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ADDITIONAL INFORMATION, PATENT APPLICATION
HWIR-672, AEC Case S-11,200

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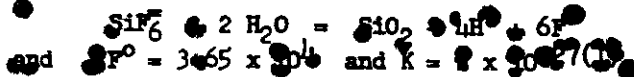
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The following information has been furnished to supplement Invention Report HWIR-672, HW-40996. This information is taken from Secret Notebooks HWN-930, HWN-1396, and HW-5452-T, and from Secret documents HW-39751H and HW-40126H.

Filterable $\text{PuF}_4 \cdot 2.5 \text{H}_2\text{O}$ can be precipitated homogeneously from plutonium nitrate-nitric acid solutions by the addition of fluosilicic acid followed by the addition of hydrofluoric acid after precipitation has started. The fluosilicate anion ionizes by the following:



The fluoride ion in equilibrium with the fluosilicate is complexed by $\text{Pu}(\text{F})_4$ and a solid is formed.

The precipitation has been made from $\text{Pu}(\text{NO}_3)_4$ solutions with plutonium concentrations from 40 to 80 g/l and acid concentrations up to 1.6 M HNO_3 at room temperature.

A typical procedure for the precipitation would be the rapid addition of one mole of 31 per cent fluosilicic acid per mole plutonium to a solution of 40 g/l $\text{Pu}(\text{IV})$ and 1.2 M HNO_3 . The solution was agitated to distribute the fluosilicic acid. Solids became apparent after 20 minutes and after 40 to 60 minutes hydrofluoric acid was added to complete the precipitation and converted any silicic acid or silica formed from the first reaction to soluble fluosilicic acid. The fluoride can be filtered immediately. This fluoride is more crystalline as evident by settling rates and ease of filtration than the fluoride produced by hydrofluoric acid precipitated fluoride. Sufficient hydrofluoric acid was added to make the slurry 0.01 to 0.1 molar excess.

The high plutonium content and the necessity of reprocessing of the filtrates from 0.4 to 1.0 g/l plutonium, in the filtrates, prompted an investigation into the precipitation of the trifluoride with fluosilicic acid. The solubility of plutonium trifluoride in hydrofluoric acid-nitric acid systems was known to be 0.02 to 0.1 g/l Pu. Filtrates produced from such a process could be cribbed.

Attempts to precipitate the trifluoride with fluosilicic acid were not successful. A solution containing 20 g/l $\text{Pu}(\text{III})$ and 0.8 M HNO_3 with one mole fluosilicic acid per mole plutonium showed no evidence of solids after four days at room temperature. This behavior is attributed to the less favorable

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oxidation state to atomic radius quotient for Pu(III).

The rate of the fluoride formation with fluosilicic acid is dependent upon the acidity of the solution. Solutions with a nitric acid concentration greater than 1.6 molar are very slow in forming solids. One precipitation with 40 g/l Pu(IV) as the nitrate and 2.2 M HNO₃ gave no solid after 1.5 hours; however, after 16 hours solids were apparent. The reaction was completed by the addition of hydrofluoric acid.

Filtrate losses, as determined with filters having 10 to 15 micron nominal pore size varied from 0.4 to 1.0 g/l plutonium with various concentrations of excess hydrofluoric acid. The fluoride cake was readily washed with 0.5 M to 1.0 M HF and 0.5 M HF - 2.0 M HNO₃ with no evidence of peptizing. Wash losses of ca. 0.1 g/l plutonium were obtained.

Homogeneous precipitation of PuF₄ · 2.5 H₂O with fluosilicic acid as described, produces powders with greater purity than PuF₄ · 2.5 H₂O prepared by precipitation with aqueous hydrofluoric acid. The literature reports no separation of aluminum and iron in the precipitation step with hydrofluoric acid precipitated fluoride. The fluoride produced by the successive fluosilicic acid and hydrofluoric acid additions has produced separation factors of 80 for aluminum with feed concentration of 8000 ppm aluminum, and greater than 100 for iron with feed concentration greater than 20,000 ppm iron. The fluoride cake content was 200 ppm iron. Samples of the fluoride were converted to oxide for impurity analyses on the emission spectrograph by heating the fluoride at 500 C for one hour in moist air. Silicon analyses of 50 ppm have been obtained for hydrofluoric acid washed fluorides. X-ray diffraction data have shown the precipitated compound to be PuF₄ · 2.5 H₂O with no evidence of fluosilicate structure. Chemical analyses have shown a plutonium-to-fluoride ratio of one to four.

The PuF₄ · 2.5 H₂O can be dried in anhydrous hydrogen fluoride at 350 C and reduced satisfactorily to metal. Drying of the fluoride in inert gases produces mixtures of PuF₃ and PuO₂ in quantities dependent upon the drying conditions.

The effects of temperature upon crystallinity (filterability) and rate of precipitation have not been investigated.

The plutonium bulk density of the precipitated fluoride, as filtered, was ca. 0.4 g/cc.

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Spectrochemical Data on a Typical PuF₃ · 2.5 H₂O Prepared Homogeneously

<u>Element</u>	<u>Feed ppm (1)</u>	<u>Fluoride (2) ppm</u>	<u>Metal ppm</u>
Al	8000 (3)	~130	130
Ca	320	10	25 (4)
Cr	4000	50	200
Fe	>20,000	200	50
Mg	1000	10	100 (5)
Mn	2000	5	50
Ni	2000	200	50
Si	1000	2 to 500 (6)	5 (5)

- (1) Parts impurity per million parts plutonium.
- (2) The precipitated fluoride washed with 0.5 M HF - 2.0 M HNO₃, dried in anhydrous HF at 350 C for one hour. Reduced with Ca, and I₂ used as a booster.
- (3) One run made with 10,000 ppm Al added to this feed. Spectrochemical assay indicated less than 100 ppm Al in the fluoride after it was water-washed and heated at 500 C for conversion to oxide of spectrochemical analyses.
- (4) Calcium used as the reductant.
- (5) Magnesium oxide used for the reduction and they have ca. one per cent silicon by weight.
- (6) Some evidence of HF wash lowering Si content.

Equations for PuF₃ · 2.5 H₂O Precipitation

1. $\text{H}_2\text{SiF}_6 = 2 \text{H}^+ + \text{SiF}_6^-$ $K = 7$
2. $\text{SiF}_6^- + 2\text{H}_2\text{O} = \text{SiO}_2 + 4\text{H}^+ + 6\text{F}^-$ $K = 2 \times 10^{-27}$
3. $3\text{Pu}(\text{NO}_3)_4 + 2 \text{H}_2\text{SiF}_6 + x\text{H}_2\text{O} = 3 \text{PuF}_4 + 2 \text{SiO}_2 \cdot \frac{x}{2} \text{H}_2\text{O} + 4 \text{HNO}_3$
4. $\text{SiO}_2 \cdot x \text{H}_2\text{O} + 6\text{HF} = \text{H}_2\text{SiF}_6 + (x+2) \text{H}_2\text{O}$

Reference:

- (1) Wendell M. Latimer, Oxidation Potentials, Prentice Hall, Inc., New York, New York, 2nd edition, 1953.

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