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WET FLUORIDE STUDIES: CALCIUM PLUTONIUM(IV) FLUORIDE

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WET FLUORIDE STUDIES: CALCIUM PLUTONIUM(IV) FLUORIDE

INTRODUCTION

At the present time, the Hanford process for preparing plutonium metal includes the following steps:

a. Reduction of plutonium in P-2 cake solution, or in concentrated Redox IIIBP solution, to the tetravalent state by hydrogen peroxide, and precipitation of plutonium(IV) oxalate.

b. Drying of the oxalate followed by hydrofluorination to plutonium tetrafluoride.

c. Reduction of the fluoride to plutonium metal by calcium in a stationary bomb.

The corrosion resulting from step "b" above is excessive, so that considerable equipment maintenance and replacement costs are incurred. For this reason, a program was initiated to investigate methods which could be substituted for the present process, and which would minimize the corrosion problem.

OBJECTIVES

The experiments described herein were performed in order to establish conditions for the precipitation of a plutonium-fluorine compound which could successfully be reduced to plutonium metal. In addition, it was desirable to show possible savings by shortening the time cycle between reception of the final plant plutonium solution and the bomb reduction of a plutonium compound to metal.

SUMMARY AND CONCLUSIONS

Precipitation and Washing

Calcium plutonium fluoride can be precipitated at room temperature by rapid addition of hydrofluoric acid to plutonium(IV) nitrate solutions having concentrations in the range of 1 to 10 M HNO_3, 25 to 75 g Pu/l, and with calcium ion made equimolar to plutonium.

Precipitates which are formed in solutions having initial concentrations in the range of 1 to 2 M HNO_3, 2 M HF, and 40-65 g Pu/l are found to exhibit favorable physical properties and low precipitate solubilities. The precipitate settles rapidly and can be filtered easily after being washed with water.

Drying

The filter cake can be dried to the anhydrous salt, $CaF_2 \cdot PuF_4$, at 300 C in a stream of dried, deoxygenated argon. The dried cake is quite hard and must be crushed before it is suitable for reduction in a stationary bomb. Bulk density of the crushed cake is approximately 1 g Pu/cm^3.

Reduction

The most successful reductions of calcium plutonium(IV) fluoride were made using 25 per cent excess calcium reductant and 1 to 1.2 moles calcium-iodine booster per mole plutonium. Yields for eleven reductions averaged 86.3 per cent, the highest yield being 95.3 per cent. In all reductions, the metal button was cleanly separated from the slag and was smooth on top but rough or cracked on the bottom. Small pellets of plutonium metal were found in the slag from most reductions, indicating that better coalescence of the metal formed would give much higher yields. It is likely that larger scale (300-400 g Pu) reductions of the calcium double salt will show improved button yields.

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Time Cycle

The time required for the wet chemistry portion of this process is probably about the same as for the present plutonium(IV) oxalate process, although this can be shown definitely only on a production scale. Subsequent drying time is certainly far less than the time required for drying, calcination, and hydrofluorination of the oxalate.

Recommendation

It is recommended that large batches of calcium plutonium fluoride be reduced to the metal to ascertain whether the button yield is a function of batch size. A suitable batch size is approximately 300 g Pu. Since plutonium pellets are found in the slags of small scale reductions, it is apparent that the slag solidifies before all the plutonium pellets settle and coalesce with the main reduction button. Since the production bombs are much larger, it is likely that the slags will remain molten for a long period of time and greater button yields will be realized.

A large scale preparation and reduction of calcium plutonium fluoride will also provide plant time cycle information which cannot readily be obtained on a small laboratory scale.

EXPERIMENTAL DETAILS

Equipment

For small-scale solubility experiments involving less than 1 g Pu, lusteroid precipitation tubes, sintered platinum filter crucibles, and small platinum drying boats were used.

For 20 to 25 g batches, precipitation and washing steps were carried out in a polyethylene beaker. When most of the fluoride ion in solution had been removed by washing, a sintered glass Buchner funnel could be used

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for filtering the precipitates. Filter cakes were dried in platinum boats placed in a 2 inch diameter tube furnace. Argon was deoxygenated and dried by passing it over hot copper turnings and through two Drierite towers. The fifty gram size steel bombs with magnesia liners used for reductions were heated by means of an induction coil.

VARIABLES STUDIED

Conditions for Precipitation

Effects of solution concentrations upon the physical properties of the precipitate and upon supernatant solution waste losses were studied on a 0.5 g Pu scale. The ranges of concentrations investigated were 1 to 11 M HNO_3, 1 to 5 M HF, 25 to 72 g Pu/l, and 0.3 to 1.0 moles of calcium per mole of plutonium. Solubilities were determined by analyzing the supernatant solutions which were sampled as soon as the precipitates had settled. Therefore, the results shown in Table I are not equilibrium solubility values, but merely represent typical solubilities such as might be encountered in plant practice.

TABLE I

SOLUBILITY OF $CaF_2 \cdot PuF_4 \cdot nH_2O$ AS A FUNCTION OF HYDROFLUORIC ACID AND NITRIC ACID CONCENTRATIONS

Initial Pu Concentration - 40 g/l
Initial Ca Concentration - 6.7 g/l

Plutonium Solubility - g/l

HF M \ HNO_3 M	1.0	1.4	2.0	3.0	4.0	6.0*	8.0	10.0*	11.0*
1.0	0.34	0.60	0.71	0.16	0.38	--	--	--	--
2.0	0.17	0.20	0.27	1.0	0.062	0.056	0.046	0.043	0.066
3.0	0.22	0.29	0.28	0.17	0.091	--	--	--	--
4.0	0.33	0.24	0.28	0.16	0.12	--	--	--	--
5.0	0.25	0.20	0.019	0.028	0.098	--	--	--	--

* Initial Pu concentration - 56 g/l, initial Ca concentration - 9.2 g/l

In general, settling times decreased and bulk densities of the settled precipitates increased with lower nitric acid concentrations, higher plutonium concentrations, or lower calcium to plutonium ratios. Bulk densities ranged from 0.3 g Pu/cm^3 at 1 M HNO_3, to 0.08 g Pu/cm^3 at 11 M HNO_3. Neither heating the solutions prior to precipitation nor varying the concentration or rate of addition of hydrofluoric acid had any apparent effect upon the physical properties of the precipitates.

Washing

In all cases studied, the precipitates could be washed as well with water as with a dilute acid solution, and, in fact, settled better after being washed than before. The precipitates having higher bulk densities could be filtered quite rapidly, but caked badly when dried. In attempts to improve the properties of the dried cake, samples of the precipitate were washed with acetone or with ethyl alcohol. The acetone-washed precipitates were sticky and more difficult to handle while wet than alcohol-washed precipitates. Both alcohol- and acetone-washed salts yielded slightly softer dried cakes than did the water-washed salts, but their bulk densities were only about 0.6 g Pu/cm^3 as compared with 1.0 g Pu/cm^3 for water-washed precipitates.

Drying

The calcium double salt, when air-dried at 400 C to remove water of hydration, was partially converted to the oxide, PuO_2. However, it remained as the fluoride when dried at 400 C in a stream of Freon-12 or in dried, deoxygenated argon. Analysis of the dried compound showed it to be $CaF_2 \cdot PuF_4$. A temperature - weight loss curve was recorded during the drying cycle of one batch of fluoride. It was found that when 300 C was reached, all the water of hydration had been removed. Each dried cake had to be ground to a powder before it could be reduced to metal.

Reduction

Thirteen batches of fluoride were prepared for reduction to metal. For all runs, 25 per cent excess calcium reductant was used. Calcium-iodine booster was employed, varying in amount from 0.55 to 1.4 moles per mole plutonium. The reduction bombs were heated in the coil of an induction heater; "firing" occurred in the range from 525 to 850 C as indicated by the external bomb thermocouple. The temperature was maintained at the peak firing temperature for 3 to 5 minutes after firing. It was found, as expected, that somewhat better coalescence of metal took place with longer holding periods at the highest temperature. Reduction yields, along with run conditions are shown in Table II.

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TABLE II

RESULTS OF REDUCTIONS OF CALCIUM PLUTONIUM(IV) FLUORIDE

Precipitation conditions: 1 M HNO_3, 2 M HF, 1 mole calcium per mole plutonium
For all reductions: 25 per cent excess calcium reductant, calcium-iodine booster

Run No.	Initial Plutonium Conc., g/l	No. Water Washes	Drying Conditions		Dried Product			Booster/ Pu Mole Ratio	Reduction Yield(b) Per Cent
			Temp. °C	Gas	Appearance	Bulk Density g Pu/cm³	Per Cent Pu(a)		
27	25	3	400	Freon-12	Small amount of oxide on top	1.0	61.4	0.55	0
28	25	3	400	Freon-12	More oxide	1.0	61.0(c)	1.0	95.3
29	38	3	400	Untreated argon	Same as 28	1.0	61.0	1.0	85.4
30	31	3	380	Same as 29	Large amount oxide	1.0	62.8	1.0	80.8
31	31	3	400	Treated argon(d)	No oxide visible	1.0	60.9	1.0	85.2
32	31	3	400	"	No oxide visible	1.0	61.2	1.2	92.4
33	31	3	400	"	No oxide visible	1.0	61.2	1.4	86.3
34	31	3	400	"	No oxide visible	1.0	62.1	1.2	86.9
35	31	2 and 2(e)	400	"	Small amount of oxide	0.6	No analysis obtained	1.2	87.2
36	31	2 and 2(e)	300	"	No oxide visible	0.6	56.8	1.2	78.1
37	31	2 and 2(f)	300	"	No oxide visible	0.6	57.8	1.2	81.6
38	31	2 and 2(f)	300	"	No oxide visible	0.6	57.3	1.2	89.9
39	72(g)	3	300	"	No oxide visible	1.2	61.0	1.2	86.3
40	63(h)	3	300	"	No oxide visible	1.2	68.8	1.0	72.7

(a) Theoretical weight per cent plutonium in $CaPuF_6$ = 60.8.
(b) Main button only.
(c) Not analyzed; estimate based on calculated amount of Pu in initial solution; yield probably high.
(d) Dried, deoxygenated.
(e) The two water washes were followed by two acetone washes.
(f) The two water washes were followed by two ethyl alcohol washes.
(g) 1.79 M HNO_3.
(h) 1.36 M HNO_3, 1/2 mole Ca/mole Pu.

ABSTRACT

Laboratory studies have shown that the double salt, $CaF_2 \cdot PuF_4$, can be precipitated by rapid addition of hydrofluoric acid to solutions containing 25 to 75 g Pu/l, calcium equimolar to plutonium, and 1 to 10 M HNO_3. The precipitate, which is subsequently washed with water and dried to 300 C in dehumidified, deoxygenated argon, can be reduced thermally by calcium to give high yields of plutonium metal.