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THE USE OF METALLIC IRON IN THE PREPARATION OF URANIUM(IV) FLUORIDE SALTS FROM URANYL SULFATE

E. J. WHEELWRIGHT

FEBRUARY 26, 1957

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THE USE OF METALLIC IRON IN THE PREPARATION OF URANIUM(IV) FLUORIDE SALTS FROM URANYL SULFATE

I. INTRODUCTION

In an attempt to circumvent the large excess of hydrofluoric acid needed for a satisfactory reduction of uranyl nitrate by iron(II) chloride(1), several experiments were conducted using the much stronger reducing agent, powdered metallic iron. Unfortunately, the nitrate ion is also easily reduced by metallic iron. This causes the yield of uranium(IV) to be unsatisfactorily low due to the great amount of reoxidation of the uranium(IV) by reduced nitrate species. A preliminary conversion of uranyl nitrate to uranyl sulfate, followed by the reduction of the uranyl sulfate to uranium(IV) sulfate by powdered iron offered an attractive solution to the problem.

II. OBJECTIVE

The objective of this research was to determine the conditions under which uranyl sulfate could be reduced to uranium(IV) by metallic iron, and to determine the minimum amount of hydrofluoric acid necessary for complete recovery of the uranium from the sulfate solution as sodium uranium(IV) fluoride.

III. SUMMARY AND CONCLUSIONS

Anhydrous sodium uranium(IV) fluoride ($NaUF_5$) can be prepared from aqueous uranyl nitrate by a process which involves the following three steps:

1. The cation-exchange conversion of aqueous uranyl nitrate to aqueous uranyl sulfate.

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(1) Wheelwright, E. J., "The Preparation of Sodium Uranium(IV) Fluoride from Aqueous Uranyl Nitrate by Iron(II) Reduction," HW-45139, March 5, 1957 (Confidential).

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2. The reduction of uranyl sulfate to uranium(IV) sulfate by the action of powdered iron in 0.05 molar sulfuric acid solution.

3. The precipitation of the desired salt by the concurrent addition of hydrofluoric acid and uranium(IV) sulfate to a stirred sodium chloride solution.

The operations and reactions described in steps 2 and 3 have been investigated and demonstrated by the author. The operations and reactions involved in step 1 have been investigated at Oak Ridge.(2, 3) Since the ion-exchange step is a simple operation, the equipment inexpensive, and sulfuric acid the only chemical necessary, the nitrate to sulfate conversion should cost only two or three cents per pound of uranium and would be expected to give considerable decontamination.

Uranyl sulfate can be easily and quickly reduced to uranium(IV) sulfate by the addition of powdered metallic iron and dilute sulfuric acid to a uranyl sulfate solution. Only 15 to 20 per cent excess hydrofluoric acid is necessary for the recovery of 99.9 per cent of the uranium(IV) as the anhydrous sodium uranium(IV) fluoride salt. The average iron contamination of the product was 118 ppm of uranium. The chemical costs for steps 2 and 3 of the process would be approximately $300 per ton of uranium.

IV. DISCUSSION

The Reduction of Uranyl Sulfate

When metallic iron and aqueous uranyl sulfate are mixed together under acid conditions, two reactions can take place. The iron can reduce the uranyl ion to uranium(IV), or it may reduce the hydrogen ion to elemental hydrogen. In the experiments conducted during the course of this research, conditions were chosen to minimize hydrogen formation; namely, a low acid concentration and a low reduction temperature.

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(2) Overholt, D. C., D. A. Orth, F. W. Tober, R. H. Rainey, and D. G. Karraker, "Progress Report No. IV. Ion-Exchange Isolation Processes for Plutonium and Uranium." ORNL-1585, October 23, 1953 (Secret).

(3) Higgins, I. R. and J. T. Roberts, "Development of the Excer Process I." ORNL-1696, April 13, 1956 (Confidential).

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The reductions were achieved by adding 0.345 moles of powdered iron (a 15 per cent excess) and 100 milliliters of six molar sulfuric acid simultaneously and in small increments to 1000 milliliters of 0.3 molar uranyl sulfate. No difficulty was experienced in controlling the reaction rate and acidity. The simple procedure used was to add the powdered iron at a predetermined rate, monitor and pH of the solution, and add acid as needed to keep the pH at a value of 1 ± 0.3. If the additions took place over a 20 to 30 minute period, the solution temperature did not exceed 38 C. It was not determined whether acidities in excess of pH 1 or temperature higher than 38 C would be particularly detrimental to the reduction yield.

In the experiments conducted, the excess unoxidized iron was removed by filtration prior to the precipitation step. On a production scale, this step would be ideally performed by centrifugation since the volume of liquids would be quite large and the amount of solid residue very small.

The Precipitation of $NaUF_5$

The experimental scale precipitations were accomplished by simultaneously adding the filtered uranium(IV) sulfate solution and dilute hydrofluoric acid to 200 milliliters of a stirred solution of 1.8 molar sodium chloride. The concentration of the hydrofluoric acid and the rates of addition of the uranium and hydrofluoric acid solutions were such that uranium(IV) and fluoride were combined in a molar ratio of 1:5 in the presence of an excess of sodium ion. This method of precipitation minimizes the concentration of both fluoride and uranium(IV) in solution and prevents the formation of hydrous uranium tetrafluoride.

The sodium uranium(IV) fluoride precipitated by the above method is dense and crystalline and can be separated from the mother liquid by decantation. In the experimental runs, the salt was washed by decantation three times with a 0.2 molar sodium chloride-hydrofluoric acid wash

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solution; then dried with alcohol, petroleum ether, and finally in an oven at 150 C.

A series of five experiments was performed to determine the minimum amount of hydrofluoric acid needed to completely precipitate the uranium from uranium(IV) sulfate solutions as $NaUF_5$. Uranium(IV) sulfate, which had been reduced from uranyl sulfate as previously described, was precipitated by various amounts of hydrofluoric acid. The completeness of reduction and precipitation was ascertained by determining the total uranium content of the aqueous supernate solution from which the $NaUF_5$ had been precipitated. The results are presented in Table I.

TABLE I

THE EFFECT OF EXCESS HYDROFLUORIC ACID UPON THE RECOVERY OF URANIUM(IV)

	Run 10-I	Run 10-II	Run 10-III	Run 10-IV	Run 9-IV
% excess HF used in precipitation	0	5	10	15	20
% loss of uranium	3.4	0.42	0.84(?)	0.14	0.06
Tap density of $NaUF_5$ (gms/cc)	1.59	1.60	1.03	1.04	1.43
Iron contamination of $NaUF_5$ (ppm of uranium)	100	128	128	114	--

The amount of excess hydrofluoric acid needed is determined by the amount of uranium that can be sacrificed to waste. The information given above indicates that 99.9% of the uranium can be recovered by using 15 to 20 per cent excess hydrofluoric acid.

Process Cost Estimates

The chemical costs of producing $NaUF_5$ from uranyl sulfate by this process would be $316 per ton of uranium based upon a cost of $0.24 per

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pound for hydrofluoric acid (anhydrous), $0.085 per pound for powdered iron, and using 15 per cent excess iron for the reduction and 15 per cent excess hydrofluoric acid in the precipitation step. The cost would be advanced to $326 per ton if a 20 per cent excess of hydrofluoric acid were needed. The price of hydrofluoric acid could probably be reduced to around $0.20 per pound for a large scale plant process, reducing the chemical cost figures given above to $277 and $286, respectively.

It should be pointed out that hydrofluoric acid is used only in the precipitation step, so the equipment used in steps 1 and 2 need not be fluoride or chloride resistant

Other Uranium(IV) Fluoride Products

Some preliminary experiments have been conducted which indicate the adaptability of this process to the production of other fluoride salts. In one experiment, aqueous uranium(IV) sulfate and hydrofluoric acid were combined in the presence of ammonium sulfate, resulting in the precipitation of ammonium uranium(IV) fluoride. The ammonium salt had a tap density of 1.58 g/cc and contained 114 ppm iron. In this preliminary experiment, 99.48 per cent of the uranium(IV) was recovered when 15 per cent excess hydrofluoric acid was used for the precipitation.

Two experiments have been performed in which hydrated uranium tetrafluoride salts were precipitated. In each case the precipitation was achieved by adding uranium(IV) sulfate solution and hydrofluoric acid to water maintained at 90 C. The iron contents of the resulting hydrated salts were 280 and 171 ppm, respectively. Only 95 per cent of the uranium was recovered in the first experiment and 98.5 per cent in the second experiment. Fifteen per cent excess hydrofluoric acid was used in each experiment. The hydrated salts were very finely divided and had tap densities of 1.8 and 2.2 g/cc, respectively. The uranium recovery could undoubtedly be improved by the use of precipitation conditions more nearly optimum.

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