

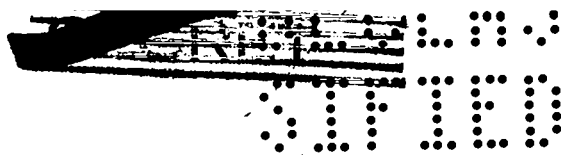
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PRODUCTION OF URANIUM TETRAFLUORIDE ON A 200-GRAM SCALE

WORK DONE BY:

T/5 D. Lasovick

K. A. Walsh

REPORT WRITTEN BY:

T/5 D. Lasovick

K. A. Walsh

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ABSTRACT

Conversions of different uranium compounds such as U_3O_8 , UO_3 , UO_4 , and UO_2CO_2 to uranium tetrafluoride for reduction to metal were made in the customary two-stage process of reduction to UO_2 by means of hydrogen and hydrofluorination of the UO_2 to UF_4 . Of these starting materials U_3O_8 , UO_3 , and UO_2CO_2 of -100-mesh particle size were most satisfactory. Temperatures of 650° to 750° C in step one and 550° to 650° C for step two were best for conversion of U_3O_8 . Temperatures between 550° and 600° C for both steps involving conversion of UO_3 were best. Use of a mixture of hydrogen and hydrogen fluoride in the second step proved more advantageous than the usual procedure using anhydrous hydrogen fluoride alone. This prevented caking of the UF_4 so the product was of the same particle size as the original material. Removal of impurities by volatilization of their fluorides is partially accomplished for those elements such as carbon, silicon, and boron.

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PRODUCTION OF URANIUM TETRAFLUORIDE ON A 200-GRAM SCALE

I. INTRODUCTION

Since UF_4 seems to be the best starting material in the production of uranium metal, a system was set up to produce UF_4 locally. The highest degree of conversion from the initial materials to the tetrafluoride was sought to insure the best possible yields of metal in reduction. Methods were also investigated to reduce the time of conversion to tetrafluoride. These objectives were to be accomplished without decreasing the bulk density of the UF_4 produced.

II. APPARATUS

The general commercial practice in the production of UF_4 is a two-stage operation. The first stage consists of reduction of an oxide of uranium to UO_2 by the use of hydrogen. The UO_2 is then converted in the second step to UF_4 with anhydrous hydrogen fluoride.

Because of the corrosive nature of HF and the high temperatures involved, a reactor tube of nickel was used. For conversions on a 200-gram scale a nickel tube 15 inches long, 3 inches outside diameter, and 1/4 inch wall thickness was employed. The opening was closed by a steel plate and rendered gastight by use of a sharp edge on the steel plate which cut into a copper washer. A diagram of the complete assembly is shown in Fig. I. *W. H. Beck*

All connecting tubes not subject to high temperatures were made with 3/8-inch-OD annealed copper tubing connected with standard brass refrigerator fittings. Other connections were made with hard solder. Kerotest valves with annealed copper seats were used at the point of introduction of the various gases. Hoke needle valves were installed where it was necessary to regulate gas flow. Corrosion of the needle points was reduced by use of special fluorocarbon greases.

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Since it was found that passage of a mixture of hydrogen and HF was advantageous, a copper trap was filled with liquid anhydrous HF through which H₂ could be bubbled by extending the inlet tube of this trap to the bottom. A by-pass was provided for direct use of hydrogen alone. Relative concentrations of hydrogen and HF could be controlled by regulating the temperature of the trap.

Commercial hydrogen contains small amounts of oxygen which may not permit complete reduction of uranium compounds to UO₂. Purification of the hydrogen was accomplished by passing it over powdered uranium metal in a nickel tube heated to 400° C. The anhydrous hydrogen fluoride used was the commercial grade supplied by Matheson. For sweeping and cooling purposes in an inert atmosphere, nitrogen gas was used.

The samples for conversion were placed in platinum trays resting on nickel supports. The trays were covered with a platinum canopy to prevent nickel fluoride formed on the walls of the reactor tube from dropping into the sample.

The rate of flow of gases passed through the system was observed by bubbling the gases from the reactor through concentrated sulfuric acid in a copper cup.

III. EXPERIMENTAL PROCEDURES

Various aspects of the conversion process were investigated to determine the best conditions for conversion from the standpoint of time and degree of conversion. The rate of reaction is influenced by such factors as the starting material, particle size, depth of material in the tray, temperature, and rate of flow and composition of gases over the sample.

Numerous runs were made involving the use of U₃O₈, UO₃, UO₄ and UO₂C₂O₄ as the starting material to be converted to UF₄. These experiments were conducted not only to determine the material best suited for conversion, but also the best conditions

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for each material, inasmuch as no decision had been reached as to the probable starting material in production of the enriched uranium tetrafluoride.

Tests on the particle size of the initial material were made principally on U_3O_8 which was sieved to give separations of -100, +100 to -60, and +60 mesh fractions. A few tests were made to determine the degree of penetration of the gases into the sample piled at different depths.

Caking of the material on the surface led to tests involving use of a mixture of hydrogen and hydrogen fluoride to sweep out the water formed in the hydrofluorination of UO_2 which was found to be the source of the caking tendency. Variation of the temperature of the liquid HF altered the ratio of hydrogen and hydrogen fluoride passing over the sample.

Different temperatures for both the reduction and hydrofluorination steps were studied to find the shortest time necessary for conversion and to increase the degree of conversion on the different starting materials.

The degree of conversion was determined by igniting a weighed sample of the UF_4 to U_3O_8 . From this weight of U_3O_8 , theoretical values for the weight of the sample were calculated if it were 100% UO_2 or 100% UF_4 . From these values the percentage conversion in different runs was calculated through use of

$$\% \text{ conversion} = \frac{\text{wt sample} - \text{theoretical wt } UO_2}{\text{theoretical wt } UF_4 - \text{theoretical wt } UO_2} \times 100.$$

It must be remembered that oxygen remaining in the sample may be present as U_3O_8 or as oxyfluorides rather than as UO_2 , through the nature of the oxycompound does not greatly affect the percentage conversion if it is nearly complete.

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IV. EXPERIMENTAL RESULTS

A. Use of Different Starting Materials

The following table gives a comparison of time, temperature and degree of conversion for the different starting materials under the best conditions found for each compound.

Starting Material	H ₂ reduction		Hydrofluorination*		% Conversion
	Time hrs.	Temperature °C	Time hrs.	Temperature °C	
U ₃ O ₈	3	650	6	650	99.61
	5	650	8	600	99.70
	5	750	6	650	99.66
UO ₃	4	500	6	635	99.89
	7	600	6	550	99.48
	3	600	5	600	99.47
UO ₄	3	580	6	580	100.1
	5	600	6	600	100.0
	1½	550	6	580	98.7
UO ₂ C ₂ O ₄	4	500	6	635	99.6
	3	580	6	580	100.2
	3	575	6	600	99.5

* Mixture of H₂ and HF

B. Particle Size and Depth of Material

After the mixture of hydrogen and HF was used in step 2 of the conversion to prevent formation of a hard surface which hindered penetration by the gases, it was found that conversion of layers up to 3/4 inch in thickness was complete. No difficulties were encountered in failure of the bottom of the material to convert.

Particle size assumes an important role in the possible formation of an outer coating of UF₄ and subsequent failure of the gases to penetrate the core of an individual particle. Studies were carried out on U₃O₈ to find the effect of particle

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size. Three samples of different particle size were placed in the reactor for duplication of conditions in two different runs.

Run No.	Particle Size	H ₂ reduction		Hydrofluorination		% Conversion
		Time hrs.	Temperature °C	Time hrs.	Temperature °C	
1	-100 mesh	7	650	5	650	99.7
	+100 to -60	7	650	5	650	95.2
	+60	7	650	5	650	79.1
2	-100 mesh	8	600	6	600	99.2
	+100 to -60	8	600	6	600	98.4
	+60	8	600	6	600	81.9

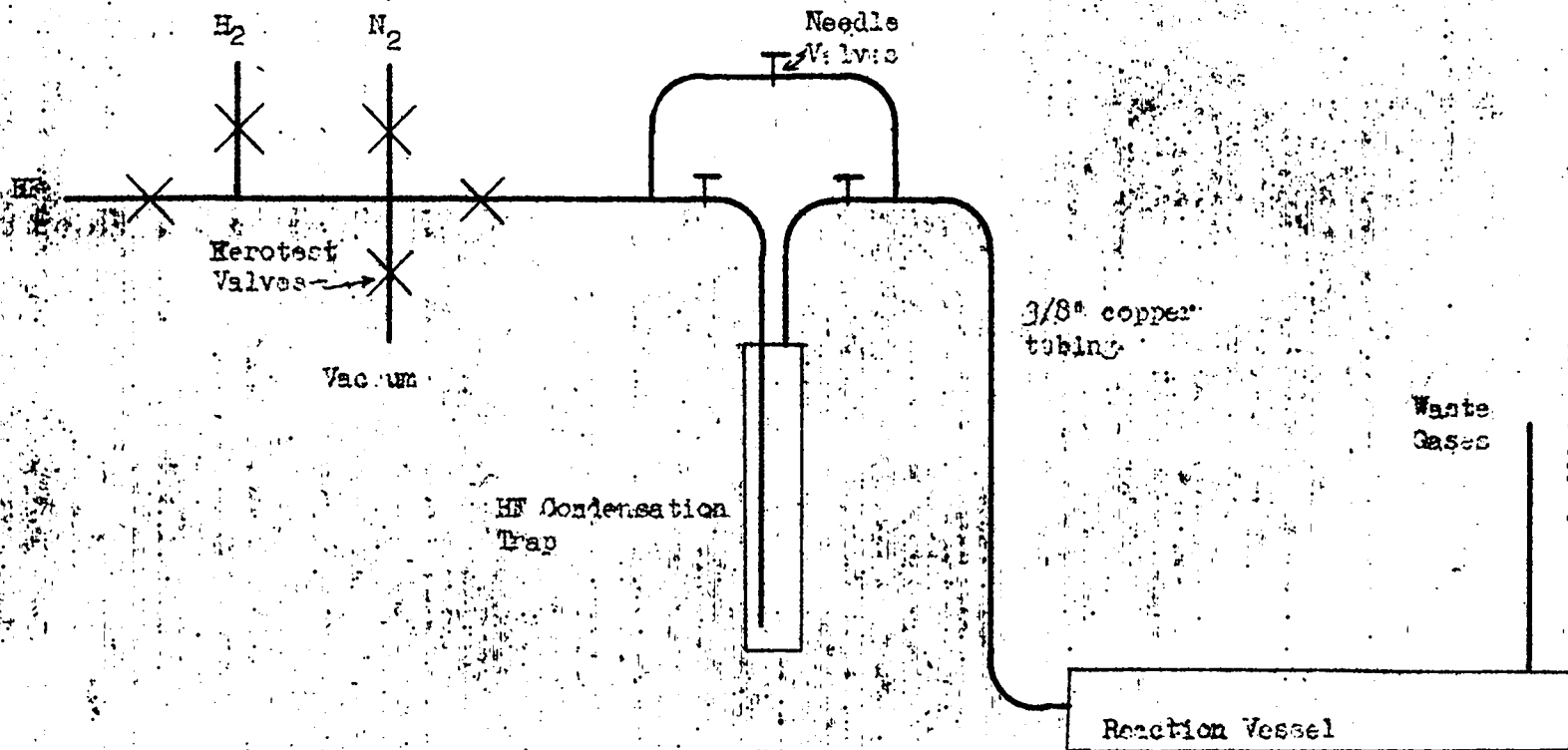
C. Rate of Flow of Gases

A hydrogen flow rate of about 100 cc per minute was used in the first step (reduction). An equal rate of flow of H₂ through the liquid HF was used in the second step (fluorination). In controlling the ratio of hydrogen and HF passing over the sample, a temperature of -25° C for the liquid HF did not allow enough HF to pass for rapid or complete conversion. Maintenance of the temperature of the liquid HF at 0° C during the second step provided sufficient HF for conversion to UF₄. Later it was found that leaving the trap at room temperature was satisfactory, because the cooling effect of the vaporization of liquid HF retained a ratio of hydrogen and HF which gave complete conversions. The development of special HF-resistant flow meters has allowed mixing the H₂ and HF as gases in any desired ratio.

The rate of reduction of U₃O₈ to UO₂ has been determined at another laboratory (Brown and Hill, Report CN-261, p. 8) as a function of hydrogen flow and was found to be inversely proportional to the flow rate; the product of reaction time and flow rate was equal to about 25,000 cc at 650° C.

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HF PRODUCTION SYSTEM



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K. A. Walsh & D. Lasovick
September 1, 1944

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