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HW-35815

# AEC RESEARCH AND DEVELOPMENT REPORT

## CALCIUM URANIUM(IV) FLUORIDE; PRECIPITATION AND REDUCTION TO METAL

By

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CALCIUM URANIUM(IV) FLUORIDE;  
PRECIPITATION AND REDUCTION TO METAL

INTRODUCTION

Uranium metal for fabrication into pile fuel material is currently prepared by the reduction of uranium tetrafluoride with magnesium in an hermetically sealed reactor. This bomb reduction technique, a batch process, is quite efficient. Reduction yields are high and metal purity is satisfactory. Uranium tetrafluoride feed material is prepared from crude uranium ore in several steps. The raw material is digested with 55 per cent nitric acid at 95 C, producing a nitric acid slurry containing uranium nitrate. The "Slurex Process" a pulse column solvent extraction system, uses this slurry and yields a UNH solution called the OK liquor. Uranium trioxide prepared by denitrification of the OK liquor is reduced to uranium dioxide by reaction with dissociated ammonia at 650 C. The dioxide is in turn converted to uranium tetrafluoride by reaction with anhydrous hydrogen fluoride at temperatures of 375 to 625 C.

OBJECTIVES

Previous work in this laboratory has shown that calcium plutonium(IV) fluoride can be precipitated from aqueous solutions, washed, dried, and reduced to the metal.<sup>(1)</sup> Likewise, uranium(IV) ammonium fluoride has been precipitated, decomposed to uranium tetrafluoride, and converted to metal by bomb reduction.<sup>(2)</sup> In both cases easily handled precipitates and satisfactory reduction yields are obtained. The objectives of this investigation were to study the preparation of the double salt calcium uranium(IV) fluoride by precipitation from a uranyl nitrate solution and to study the reduction of this salt to metal by the conventional bomb technique. Since the reduction of uranyl nitrate solution to uranium(IV) and precipitation of the double salt would be accomplished simultaneously, such a process

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would eliminate the denitrification to uranium trioxide, the reduction to uranium dioxide, and the hydrofluorination steps.

SUMMARY AND CONCLUSIONS

Using ferrous ion in the presence of fluoride for reducing uranium(VI) to the four state, the salt calcium uranium(IV) fluoride can be precipitated from uranyl nitrate solutions. X-ray studies have shown that the precipitate is a true double salt and not a mixture of the two insoluble fluorides of calcium and uranium. The salt settles rapidly and can be either filtered or centrifuged. Waste losses during precipitation and washing were on the order of 2.0 and 0.4 per cent, respectively. These waste losses are not primarily solubility losses. During filtration of the supernates some fines were not removed by the sintered glass filter, and post-precipitation was also noticed. The hydrated salt contains approximately one mole of water which can be removed without hydrolysis by drying at 250 C in an atmosphere of deoxygenated argon. Dry calcium uranium fluoride prepared in this manner is free flowing with a bulk density of about 1.25 g/cm<sup>3</sup>.

Calcium reduction by the bomb technique has been demonstrated on a twenty-gram scale with an average metal yield of 96.1 per cent. However, the uranium metal is contaminated with approximately 0.6 per cent iron. The double salt also appears to be a satisfactory feed for electrolytic reduction from a fused salt bath. Needles one to three millimeters long were obtained with a current efficiency of 35 per cent when a 30 per cent solution of the double salt in KCl-LiCl eutectic was electrolyzed at a current density of one ampere per cm<sup>2</sup>. About two grams of metal were recovered which represented 30 per cent of the uranium dissolved in the bath.



DISCUSSION

Previous work has indicated that ferrous ion in the presence of fluoride will reduce uranium(VI) nitrate solutions to the (IV) state. A precipitation of the uranium(IV) fluoride occurs simultaneously. The use of ferrous ion in the presence of fluoride appears to be the most promising method of chemical reduction and was employed in the following experiments.

A. Reduction to Uranium(IV) and Precipitation

All precipitations were carried out at room temperature. A 20 per cent excess of ferrous chloride tetrahydrate was employed over the stoichiometric amount required for reduction while one hundred per cent excess hydrogen fluoride was used in each precipitation. Several methods of carrying out the precipitation were studied. Forty-eight per cent hydrogen fluoride was added slowly to 0.5 and 0.3 M uranyl nitrate solutions in which the calcium and ferrous ions, added as the chlorides, were dissolved. Increasing the uranyl nitrate concentration when precipitating with 48 per cent hydrogen fluoride reduced the ease of handling the precipitate. Double salt precipitated from 0.5 M uranyl nitrate solution proved difficult to filter and peptized badly during washing while that from the 0.3 M solution exhibited much better precipitate characteristics with some peptization occurring. In one run a ten per cent solution of hydrofluoric acid was added to 1.48 M uranyl nitrate in which the ferrous and calcium salts were dissolved. The precipitate was easily washed and dried; however, waste losses during precipitation were about three per cent. When precipitation was carried out with one half mole of calcium per mole of uranium, a precipitate was formed which could not be processed. Peptization occurred which prevented efficient washing. The best precipitating condition tested appears to be a slow addition of 10 to 11 per cent hydrofluoric acid to a solution 0.9 M in UNH in which the proper amounts of calcium and ferrous chlorides have been dissolved. The precipitate is

quite coarse and can be rapidly washed by filtration, decantation, or centrifugation. The product is free flowing with a bulk density of about  $1.25 \text{ g/cm}^3$ . Waste losses during precipitation were about 2.0 per cent uranium. It would be expected that this loss could be considerably reduced by a more detailed study of precipitating conditions. Since waste losses are reasonably low and the precipitate itself is satisfactory, a more detailed study was not undertaken at this time. Results of the precipitations are presented in Table I.

#### B. Washing and Drying

The precipitates were washed with 0.5 M hydrogen fluoride solution. Washing was a simple task as the precipitates settled rapidly and could be filtered on a medium sintered glass filter almost as rapidly as the slurry could be added. Alcohol and ether were used to further dry the salt. The water content of the calcium uranium fluoride after air drying with ether is about 4.0 per cent. However, the double salt can be dehydrated at 250 C under an atmosphere of argon without hydrolysis occurring. Dried calcium uranium fluoride is free flowing and can be reduced to the metal in an hermetically sealed bomb.

#### C. Reduction to Metal

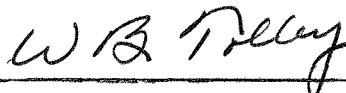
Calcium reductions of the calcium uranium fluorides were made using the bomb technique. One mole of iodine-calcium booster per mole of uranium was employed to aid in the coalescence of a button by lowering the melting point of the calcium fluoride slag and by adding additional heat within the charge. The charges were packed in a magnesia crucible and hermetically sealed in a steel bomb. Reaction was initiated by heating the bomb by induction. Well formed buttons with an average yield of 96.1 per cent were obtained. No special problems were encountered in removing the metal from the slag. The quantity of booster required to obtain high button yields can be reduced as charge size increases, and it would be

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expected that the booster could be eliminated on production size charges. The double salt contains about 0.5 per cent iron. This iron was apparently reduced and coalesced with the uranium, resulting in an average iron impurity of 0.61 per cent in the metal. Since iron is apparently co-precipitated with the double salt, it may be impossible to obtain pure uranium by bomb reduction from calcium uranium(IV) fluoride prepared using ferrous iron as a reductant unless iron can be complexed and extracted or washed from the salts at the time of precipitation. Results of bomb reductions are presented in Table II, while the photograph on page 13 shows the shape and size of some of the metal buttons. The double salt can be used as feed for the electrolytic reduction of uranium to metal. Thirty per cent calcium uranium fluoride was dissolved in lithium chloride-potassium chloride eutectic. A platinum cathode and a graphite anode were employed. The salt was fused and held at 500 C under argon. When electrolyzing at a current density of 1.0 ampere per  $\text{cm}^2$ , the current efficiency was 35 per cent. Approximately thirty per cent of the uranium was recovered as dendritic crystals, one to three mm in length. The iron impurity in the electrolytically reduced uranium was 250 ppm compared to 3400 ppm in the double salt.

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- (1) Branin, P. B., Wet Fluoride Studies: Calcium Plutonium(IV) Fluoride, HW-30039, December 22, 1953 (SECRET).
- (2) Tolley, W. B., Precipitation of Uranium Ammonium Fluoride from UNH Solution as an Intermediate in the Preparation of Uranium Tetrafluoride, HW-35814, February 1, 1955 (SECRET).

TABLE I

RESULTS OF PRECIPITATIONS

Precipitation Conditions

100 per cent excess HF  
 20 per cent excess  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$   
 30 grams uranium per run  
 One mole  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  per mole uranium

Run	HF Conc. Per Cent	UNH Molarity	Pre Cent Waste Loss		Product Composition <sup>b</sup>	Actual Mole Ratio	
			Precipitation	Washing		Ca/U	F/U
1	48	0.3	1.5	0.23	$\text{UCaF}_6 \times 1.1\text{H}_2\text{O}$	0.92	6.21
2	48	0.5	2.6	0.94	$\text{UCaF}_6 \times 0.7\text{H}_2\text{O}$	0.95	5.90
3	9.5	1.48	3.0	0.43	$\text{UCaF}_6 \times 1.2\text{H}_2\text{O}$	0.99	6.02
4	11.5	0.9	0.64	0.59	$\text{UCaF}_6 \times 0.6\text{H}_2\text{O}$	1.05	6.07
5 <sup>a</sup>	9.1	0.9	3.4	0.11	$\text{UCaF}_6 \times 1.1\text{H}_2\text{O}$	0.93	6.10

a 150-gram batch of uranium

b All compounds contain about one-half per cent iron.

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TABLE II

RESULTS OF REDUCTIONS

1.0 mole Ca-I<sub>2</sub> Booster/mole U

30 per cent excess calcium, 20 grams U/reduction

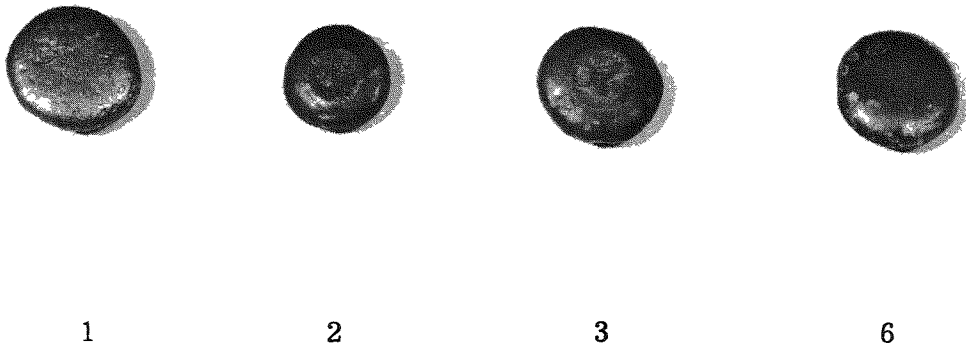
<u>Run</u>	<u>Per Cent Yield</u>	<u>Density</u>	<u>Per Cent Iron</u>
1	99.0	18.32	0.75
2	98.8	18.27	0.78
3	91.4	17.38	0.41
4	99.2	18.29	0.47
5	92.6	--	0.70
6 <sup>a</sup>	95.3	18.19	0.66

a Two twenty-gram reductions were made using salt prepared in run 5.

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URANIUM BUTTONS FROM  $UCaF_6$

Actual Size



Rough surface on buttons 2 and 3 formed by a calcium cap which was dissolved. Average yield was 96.1 per cent.

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ABSTRACT

The double salt calcium uranium(IV) fluoride can be precipitated from uranyl nitrate solution. In the presence of fluoride and calcium ions, ferrous salts will reduce uranium(VI) nitrate to the four state precipitating calcium uranium(IV) fluoride. X-ray studies have shown that the compound is a true double salt. The salt can be dehydrated under argon at 250 C and reduced to metal by the bomb technique. Reduction yields are high, but co-precipitated iron in the salt is concentrated in the uranium button, resulting in iron impurities of approximately 0.6 per cent. The double salt is a suitable feed for fused salt electrolysis. Electrolyzing from a solution of 30 per cent double salt dissolved in LiCl-KCl eutectic dendritic uranium was recovered with a current efficiency of 35 per cent. Iron impurity in the electrolytically prepared uranium was reduced from an expected concentration of 5700 ppm to an actual concentration of 250 ppm.

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