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# PREPARATION OF SODIUM URANIUM(IV) FLUORIDE FROM AQUEOUS URANYL NITRATE BY IRON(II) REDUCTION

BY

E. J. WHEELWRIGHT

HANFORD LABORATORIES OPERATION

MARCH 5, 1957

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Chemical Research  
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PREPARATION OF SODIUM URANIUM(IV) FLUORIDE  
FROM AQUEOUS URANYL NITRATE BY IRON(II) REDUCTION

I. INTRODUCTION

• Anhydrous uranium tetrafluoride is presently prepared from aqueous uranyl nitrate by a three-step process which involves (1) evaporation and denitrification, (2) reduction of uranium trioxide to uranium dioxide, and (3) fluorination with hydrogen fluoride at elevated temperature. Because of the temperature and the presence of water vapor, the fluorination step is subject to serious corrosion problems.

• The uranium tetrafluoride so produced can either be reduced to massive uranium metal by magnesium or converted to the hexafluoride with elemental fluorine.

The objective of this research was to investigate possible competitive methods of directly preparing, from uranyl nitrate solution, a uranium salt which could be subsequently reduced to the massive metal or fluorinated to uranium hexafluoride. Emphasis was placed on minimizing the number of operational steps and simplifying the process so as to reduce operational maintenance and manpower needs to a minimum.

The reduction of uranyl nitrate by iron(II) and the concurrent precipitation of uranium(IV) fluoride salts has been reported by W. B. Tolley<sup>(1,2)</sup>, but a detailed study of the precipitation conditions was

- (1) Tolley, W. B., Precipitation of Uranium Ammonium Fluoride from UNH Solutions as Intermediate in the Preparation of Uranium Tetrafluoride, HW-35814, February 1, 1955 (Secret).
- (2) Tolley, W. B., A Process for the Preparation of Uranium(IV) Fluorides from Aqueous Uranyl Nitrate, HW-39087, September 19, 1955 (Unclassified).

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not made. In six runs, Tolley was able to prepare uranium fluoride salts in which the iron contamination ranged from 0.19 per cent to 0.84 per cent and averaged 0.33 per cent. The minimization or elimination of this iron contamination seemed both feasible and desirable.

## II. SUMMARY AND CONCLUSIONS

Anhydrous sodium uranium(IV) fluoride can be prepared from aqueous uranyl nitrate solutions by the use of iron(II) chloride in the presence of excess fluoride ion. The sodium uranium(IV) fluoride ( $\text{NaUF}_5$ ), contaminated with iron, can be purified by a process which includes the conversion of the fluoride salt to uranium(IV) hydroxide, dissolution of the hydroxide in sulfuric acid, and reprecipitation of iron-free  $\text{NaUF}_5$ . The entire process can be carried out at room temperature in plastic lined tanks.

Iron contamination of the  $\text{NaUF}_5$  obtained by the concurrent reduction of uranyl nitrate and precipitation with hydrofluoric acid ranged from 2160 to 4500 ppm of uranium for nine experimental runs, and averaged 3200 ppm of uranium. In four reprecipitation runs using  $\text{NaUF}_5$  contaminated by iron to the extent of 3600 ppm of uranium and one run using  $\text{NaUF}_5$  containing 4500 ppm as starting feed, the iron contamination of the reprecipitated salts ranged from 75 to 135 ppm of uranium and averaged 100; the average iron decontamination factor was 40.

Decontamination from a group of non-radioactive metallic ions commonly found in plant streams was found to be very good. However, beta and gamma decontamination factors obtained by the process were only 3 and 11, respectively.

Since iron(II) is not a strong reducing agent, it is necessary to add approximately three moles of hydrofluoric acid per mole of iron in excess of the five moles of hydrofluoric acid per mole of uranium necessary to precipitate the  $\text{NaUF}_5$  salt. The excess fluoride strongly complexes iron(III) and shifts the reduction potential of the iron(II) - iron(III) couple to a more favorable value.

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The process as described in this report is not economically competitive at the present time because of the large excess of hydrofluoric acid necessary for the complete reduction of uranyl nitrate by iron(II). The process would, however, be economically feasible if the cost of hydrofluoric acid should decline or if a suitable recovery system could be devised.

### III. DISCUSSION

The process for the chemical preparation of sodium uranium(IV) fluoride described in this report involves four distinct steps. They are as follows:

1. The reduction of uranyl nitrate by iron(II) in the presence of hydrofluoric acid and the simultaneous precipitation of the reduced uranium as the sodium uranium(IV) fluoride double salt.
2. The solid state metathetical conversion of sodium uranium(IV) fluoride to uranium(IV) hydroxide by aqueous sodium hydroxide.
3. Dissolution of uranium(IV) hydroxide in sulfuric acid.
4. The reprecipitation of sodium uranium(IV) fluoride by the concurrent addition of aqueous uranium(IV) sulfate and hydrofluoric acid to a sodium chloride solution.

If the product obtained from step 1 is of adequate purity for subsequent processing, i. e., reduction to metal or conversion to uranium hexafluoride, the remaining three steps would be superfluous.

#### A. Reduction and Precipitation

The procedure for the preparation of insoluble sodium uranium(IV) fluoride involves the slow addition of an aqueous iron(II) chloride-hydrofluoric acid solution to a well stirred aqueous uranyl nitrate solution containing sodium chloride or sulfate. Experiments have been conducted using solution concentrations ranging from 0.2 to 0.6 molar in uranyl nitrate. Although the exact uranium concentration is not critical, the ratio of the concentrations of fluoride, sodium and iron(II) to uranium is very important.

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The effect of hydrofluoric acid concentration on the completeness of reduction was studied in a series of eight experiments. The iron(II), sodium and uranium concentrations were kept constant. The iron(II) was 15 per cent in excess of the amount required to reduce all of the uranium; sodium was three times the uranium concentration; and the hydrofluoric acid was varied from 5 to 14 moles per mole of uranium. In each experiment, 1200 ml of solution, containing 2.3 moles of iron(II) chloride and various amounts of hydrofluoric acid, was added at a rate of 500 ml per hour to two liters of a stirred solution containing one mole of uranyl nitrate and three moles of sodium chloride. The resulting slurry was stirred overnight to ensure a maximum reduction of the uranyl nitrate. The precipitate was then allowed to settle, the aqueous supernate decanted off, and the precipitate washed three times by decantation using 600 ml of 0.2 molar sodium fluoride each time. In each case the per cent reduction was determined from the uranium analysis of the supernate and wash solutions. The results are shown in Table I.

TABLE I  
THE EFFECT OF EXCESS HYDROFLUORIC ACID UPON THE  
REDUCTION OF URANYL NITRATE BY IRON(II) CHLORIDE

<u>Mole Ratio</u> <u>HF/U</u>	<u>% of U in</u> <u>Supernate</u>	<u>% of U in</u> <u>Wash</u>	<u>% U Reduced</u>
5	36	2.7	61
7	22	3.2	75
9	4.2	0.60	95
10	0.50	0.08	99
11	0.15	0.10	99.75
12	0.06	0.06	99.88
13	0.02	0.06	99.92
14	0.01	0.05	99.94

These results indicate that 140 to 160 per cent excess hydrofluoric acid must be used to ensure complete reduction and consequent recovery of uranium. The excess hydrofluoric acid is needed to complex the iron(III) ion and shift the potential of the Fe(II) - Fe(III) couple to a more favorable value. ●

A series of experiments was conducted to determine what effect changes in uranium feed concentration would have upon the amount of iron occluded by the product and upon the tap density of the product. Both sodium chloride and sodium sulfate were used as sodium ion sources. In each experiment, the molar ratios of sodium, fluoride and iron(II) to uranyl were maintained at 3:1, 14.2:1, and 2.3:1 respectively. The information obtained from these experiments is presented in Table II. It will be noted that the tap density and iron content of the product are but little affected by replacement of sodium chloride with sodium sulfate. However, an increase in the uranium concentration of the feed solution (and a corresponding increase in the iron concentration) resulted in a slight increase in the amount of iron occluded in the final product. That the sodium uranium(IV) fluoride product is  $\text{NaUF}_5$ , within the limits of analysis, is shown in Table III.

TABLE II

THE EFFECT OF THE URANIUM CONCENTRATION  
UPON IRON CONTAMINATION OF  $\text{NaUF}_5$

Run No.	Source of Na	Uranium Conc. in Feed (molar)	Moles of U Involved	Product Tap Density gms/cc	% Iron in Product
11-II	$\text{Na}_2\text{SO}_4$	0.24	0.12	1.0	0.16
12-I	$\text{NaCl}$	0.24	0.48	1.6	0.14
12-V	$\text{NaCl}$	0.24	0.12	1.2	0.16
12-VI	$\text{NaCl}$	0.24	0.12	1.0	0.19
12-VII	$\text{NaCl}$	0.24	0.12	1.1	0.19
2-I	$\text{NaCl}$	0.50	1.0	1.4	0.24
2-II	$\text{Na}_2\text{SO}_4$	0.50	1.0	1.6	0.30
2-III	$\text{NaCl}$	0.59	1.0	1.3	0.24
2-IV	$\text{Na}_2\text{SO}_4$	0.59	1.0	1.5	0.30

All of the reduction-precipitation runs were conducted at room temperature. No kinetic studies were made, but visual observation indicated that reduction was 95 - 98 per cent complete in 30 minutes and reached completion in one to two hours when the hydrofluoric acid to uranium ratio was 13 or 14 to one. In these experiments, the product salt was washed three times by decantation using 400 to 600 ml of a dilute sodium chloride-hydrofluoric acid wash solution (0.1 to 0.2 molar in each) each time, and then dried at 110 C for 16 hours. The salts had excellent physical properties.

TABLE III

COMPOSITION OF SODIUM URANIUM(IV) FLUORIDE  
PRODUCT FROM TYPICAL REDUCTION-PRECIPITATION RUNS

<u>Run No.</u>	<u>% U</u>	<u>% Na</u>	<u>% F</u>	<u>F/U</u>	<u>Na/U</u>
11-II	68	7.3	26	4.8	1.11
12-I	67	6.9	26	4.9	1.06
12-V	67	7.3	26	4.9	1.13
12-VI	69	7.4	26	4.7	1.11
12-VII	70	7.3	25	4.5	1.08
2-I	70	7.0	26	4.7	1.04
2-II	70	6.9	26	4.7	1.02
2-III	70	7.0	26	4.7	1.04
2-IV	68	7.1	25	4.6	1.08

B. Metathetical Preparation of Uranium(IV) Hydroxide

Sodium uranium(IV) fluoride, prepared as described in the previous section, can be easily and quickly converted to insoluble uranium(IV) hydroxide by slurring it in a sodium hydroxide solution for 20 to 30 minutes. Only a small excess of sodium hydroxide is necessary.

Excellent results have been achieved using sodium hydroxide concentrations ranging from 1 to 5 molar. The hydroxide precipitate prepared in this manner is quite crystalline and settles rapidly. A single decantation

wash with 0.1 molar sodium hydroxide is sufficient to remove the fluoride ion and render the precipitate soluble in sulfuric acid. In a working process, the hydroxide mother liquor and wash solutions would be recycled to the reduction - precipitation step to conserve fluoride.

C. Dissolution of Uranium(IV) Hydroxide

Uranium(IV) hydroxide, which has been washed free of fluoride, can be easily and quickly dissolved in sulfuric acid. Acid concentrations ranging from 0.6 to 2.2 molar have been used. The less concentrated solutions require two to three hours to complete the dissolution. In the more concentrated solutions, enough reaction heat is liberated to increase the reaction temperature from room temperature to 50 - 60 C, and the dissolution is complete in about ten minutes.

Some reoxidation takes place during this step and results in a diminished yield in the reprecipitation of the double fluoride. In eight runs, the uranium content of the supernate after precipitation of all of the uranium(IV) as  $\text{NaUF}_6$  ranged from 1.9 to 4.9 per cent and averaged 3.2 per cent. This information is summarized in Table IV. Moderate heating during dissolution did not increase the extent of oxidation. A two to three per cent oxidation of the uranium would not be serious since recycling the uranyl fluoride supernate to the iron reduction - precipitation step (as a hydrofluoric acid economy measure) would result in its recovery.

TABLE IV

URANIUM OXIDATION DURING DISSOLUTION

<u>Run No.</u>	<u>Temperature</u>	<u>Grams of Uranium Involved in Run</u>	<u>Per Cent of Uranium Oxidized</u>
1-I	25	93	3.4
1-II	25	29	4.9
1-III	50 - 60	166	1.9
3-I	40 - 50	60	3.4
3-II	40 - 50	60	3.3
3-III	40 - 50	60	2.5
3-IV	40 - 50	60	3.2
3-V	40 - 50	60	2.8



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D. Reprecipitation of  $\text{NaUF}_5$

The physical properties and, to a limited extent, the iron decontamination depend upon the conditions under which the fluoride salt is reprecipitated. The sodium ion concentration must be sufficiently high in the immediate region of the formation of the  $\text{NaUF}_5$  particles to prevent the formation of hydrous  $\text{UF}_4$ . Best results have been obtained under conditions such that the sodium ion concentration is high, while both the uranium and fluoride ion concentrations are low. This can be accomplished by adding uranium(IV) sulfate (obtained from the sulfuric acid dissolution of the hydroxide) and dilute hydrofluoric acid from two separate sources, and at a molar ratio of 1:5, to a well stirred sodium chloride or sodium sulfate solution. Slight modifications of this general procedure such as adding part or all of the sodium along with the uranium(IV) sulfate solution have been examined, but the product obtained is less desirable. If the reprecipitation is carried out at 70 - 80 C, the sodium uranium(IV) fluoride is precipitated as larger crystals than when the precipitation is done at room temperature. Of course, the larger crystals result in a product of lower tap density. Data from some typical experiments are given in Table V on the following page.

Under the conditions described above, the product which is obtained is a dense crystalline salt which settles rapidly and can be washed by decantation if desired. The mother liquor from the precipitation contains the 10 to 15 per cent excess fluoride added to ensure a complete precipitation and the reoxidized uranium produced in the sulfuric acid dissolution step. In a plant process, this solution would be recycled to the initial reoxidation - precipitation step.

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TABLE

THE EFFECT OF THE METHOD OF REPRECIPITATION UPON THE QUALITY OF THE NaUF<sub>5</sub> PRODUCT

Run No.	Temp. C	Iron ppm of Uranium	Iron Decantation Factor	Tap Density gms/cc	Solution A	Solution B	Solution C
3-8	25	135	27	0.9	HF	U(SO <sub>4</sub> ) <sub>2</sub> + Na <sup>+</sup>	H <sub>2</sub> O
3-13	25	90	40	0.6	HF	U(SO <sub>4</sub> ) <sub>2</sub> + 1/2 Na <sup>+</sup>	1/2 Na <sup>+</sup>
3-21	25	76	43	1.6	HF	U(SO <sub>4</sub> ) <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>
3-24	25	97	37	1.8	HF	U(SO <sub>4</sub> ) <sub>2</sub>	NaCl
3-28	70-80	105	49	0.7	HF	U(SO <sub>4</sub> ) <sub>2</sub>	Na <sup>+</sup>

\* In each experiment, Solutions A and B were added concurrently to stirred Solution C at rates of about 500 ml per hour. In each case, a 200 per cent excess of sodium ion was used and the relative concentrations of A and B were adjusted such that the uranic and fluoride ions would combine at a molar ratio of 1:5.

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E. Process Decontamination

The process has been examined from the standpoint of decontamination of various non-radioactive metallic ions. In one run, Cu, Cr, Co, Ni, Mn, Sn, Al, and Mg were each added to an aqueous uranyl nitrate solution to the extent of 1000 ppm of uranium. The uranium was then reduced and precipitated as  $\text{NaUF}_5$ . The product was spectrographically free from Cr, Co, Ni, Mn, Mg, and Cu; but contained 150 ppm Sn and 20 ppm Al. The tin and aluminum were completely removed by the reprecipitation process.

Several runs have been conducted using Purex 2DF solution as the starting feed material. Beta and gamma decontamination factors of 3 and 11 were obtained for the complete process. It was found that the addition of a trace of ethylenediaminetetraacetic acid to the uranium(IV) sulfate solution prior to reprecipitation improved the gamma decontamination by a factor of two but did not affect the beta decontamination.

  
E. J. Wheelwright

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