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EFFECTS OF CERTAIN VARIABLES UPON THE
REACTIONS FOR PREPARATION, BY THE DRY
METHOD, OF UF_4 FROM U_3O_8

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For The Atomic Energy Commission

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TECHNOLOGY--FEED MATERIALS

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ABSTRACT

The effects of certain process variables on the production of uranium tetrafluoride from U_3O_8 on the 250 g. (uranium) scale, and smaller scales in a few cases, have been studied.

It was found that the initial step (reduction of U_3O_8 to UO_2 by hydrogen) is essentially complete in 15 minutes at $700^\circ C$. The rate of conversion was shown to be temperature dependent, the greatest increase in rate of conversion occurring in the vicinity of $500^\circ C$.

In the conversion of UO_2 to UF_4 by hydrogen fluoride, the optimum temperature was found to be about $600^\circ C$. For a reaction time of 5-1/2 hours, both higher and lower temperatures yielded less completely converted products.

An increase in rate of conversion, both in reduction and hydrofluorination, resulted when smaller quantities of material were used.

Changes resulting from the present study and yielding an increased efficiency in the production process are described.

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1. Introduction

When it became necessary to prepare uranium tetrafluoride at the Los Alamos Scientific Laboratory, the process adopted was that developed by R. D. Fowler and co-workers at Johns Hopkins and converted to plant scale operation by Harshaw, duPont and Mallinckrodt [Refs. 26 (p. 9), 32, 40]. In the summer of 1947 a decision was made to study the variables of the process as then used at Los Alamos in order to improve the process if possible. Some work along these lines had been done (Refs. 5, 13, 14, 32, 41) but it was felt that there was still much that could and should be done. Subsequent to the starting of this work, pertinent findings by other laboratories have been reported. (Refs. 4, 6, 8, 11, 16, 17, 20, 21, 22, 23, 25, 28, 29, 35, 37, 38) The following references describe some of the early work here and at other laboratories: 1, 7, 18, 24, 26, 27, 30, 31, 40, 42, 43.

Briefly, the preparation of UF_4 consists in the reduction of U_3O_8 by hydrogen to UO_2 and the conversion of UO_2 to UF_4 by hydrogen fluoride in a reducing atmosphere.^{12, 15} The variables studied were temperature, time, and size of charge. It was known, of course,^{3, 10, 44} that different samples of U_3O_8 varied widely in their behavior in reference to the preparation of UF_4 . However, this variation was not made a part of the present study.

2. Production Process

Details of the process in use in 1947 were as follows:

Two hundred and fifty grams of uranium as U_3O_8 were weighed out in a platinum-10% rhodium boat. The boat was roughly semicircular in cross section and had a flattened bottom. The dimensions were: length, 7 in.; width at the open top, 2 in.; depth, 1-1/4 in. The boat was provided with a cover, open at each end, designed to prevent dust, etc., from falling into the boat, and yet permit the gases to have free access to the uranium compounds. Two such boats were placed in tandem in a horizontal tubular nickel reactor of the following dimensions: length, 24 in.; outside diameter, 3 in.; wall thickness, 5/32 in.

At one end the nickel reactor was provided with a flange to which the reactor lid was bolted. An annealed copper gasket between the lid and the reactor provided a gas-tight seal. The reactor lid carried the inlet for the gases; the exhaust gases left the reactor through a tube joined to the closed end. The reactor was mounted in a 3 in. tube furnace, which could be opened for cooling. An electric fan provided additional cooling. The flow of hydrogen was

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measured by means of a rotameter; the flow of hydrogen fluoride was controlled by means of an orifice designed to give a flow of 200 g./hr. under normal tank pressure.

The conditions used in preparing the uranium tetrafluoride were as follows:

Temp. (°C.)	Time (hrs.)	Rates of Gas Flow	
		H ₂ (l./min.)	HF (g./hr.)
25 to 800	1.5	2	0
800	2.5	2	0
800 to 500	0.2	2	0
500	5.5	1	200
500 to 800	0.8	1	200
800	5.0	0.5	200
800 to 300	0.5	0.5	200
Total	16.0		

A conversion of at least 98.5% is considered essential for subsequent processing of the fluoride to uranium metal.

3. Experimental Equipment and Procedure

Since there was a considerable temperature variation along the length of the production process reactors, these were unsuitable for a study of process variables. A reactor was designed which could be completely enclosed in one of the 3 in. tube furnaces, and which was large enough to hold one of the platinum-rhodium boats. The closure, which is the essential feature of this reactor, is shown in Fig. 1. This reactor had a temperature variation of $\pm 2.0^{\circ}\text{C}$. along its length at a temperature of 700°C . and at a hydrogen flow of 2 l./min. The gases were introduced through a tube joined to the closed end of the reactor and extending through the reactor almost to the reactor closure. A gas preheater was constructed and used to bring the gases to temperature before they entered the reactor.

Because of the known variability of different samples of U_3O_8 , considerable quantities of U_3O_8 were prepared to serve as standard materials. The method of preparation and other details are discussed in the appendix. Except where otherwise stated, 250 g. of uranium as U_3O_8 were used in each experiment. A small brass "rake" was used to distribute the oxide uniformly in the boats, which were the same as the boats described in Sec. 2.

An atmosphere of argon was used during the heating of the starting materials to the reaction temperature. Argon was also used as a purge gas at the end of the reaction time.

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The argon was purified by passing it over calcium at 400°C. and then over indicating calcium sulfate.

The hydrogen was purified by passing it over nickel scrap at 500°C. and then over indicating calcium sulfate.

Tank anhydrous HF was used without further purification.

Calibrated rotameters were used for measuring the rates of flow of the gases. The rotameters used for hydrogen and helium were calibrated by means of a wet-test meter. The rotameter used for HF was calibrated by condensing and weighing the HF passed through the rotameter at various indicated flow rates.

Solenoid valves were used to start and stop the flow of hydrogen and argon; HF flow was controlled by the manual operation of valves. The precision of the reaction times was kept within 5 seconds for times of less than 30 minutes and within 1 minute for longer times.

Temperatures were determined by means of calibrated thermocouples placed in wells inside the reactor, above and below the position of the platinum boats.

Weighings were made on a large-capacity analytical balance with as little delay as possible after the materials had cooled in the reactor under argon to room temperature. The extent of conversion was calculated from the weight change.

In the hydrofluorination studies, U_3O_8 was used as the starting material. After reduction (1 hr. at 700°C.), the product (UO_2) was cooled in the reactor under hydrogen to the desired temperature and, without removal from the reactor, was then hydrofluorinated.

The general procedure was to react the material for a specified time at a given temperature, determine the conversion, and then react for additional time to obtain the value for the next longer specified time at the given temperature. Experiments showed that such a stepwise procedure gave results which did not differ significantly from the results of non-stepwise experiments over the same total time. A flow rate of 2 l./min. of hydrogen was used in the reduction step. Flow rates of 1 l./min. of hydrogen and 200 g./hr. of the HF were used in the hydrofluorination step.

4. Experimental Results

The results obtained are presented in Tables I and II, and plotted in Figs. 2 through 7.

5. Discussion

The reduction studies indicate a continuous increase in the rate of conversion of U_3O_8 to UO_2 with increasing temperature (Fig. 2). The greatest increase in the rate of conversion of U_3O_8 to UO_2 takes place in the vicinity of 500°C. (Fig. 3). From these results it was

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evident that the time required in the reduction step of the production process could be shortened considerably without affecting the results.

It will be noticed that the reduction appears to be incomplete in all cases. Although this may be the case,²⁶ it is also probable that there is reoxidation on exposure to air. (Refs. 2, 19, 33, 34, 39)

The hydrofluorination results indicate that the rate of conversion of UO_2 to UF_4 increases up to about 600°C . (See Figs. 4 and 5.) Above 600°C ., the rate of conversion decreases with increasing temperature. This effect is attributed to a sintering action, which, it is believed, renders the unreacted material less accessible to the hydrogen fluoride.⁴¹ The melting point of UF_4 is variously stated to be $960 \pm 5^\circ\text{C}$.⁹ and 1036°C .³⁶ (In the production process, the higher temperatures at the end of the hydrofluorination provide an additional "kick" which boosts the extent of conversion. In addition, the sintering effect of the higher temperature produces a UF_4 that is less "dusty" and therefore easier to work with in transfer operations.)⁷ The terminal high-temperature hydrofluorination increased the rate of conversion in those experiments which had initial hydrofluorination temperatures of up to and including 600°C . In the case of higher initial temperatures, the sintering operation did not seem to change the rate of conversion.

The experiments in which the size of charge was changed show that this variable has a very important effect on the rate of conversion. Both in reduction and in hydrofluorination, decreasing the size of the charge resulted in a marked increase in the rate of conversion (Figs. 6 and 7). Probably layer thickness is the more fundamental factor here, but because of the shape of the boats it does not appear that it would be a valid procedure to attempt a correlation between layer thickness and rate of conversion in the present case.

The experiments at 125°C . show that there is no advantage to an initial "seasoning" before carrying out the hydrofluorination at a higher temperature. (This procedure has been found to be advantageous in work with plutonium.)

In both reduction and hydrofluorination, the rate of conversion is a function of extent of reaction. The rate of conversion, depending on the temperature, is relatively rapid initially and then becomes slower as the extent of conversion increases. Because of the effect of size of charge, any attempt at a theoretical interpretation of the relation between rate of conversion and extent of conversion does not appear to be justified for the data presented here, although these results do indicate some of the variables which must be considered in possible future fundamental studies.

It should be pointed out that the results reported here are specific for the oxides used. Probably the interrelation of effects would remain the same, but the specific effects would vary with different samples of oxide.

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The results reported here have been the basis for appreciable reductions in processing time in the production process. The present schedule (July 1954) is as follows:

Temp. (°C.)	Time (hrs.)	Gas Flow	
		H ₂ (l./min.)	HF (g./hr.)
25 to 660	1	4	0
660	1	4	0
660 to 550	0.1	4	0
550	5.5	3	350
550 to 740	0.5	2	200
740	0.5	2	200
740 to 400	0.3	2	200
400 to 350	0.1	2	0
Below 350	0.1	0	0
Total	9.1		

A further simplification has been the use of larger furnaces, larger reactors and larger boats. As in the experimental reactor, the gases are brought in through a tube joined to the closed end of the reactor and extending inside the reactor almost to the reactor closure. The boats, which will accomodate 1000 g. of uranium in compound form, are 14 in. long. The width is 4-1/4 in. at the top and 4 in. at the bottom. The depth is 1-1/2 in.

Summary

1. It is shown that conversion of U_3O_8 to UO_2 can be accomplished in appreciably shorter times than were originally used in the first stage of the process for producing UF_4 on the 250 g. (uranium) scale.
2. A temperature of about 600°C. was found to be optimum for preparing UF_4 by the hydrofluorination of UO_2 .
3. Under a given set of conditions, the extents of conversion in both reduction and hydrofluorination were markedly affected by the quantity of material used.
4. As a result of the present study, the time required in processing U_3O_8 to UF_4 has been reduced from 16 hrs. to 9.1 hrs.

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Appendix

Preparation of U_3O_8

Procedure

A uranyl nitrate solution is prepared by dissolving 250 g. of uranium (as U_3O_8 , Mallinckrodt, reagent grade) in 210 ml. of concentrated HNO_3 . The solution is diluted to 3 liters. To the solution is added 20 g. of malonic acid and 4 g. of citric acid and the pH is adjusted to 1.5. A 20% excess of 30% H_2O_2 is added at a rate of about 10 ml./min. while maintaining the pH at 1.5 by the simultaneous addition of dilute NH_4OH (1:1). The mixture is stirred mechanically during the precipitation, and stirring is continued for a few minutes after the addition of the H_2O_2 is complete. After filtration, the precipitate ($UO_4 \cdot 2H_2O$) is ignited for 15 hours at $900^\circ C$. The product (U_3O_8) is passed through a sheet-metal sieve (5/64 in. holes) to break up the lumps.

For the reduction studies, about 23-1/2 kg. of U_3O_8 was prepared by the above method. An additional 40 kg. of U_3O_8 was prepared for the hydrofluorination studies. Comparisons in reduction showed that this second batch of U_3O_8 was somewhat less reactive than the first:

Temp. ($^\circ C$.)	Time (min.)	Batch 1 % UO_2	Batch 2 % UO_2
600	10	87.36	78.69
600	15	97.79	95.68
700	7.5	72.76	66.43

Electron micrographs indicated that the second batch had a somewhat larger particle size than the first.

In each case, the batches of oxide were thoroughly mixed and the portions used were obtained by means of a sample splitter. It was found that samples of the U_3O_8 lost a small amount of weight on ignition. This loss in weight was attributed to adsorbed moisture. Appropriate corrections for the extraneous weight in the U_3O_8 were made in calculating the conversions in reduction and in hydrofluorination.

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Notebook references: Los Alamos Notebooks 1683, 2020, 2368, 3007.

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TABLE I

REDUCTION OF U_3O_8 TO UO_2

Temp. (°C.)	Time	Per Cent Conversion	Temp. (°C.)	Time	Per Cent Conversion
300	30 min.	0.10	700	2.5 min.	25.38
350	30 min.	2.32		2.5 min.	24.72
400	30 min.	8.06		5 min.	52.42
	30 min.	8.33		5 min.	54.39
	1 hr.	11.22		7.5 min.	72.77
	2.5 hrs.	15.19		10 min.	89.16
425	30 min.	11.22		10 min.	91.00
450	30 min.	18.08		12.5 min.	97.42
	30 min.	19.82		15 min.	97.44
	1 hr.	17.15		20 min.	97.49
	1 hr.	22.16		30 min.	97.43
	1 hr.	25.60		2.5 hrs.	96.74
	2.5 hrs.	48.13		2.5 hrs.	96.76
475	30 min.	27.59		2.5 hrs.	97.07
500	30 min.	55.83		2.5 hrs.	97.75
	1 hr.	93.57		2.5 hrs.	97.49
	1 hr.	83.77	750	2.5 min.	30.27
	70 min.	86.86	800	2.5 min.	28.02
	100 min.	94.61			
512.5	30 min.	74.73		1/4 charge (62.5 g. U)	
525	15 min.	75.83			
	30 min.	88.05	700	2.5 min.	53.65
	45 min.	95.55		5 min.	97.46
537.5	30 min.	96.68		15 min.	97.93
550	15 min.	91.73			
	30 min.	96.52		1/2 charge (125 g. U)	
600	10 min.	87.37	700	2.5 min.	41.23
	15 min.	97.79		5 min.	82.33
	30 min.	97.20		7.5 min.	98.02
	1 hr.	97.69		15 min.	98.02

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TABLE II

HYDROFLUORINATION OF UO_2 TO UF_4

Hydrofluorination				Sintering			
Temp. (°C.)	Exp. No.	Total Time at Temp. (hrs.)	Per Cent Conversion	Temp. (°C.)	Exp. No.	Total Time at Temp. (hrs.)	Per Cent Conversion
125	21b	1	3.63	600 ^(a)	21f	1	44.85
	21c	2	5.80		21g	3	85.07
	21d	4-1/2	10.90		21h	5-1/2	95.41
	21e	5-1/2	12.50				
	27	5-1/2	10.41	600 ^(a)	22a	1	37.11
	22a	1	-		22b	2	78.57
200	19a	1	19.05	850	19f	1	44.38
	19b	2	25.82				
	19c	3	31.05				
	19d	4	34.89				
	19e	5-1/2	39.34 ^(b)				
	25	5-1/2	35.62				
	28a	7-1/2	36.80				
	28b	13-1/2	48.06				
	28c	26-1/2	64.42				
	28d	34	70.02				
	28e	41-1/2	74.18				
400	8b	1	51.81	850	8g	1	93.85
	8c	2	71.80		8h	2	96.76
	8d	3-1/4	81.70				
	8e	4-1/2	86.47				
	8f	5-1/2	89.07				
500	7b	1	53.35	850	7g	1	97.79
	7c	2	79.89		7h	2	98.66
	7d	3-1/4	90.15				
	7e	4-1/2	93.35				
	7f	5-1/2	94.61	850	20f	1	94.82
	20a	1 ^(c)	36.15 ^(c)		20g	2	97.42
	20b	2	57.41				
	20c	3-1/4	77.97				
	20d	4-1/2	87.27				
	20e	5-1/2	90.69				
550	17b	1	48.65	850	17f	1	98.27
	17c	2	77.39		17g	2	98.77
	17d	3-1/4	91.76				
	17e	5-1/2	94.95				
	14	4-1/2	95.07				

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TABLE II (continued)

Hydrofluorination				Sintering			
Temp. (°C.)	Exp. No.	Total Time at Temp. (hrs.)	Per Cent Conversion	Temp. (°C.)	Exp. No.	Total Time at Temp. (hrs.)	Per Cent Conversion
600	9b	1	43.08	850	9g	1	98.66
	9c	2	69.86		9h	2	98.92
	9d	3	87.71				
	9e	4-1/2	95.19				
	9f	5-1/2	96.51				
	13	4-1/2	95.26				
	26b	5-1/2	96.50	850	26c	2	99.01
650	18a	1	30.46	850	18f	1	97.56
	18b	2	54.62		18g	2	98.26
	18c	3-1/4	78.00				
	18d	4-1/2	91.56				
	18e	5-1/2	95.35				
700	16a	1	26.27	850	16e	1	89.29
	16b	2	42.54		16f	2	92.24
	16c	3	58.11				
	16d	5-1/2	85.71				
	10	4-1/2	78.94				
800	15a	1	11.52	850	15e	1	53.01
	15b	2	21.00		15f	2	57.37
	15c	3	30.74				
	15d	5-1/2	48.32				
	11	4-1/2	42.89				
600	30b ^(d)	1	90.06				
	30c	2-1/2	96.42				
	30d	5-1/2	98.32				
600	32a ^(e)	1/2	44.92				
	32b	1-1/4	81.83				
	32c	3	95.71				
	32d	5-1/2	97.93				
800	31b ^(d)	1/4	10.03				
	31c	1	36.46				
	31d	3	78.12				
	31e	5-1/2	91.14				
800	33c ^(e)	1	20.10				
	33d	3	53.87				
	33e	5-1/2	78.94				

Notes:

- (a) This is not a "sintering" temperature. The effect of "seasoning" at 125°C. was being studied.
- (b) X-ray analysis indicated that the product was all UO₂.
- (c) HF was admitted at 700°C. and the reactor cooled to 500°C. in 1 hr.
- (d) The charge was 1/4 the usual size (62.5 g. U).
- (e) The charge was 1/2 the usual size (125 g. U).

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Fig. 1--Closure of the reactor.

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Fig. 2--Reduction of U_3O_8 .

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Fig. 3--Effect of temperature on extent of reduction at constant time.

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Fig. 4--Hydrofluorination of UO_2 .

Fig. 5--Effect of temperature on extent of hydrofluorination for various times.

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Fig. 6--Effect of size of charge on extent of reduction.

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Fig. 7--Effect of size of charge on extent of hydrofluorination.

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