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ENGINEERING DEVELOPMENT OF FLUID-BED
FLUORIDE VOLATILITY PROCESSES

*PART 6. PREPARATION OF DENSE URANIUM DIOXIDE PARTICLES
FROM URANIUM HEXAFLUORIDE IN A FLUIDIZED BED*

by

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ENGINEERING DEVELOPMENT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 6. Preparation of Dense Uranium Dioxide Particles from Uranium Hexafluoride in a Fluidized Bed

by

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ABSTRACT

A fluid-bed process for the preparation of dense, spheroidal uranium dioxide particles directly from uranium hexafluoride for dispersion and compacted fuel element applications has been developed. In the process, uranium hexafluoride is reacted with mixtures of steam and hydrogen in a bed of uranium dioxide fluidized by the reactant gases and maintained at 650 to 700°C. The solid reaction products deposit 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. Product is withdrawn at the end of each cleanup period. Seed particles may be added to offset the growth of the particles in the bed and allow a uniform average particle size to be maintained. The feasibility of an in-situ method of seed preparation, in which the reduction of bed particle size is obtained by oxidative fracturing of the UO_2 particles, was established.

Uranium dioxide particles in the size range -18 +140 mesh and having densities up to 9.75 g/cc (89% of theoretical density) were reproduced. Uranium hexafluoride feed rates in the range from 17 to 50 g/min [30 to 88 lb uranium/(hr)(sq ft reactor cross section)] were tested, the higher rates giving a product of somewhat lower density (~9 g/cc). The average residual fluoride content of the product was about 250 ppm.

Steam/uranium hexafluoride mole ratios proved to be another important variable, ratios of about 2:1 giving material of the highest density. The effect on uranium dioxide density of other process variables, such as hydrogen concentration, bed depth, and location of the uranium hexafluoride inlet, was also determined.

Densification of the uranium dioxide particles to about 10.5 g/cc (96% of theoretical density) and reduction of the fluoride content to about 5 ppm was achieved by sintering in hydrogen at about 1700°C.

I. INTRODUCTION

Significant potential for the reduction of fabrication costs of reactor fuel elements is indicated in the current development work on compacted-powder fuels.^(1,2) Fuel elements prepared by compaction techniques utilize loadings of dense fuel particles into fuel tubes with final densification of the powder being achieved by vibratory compaction, mechanical working, or other means. An investigation of the direct preparation of uranium dioxide (UO₂) particles from uranium hexafluoride (UF₆) for application to compacted-powder fuel elements was undertaken as part of a fluoride volatility reprocessing scheme currently under development. Since UF₆ is the most common starting material from which slightly enriched UO₂ fuel is prepared, a direct conversion process could have wide application.

Earlier work^(3,4) had shown that fluidization and gas-solid reaction techniques could be used for a hexafluoride-to-oxide conversion process. Further study has shown that spheroidal particles of high density can be produced by proper choice of operating conditions and procedures. The process consists of reacting UF₆ with mixtures of steam and hydrogen at 650 to 700°C in a fluidized bed of UO₂ particles. The solid reaction products are deposited as a dense layer on the surface of the bed particles. A cyclic operating procedure is used in which periods of UF₆ feed are alternated with periods of fluoride cleanup; in the latter only steam and hydrogen are fed.

This report summarizes the work with UF₆ which has led to the development of a practical process for the preparation of dense UO₂ particles. Application of this process to the conversion of mixtures of uranium and plutonium hexafluorides to dense, mixed-oxide particles is planned for investigation, and equipment installation in a glovebox facility is currently in progress.⁽⁵⁾

II. PROCESS CHEMISTRY

Uranium hexafluoride is converted to UO₂ by reaction with steam and hydrogen through a series of concurrent and consecutive reactions. The overall reaction,

represents the net consumption of reactants and formation of products. Initially, reactions occur between UF₆ and the hydrogen and steam, producing as solid products uranium tetrafluoride (UF₄) and uranium oxide (U₃O₈):^(6,7)

Although the low-temperature hydrolysis of UF_6 leads to the formation of uranyl fluoride, reaction at elevated temperatures, as in this process, results primarily in the above products, due perhaps to further reaction of any UO_2F_2 formed. The intermediate solid products UF_4 and U_3O_8 are converted to UO_2 by reaction with additional quantities of steam and hydrogen:

The kinetics of these latter reactions establishes the duration of the cleanup period in which reaction to the dioxide is carried to completion.

III. APPARATUS AND PROCEDURE

The experimental work on the hexafluoride-to-oxide conversion process was performed in a Monel column, shown schematically in Figure 1. The reactor section was 3 in. in diameter, 30 in. high, and had a 60° cone bottom. A $1\frac{1}{4}$ -in.-OD tube, which passed through the apex of the cone and extended about $3\frac{1}{2}$ in. into the bed, served as the UF_6 feed inlet. The fluidizing and/or reactant gases entered through the annulus surrounding the UF_6 inlet. Product was withdrawn from an outlet on the cone. A solids feed line for the addition of seed particles was provided at a point 20 in. from the bottom of the reactor section.

Solids entrained from the bed were retained in the system by Monel sintered metal filters* contained in an 8-in.-diameter section surmounting the reactor section. The filters were 9-in.-long cylinders, 3 in. in diameter, and had an average pore size of 10μ . An automatic pulse blowback system (40 pulses per hr per filter) using 80-psig nitrogen discharged accumulated solids from the filters. For the majority of the work reported here, the 8-in.-diameter section was mounted directly above the bed so that during blowback the fine particles that had accumulated on the filters were returned to the bed. In some of the initial runs, however, this section was detached from the main reactor so that fine particles which were elutriated from the bed were collected separately. The former arrangement was preferable since it eliminated handling of a separate fines stream. No changes in product properties were noted from the change in operation.

*Poro-Klean sintered metal filter elements, Cuno Engineering Corporation, Meriden, Connecticut.

The off-gas from the filter section passed to a Monel condenser where the waste steam and hydrofluoric acid were condensed and collected.

Figure 1
SCHEMATIC DRAWING OF
FLUID-BED COLUMN FOR
THE PREPARATION OF
DENSE UO_2 FROM UF_6

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when only steam and hydrogen were fed. These periods were generally of 30-min duration each. Product was withdrawn from the reactor at the end of each cleanup period. Seed particles (obtained by grinding a portion of the product or by an *in-situ* technique described in the Appendix) were added as necessary to offset particle growth which results from the solid reaction products being deposited on the bed particles. With proper seed addition, a uniform average particle size was maintained in the fluidized bed.

In order to evaluate a given variable, the run duration was sufficient to displace a major fraction of the starting bed particles with new UO_2 product. Usually, after the formation of UO_2 product equal in weight to the starting bed of UO_2 , no further change in particle density was observed. The starting bed for each test was the final bed of the previous test except where otherwise specified.

The noncondensable gases passed to a packed scrub tower for final cleanup by circulating potassium hydroxide solution. The off-gas condensate and the caustic scrub solution were sampled and analyzed for uranium content to check on the efficiency of the filters.

The run procedure involved, first, starting of the nitrogen purge and fluidizing gas streams, and charging and heating of the starting UO_2 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. The superficial velocity in the column (exclusive of UF_6 feed and nitrogen purges) was maintained at 1.0 ft/sec in most experiments. Where changes were made in the amount of steam fed, the hydrogen rate was adjusted to compensate for the change. When operating conditions were stabilized, the UF_6 feed was introduced.

The operating procedure was cyclic in nature; periods of UF_6 feed were alternated with cleanup periods

IV. RESULTS AND DISCUSSION

A. Effect of Process Variables on the Density of the UO_2 Particles

The variables studied and their ranges were as follows:

UF_6 rate	17 to 50 g/min
steam/ UF_6 mole ratio	0 to 23/1
hydrogen/ UF_6 mole ratio	4/1 to 17/1
reactor temperature	650 to 700°C
bed depth	9 to 17 in.
UF_6 inlet location	1/2 and 3 1/2 in. into the bed.

Reaction of the hexafluoride to form solids was essentially complete under all conditions tested. Losses of uranium to the off-gas were less than 0.01% of the hexafluoride fed. The bulk of the newly formed solids was deposited on the particles of the bed.

The UO_2 product was characterized in regard to its density, fluoride content, and oxygen/uranium ratio or hexavalent uranium content. The density was measured by a mercury displacement technique⁽⁸⁾ at atmospheric pressure, so that an overall particle density, not skeletal density, was measured.

1. Effects of Reactant Rates

Steam. The effect of the steam rate on the density of the UO_2 particles was studied in a series of tests with a constant UF_6 feed rate of 25 g/min. The tests were made at 650°C with a 6-kg bed of UO_2 particles (bed depth about 9 in. static). The durations of the UF_6 feed period and of the cleanup period were each 30 min. The steam rate was varied from 0 to 8.2 g/min (steam/ UF_6 mole ratio of 0 to 6.4/1). The hydrogen rate was adjusted so that a constant superficial velocity in the column of 1 ft/sec at operating conditions was maintained; the H_2/UF_6 mole ratio was relatively high (9/1 to 20/1) in all the tests. In those tests in which no steam or small amounts of steam were fed with the UF_6 , steam was added during the cleanup period to ensure fluoride removal. Run duration ranged from 6 to 24 hr. The mean volume-surface diameters,⁽⁹⁾ $D_{v/s}$, of the bed particles ranged from a minimum of 316 to a maximum of 439 μ . Seed particles (of average diameter about 160 μ) were added as needed to offset excessive particle growth.

A steam rate which provided a steam/ UF_6 mole ratio of about 2/1 was found to produce the densest UO_2 particles (see Table 1 and Figure 2), the highest value in this series being 9.5 g/cc or about 86.5% of theoretical density (TD). Smaller amounts as well as larger amounts of steam resulted in a product of lower density. In earlier tests at slightly lower UF_6 rates (10 g/min) with steam/ UF_6 mole ratios of 23/1, particle densities as low as 6.6 g/cc were obtained.

Table 1

EFFECT OF STEAM/UF₆ MOLE RATIO ON THE
DENSITY OF UO₂ PARTICLES PRODUCED BY
REACTION OF UF₆ WITH STEAM AND HYDROGEN

Temperature:	650°C
UF ₆ Rate:	25 g/min
Bed Weight and Height:	5.5 to 6.5 kg, 8 to 10 in. (static)
H ₂ /UF ₆ Mole Ratio:	9/1 to 20/1
Duration of UF ₆ Feed Period:	30 min/hr
Average Bed-particle Diameter:	316 to 439 μ

Steam/UF ₆ Mole Ratio	UO ₂ Density ^a (g/cc)
0	8.7
0.8	8.7
1.5	9.3
2.2	9.3
2.5	9.5
2.7	9.3
3.8	8.9
5.6	8.5
6.4	8.5

^a Measured by mercury displacement.

Figure 2

THE EFFECT OF STEAM/UF₆ MOLE RATIO ON THE
DENSITY OF UO₂ PARTICLES PRODUCED BY
REACTION OF UF₆ WITH STEAM AND HYDROGEN

Run Conditions

Temperature:	650°C
UF ₆ Rate:	25 g/min
Duration of Feed Period:	30 min/hr
Bed Depth (Static):	9 in.

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A similar effect of steam rate on particle density was indicated in tests at higher UF₆ rates near 50 g/min (see Table 2). The highest density, 8.8 g/cc, was obtained with a steam/UF₆ mole ratio of 2.7/1; lower densities, 8.2 and 8.5 g/cc, were obtained at lower and higher steam/UF₆ mole ratios, 1.3/1 and 3.2/1, respectively. Some variation in bed depth existed in these tests, but the primary effect of steam/UF₆ ratio was clear.

Table 2

EFFECT OF STEAM/UF₆ MOLE RATIO ON THE
DENSITY OF UO₂ PARTICLES PRODUCED AT
HIGH UF₆ FEED RATES

Temperature:	650°C
UF ₆ Rate:	48 to 52 g/cc
Bed Weight and Height:	5.7 to 8.8 kg, 8 to 14 in. (static)
H ₂ /UF ₆ Mole Ratio:	6.1 to 8.8
Duration of UF ₆ Feed Period:	30 min/hr
Average Bed-particle Diameter:	196 to 303 μ

Steam/UF ₆ Mole Ratio	UO ₂ Density ^a (g/cc)
1.3	8.2
2.7	8.8
3.2	8.5

^a As measured by mercury displacement.

Hydrogen. The H₂/UF₆ ratio was varied in a run in which a portion of the hydrogen was replaced with nitrogen while maintaining the steam/UF₆ ratio (and other operating conditions) constant. The run consisted of a 17-hr period at a hydrogen/UF₆ ratio of 17/1, followed by a 12-hr period with the hydrogen/UF₆ ratio reduced to 3.8/1. A deep bed (11 kg, 17 in. static depth) was used.

No change in particle density was observed, a value of 9.6 g/cc being maintained throughout the run (the relatively high density is attributed to the greater bed depth, as discussed later). However, both the fluoride and hexavalent uranium contents of the products increased by a factor of about two, from 0.04 to 0.08 w/o, and from 0.5 to 1.0 w/o, respectively.

Uranium Hexafluoride. The effect of UF₆ feed rate on product density was also studied. The hexafluoride input ranged from 17 to 48 g/min. Tests were made at 650°C with starting beds of about 6 kg of UO₂ particles (static bed depth about 9 in.). The steam/UF₆ mole ratio was held at about 2.5/1. The H₂/UF₆ mole ratio was 27/1 at the low UF₆ rate and 7.6/1 at the high UF₆ rate. The UF₆ feed period and the cleanup period were each 30 min in duration.

A continual decrease in density of the UO₂ product was observed as the UF₆ rate was increased (see Table 3, and Figure 3). The density values ranged from 9.6 g/cc to 8.8 g/cc. Comparison of tests with deeper beds (11 kg, static bed depth about 17 in.) at UF₆ rates of 25 and 50 g/min showed a similar trend of decreased product density with increased feed rate.

Table 3

EFFECT OF UF_6 RATE ON THE DENSITY OF
 UO_2 PARTICLES PRODUCED BY REACTION
 OF UF_6 WITH STEAM AND HYDROGEN

Temperature: 650°C
 Steam/ UF_6 Mole Ratio: 2.3/1 to 2.7/1
 Bed Weight and Height: 5.5 to 6.8 kg, 8 to 10 in. (static)
 H_2 / UF_6 Mole Ratio: 7.6/1 to 27/1
 Duration of UF_6 Feed Period: 30 min/hr
 Average Bed-particle Diameter: 298 to 479 μ

UF_6 Rate (g/min)	UO_2 Density ^a (g/cc)
17	9.6
25	9.3
34	9.1
48	8.8

^a Measured by mercury displacement.

Figure 3

THE EFFECT OF UF_6 RATE ON THE
 DENSITY OF UO_2 PARTICLES
 PRODUCED BY REACTION OF UF_6
 WITH STEAM AND HYDROGEN

Run Conditions

Temperature: 650°C
 Steam/ UF_6 Mole Ratio: 2.3/1 to 2.7/1
 Duration of Feed Period: 30 min/hr
 Bed Depth (static): 9 in.

2. Effect of Bed Depth

An effect of bed depth (or bed inventory) on the density of the UO_2 particles was observed in tests with average bed depths (static) of 9 and 17 in. (bed weights of 6.0 and 11.2 kg). The tests were made at 650°C with UF_6 rates of 25 and 50 g/min, steam/ UF_6 mole ratio of about 2.5/1, and H_2/UF_6 mole ratios of from 7/1 to 17/1. The UF_6 feed period and the clean-up period were each 30 min in duration.

The density of the UO_2 particles was found to be higher when a greater bed depth was used (see Table 4). In tests at a UF_6 rate of 25 g/min, the density of the particles produced with a deep bed was 9.6 g/cc as compared with a particle density of 9.3 g/cc obtained with the shallow bed; at a UF_6 rate of 50 g/min, the particle densities obtained were 9.1 g/cc with the deeper bed and 8.8 g/cc with the shallow bed. It is also noted that at similar "UF₆ rate/bed depth" ratios, a slightly higher density was obtained at the lower UF_6 rate, indicating the effect of bed depth is not one of total surface area alone.

Table 4

EFFECT OF BED DEPTH ON THE DENSITY OF UO_2 PARTICLES PRODUCED BY REACTION OF UF_6 WITH STEAM AND HYDROGEN

Temperature:	650°C	
Steam/ UF_6 Mole Ratio:	2.3/1 to 2.7/1	
H_2/UF_6 Mole Ratio:	7/1 to 17/1	
Duration of UF_6 Feed Period:	30 min/hr	
Average Bed-particle Diameter:	267 to 439 μ	
Static Bed Depth (in.)	UO_2 Density ^a (g/cc)	
	25 g/min UF_6	50 g/min UF_6
9	9.3	8.8
17	9.6	9.1

^a Measured by mercury displacement.

3. Effect of Reaction Temperature

Particle density increased with increased bed temperature. Uranium dioxide particles with a density of 9.75 g/cc were obtained at 700°C (as compared with 9.3-9.5 g/cc obtained at 650°C) in experiments conducted with a UF_6 feed rate of 26 g/min, steam/ UF_6 mole ratio of 2.3/1, H_2/UF_6 mole ratio of 17/1, and a 6-kg bed (9-in. static depth). Temperatures lower than 650°C were not investigated.

4. Effect of the Location of the UF₆ Inlet

During the course of the experimental work, the UF₆ inlet nozzle was repositioned so that it extended only 3/4 in., rather than 3 1/2 in., into the bed of particles. Tests showed a lower density product was produced when the shorter UF₆ nozzle was employed. This effect was reproduced at four different steam/UF₆ mole ratios, as shown in Table 5.

Table 5

EFFECT OF UF₆ NOZZLE POSITION ON THE DENSITY OF UO₂ PARTICLES PRODUCED BY REACTION OF UF₆ WITH STEAM AND HYDROGEN

Temperature:	650°C	
UF ₆ Rate:	25 g/min	
Bed Weight and Height:	5.2 to 6.5 kg, 8 to 10 in. (static)	
H ₂ /UF ₆ Mole Ratio:	9/1 to 20/1	
Average Bed-particle Diameter:	301 to 439 μ	
Duration of UF ₆ Feed Period:	30 min/hr	
Steam/UF ₆ Mole Ratio	UO ₂ Density ^a (g/cc)	
	Short Nozzle (3/4 in.)	Long Nozzle (3 1/2 in.)
0.2	8.4	8.7 ^b
2.6	9.0	9.4 ^b
2.8	8.5	9.3 ^b
3.1	8.0	9.2 ^b

^a Measured by mercury displacement.

^b Interpolated values obtained from Figure 2.

For each of the nozzle positions, particle density was highest when the steam/UF₆ mole ratio was optimum (near 2.5/1). A maximum particle density of 9.0 g/cc was obtained with the shorter nozzle as compared to 9.3 to 9.5 g/cc obtained with the longer nozzle.

5. Discussion of Density Effects

The initial reactions of the UF₆ with steam and hydrogen are of the vapor-deposition type which usually give dense solid reaction products. The subsequent gas-solid reactions during the conversion of the intermediates to the dioxide may result in porosity and an overall lowering of particle density. This latter effect, however, is believed to be partially offset by a sintering of the uranium oxide-UF₄ mixtures occurring at operating temperatures. Melting points of mixtures of UF₄ and UO₂ have been found to be in

the range from 910 to 940°C,⁽¹⁰⁾ with sintering being important at temperatures as low as 500°C.⁽¹¹⁾ Also, U_3O_8 has been found to be quite sensitive to sintering at temperatures above 600°C.⁽¹²⁾

The effects of the reactant feed rates and other operating conditions on the density of the UO_2 product can be related to the above sintering mechanism. Variation of the steam/ UF_6 mole ratio was observed to produce changes in the relative proportions of UF_4 and U_3O_8 formed during the UF_6 feed period, apparently resulting in different degrees of sinterability. At the optimum ratio of about 2.5/1, about 30% of the UF_6 reacts to form UF_4 with the remainder going to U_3O_8 . The composition of the deposited solids changed only slightly when the amount of hydrogen fed was reduced, thereby explaining the absence of any effect of the hydrogen feed rate on the product density.

The effects on product density of the UF_6 feed rate, bed depth, and the UF_6 inlet location also may be related to the sintering mechanism. Density variations obtained at different rates and operating conditions appear to be a function of the differences in the rate of deposition and the thickness of the layer of the newly formed solids. Lower densities were obtained at the higher UF_6 rates, with shallow beds (less surface area available for deposition), and when the UF_6 inlet was located in the cone region (where solids circulation might be nonuniform). Other factors, such as bed-depth effects on solids circulation patterns, may be involved in the tests at comparable " UF_6 rate/bed depth" ratios in which similar densities were expected but not obtained.

Consistent with the other effects, that of reactor temperature can be attributed to the degree of sintering occurring at different temperatures.

B. Densification of Low-density Oxide

Instances of unexpectedly rapid increases in product density were noted in tests in which starting beds of relatively low-density UO_2 were used. A study was made, therefore, of the rate of increase in density of low-density material to establish whether overall densification was occurring. Conditions were maintained similar to those of previous tests in which product densities of 9.3 g/cc were obtained (reactor temperature 650°C, UF_6 rate 25 g/min, steam/ UF_6 mole ratio 2.5/1, H_2 / UF_6 mole ratio 16/1, bed weight 5.5 kg, duration of feed and cleanup periods 30 min each). The starting bed had a density of 6.9 g/cc and an average particle diameter of about 192 μ ; no seed particles were added during the run.

An increase in density of the bed particles of 24%, from 6.9 to 8.6 g/cc, was obtained in the 8-hr run (see Figure 4). Measurements on the -100 +140 mesh and -40 +60 mesh fractions showed similar percentage

increases in density in spite of a difference in starting densities. A reduction in surface area of the particles reflected the increase in density; typically, the area of the -40 +60 mesh fraction decreased from 0.7 sq m/g to 0.3 sq m/g during the run.

Figure 4
INCREASE IN DENSITY OF UO_2 BED PARTICLES
DURING THE UF_6 REACTION PERIOD

Run Conditions

Temperature:	650°C
UF_6 Rate:	25 g/min
Steam/ UF_6 Mole Ratio:	2.6/1
Duration of Feed Period:	30 min/hr
Bed Depth (static):	9 in.

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If the deposition of UO_2 with a density of 9.3 g/cc (normally obtained at steady state at these operating conditions) is assumed, only about 70% of the observed increase in density can be attributed to the newly deposited layers of denser oxide. The remainder of the increase is attributed to in-situ densification. A comparison of starting and final bed material by microscopic examination also supports this densification hypothesis. Large voids observed in the starting material were eliminated entirely from the particles in the smaller-size fraction in the final bed and were also eliminated, but to a lesser extent, in the coarser particles.

Another indication of the apparent densification of the starting material was the absence of any significant particle growth. Based on the volume of solids deposited on the bed particles, a 19% increase in average particle diameter had been expected. Towards the end of the run, sieve analyses of bed samples showed growth of the smallest size fraction into the next size range. This fraction would have attained a maximum density first. Continued run time would be expected to result in a maximum (or steady-state) density value being achieved for each of the succeeding particle size fractions.

C. Fluoride Removal and U^{+6} Reduction during the Cleanup Step

A cleanup period in which only steam and hydrogen were fed was used to complete the conversion to the oxide of the intermediate reaction products (UF_4 , U_3O_8) formed during the UF_6 feed period. The fluoride and hexavalent uranium content of the bed at the end of the UF_6 feed period ranged from 0.3 to 1.6% and from 0.9 to about 9%, respectively, with variation in starting bed weight and UF_6 feed rate. To obtain adequate rates of fluoride removal during the cleanup step, especially in the tests at high UF_6 feed rates, the steam concentration in the cleanup stream was increased over that used in the UF_6 feed period to a 1/1 steam/hydrogen mole ratio.

Final values of about 0.025% fluoride and of 0.5 to 1.0% hexavalent uranium (O/U of 2.02 to 2.04) were achieved in a 30-min cleanup step. The rate of fluoride removal for starting values in the range 0.1 to 1.6% fluoride in the bed averaged about 0.1%/min; below 0.1% fluoride content, the rate of removal decreased sharply to about 0.005%/min. Final fluoride contents were somewhat lower when shallower beds were used. The rate of reduction of low (<1%) levels of hexavalent uranium also was observed to be quite low, about 0.01%/min. Above this level, rates of about 0.2%/min were obtained in the initial part of the 30-min cleanup period.

Requirements as to residual fluoride content and O/U ratio establish required cleanup times; the 30-min cleanup period was adequate for test purposes. Optimization of overall cycle times was not attempted.

D. Particle Size Control and Seed Requirements

The deposition of the solid reaction products on the particles of the bed results in an increase in the size of the particles. Growth rates in the absence of seed addition may be calculated (assuming formation of concentric shells) for the case of complete deposition of newly formed solids on the particles. The calculated rates for current operating situations range from about 6 μ per 30 min of UF₆ feed (11-kg bed, average particle diameter of 250 μ , and UF₆ rate of 25 g/min) to 21 μ per 30 min of UF₆ feed (6-kg bed, average particle diameter of 350 μ , and UF₆ rate of 50 g/min).

A side stream of seed particles (average diameter about one-half that of the average bed particle diameter) was used as needed to offset particle growth. The seed particles were obtained by grinding a portion of the UO₂ product to a suitable size or by an in-situ technique (described in the Appendix) in which particle breakup was obtained by oxidation of the UO₂ to U₃O₈.

Under actual run conditions, seed-particle requirements were expected to be reduced by the production of small particles (fines of <325 mesh size) in the bed by vapor-phase reaction of the hexafluoride feed. In early tests in which these fines were elutriated from the bed and collected separately in the filter vessel, the amount of fines formed was found to range from 2 to 14% by weight of the UF₆ feed, averaging about 7.4%. Larger amounts of fines were formed when higher steam/UF₆ mole ratios were used, and, in a single experiment with a deep bed (11 kg, 17-in. deep, static), a higher-than-average rate of fines formation (13.6% of the UF₆ feed) was observed. In these tests in which the fines were elutriated from the bed, the addition of seed particles (average particle diameter of 160 μ) in amounts equal to 10 to 12% of the UF₆ feed rate was required to offset particle growth.

During operations with the filter vessel directly above the bed, the amount of seed particles required was found to vary with bed height. In tests at the high UF₆ rate, 50 g/min, the amount of seed particles required to offset

particle growth ranged from 14.6% of the UF_6 feed rate when a 6-kg bed was used to no seed requirement when an 11-kg bed was used. In tests with an intermediate bed size, 8.9 kg, and with finer seed particles (all -120 mesh prepared by an oxidation-reduction procedure - see Appendix), seed requirements were equivalent to only about 5.5% of the UF_6 feed rate. Since fines generation in the bed appears to be a function of bed height and these fines are expected to behave as seed particles, this effect of bed height on seed addition requirements was anticipated.

The particle size distribution of the seed material also may require consideration. For example, in a 12-hr experiment (Run PY-80) made with a seed stream containing a considerable fraction of fines (<325 mesh), the bulk of this fraction was apparently not retained in the bed. A quantity of fines equivalent to about 2/3 of those fed were found held up in the filter section, probably on the walls as well as on the filters. Rapping on the column at regular intervals in a subsequent experiment (Run PY-81) in which the same seed material (size distribution given in Table 6) and the same seed addition rate were used, resulted eventually in a high fines content in the bed. In time (after 17 hr of a 24-hr planned period), the UF_6 nozzle plugged, the plugging being attributed to the high fines content of the bed and the resulting poor quality of fluidization.

Table 6

SIZE DISTRIBUTION OF SEED PARTICLES^a
USED FOR RUNS PY-80 AND PY-81

Mesh Size	w/o
+120	0.6
-120 +140	8.2
-140 +170	21.6
-170 +230	17.6
-230 +270	16.3
-270 +325	12.4
-325	23.3
	<u>100.0</u>

^aSee Appendix for method of preparation.

The control of bed-particle size by the addition of seed particles proved reasonably satisfactory with the following reservations: (1) with the filters mounted directly above the bed and fine particles being returned to the bed during blowback, seed requirements had to be established experimentally, and (2) the seed particle stream should contain minimum amounts of -325 mesh particles.

E. Particle Sintering Tests

Hydrogen sintering of representative samples of the UO_2 product resulted in further densification and fluoride removal (see Table 7). Particles with as-produced densities ranging from 72 to 89% of TD were sintered in hydrogen for 2.5 hr at 1700°C . Final densities of 95 to 96.5% of TD were achieved, the highest density being obtained with particles having the highest as-produced density. The residual fluoride content of all samples was reduced to 5 ppm; the O/U ratio was reduced to an average value of 2.03. The fine-grained layered structure of the particle before sintering and the denser randomized structure after sintering are shown in Figures 5 and 6.

Table 7

RESULTS OF SINTERING TESTS ON DENSE UO_2 PARTICLES PRODUCED BY REACTION OF UF_6 WITH STEAM AND HYDROGEN

Particle Size: -20 +200 mesh
Sintering Atmosphere: Hydrogen (300 ppm oxygen impurity)
Sintering Temperature: 1700°C for $2\frac{1}{2}$ hours

Before Sintering			After Sintering		
Particle Density (g/cc)	F (w/o)	O/U	Particle Density (g/cc)	F (w/o)	O/U
9.75	0.0400	2.03	10.6	0.0005	2.02
9.0	0.0360	2.06	10.4	0.0005	2.04
8.5	0.0420	2.06	10.4	0.0005	2.02

Figure 5

CROSS SECTION OF DENSE UO_2 AS PRODUCED BY REACTION OF UF_6 WITH STEAM AND HYDROGEN

Particle Density, 9.7 g/cc
(Magnification - 533X)

Figure 6
CROSS SECTION OF UO_2 AFTER
DENSIFICATION BY SINTERING
IN HYDROGEN AT 1700°C

Particle Density, 10.6 g/cc
(Magnification - 533X)

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A number of additional sintering tests with 2- to 3-kg batches of -60 +100 mesh particles were carried out in vacuum. Sintering time was $1/2$ hr at 1750°C . Sintered densities were good, being in the range from 10.1 to 10.5 g/cc, but residual fluoride contents were higher than those achieved in the hydrogen sintering tests. Also, some instances of sintering together of the particles occurred; this caking was eliminated by pretreatment with hydrogen at a temperature of 1400°C for 4 hr.

V. CONCLUSION

A semicontinuous fluid-bed process for the preparation of high-quality dense UO_2 particles directly from UF_6 by reaction with steam and hydrogen in a fluidized bed has been developed. Spheroidal particles of UO_2 with densities up to 9.75 g/cc (89% TD) have been produced. Uniformity of product is ensured since excellent control over process parameters is possible. Final densification to over 95% TD and reduction of fluoride content to 5 ppm can be achieved by hydrogen sintering at a high temperature. Direct application of this process to the conversion of mixtures of the hexafluorides of uranium and plutonium to dense mixed-oxide particles is believed feasible, and work in this direction is in progress.

APPENDIX

Particle-size Reduction of UO_2 by Oxidation-reduction Procedures

A brief study was made of an in-column seed-preparation technique in which particle-size reduction (breakup) is achieved by oxidizing the UO_2 partially or completely to U_3O_8 . The oxidized material is then reduced back to UO_2 with hydrogen before use. In practice, either a portion of a bed might be treated and then recycled as seed or an entire bed which has grown through the hexafluoride-conversion process to a practical limit may be re-sized in place. Both schemes were demonstrated after a study of the effect of oxidation on the extent of size reduction.

A. Studies of UO_2 Particle-size Reduction by Oxidation-reduction - Small Batch Tests

A series of seed-preparation tests were carried out in the 3-in.-diameter fluid-bed reactor system with relatively small amounts of material, 1.0- and 1.5-kg beds of +80 mesh particles of UO_2 . In one case, a bed of -20 +40 mesh particles was used. Oxidation was conducted at either 400°C or 650°C, with either 10% or 20% air in nitrogen. The quantity of air used ranged from 0.56 to 1.20 times the stoichiometric amount required for conversion of UO_2 to U_3O_8 . Oxidation periods ranged from 29 to 58 min. The reduction of the oxidized particles was conducted at 650°C with essentially 100% hydrogen (some dilution by nitrogen purge). The reactor was purged with nitrogen before and after the reduction step.

In sequence, the UO_2 charge was heated to the reaction temperature while being fluidized with nitrogen, then oxidized for the required time

with the air-nitrogen mixture; the system was then purged with nitrogen for a minimum of 20 min or until the bed was heated to 650°C. Hydrogen was fed for 30 min to reduce the oxidized material. The operating conditions and results are summarized in Table 8. The extent of particle breakup is shown by the amount of -80 mesh particles formed except in Run 12, in which the starting bed consisted of -20 +40 mesh particles. Here the amount of -40 mesh material is used to indicate the extent of breakup.

Table 8

CONDITIONS AND RESULTS OF OXIDATION-REDUCTION TESTS

Equipment:	3-in.-diameter Monel reactor					
Superficial Gas Velocity:	1.0 ft/sec (except Run 12, 1.75 ft/sec) during oxidation					
Starting Bed:	-18 +80 mesh, except Run 12, -20 +40 mesh					
Reduction Conditions:	100% hydrogen, 650°C, 30-min duration (except Run 7 and Run 12, 45 min)					
Starting Bed Weight:	1.5 kg, except Run 6, 1.0 kg					
Starting Particle Density: ^a	8.9 g/cc					
Run No.	6	7	12	10	9	11
Oxidation Conditions:						
Temperature (°C)	650	400	400	400	400	650
Air Concentration (% in nitrogen)	10	10	20	20	10	20
Equivalents Oxygen Fed ^b	0.70	0.80	1.20	1.20	1.20	1.18
O/U after Oxidation	2.38	2.46	2.48	2.53	2.55	2.61
Amount in -80 mesh fraction (%):						
After Oxidation	17.1	14.7	54.7	64.5	64.9	83.4
After Purging	23.7	20.9	50.6	74.6	66.3	84.8
After Reduction	26.8	52.0	57.4	77.1	70.8	-
Final Bed	42.2	61.3	59.7	76.7	70.8	86.6
-325 mesh/-80 mesh in Final Bed	0.45	0.20	0.30	0.31	0.34	0.44
Particle Density, ^a -80 +170 mesh						
Fraction (g/cc)	8.3	8.0	6.5	7.1	6.6	7.9

^aMeasured by mercury displacement after the reduction step.

^bExpressed as the ratio of oxygen fed to the reactor to the stoichiometric equivalents of oxygen required for oxidation of UO_2 to U_3O_8 .

In these tests, it was found that adequate particle breakup

was obtained with partial oxidation to U_3O_8 (0.7 stoichiometric equivalent of oxygen fed, as in Run 6) and that excessive amounts of -325 mesh particles were formed when the oxidation was carried to near completion. Particle breakup continued during all phases of the test after oxidation, e.g., in Run 6 the amount in the -80 mesh fraction was only 17% after oxidation, 24% after purging, 28% after reduction, and 43% after cooling down. Overall particle breakup was proportional to the degree of oxidation; typically, 43% breakup occurred in Run 6 for which the final O/U was 2.38, and up to 87% breakup in Run 11 for which the final O/U was 2.61. The percent -325 mesh in the -80 mesh fraction was relatively high in all cases, ranging from 20 to 45%.

Oxidation temperature affected size distribution. Sieve analyses of the final beds showed that a smaller proportion of the -80 mesh material was in the -325 mesh fraction when the oxidation was carried out at 400°C rather than at 650°C (0.20 to 0.34 at 400°C as compared with 0.44 and 0.45 at 650°C). The higher air concentration (on the basis of the results of Runs 9 and 10) gave greater particle breakup, a slightly better (lower) -325 mesh/-80 mesh ratio, and denser particles. Finally, the particle density of the -80 +170 fraction after reduction was higher, on the average, when the higher oxidation temperature was used, the density values being 8.1 as compared with 7.0 g/cc.

B. In-place Particle-size Reduction of Entire Beds

A test of the use of the oxidation-reduction technique for in-place particle-size reduction of an entire bed was carried through four cycles of particle-size reduction (oxidation-reduction) and three of particle growth (hexafluoride-to-oxide conversion). It was desired to control the bed-particle size in the range from 200 to 400 μ . To shorten the amount of time needed to carry out the growth portions in the test, the bed weight was held to 6 kg by hourly withdrawal of product; an alternative procedure in which solids handling was minimized was demonstrated in a 7-hr period in which the bed was permitted to increase to about 12 kg before any product was drawn.

Oxidation was conducted at 400°C with 20% air diluted with nitrogen. The quantity of air used ranged from 0.25 to 0.52 times the stoichiometric amount required for conversion of UO_2 to U_3O_8 , somewhat smaller amounts than those used in earlier tests in which extensive size reduction occurred. The oxidized particles were reduced for 1 hr at 650°C with hydrogen diluted slightly with a small amount of purge nitrogen. Operating conditions for the hexafluoride-conversion portions of the test (nominal conditions used in previous tests) are shown in Table 9.

Size reduction and particle growth were successfully carried through the operating cycles. The process steps and particle-size behavior are summarized in Table 10. Normal solids deposition occurred

during the hexafluoride-to-oxide conversion periods, which ranged from 10 to 17 hr. The average weight of UO_2 produced per cycle was equal to 2.7 times the weight of the UO_2 bed. A flattening of the particle-size distribution of the bed was noted during the whole operation, but adequate breakup of the coarse particles occurred during the run. Final particle density varied in the range from 8.0 to 8.4 g/cc.

Table 9

OPERATING CONDITIONS FOR UF_6 CONVERSION PERIODS
IN A PARTICLE-SIZE-REDUCTION TEST

Temperature:	650°C
Superficial Gas Velocity:	1.0 ft/sec
UF_6 Feed Rate:	50 g/min
Steam/ UF_6 Mole Ratio:	2.6/1
H_2 / UF_6 Mole Ratio:	6.7/1
Duration of UF_6 Feed Period	30 min/hr
Steam/ H_2 Mole Ratio during Cleanup:	1/1
Bed Weight and Height:	6 to 12 kg, 9 to 18 in. (static)

Table 10

SUMMARY OF UF_6 CONVERSION
AND OXIDATION-REDUCTION CYCLES

Equipment: 3-in.-diameter Monel reactor

Cycle Process Step	Duration (hr)	Average Particle Diameter (μ) in Bed	
		Initial	Final
First Oxidation-reduction	3	360	154
UF_6 Conversion	16	185 ^a	386
Second Oxidation-reduction	3	386	(180) ^b
UF_6 Conversion	17	(180) ^b	379
Third Oxidation-reduction	3	379	171
UF_6 Conversion	10	202 ^a	402

^aAfter particle-size adjustment by removing a portion of the -120 mesh particles.

^bEstimated value.

In the first three oxidation-reduction cycles, somewhat greater particle breakup occurred than that expected on the basis of the data obtained in the earlier tests with 1.0- to 1.5-kg beds (see above). In one of the earlier tests with shallow beds, the -80 mesh fraction formed was

about 42% when 0.70 stoichiometric equivalent of oxygen were fed; in the current test, breakup was almost as extensive (30% minus 80 mesh) when only about half as much oxygen (0.37 equivalent) was used. This difference is attributed to two factors: increased utilization of the oxygen in the deeper beds, and additional particle breakup during purge periods when fluidization was continued with nitrogen after the completion of the oxidation-reduction treatment.

The ratio of -325 mesh to -80 mesh fraction was low in these tests, in the range from 0.04 to 0.07; however, some holdup of -325 mesh material on the filters may have occurred. To avoid the use of starting beds containing excessive amounts of fines in the hexafluoride conversion, a portion of the -120 mesh fraction was removed after the first and third reduction treatments to adjust the average particle diameter as shown in Table 10. In the second cycle, sieve analyses of bed samples after oxidation-reduction did not indicate that excessive fines were present (the average particle diameter shown in Table 10 is actually an estimate based on subsequent analyses), and the hexafluoride conversion period was started without removing any bed material. Later samples, however, showed the presence of excessive amounts of fines, and the bed was withdrawn prior to the third cycle for partial sieving. The screened bed was recharged and the cycle completed.

The fourth oxidation-reduction treatment was carried out on the final bed to determine the extent of particle breakup during subsequent periods of fluidization. The amount of oxygen fed was the least of all the tests, equal to 0.25 equivalent; other operating conditions were the same as above. Particle breakup, expressed as cumulative values for the -80 mesh fraction, was as follows:

After oxidation:	2.2%
After reduction:	4.1%
After 8 hr of fluidization:	11.8%
After 16 hr of fluidization:	16.0%
After 24 hr of fluidization including heating to 650°C and treating with steam and hydrogen for 1 hr:	20.6%

The continuing particle breakup included breakup of the coarser fractions (+45 mesh); all of the individual fractions below the 80 mesh sieve size also increased. The -325 mesh/-80 mesh ratio increased from 0.06 at the end of the reduction period to a final value of 0.18. It is apparent that the breakup which continues during fluidization must be taken into consideration when given amounts of particle breakup by the oxidation-reduction method are desired.

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