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HW-39087
AEC RESEARCH AND DEVELOPMENT REPORT
METALLURGY AND CERAMICS

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

BY

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PILE TECHNOLOGY SECTION
ENGINEERING DEPARTMENT

SEPTEMBER 19, 1955

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

GENERAL ELECTRIC

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(TID-4500, 10th Ed.)

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Operated for the Atomic Energy Commission by the
General Electric Company under Contract #W-31-109-Eng-52

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price 15 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

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INTRODUCTION

Massive uranium metal for use as a reactor fuel material is prepared in the United States by reduction of uranium tetrafluoride with magnesium in a steel reactor. This bomb reduction process produces high quality metal with an efficiency greater than 97 per cent. The preparation of the uranium tetrafluoride is, however, a complicated step in the process. A uranyl nitrate solution is obtained by a nitric acid digestion of the raw feed followed by a pulse column solvent extraction cycle. Conversion of the uranyl nitrate solution to uranium tetrafluoride involves the following steps. The uranyl nitrate solution is converted to uranium trioxide by boil-down and denitrification. The trioxide is reduced to uranium dioxide by reaction with dissociated ammonia at 650 C, and the dioxide is then converted with anhydrous hydrogen fluoride at temperatures of 375 to 625 C to uranium tetrafluoride.

OBJECTIVES

Studies aimed at simplifying the present process of recovering uranium metal for fuel element fabrication have been investigated. Such studies include the reduction of the oxides directly,[1] the dry preparation of uranium compounds which can be reduced to metal,[2] and the precipitation of uranium compounds for reduction to metal. The most promising results to date have been achieved with the precipitation reactions. Uranium ammonium fluoride has been precipitated from uranyl nitrate solution, thermally decomposed to uranium tetrafluoride and reduced to metal.[3] Uranium calcium fluoride has also been precipitated, dehydrated in argon and reduced to metal.[4] The objectives of this investigation were to determine the possibility of precipitating a uranium sodium salt

from uranyl solution, to obtain some solubility data during precipitation, and to classify the structure of the compound obtained. It was also within the scope of this investigation to study the reduction to metal of the sodium uranium salt by the conventional bomb technique. The reaction being investigated would convert uranyl nitrate directly to $UNaF_5$, thereby eliminating the denitrification to uranium trioxide, the reduction to uranium dioxide and the hydrofluorination steps presently employed in the preparation of UF_4.

SUMMARY AND CONCLUSIONS

Ferrous salts in the presence of fluoride ions will reduce uranyl solutions to uranium(IV) with the simultaneous precipitation of uranium tetrafluoride. The double salt uranium sodium fluoride, $UNaF_5$, is precipitated if sodium ions are introduced into the solutions. X-ray studies have shown that a compound which is not a mixture of UF_4 and NaF is obtained from the precipitations. Slight variations in the x-ray patterns are noticed, but in general, the compounds appear identical. The reduction and precipitation reactions are rapid; however, post-precipitation does occur, and a hold-up of an hour or longer will decrease waste losses considerably. When the precipitate was filtered and washed immediately, the waste losses were reasonably low, averaging about 4.7 and 1.0 per cent uranium, respectively. However, when allowed to settle for 12 hours, the losses were reduced to 0.69 and 0.092 per cent uranium during the filtering and washing cycles.

The salt $UNaF_5$ apparently is not hydrated. Drying at 110 C in air removed essentially all traces of water, leaving a free flowing salt with a tap density of about 1.3 g/cm^3. This dry salt can be used directly in bomb reduction experiments without further processing.

Reduction of $UNaF_5$ with calcium by the bomb technique has been demonstrated to be extremely efficient. An average metal button yield of 96.0 per cent was obtained from six reductions on a twenty-gram scale. One small scale run of the $UNaF_5$ salt as feed for an electrolytic reduction from a fused-salt bath was performed. Uranium needles one to three millimeters in length were obtained with a current efficiency of 58 per cent. About a thirty per cent solution of the double salt in fused KCl - LiCl eutectic was electrolyzed at a current density of one ampere per cm^2. Thirty per cent of the uranium dissolved in the bath was recovered.

DISCUSSION

It has been known for some time that ferrous ions will reduce uranyl solutions to the uranium(IV) valent state if fluoride ions are present in the solution. In such a reduction, the salt UF_4 precipitates almost as soon as the uranium(IV) becomes available. Uranium tetrafluoride prepared by the wet method is difficult to handle. The precipitate is generally gummy and extremely slow filtering. A hydrate $UF_4 \cdot 2.5\ H_2O$ is obtained by the wet method which must be dried prior to reduction in the hermetically sealed bombs. Unless the hydrated salt is dried in an atmosphere of hydrogen fluoride at a temperature of 250 C, hydrolysis occurs. This dehydration process does not eliminate the high temperature corrosion problems found in the hydrofluorination process presently employed at production sites. Secondly, if an anhydrous hydrogen fluoride line is to be maintained, it would be more economic to use it for the complete hydrofluorination of the oxide rather than as a drying train for the precipitated tetrafluoride. However, the double salt, $UNaF_5$, can also be precipitated from uranyl solutions in a manner similar to that described above for UF_4. By comparison with UF_4, the physical properties of $UNaF_5$ are excellent. The salt can be filtered and washed with ease. Any water in the salt can be removed by drying in air at 110 C as hydrolysis does not occur at this low temperature.

A. Reduction to Uranium(IV) and Precipitation

The precipitation of $UNaF_5$ is carried out at room temperature so corrosion problems due to acid chloride solutions are non-existent. Since corrosion is not a problem, chlorides were employed as precipitating agents in this study solely for economic reasons. Any soluble ferrous and sodium salts could be used as effectively as reagents.

A stoichiometric plus 20 per cent excess of ferrous chloride tetrahydrate was employed to reduce uranyl nitrate solutions to the uranium (IV) valent state while a 100 per cent excess of a ten per cent hydrogen fluoride solution was used in the precipitations. In the preparation of $UCaF_6$[4] the ferrous chloride has been added to the uranyl solutions prior to fluoride additions. Some air oxidation of Fe^{++} to Fe^{+++} always occurred. If, however, the ferrous chloride is added to the hydrogen fluoride solution, the ferrous state becomes quite stable with little tendency to oxidize to ferric before uranyl nitrate is added. A detailed study of precipitating conditions was not undertaken at this time. Enough runs were made to indicate that the conditions necessary to obtain a good precipitate are not critical. Post-precipitation does occur, and a hold-up before filtering lowers the waste losses considerably. In the first run a 12-hour hold-up reduced the uranium solubility loss to 0.69 per cent compared to an average of about 4.7 per cent in the other runs. In run six the excess HF was cut from 100 to 48 per cent, and solubility losses rose to 17 per cent uranium. Since a large excess of hydrogen fluoride appears to be necessary to maintain low solubility losses, a system for recycle of the excess fluoride would prove desirable. The best precipitation conditions tested appear to be a slow addition of a 10 per cent solution of HF containing stoichiometric plus a 20 per cent excess of $FeCl_2 \cdot 4\ H_2O$ to a 0.3 to 0.6 molar uranyl nitrate solution containing one mole of NaCl per mole of uranium.

The green salt $UNaF_5$ can be easily washed and filtered or centrifuged. The product has a tap density of about 1.3 g/cm^3 and is a free flowing fine-grained material. The precipitation data are presented in Table I.

B. Washing and Drying

Uranium sodium fluoride is apparently not hydrated. The salt can be completely dried at 110 C in air. Several wash solutions were used in an effort to remove an average iron impurity of 0.33 per cent. Dilute HF, HCl, and water washes did not prove effective in removing the iron contamination. Several methods for clean-up of iron have been suggested and should be tested. Most methods involve a complexing of the iron with suitable agents as thiocyanate and their removal by solvent extraction means.[5] The dried salt can be reduced to the metal electrolytically or by the bomb method without additional processing after drying at 110 C.

C. Reduction to Metal

Small scale reductions, 20 grams of metal, were made using the bomb technique. Calcium metal was used as reductant and one mole of iodine-calcium booster per mole of uranium was employed as a heat source and as a slaging agent. A large amount of booster was used, but as charge size increases, the booster needed to obtain satisfactory metal button yields can be reduced. Reduction of production sized charges should not require a booster for efficient reduction yields. The charge which consisted of $UNaF_5$, calcium reductant, and booster was packed in a magnesia crucible which was hermetically sealed in a steel bomb. Reaction was initiated by soaking the bomb in a furnace held at 1000 C or by induction heating. Efficiency of the small scale reductions was extremely good as an average button yield of 96 per cent was obtained. The iron present in the double salt is reduced and coalesced with the uranium button. Iron impurity in the metal averaged 0.42 per cent while sodium pick-up was negligible. Since iron is concentrated in the uranium metal, methods for

its removal from the salt have to be forthcoming before such a process for uranium production is feasible. One experiment was performed using the $UNaF_5$ salt as a feed for electrolytic reduction from fused salts. A thirty per cent solution of $UNaF_5$ in KCl - LiCl eutectic was electrolyzed under an atmosphere of argon. The salt was contained at approximately 500 C during the run in a platinum dish equipped with a platinum cathode and graphite anode. A current efficiency of 58 per cent was realized when electrolyzing at a current density of 1.0 ampere per cm^2. Approximately one third or two grams of uranium was recovered as dendritic crystals. The iron impurity was reduced from 3900 ppm in the salt to 134 ppm in the metal. A photograph of the metal buttons obtained is shown in Figure 1. Results of the reduction studies appear in Table II.

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WBT:jw

REFERENCES

(1) Cadwell, J. J., HW-36054, May 16, 1955, (SECRET).

(2) Cadwell, J. J., HW-32236, July 16, 1954, (SECRET).

(3) Tolley, W. B., HW-35814, February 1, 1955, (SECRET).

(4) Tolley, W. B., HW-35815, March 17, 1955, (SECRET).

(5) Roake, W. E., Private Communication.

TABLE I

PRECIPITATION RESULTS

CONDITIONS

100 per cent excess of 10 per cent HF
20 per cent excess $FeCl_2 \cdot 4H_2O$
30 grams uranium per run

Run	UNH Molarity	Per Cent Waste Losses		Product Composition	Actual Mole Ratio		Tap Density	Per Cent Iron
		Precipitation	Washing		Na/U	F/U	g/cm^3	
1[a]	0.3	0.69	0.09	$UNaF_5$	0.92	4.92	1.2	0.39
2	0.3	3.3	1.1	$UNaF_5$	0.99	5.52	1.8	0.13
3	0.3	7.5	1.1	$UNaF_5$	.10	5.75	1.5	0.21
4	0.3	4.4	1.7	$UNaF_5$	0.86	5.10	1.0	0.84
5	0.3	3.8	1.3	$UNaF_5$	1.14	5.32	1.0	0.19
6[b]	0.5	17.8	--	$UNaF_5$	1.11	5.36	--	0.21

a. Waste losses were low. Precipitate stood for 12 hours before filtering and washing.

b. Excess HF was reduced from 100 to 48 per cent.

TABLE II

REDUCTION DATA

1.0 mole Ca-I_2 booster per mole U
30 per cent excess calcium reductant

Run	Per Cent Yield	Density	Per Cent Iron	Sodium, ppm(a)	Calcium, ppm
1	86.3	--	0.29	--	
2	100.6	18.54	0.21	not detected	<50
3	94.0	18.79	0.27	200	1000
4	101.5	18.48	1.03	not detected	1000
5	95.5	18.76	0.28	not detected	100
6	97.8	--	--	--	

(a) Limit of detection of Na is less than 10 ppm

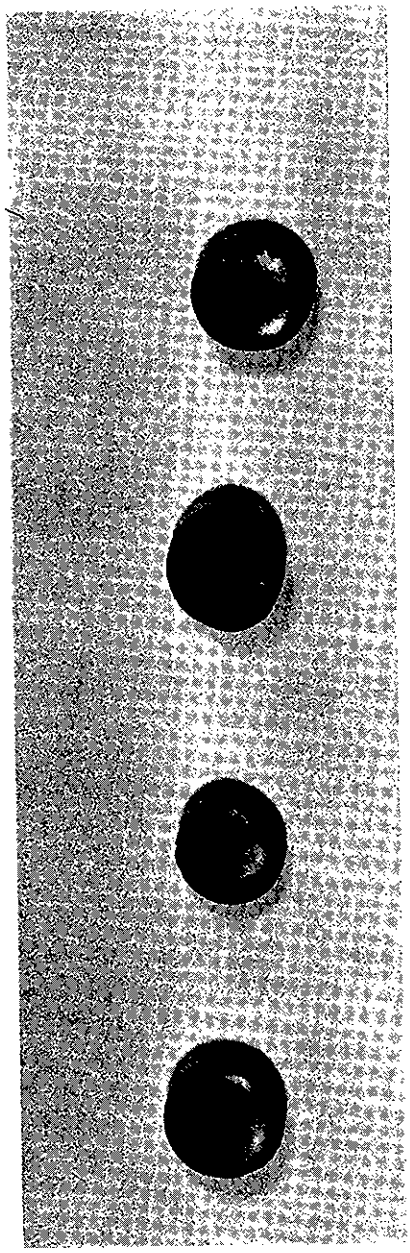

FIGURE 1
BUTTONS FROM $UNaF_5$ REDUCTIONS
Actual Size

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ABSTRACT

The double salt $UNaF_5$ can be quantitatively precipitated from uranyl nitrate solutions. Ferrous ions in the presence of fluoride ions will reduce uranyl solutions to the uranium(IV) valence state. If sodium ions are present the salt $UNaF_5$ is precipitated instead of $UF_4 \cdot 2.5\ H_2O$. $UNaF_5$ can be completely dried in air at 110 C and is then a suitable feed for reduction to metal by the bomb technique. Using calcium as reductant the button yields from reduction averaged 96 per cent. Iron impurity in the $UNaF_5$ salt is co-reduced and coalesced with the uranium metal resulting in an average iron contamination in the metal of 0.41 per cent. Electrolysis of the double salt dissolved in LiCl - KCl eutectic held at 500 C produced fine uranium needles at a current efficiency of 58 per cent. Iron impurity was reduced to 0.0134 per cent in the electrolytically reduced metal.