INORG. NUCL. CHEM. LETTERS Vol. 13, pp. 175-178, 1977. Pergamon Press. Printed in Great Britain.

A NOVEL PREPARATION OF ANHYDROUS UF_4

by

E. R. Russell and M. L. Hyder

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina 29801

(*Received* 2 *August* 1976; *in revised form* 18 *February* 1977)

Uranium is commonly recovered from its ores or from nuclear fuel reprocessing in the hexavalent state as aqueous uranyl ion or a solid oxide compound. Conversion to UF_6 for isotopic enrichment, or to the metal for fuel fabrication, involves a sequence of operations that may include denitration, precipitation, dehydration, high temperature hydrogen reduction, and hydrofluorination to yield anhydrous UF_4 (1). This intermediate may be readily converted to metal or UF_6. We report here a method for the direct production of anhydrous UF_4 by the electrolytic reduction of uranyl formate in the presence of fluoride ion.

Electrolytic reduction of uranium in aqueous solution to produce UF_4-hydrate has been reported by others. Michal (2) dissolved UO_3 in H_2SO_4-HF solution, then precipitated UF_4-hydrate by electrolytic reduction. Higgins, Neill, and McNeese (3) studied continuous electrolytic reduction of uranium from chloride solutions. Both sulfate and chloride solutions require special materials for handling because they corrode stainless steel.

Allen, Anderson, McGill, and Powell (4) have made an extensive study of the low-temperature electrolytic reduction and precipitation of UF_4 from HF solutions. At temperatures below 35°C, the reduction of uranyl ion in the presence of excess HF causes precipitation of $UF_4 \cdot 2.5\ H_2O$. This hydrate could not be dehydrated thermally without oxidation (4). To prepare anhydrous

UF_4, it was first necessary to digest $UF_4 \cdot 2.5\ H_2O$ in boiling water to produce $UF_4 \cdot 0.75\ H_2O$. $UF_4 \cdot 0.75\ H_2O$ was then dehydrated to UF_4 by heating in a nitrogen atmosphere (5).

Formic acid solutions are not corrosive to stainless steel, and uranium(IV) is stable in formic acid solution. Because formate-fluoride solutions are less corrosive than sulfate or chloride-fluoride solutions, we undertook a study of the use of formate-fluoride solutions for the electrolytic reduction of uranyl ion. We previously reported the reduction of uranyl ion by formic acid or formate under various conditions, including the thermal decomposition of solid uranyl formate to UO_2 (6).

RESULTS AND DISCUSSION

Uranyl nitrate was metathesized to uranyl formate by sorption of UO_2^{2+} on "Dowex" 50W* cation exchange resin and elution with 1M formic acid and various concentrations of ammonium formate. (Formic acid is very inefficient in eluting uranium from "Dowex" 50W resin. Addition of ammonium formate to increase the formate complexing action and supply sufficient NH_4^+ to replace UO_2^{++} is necessary.) The solution was adjusted to 2M HF and transferred to a platinum dish for electrolysis. The uranium concentration was about 150 g/l. Electrolysis of $\sim$250 ml at 6V was performed with the dish as cathode. A platinum rod suspended in the solution served as the anode. An emerald green ammonium uranous fluoride double salt deposited at the cathode. Electrolysis was continued until practically all of the uranyl color disappeared and the current decreased to less than one ampere.

The composition of the ammonium fluoride-uranous fluoride salt varied according to the ammonium concentration of the electrolysis mixture. The several compounds produced were identified by x-ray diffraction and are listed in Table I. The formation of the $NH_4F - UF_4$ double salts is influenced by the NH_4^+ concentration

---

* Trademark of Dow Chemical Co.

and temperature (7). Low temperatures during precipitation produce mixtures of the double salts at all NH_4^+ concentrations.

All of the double salts are anhydrous and may be decomposed without oxidation by heating in the absence of oxygen. Anhydrous UF_4 was produced from each salt by slowly heating to 450°C in a nitrogen atmosphere to volatilize NH_4F.

Precipitation of the double salt should provide additional decontamination of the uranium from fission products and other contaminating cations. To test this possibility, and to evaluate the UF_4 product as feed for production of uranium metal, a uranium formate solution was contaminated with approximately 20,000 ppm each of Fe, Al, Zr, Ru, and Cs. Uranium was electrolytically reduced and precipitated as $NH_4U_2F_9$ from a 2M HF – 1M HCOOH – 0.5M $HCOONH_4$ solution. After NH_4F was removed by heating, a 30-gram uranium button (>85% yield) was produced by bomb reduction of the UF_4 with calcium. Emission spectroscopic analysis showed that the product contained ≤0.01% of each contaminant.

ACKNOWLEDGMENT

The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Energy Research and Development Administration.

TABLE I

Reduction and Precipitation of Uranium
(U = 150 grams/liter)
(2M HF)

Elutriant Composition	Temp., °C	Product
HCOOH – $HCOONH_4$		
1M – 1M or less	90	$NH_4U_2F_9$
1M – 1-2M	90	NH_4UF_5
1M – 2M	90	$(NH_4)_2UF_6$
1M – 2M	50	Not identified

REFERENCES

1. S. H. SMILEY and D. C. BRATER. "Conversion of Uranium Trioxide to Uranium Tetrafluoride." *Progress in Nuclear Energy,* Series III, Vol. 2, Process Chemistry, pp 107-121 (1958).

2. EUGENE J. MICHAL. USAEC Report MITG-A35, Massachusetts Institute of Technology, Cambridge, Massachusetts (1947).

3. I. R. HIGGINS, W. J. NEILL, and L. E. McNEESE. USAEC Report ORNL-2490, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1958).

4. A. L. ALLEN, R. W. ANDERSON, R. M. McGILL, and E. W. POWELL. USAEC Report K-680, Union Carbide and Carbon Corporation, K-25 Plant, Oak Ridge, Tennessee (1950).

5. R. W. ANDERSON, A. L. ALLEN, and E. W. POWELL. USAEC Report K-681, Union Carbide and Carbon Corporation, K-25 Plant, Oak Ridge, Tennessee (1950).

6. E. R. RUSSELL and M. L. HYDER. "Thermal Decomposition of Uranyl Formate and the Preparation of Ammonium Uranyl Formate." *Inor. Nucl. Chem. Letters 12* (3), 247-50 (1976).

7. R. A. PENNEMAN, F. H. KRUSE, R. S. GEORGE, and J. S. COLEMAN. *Studies of the Ammonium Fluoride-Uranium Tetrafluoride-Water System. Properties of* $(NH_4)_4UF_8$*,* $(NH_4)_2UF_6$*,* $7NH_4F{\cdot}6UF_4$*, and of U(IV) in Aqueous* NH_4F*.* Inorg. Chem. *3*, 309 (1964).