Conf-117-33

(1, d)

UO_2

PREPARATION OF DENSE URANIUM DIOXIDE PARTICLES FROM URANIUM HEXAFLUORIDE IN A FLUIDIZED BED

by

Irving E. Knudsen, Norman Levitz, and Albert A. Jonke

Prepared for presentation at the
145th Meeting of the American Chemical Society
September 8 to 13, 1963
New York City

Argonne National Laboratory
Chemical Engineering Division
9700 South Cass Avenue
Argonne, Illinois

Operated by the University of Chicago
under
Contract W-31-109 eng-38
with
the U. S. Atomic Energy Commission

September 1, 1963

American Chemical Society
145th National Meeting
New York, N. Y.,
September 8-13, 1963

DISCLAIMER

PREPARATION OF DENSE URANIUM DIOXIDE PARTICLES FROM URANIUM HEXAFLUORIDE IN A FLUIDIZED BED

by

Irving E. Knudsen, Norman Levitz, and Albert A. Jonke

ABSTRACT

A fluid-bed method has been developed for the direct preparation from uranium hexafluoride of dense, spheroidal uranium dioxide particles for dispersion and packed fuel element applications. The uranium hexafluoride is reacted with mixtures of steam and hydrogen in a bed of uranium dioxide maintained at 650 to 700°C, the solid reaction products depositing as a dense layer on the surface of the bed particles. The operating procedure involves alternating periods of uranium hexafluoride feed with periods of fluoride cleanup when only steam and hydrogen are fed.

Uranium dioxide particles in the size range - 16 + 140 mesh and having densities of 9.5 g/cc and 9.75 g/cc (up to 89 percent of theoretical density) were produced at 650°C and 700°C, respectively, using a uranium hexafluoride feed rate of 25 g/min [44 lb uranium/(hr)(sq ft reactor cross section)]. The average residual fluoride content of the uranium dioxide was about 300 ppm. The densest material was obtained when 0.75 to 1.4 times the stoichiometric steam requirement (based on the reaction $UF_6 + 2H_2O + H_2 \longrightarrow UO_2 + 6HF$) was used. The effect on product density of other process variables such as uranium hexafluoride feed rate, hydrogen concentration, bed height and duration of hexafluoride

feed period was also determined. Further densification of the material to 10.4 to 10.6 g/cc, up to 96.5 percent of theoretical density, and reduction of the fluoride content to about 5 ppm was achieved by sintering in hydrogen at about 1700°C for 2.5 hours.

IK:ML:AJ:pso

PREPARATION OF DENSE URANIUM DIOXIDE PARTICLES FROM URANIUM HEXAFLUORIDE IN A FLUIDIZED BED

Introduction

The preparation of dense particles of uranium dioxide for use in nuclear fuel elements is currently accomplished by physical treatments of the powdered oxide. Steps such as pressing, granulating, sizing, sintering, and spherodizing are required to produce particles of suitable size, density, and shape. Dense, spheroidal particles of uranium dioxide now have been produced directly from uranium hexafluoride in a semi-continuous fluid-bed process developed at the Argonne National Laboratory. Uranium dioxide particles with densities up to 89% of theoretical density (as measured by mercury displacement), were produced in sizes ranging from 100 to 1000 microns.

The process is described by reaction (1):

$$UF_{6(g)} + 2H_2O_{(g)} + H_{2(g)} \longrightarrow UO_{2(s)} + 6HF_{(g)} \qquad (1)$$

Uranium hexafluoride is reacted with mixtures of steam and hydrogen in a fluidized bed of uranium dioxide particles. The reaction occurs preferentially on the surface of the bed particles, the solid reaction products being deposited as a dense, adherent layer. The operating procedure involves alternating periods of uranium hexafluoride feed with periods of fluoride clean-up when only steam and hydrogen are fed.

Chemistry

Uranium hexafluoride is converted to the dioxide by reaction with steam and hydrogen through a series of concurrent and consecutive reactions. Initially, gas-gas reactions occur between the uranium hexafluoride and the hydrogen or steam producing uranium tetrafluoride and U_3O_8.

$$UF_{6(g)} + H_{2(g)} \longrightarrow UF_{4(s)} + 2HF_{(g)} \quad ; \Delta H_{298^\circ K} = -60.4 \text{ kcal/mole} \qquad (2)$$

$$UF_{6(g)} + 3H_2O_{(g)} \longrightarrow 1/3\ U_3O_{8(s)} + 6HF_{(g)} + 1/6\ O_{2(g)} \quad ; \qquad (3)$$

$$\Delta H_{298^\circ K} = +16.8 \text{ kcal/mole}$$

These products are converted to uranium dioxide by reaction with additional quantities of steam and hydrogen.

$$UF_{4(s)} + 2H_2O_{(g)} \longrightarrow UO_{2(s)} + 4HF_{(g)} \quad ; \Delta H_{298^\circ K} = +44 \text{ kcal/mole} \qquad (4)$$

$$1/3\ U_3O_{8(s)} + 2/3\ H_{2(g)} \longrightarrow UO_{2(s)} + 2/3\ H_2O_{(g)} \quad ; \qquad (5)$$

$$\Delta H_{298^\circ K} = -13.7 \text{ kcal/mole}$$

Reactions (4) and (5) are important, also, during the fluoride cleanup period. The kinetics of these latter reactions establishes the residence time required for cleanup.

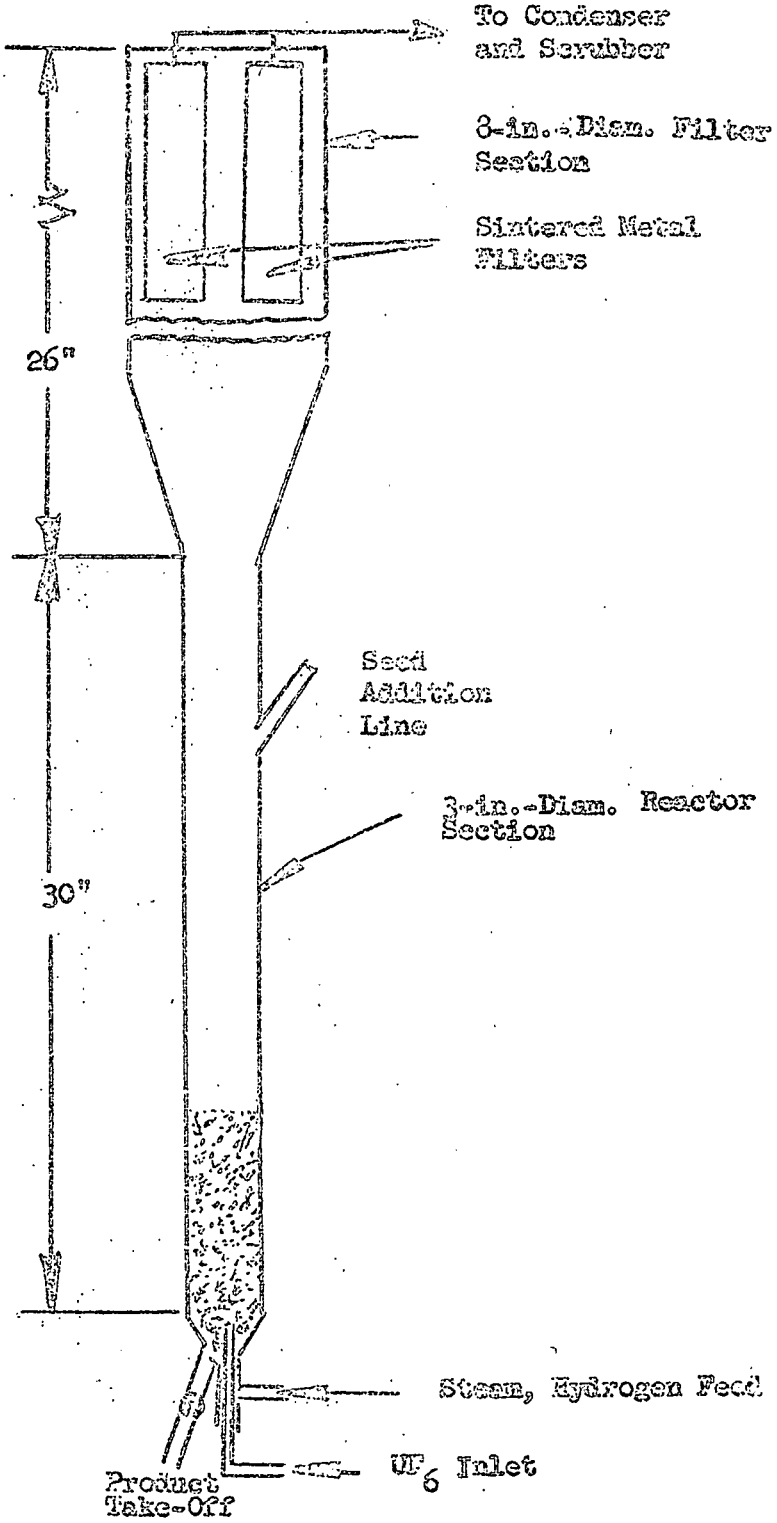
Apparatus and Procedure

The development work on the process has been carried out in a 3-inch diameter Monel column shown schematically in Fig. 1. The reactor was 30 inches high and had a 60-degree cone bottom. A 1/4-inch OD tube which passed through the apex of the cone bottom and extended about 3 1/2 inches into the bed served as the uranium hexafluoride feed nozzle. The annulus around this nozzle provided for entrance of the fluidizing and/or reactant gases. A solids feed line for the addition of seed particles was provided at a point 20 inches up the column. Product was withdrawn from an outlet located near the bottom of the cone.

An eight-inch diameter section containing sintered metal filters surmounted the reactor. Three Monel bayonet filters, 3 inches wide

Figure 1

SCHEMATIC DRAWING OF FLUID BED COLUMN FOR THE PREPARATION OF DENSE URANIUM DIOXIDE FROM URANIUM HEXAFLUORIDE



and nine inches long, were employed. An automatic jet-pulse blowback system, which utilized an 80 psig nitrogen supply, discharged accumulated solids from the filters. The off-gas passed to a Monel condenser. The hydrofluoric acid condensate was collected in plastic receivers. The noncondensable gases were scrubbed further downstream in a circulating caustic scrubber. Condensate and caustic samples were analyzed to estimate uranium losses.

The operating procedure involved, first, starting of the nitrogen purge and fluidizing gas streams and charging of the uranium dioxide bed. The flow of steam and hydrogen was started shortly before the desired operating temperature was reached; the flow of fluidizing nitrogen was then stopped. When operating conditions were stabilized, the uranium hexafluoride feed was introduced. The process was cyclic in operation; periods of hexafluoride feed were alternated with periods of fluoride cleanup when only steam and hydrogen were fed. These periods were generally of 30-minute duration, each. By adding seed particles obtained by grinding and recycling a portion of the products, particle growth (as a result of solids deposition) was offset and a uniform average particle diameter was maintained in the fluid bed. Product was withdrawn from the reactor at the end of each cleanup period.

Typical operating conditions were as follows:

Reactor temperature	650°C
Steam rate	3.3 g/min
Hydrogen rate	2.5 g/min
Uranium hexafluoride rate	25 g/min
Uranium hexafluoride feed period	30 min/hr
Bed weight and depth	6.0 kg, 9 inches (static)
Seed addition rate	~15% (by weight of the UF_6 rate)

Results and Discussion

The process variables which were found to affect the density of the uranium dioxide product were the steam and uranium hexafluoride rates, the operating temperature, the duration of the hexafluoride feed period, the depth of the fluidized bed, and the location of the uranium hexafluoride inlet in the fluidized bed.

In the experimental work, essentially complete conversion of the uranium hexaflouride to solids was achieved. Losses of uranium to the off-gas were less than 0.01% of the hexafluoride feed. The average coating rate was about 10 microns/hr of uranium hexafluoride feed.

Effect of Reactant Rates on Oxide Density

Uranium dioxide particles with densities up to 9.5 g/cc (about 86.5% of theoretical density) were produced at 650°C when optimum amounts of steam were used. A steam-to-uranium hexafluoride mole ratio of about 2/1, (the stoichiometric ratio based on the over-all reaction) was found to give the highest oxide density (see Fig. 2). Smaller amounts as well as larger amounts of steam resulted in lower density of the uranium dioxide product.

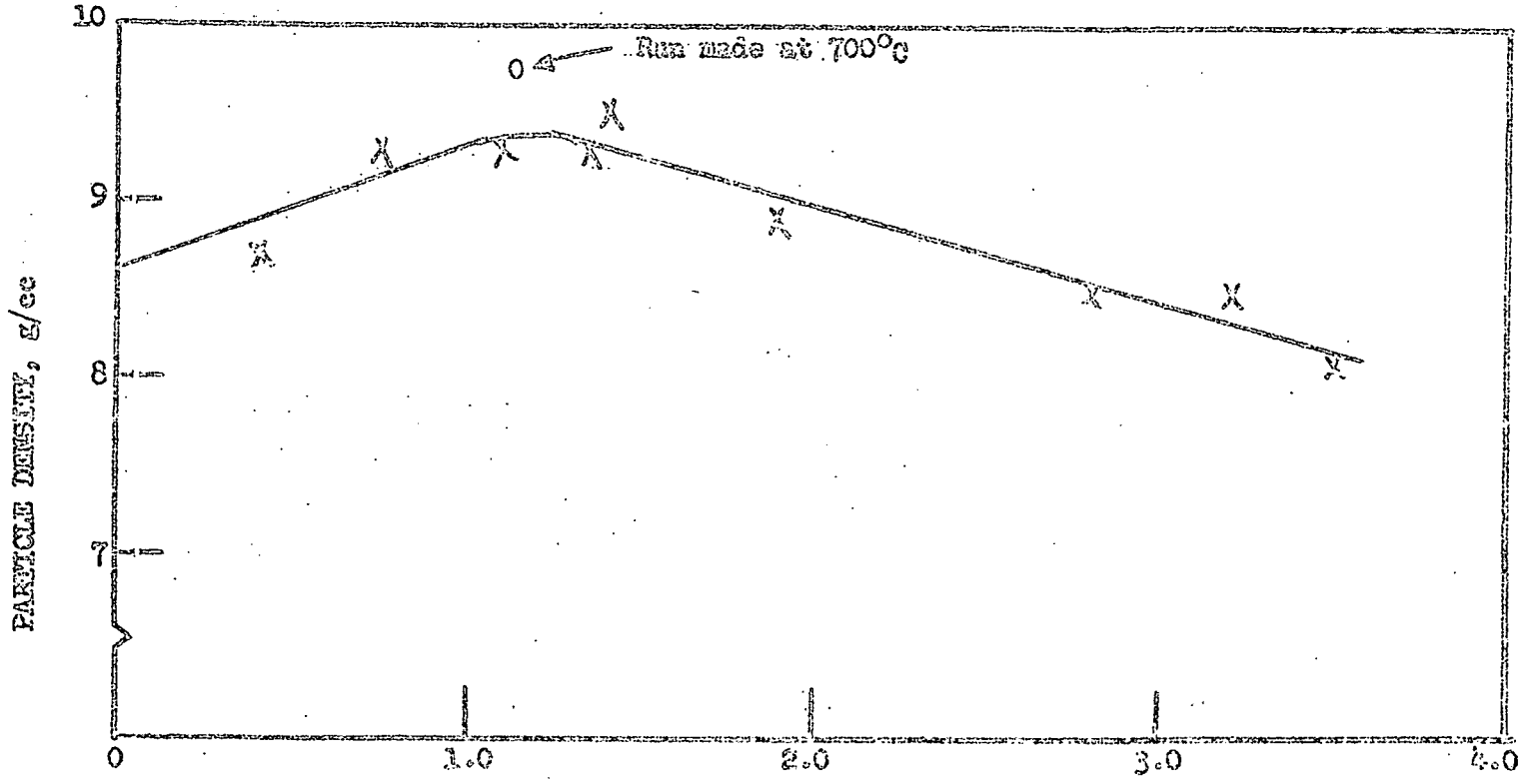
The observed density variations with steam rate are believed to be associated with the sintering on the particle surfaces of relatively low melting mixtures of uranium tetrafluoride, uranium dioxide, and U_3O_8. Sintering of mixtures of uranium tetrafluoride and uranium dioxide at these temperatures has been reported in the literature[1,2]. Actual evidence of particle sintering was obtained in a study with a starting bed of relatively low-density uranium dioxide particles. In an eight hour test, increases in density of about 24% were observed, the density increasing from 6.9 g/cc to 8.6 g/cc for the full-size range bed (see Fig. 3). Only

Figure 2

THE EFFECT OF STEAM RATE ON THE PARTICLE DENSITY OF URANIUM DIOXIDE PRODUCED BY REACTION OF HYDROGEN AND STEAM WITH URANIUM HEXAFLUORIDE

Run Conditions

Temperature:	650°C
UF_6 Rate:	25 g/min
Duration of Feed Period:	30 min/hr
Bed Depth (static):	9 in.



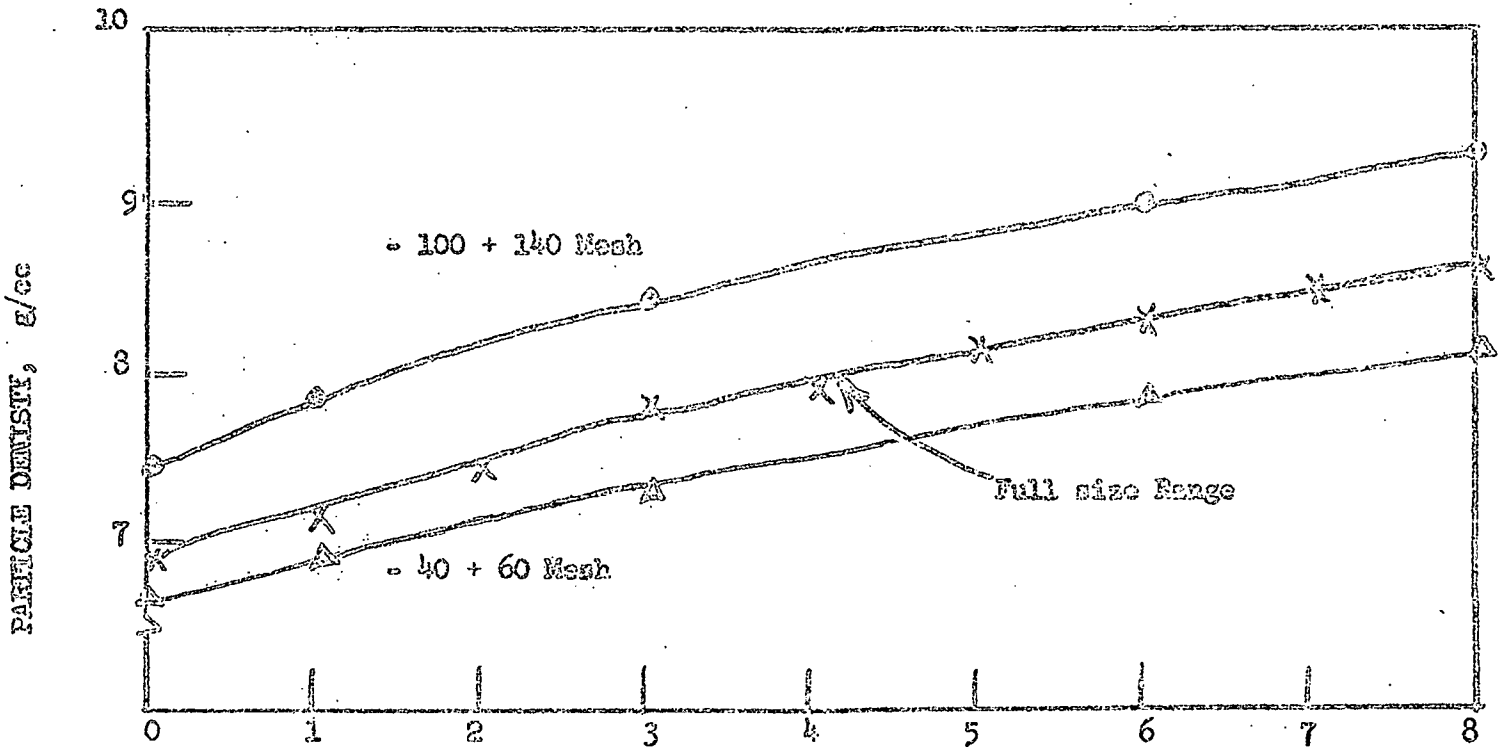
(*Based on the Reaction $UF_6 + 2H_2O + H_2 \longrightarrow UO_2 + 6HF$)

Figure 3

INCREASE IN DENSITY OF URANIUM DIOXIDE BED PARTICLES OCCURRING DURING DEPOSITION OF DENSE OXIDE FROM REACTION OF HYDROGEN AND STEAM WITH URANIUM HEXAFLUORIDE

Run Conditions

Temperature:	650°C
UF_6 Rate:	25 g/min
Steam Rate:	1.3 times stoichiometric requirement*
Duration of Feed Period:	30 min/hr
Bed Depth (static):	9 in.



(*Based on the Reaction $UF_6 + 2H_2O + H_2 \longrightarrow UO_2 + 6HF$)

about half of this increase can be attributed to the displacement of the low-density starting material by the denser oxide, the remainder resulting from sintering of the original particles. The density increases were similar for the different size fractions. Microscopic examination of the particles of the starting and final beds showed that voids had been eliminated from the interior of the starting particles during the run. Another indication of the apparent densification of the starting material was the absence of any over-all particle growth (a 10% increase in average particle diameter had been anticipated). These results suggest that this process scheme would be suitable for upgrading low-density oxide.

In contrast to the effect of the steam rate, the amount of hydrogen in the reactant stream in the range of 5 to 20 times the stoichiometric requirement (based on the over-all reaction) had no effect on the density of the uranium dioxide product. Also, since the steam rate during the fluoride cleanup period was found to have no effect on the product density, larger amounts of steam, up to 12 g/min, were used during the cleanup period to increase the rate of fluoride removal.

The effect of the uranium hexafluoride feed rate at a constant steam/hexafluoride ratio on the density of the dioxide product was investigated in the interest of increasing the capacity of the unit. Doubling the uranium hexafluoride rate from 25 to 50 g/min [from 44 to 88 lb. uranium/(hr) (sq ft reactor cross section)] resulted in about a 6% reduction in density of the dioxide product from 9.3 g/cc to 8.7 g/cc (see Fig. 4).

Effect of Other Variables on Oxide Density

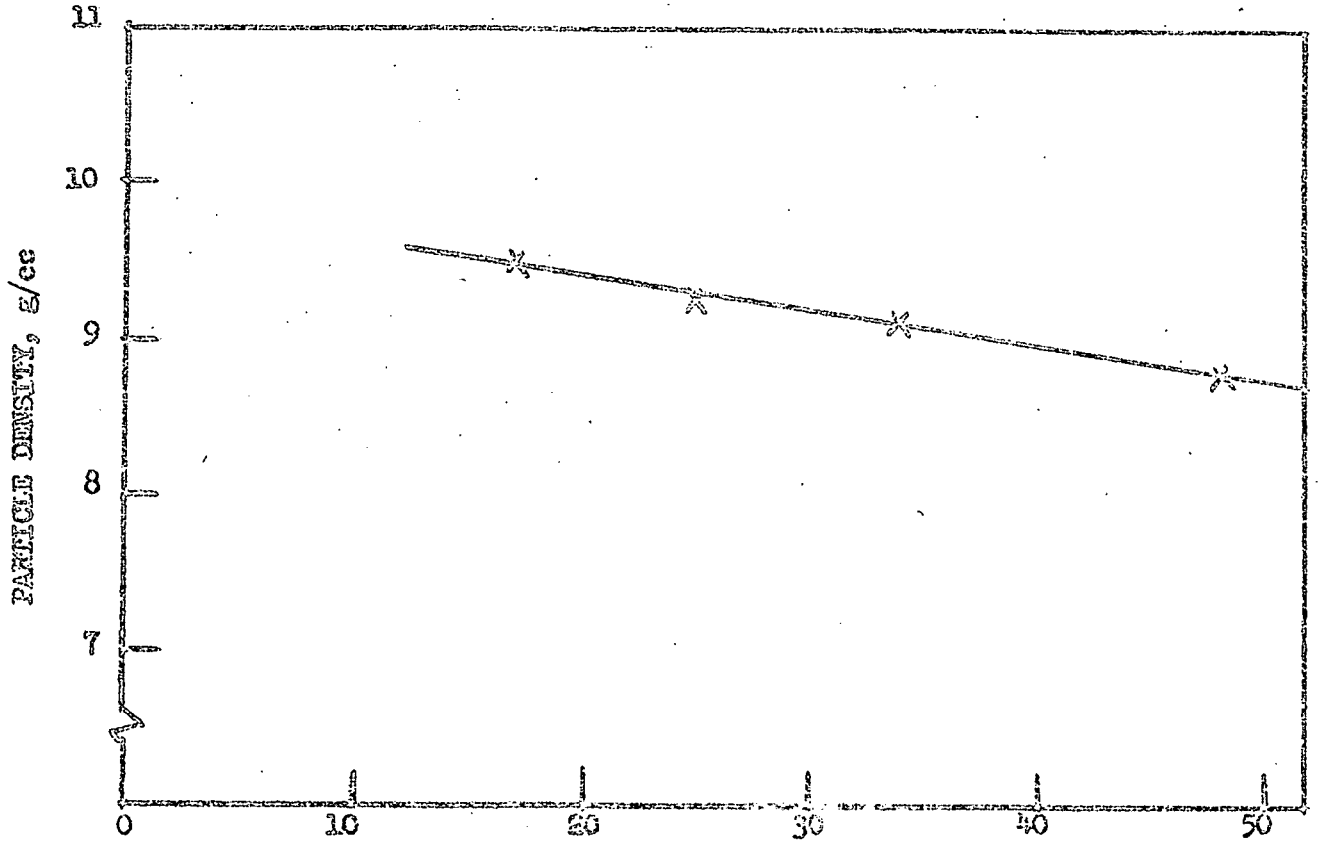
Operation at a reactor temperature higher than 650°C resulted in a denser product. Uranium dioxide with a density of 9.75 g/cc (about 89%

Figure 4

THE EFFECT OF URANIUM HEXAFLUORIDE RATE ON THE PARTICLE DENSITY OF URANIUM DIOXIDE PRODUCED BY REACTION OF HYDROGEN AND STEAM WITH URANIUM HEXAFLUORIDE

Run Conditions

Temperature:	650°C
Steam Rate:	1.15 to 1.35 times stoichiometric requirement*
Duration of Feed Period:	30 min/hr
Bed Depth (static):	9 in.



(*Based on the Reaction $UF_6 + 2H_2O + H_2 \longrightarrow UO_2 + HF$)

of theoretical density) was obtained in a test at 700°C when the 2/1 ratio of steam and uranium hexafluoride was used with a uranium hexafluoride feed rate of 25 g/min. In comparison, a density of 9.3 g/cc was obtained for similar conditions at 650°C. Temperatures below 650°C were not investigated.

The duration of the uranium hexafluoride feed period up to periods of 30 minutes had no effect on the density of the uranium dioxide. However, extending the duration of the hexafluoride feed period to one hour between cleanup periods resulted in a slight reduction in product density.

An effect of bed depth on product density was also noted. In tests at 650°C, with the optimum 2/1 steam-uranium hexafluoride ratio and a uranium hexafluoride feed rate of 25 g/min, an increase in the density of the uranium dioxide product from 9.3 g/cc to 9.6 g/cc was obtained when the bed depth (stable) was doubled from 9 to 18 inches. Doubling the bed inventory, in effect, results in halving the thickness of the deposited layer, and apparently, thinner layers densify or "sinter" more readily.

During the course of the experimental work, the uranium hexafluoride inlet was re-positioned so that it extended only 3/4 inch, rather than 3 1/2 inches, into the bed of particles. With this shorter inlet, a lower-density product was obtained, 9.0 g/cc at conditions at which product densities of 9.3 g/cc had been previously obtained. The reduction in product density with the short hexafluoride inlet was reproduced in several tests with different steam-to-uranium hexafluoride ratios and is attributed to different solids-mixing patterns in the cone section of the reactor.

Properties of the Uranium Dioxide Product

The uranium dioxide products contained about 200 to 300 ppm residual fluoride and about 1% to 2% hexavalent uranium. The oxygen-to-uranium

ratio was 2.03. Contamination of the oxide from corrosion of the Monel reactor was low; only 10 to 20 ppm copper and nickel were found in typical products.

Pore size distribution measurements* indicated that much of the porosity in the particles consisted of pores less than 0.4μ in diameter and a significant number were smaller than 0.06μ. The fine-grained structure of the particles may be seen in Fig. 5, a high-magnification (933X) photomicrograph of a sectioned particle. Figure 6 shows the smooth, spheroidal appearance of the particles as produced in the fluid-bed and Fig. 7, which shows cross sections of a number of particles, illustrates the uniform manner in which the layers are deposited.

Results of Sintering Tests

Sintering of representative samples of uranium dioxide particles in hydrogen resulted in significant further densification of the particles and further removal of fluoride. Final densities of 95% to 96.5% of theoretical density were obtained by heating material with densities ranging from 72 to 89% of theoretical in hydrogen for 2.5 hours at 1700°C (see Table 1). The highest density, 96.5% of theoretical, was obtained on the particles having the highest initial density. The residual fluoride content of all the samples was reduced to about 5ppm.

The final sintered particles were smooth-surfaced and spheroidal in appearance like the original particles (see Figs. 8 and 9). A cross-section of the sintered particle (Fig. 10) shows the elimination of the fine-grained structure previously noted.

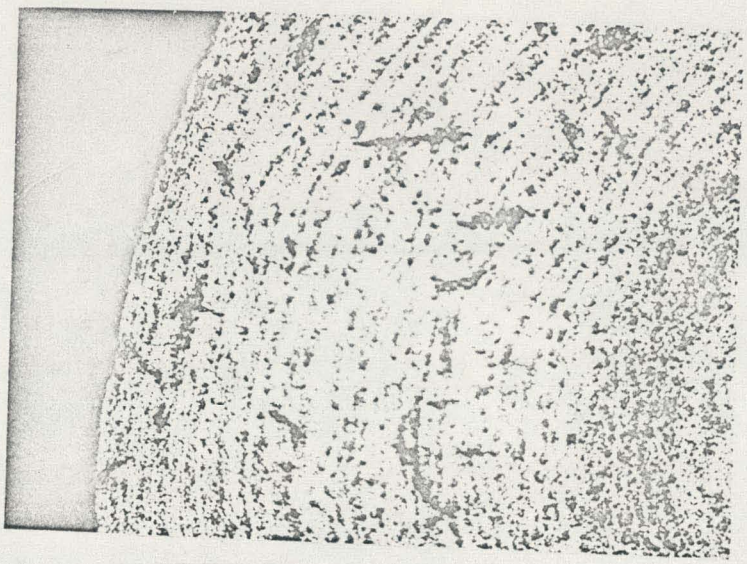
---

*Pore size distribution measured on a porosimeter by Armour Research Foundation, Chicago, Illinois.

Figure 5

CROSS SECTION OF DENSE URANIUM DIOXIDE PARTICLE

SHOWING FINE-GRAIN STRUCTURE

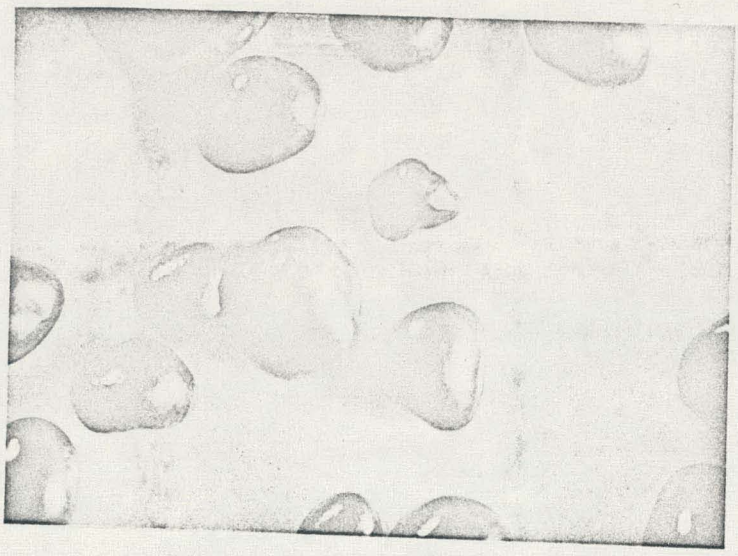


PARTICLE DENSITY, 9.7 g/cc
(Magnification - 533X)

Figure 6

DENSE URANIUM DIOXIDE PARTICLES AS PRODUCED

IN THE FLUID-BED REACTOR



1 mm

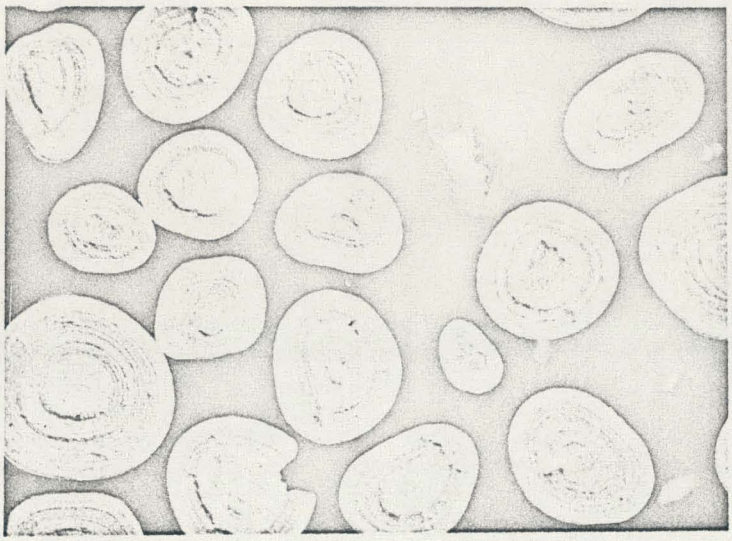
FINAL PARTICLE DENSITY, 9.3 g/cc

(Magnification - 37X)

Figure 7

CROSS SECTION OF DENSE URANIUM DIOXIDE PARTICLES

SHOWING LAYER DEPOSITION



PARTICLE DENSITY, 9.3 g/cc
ETCHED 60 SEC WITH ONE PART CONC. H_2SO_4
NINE PARTS 30% H_2O_2
(Magnification - 37X)

Table 1

SINTERING TEST RESULTS ON DENSE URANIUM DIOXIDE PARTICLES PRODUCED BY SIMULTANEOUS REACTION PROCEDURE

Particle Size:	- 20 + 200 mesh
Sintering Atmosphere:	Hydrogen (300 ppm oxygen impurity)
Sintering Temperature:	1600 - 1725°C for 2-1/2 hours

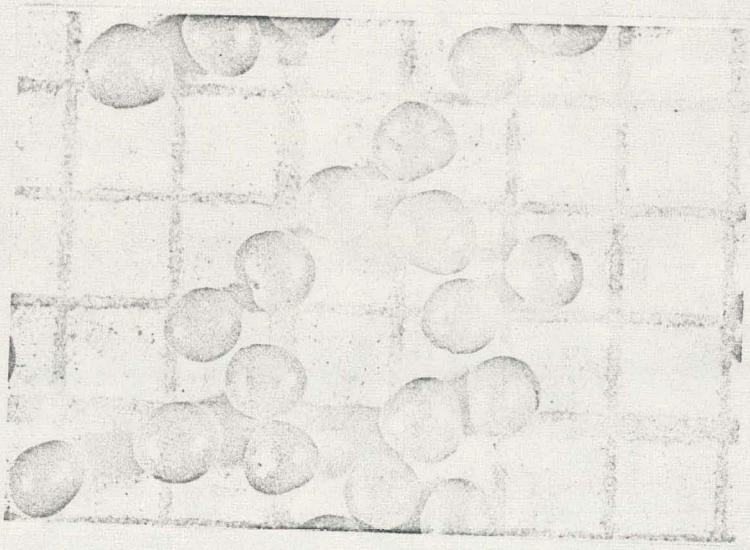
Particle Density (g/cc)	
Before Sintering	After Sintering
9.75	10.6
9.0	10.4
8.5	10.4

Figure 8

DENSE URANIUM DIOXIDE PARTICLES PRODUCED

BY THE CONVERSION OF URANIUM

HEXAFLUORIDE - AFTER SINTERING



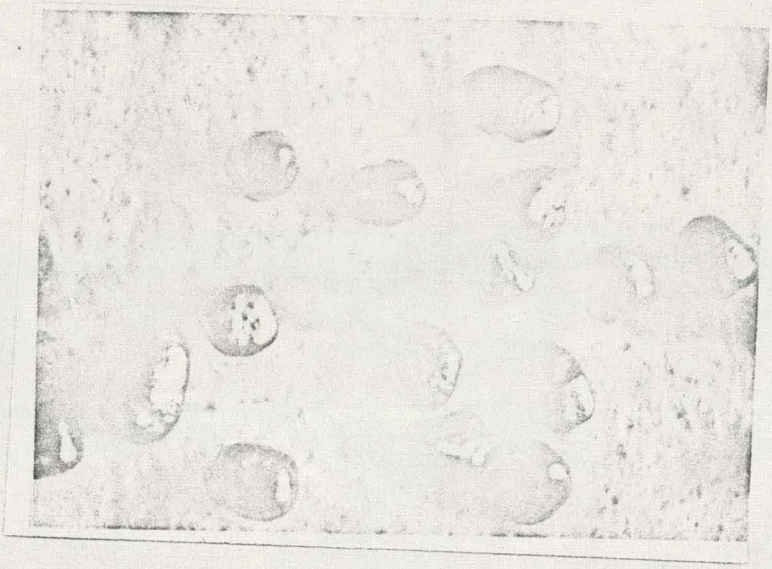
1 mm

PARTICLE DENSITY 10.6 g/cc

PARTICLE DIAMETER ~650μ

Figure 9

DENSE URANIUM DIOXIDE PARTICLES PRODUCED BY THE CONVERSION OF URANIUM HEXAFLUORIDE - AFTER SINTERING



1 mm

PARTICLE DENSITY 10.6 g/cc
PARTICLE DIAMETER 160 μ

Figure 10

CROSS SECTION OF DENSE URANIUM DIOXIDE PARTICLE SHOWING STRUCTURE AFTER SINTERING IN HYDROGEN AT 1700°C

PARTICLE DENSITY, 10.6 g/cc
(Magnification - 533X)

Conclusions

The preparation of dense uranium dioxide particles from uranium hexafluoride by reaction with steam and hydrogen in a fluidized bed has been demonstrated. The process also appears to be directly applicable for the conversion of mixtures of uranium and plutonium hexafluorides to the oxides as well as to the conversion of pure plutonium hexafluoride. Currently, work is in progress at ANL on the construction of a 2-inch diameter fluid-bed unit for the preparation of mixed-oxide particles containing up to 20% plutonium. Operation of this unit is expected to begin early in 1964.