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PRODUCTION OF URANIUM TETRAFLUORIDE ON A 200-GRAM SCALE

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ABSTRACT

Conversions of different uranium compounds such as U_3O_8, UO_3, UO_4, and $UO_2C_2O_4$ 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 $UO_2C_2O_4$ 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. where

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 fluorcarbon 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 H_2 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 UO_2. 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 U_3O_8, UO_3, UO_4 and $UO_2C_2O_4$ as the starting material to be converted to UF_4. These experiments were conducted not only to determine the material best suited for conversion, but also the best condition

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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_3O_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
$UO_2C_2O_4$	4	500	6	635	99.6
	3	580	6	580	100.2
	3	575	6	600	99.5

* Mixture of H_2 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 UF_4 and subsequent failure of the gases to penetrate the core of an individual particle. Studies were carried out on U_3O_8 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 H_2 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. Maintainence of the temperature of the liquid HF at 0° C during the second step provided sufficient HF for conversion to UF_4. 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 H_2 and HF as gases in any desired ratio.

The rate of reduction of U_3O_8 to UO_2 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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D. Effect of Temperature on Conversion

The range in temperature at which the original material was treated with hydrogen and the mixture of hydrogen and hydrogen fluoride, as well as the degree of conversion under each condition, is indicated below:

Starting Material	Temp. H_2 reduction °C	Temp. Hydrofluorination °C	% Conversion
U_3O_8	800	600	81.5
	750	650	99.7
	675	650	99.3
	650	600	99.7
	600	600	95.4
UO_3	675	700	56.5
	650	650	95.4
	600	550	99.5
	550	580	100.0
$UO_2C_2O_4$	600	600	100.3
	580	580	100.2
	550	580	100.1
	500	635	99.6
UO_4	600	600	100.0
	580	580	100.1
	550	580	98.7

E. Removal of Impurities in Conversion

A hydrofluorination at high temperatures should be effective in volatilizing out quantities of boron, silicon, and carbon as their fluorides. To check the effectiveness of this process, an analysis for carbon was made on UF_4 prepared by different methods.

Material analyzed	Carbon ppm
UF_4 by conversion of U_3O_8	50
UF_4 by conversion of UO_3	<50
UF_4 by direct conversion of $UO_2C_2O_4$	90
U_3O_8 by ignition of $UO_2C_2O_4$	80
UF_4 by conversion of U_3O_8 from $UO_2C_2O_4$ ignition	70

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The variation in these analytical results (analyses carried out by Group CM-9) is probably not very significant, although it indicates carbon content can be kept low.

V. SUMMARY

For the production of UF_4 on a 200- to 500-gram scale, either U_3O_8 or UO_3 is suitable for the starting material. In time of conversion and degree of conversion $UO_2C_2O_4$ compares favorable, but the UF_4 produced is of such low bulk density that its reduction is less favorable on such a scale.

In the conversion of U_3O_8 to UF_4 the temperature for the reduction step is most favorable between 650° and 750° C and the hydrofluorination step is best carried out between 550° and 650° C. A conversion consumes nine to twelve hours. Conversion of UO_3 to UF_4 take eight to ten hours at a temperature of 550° to 600° C for both steps in the process. The time disadvantage is overcome by better bulk density of UF_4 from U_3O_8 and the relative ease with which U_3O_8 can be prepared from most uranium salts.

Particle sizes of -100 mesh are best suited for conversions to tetrafluoride because the penetration of individual particles of this size by the gases is rapid.

In the second step of the process, a mixture of hydrogen and HF has several advantages. The hydrogen serves as a sweeping gas in removal of water formed in the reaction;

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O$$

This prevents formation of a hard surface layer which is difficult for the HF to penetrate. The excess hydrogen serves also to insure complete reduction of the starting material to UO_2, assuring better conversion. The best ratio of hydrogen and HF is obtained by keeping the trap containing the HF between 0° C and room temperature.

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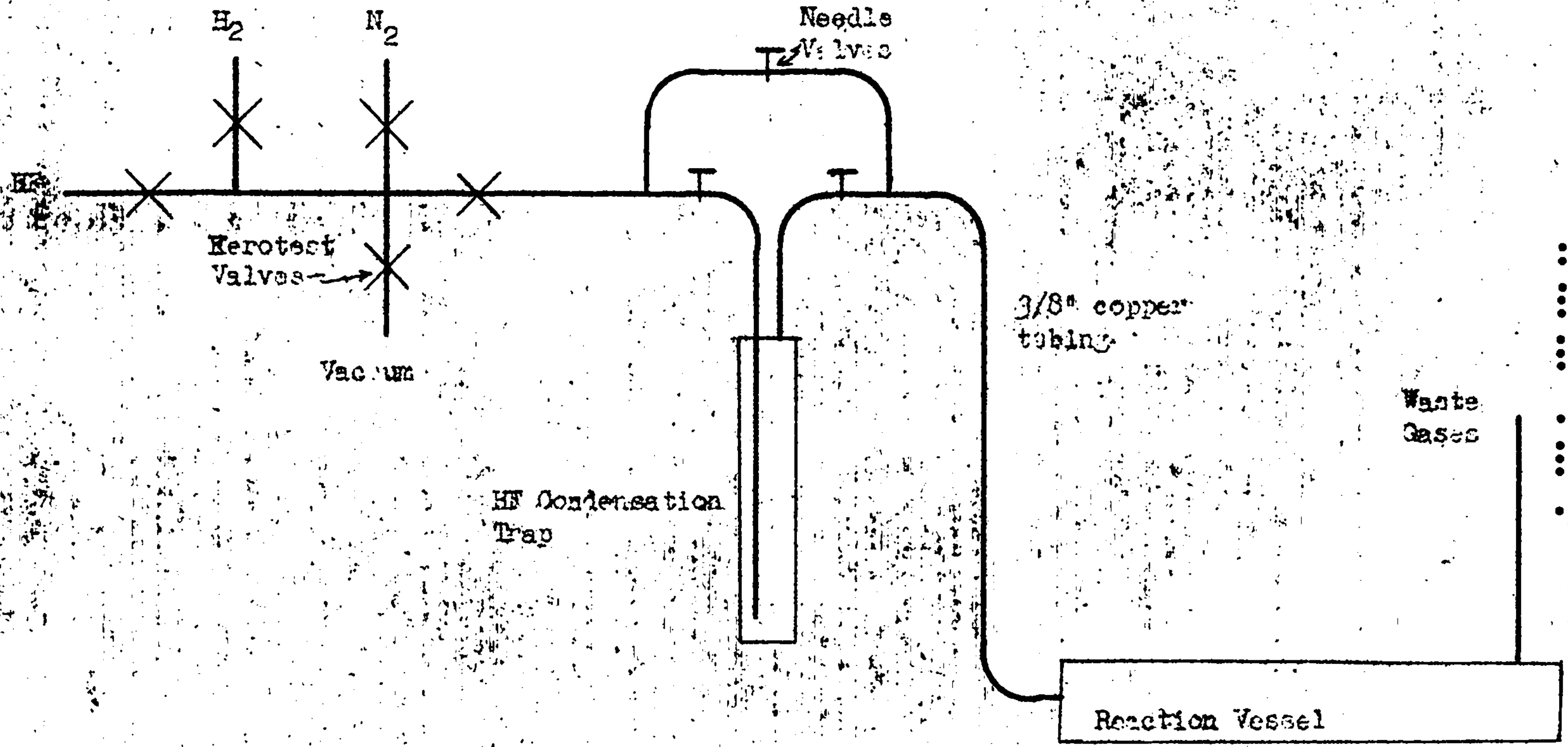
UF_4 PRODUCTION SYSTEM



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