50	< 50					< 100
Tl	< 500	< 500	< 500					< 100

- (1) Samples were taken from ten runs in Cell 3, Isolation Process, after cake dissolution: B-11-02-H-54 and 55, B-11-02-W-57 thru 61, and B-11-03-W-1, 2, and 3.
- (2) Average analyses for early runs (July to October, 1949).
- (3) Average analyses are for May 1951, except those for which no maximum and minimum are given. These have been very constant over many months and were therefore not obtained routinely during May.

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