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**PRECIPITATION OF URANIUM AMMONIUM FLUORIDE
FROM UNH SOLUTIONS AS AN INTERMEDIATE IN
THE PREPARATION OF URANIUM TETRAFLUORIDE**

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BY

W. B. TOLLEY

**FILE TECHNOLOGY SECTION
ENGINEERING DEPARTMENT**

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By

W. B. Tolley

Pile Metallurgy Unit
Metallurgy Research Sub-Section

February 1, 1955

HANFORD ATOMIC PRODUCTS OPERATION
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PRECIPITATION OF URANIUM AMMONIUM FLUORIDE
FROM UNH SOLUTIONS AS AN INTERMEDIATE IN
THE PREPARATION OF URANIUM TETRAFLUORIDE

I. INTRODUCTION

Massive uranium metal is currently prepared at the Fernald FMPC plant by reduction of uranium tetrafluoride with magnesium in a hermetically sealed reactor. High purity uranium is obtained which is then cleaned, re-melted and formed into slug material in rolling mills. The UF_4 feed material is prepared by the following procedures. Raw material is sampled and then digested with 55 per cent nitric acid at 95 C which yields uranium containing slurry in free nitric acid. This slurry is sent to a pulse column solvent extraction system "Slurex Process" which produces a UNH stream, the OK liquor. Granular uranium trioxide is prepared from the OK liquor by boil down and denitrification. The uranium trioxide is converted to uranium tetrafluoride in the "Green Salt Plant" first by reduction with dissociated ammonia at 650 C to uranium dioxide and then by hydrofluorination of the dioxide with anhydrous hydrogen fluoride at temperatures of 375 to 625 C. Since the hydrofluorination step is completed at a temperature of 625 C in the presence of water vapor the corrosion problem may become serious.

II. OBJECTIVES

The objectives of this investigation were to study and develop an alternate method of preparing uranium tetrafluoride by precipitation from a uranium-containing solution, thereby eliminating a number of steps involved in the present hydrofluorination procedure. Some emphasis was directed to the measurement of waste losses and to the development of suitable wash solutions for the precipitates. It was also practical to perform small-scale reductions of the products using conventional techniques employed at Hanford to determine if any special difficulties

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would arise from using a fluorinated uranium compound prepared by means other than hydrofluorination.

III. SUMMARY AND CONCLUSIONS

Uranyl solutions can be reduced with ferrous ion in the presence of fluoride, precipitating a uranium (IV) fluoride. Uranium tetrafluoride prepared in this manner is difficult to filter and wash and generally is not suitable as an intermediate. Dehydration can only be accomplished in a hydrogen fluoride atmosphere at elevated temperatures, thereby incorporating the difficulties experienced in the hydrofluorination process. However, uranyl nitrate solutions reduced in the presence of ammonium bifluoride or ammonium fluoride yield a double salt, uranium ammonium fluoride, which exhibits excellent precipitate characteristics. This compound can be decomposed at 375 C to uranium tetrafluoride and volatile ammonium fluoride. The ammonium fluoride is easily trapped and can be recycled for subsequent precipitations. Uranium tetrafluoride prepared by precipitation from uranyl nitrate solutions has been reduced in an hermetically sealed bomb by reaction with calcium. Reduction yields of approximately 80 per cent were realized on a twenty gram scale. During reduction the co-precipitated iron is concentrated in the uranium.

IV. DISCUSSION

Several half-gram batches of uranium tetrafluoride were prepared by reduction of UNH solutions in the presence of hydrogen fluoride. Filtering was slow and serious peptization occurred during washing. In general, uranium tetrafluoride prepared from aqueous solutions is difficult to handle. Precipitations of the tetrafluoride were discontinued for these reasons and attention was centered on the ammonium uranium double salt.

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A. Preparation of Uranium Ammonium Fluoride

A previous report⁽¹⁾ has indicated that uranyl sulfate solutions can be reduced to uranium (IV) with ferrous ion in the presence of fluoride. Preliminary work at Hanford⁽²⁾ has shown that uranyl nitrate is also a suitable starting material.

1. Reduction to Uranium (IV) and Precipitation

Several reducing agents for reduction of UNH to uranium (IV) were tested. Stannous ion reacts slowly⁽³⁾ while sulfur dioxide did not visibly reduce U(VI) either with or without fluoride present. Although the rate of reaction of stannous ion is greatly accelerated if sulfur dioxide is introduced, ferrous ion in the presence of fluoride appeared to be the most promising method of chemical reduction and was used in the following experiments. The best results were obtained when the ammonium bifluoride was dissolved in a 0.3 molar solution of UNH. The precipitation was carried out at room temperature by slowly adding an aqueous solution of ferrous chloride. In all runs 175 per cent excess ammonium bifluoride was used as the precipitating agent. However, this excess can probably be reduced to less than 30 per cent with equally efficient precipitations. When a concentrated solution of UNH was employed, $UF_4(NH_4F)_{0.4}$ was precipitated instead of the true double salt. However, this compound appeared as satisfactory in all respects as the double salt. In runs six and seven reverse strikes were made. A 1.83 molar UNH solution was added to a solution of ferrous chloride and ammonium bifluoride, making the overall solution 0.3 molar in UNH. Iron contamination was higher and waste losses were excessive, probably due to fines which could not be filtered. The product filtered rapidly and otherwise appeared satisfactory.

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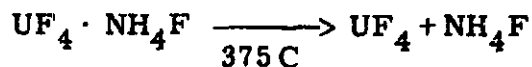
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2. Washing and Drying

● With the exception of runs six and seven, waste losses during precipitation were of the order of 0.01 to 0.02 per cent uranium. However, during washing in dilute acids waste losses were about two per cent. In order to obtain a satisfactory wash solution in which the compound has a low solubility the solubility of $\text{UF}_4 \cdot \text{NH}_4\text{F}$ in various concentrations of aqueous ammonium bifluoride was determined. Although equilibrium solubilities were not obtained, they are indicative of what may be expected during washing. The solubilities of the double salt in 1.0 to 0.5 molar ammonium bifluoride are approximately 0.2 g/l uranium. In the range 0.5 to 0.1 molar ammonium bifluoride the solubilities are slightly lower, 0.2 to 0.1 g/l uranium. ● Below 0.1 molar bifluoride the solubility of the double salt increases rapidly. Solutions of 0.2 molar ammonium bifluoride should prove satisfactory for washing this salt. Waste losses in the above solution would lie between 0.1 and 0.4 per cent uranium. The precipitate is crystalline and can be easily filtered or centrifuged. It does not tend to peptize during handling. Complete drying is easily accomplished by washing with ether followed by air drying on a sintered filter.

B. Decomposition of the Double Salt

The thermal decomposition of the anhydrous uranium ammonium fluoride has previously been studied. ⁽⁴⁾ The double salt was decomposed in vacuo at a temperature of 375 to 400 C. Volatile ammonium fluoride was easily and efficiently collected in a cold trap.



Uranium tetrafluoride prepared in this manner is free flowing with an average bulk density of 1.5 g/cm³. Approximately one-half per cent iron contamination is present in the product with small amounts of ammonium fluoride.

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C. Reduction to the Metal

The uranium tetrafluorides were reduced in a 50-gram size hermetically sealed steel reaction bomb. A magnesia crucible was used as a liner. Ground calcium metal was used as the reductant and an iodine-calcium booster was employed to aid in the button coalescence by lowering the melting point of the slag and by adding additional heat to the charge. Reaction was initiated by heating the bomb in a 1000 C resistance furnace. The time of firing was determined by a thermocouple in a well on the side of the bomb. The bomb was heated several minutes after reaction had occurred. Ratios of 0.4 to 0.6 moles of iodine-calcium booster per mole of uranium were used. The button yields were lower than expected averaging 81.6 per cent. Although as much as 0.26 mole of NH_4F was present per mole of UF_4 in one charge no excessive pressures were obtained during reduction. On large-scale reductions it is felt that the metal recovered can certainly be increased to essentially 100 per cent. However, it is apparently impossible to wash co-precipitated iron from the double salt and during reduction the iron is concentrated in the uranium metal. Using ferrous salts for the reduction of uranyl nitrate to uranium (IV) this situation evidently cannot be avoided.

Run	UNH Molarity	Double Salt	Composition Decomposed Product	Button Yield Per Cent
1	0.3	$\text{UF}_{4.18}(\text{NH}_4\text{F})_{1.13}$	$\text{UF}_{4.0}(\text{NH}_4\text{F})_{0.26}$	83.0
2	0.5	$\text{UF}_{4.2}(\text{NH}_4\text{F})_{1.02}$	Leak in decomposition reactor, product oxidized badly.	Not reduced
3	0.58	$\text{UF}_{4.07}(\text{NH}_4\text{F})_{1.13}$	$\text{UF}_{3.97}(\text{NH}_4\text{F})_{0.15}$	No button obtained
4	1.0	$\text{UF}_{4.12}(\text{NH}_4\text{F})_{1.08}$	$\text{UF}_{3.92}(\text{NH}_4\text{F})_{0.12}$	75.3
5	1.83	$\text{UF}_{4.04}(\text{NH}_4\text{F})_{0.41}$	$\text{UF}_{4.1}(\text{NH}_4\text{F})_{0.017}$	86.7
6*	0.3	$\text{UF}_{4.11}(\text{NH}_4\text{F})_{1.22}$	--	--
7*	0.3	$\text{UF}_{4.51}(\text{NH}_4\text{F})_{1.21}$	--	--

* The double salts of runs 6 and 7 were not decomposed and reduced to the metal.

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ABSTRACT

Uranium (IV) ammonium fluoride can be precipitated from uranyl nitrate solution quantitatively. Ferrous salts in the presence of ammonium and fluoride ions reduce the uranium to the four state, simultaneously precipitating the double salt. This compound can be decomposed in vacuo at 375 C, yielding uranium tetrafluoride. Reduction of the tetrafluoride with calcium by the bomb technique gives satisfactory metal yields; however, co-precipitated iron impurities are concentrated in the uranium button.

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