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PRELIMINARY REPORT ON CONVERSION OF URANIUM HEXAFLUORIDE TO URANIUM DIOXIDE IN A ONE-STEP FLUID-BED PROCESS

by

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and S. Lawroski

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I. ABSTRACT

A one-step, continuous, fluid-bed process for the conversion of uranium hexafluoride to uranium dioxide was successfully carried out in preliminary experiments in a $1\frac{1}{2}$ -inch-diameter Monel reactor. Hydrogen and steam were used for simultaneous reduction and pyrohydrolysis reactions carried out at 600 C, resulting in the formation of a dense coating of dioxide on the starting bed of uranium dioxide. The effects of uranium hexafluoride feed rate and reactant excesses on conversion were investigated. Results of fluid-bed steam pyrohydrolysis runs on uranium tetrafluoride are also presented.

II. SUMMARY

Direct conversion of uranium hexafluoride ("hex") to uranium dioxide was successfully demonstrated in preliminary runs made in a $1\frac{1}{2}$ -inch-diameter Monel fluid-bed column at a temperature of 600 C. The over-all reaction may be shown to be as follows:

A starting bed of uranium dioxide of 1000 to 1200 grams (static height of eight inches) was fluidized with steam and hydrogen (mole ratio 2:1) at a superficial velocity at column conditions of 0.5 to 0.75 ft/sec. Continuous operation with intermittent product withdrawal was maintained for periods of two to five hours with uranium hexafluoride rates ranging from 1.4 to 10.9 g/min. Reactant excesses ranged from 230 to 1500 per cent. Good conversion (97 $\frac{1}{2}$ to 99 per cent) to uranium dioxide was achieved in this system at feed rates near 6 g/min of "hex," equivalent to about 50 lb uranium per hr per cubic foot static bed volume (or about 35 lb uranium per hr per square foot column cross section) using 300 to 600 per cent excesses of steam and hydrogen. The dioxide forms as a dense coating on the surfaces of the fluidized particles. Residual fluoride content of the product was as low as 0.08 per cent. Negligible amounts of uranium were found in the off-gas condensate trap. Tapped bulk densities of 4.5 to 5.0 g/cc were obtained with absolute particle densities (by xylene displacement) near 10 g/cc. A single sintering experiment in hydrogen on a dioxide product (40 to 200 mesh particles) gave pellets with a bulk density near 8 g/cc; a small amount of

exploratory work was also done on the pyrohydrolysis of uranium tetrafluoride at temperatures of 500 to 675 C. Uranium dioxide containing 0.18 per cent residual fluoride was produced in 1.5 hours at 675 C with 300 per cent excess steam.

Early scale-up of this work to 3-inch and 6-inch-diameter units is planned in order to make a more complete study of the effect of process variables. Additional pressing and sintering tests on the dioxide will be made to get comparative data for nuclear fuel application. An alternate application of this process is to recover the fluoride as hydrofluoric acid from the substantial quantities of depleted uranium hexafluoride now being stored.

III. INTRODUCTION

The interest in uranium dioxide as a reactor fuel has grown because of its excellent stability under irradiation and ease of preparation as compared to uranium metal. Consequently, an economical process for large-scale production of enriched uranium dioxide from uranium hexafluoride is needed. A "dry" process using the fluid-bed technique with gas-solids reactions appears to offer economic advantages over the "wet" process⁽¹⁾ now being used. The "wet" process includes hydrolysis of uranium hexafluoride with water, precipitation of the uranium as the diuranate (using ammonium hydroxide), filtering, drying and calcining of the diuranate to U_3O_8 , and finally reduction of U_3O_8 to uranium dioxide with hydrogen.

Dry processes⁽²⁾ using "hot-wall" and "cold-wall" reactors have been developed at the Carbide Nuclear K-25 plant for the hydrogen reduction of uranium hexafluoride to the tetrafluoride and are in use at their Y-12 plant for enriched material and their Paducah plant for depleted material. The tetrafluoride has been converted mainly to metal and little or no uranium dioxide has been made by pyrohydrolysis of the tetrafluoride, even though horizontal rotary furnaces are in use at feed materials plants for "reverting" off-specification uranium tetrafluoride to oxides prior to solvent extraction reprocessing.

Fluid-bed "coating" has been demonstrated by workers at Battelle,⁽³⁾ where tungsten hexachloride was reduced by hydrogen to form a metallic tungsten coating on uranium dioxide powder. This work was carried out in a $1\frac{1}{2}$ -inch-diameter reactor.

IV. APPARATUS AND PROCEDURE

The fluid-bed experiments for converting uranium hexafluoride to uranium dioxide were made in a $1\frac{1}{2}$ -inch-diameter Monel column, $2\frac{1}{2}$ feet high (see Figures 1 and 2). The upper 16-inch portion of the column is an

Figure 1

SCHEMATIC DIAGRAM OF
EQUIPMENT FOR FLUID-
BED CONVERSION OF URA-
NIUM HEXAFLUORIDE TO
URANIUM DIOXIDE

Figure 2

EQUIPMENT FOR FLUID-BED CONVERSION OF UF₆ TO UO₂

expanded (3-inch diameter) disengaging section containing two porous Monel bayonet filters (Grade G, 10 micron pore size, Micrometallic Co.) to retain solids. The filters were cleaned periodically by blowing back with a heated nitrogen stream. Thermoshell (Cooley Mfg. Co.) pipe heating elements were used to heat the reactor. Thermocouples were installed in the gas inlet, at two points in the bed zone, and in the filter zone. The weight of the bed was indicated by a manometer connected to pressure taps in the reactor. A fluidized bed of sand served as a preheater for the reactant fluidizing gases which entered the reactor at the apex of the sixty-degree cone bottom. The steam was fed from a boiler charged with distilled water and heated to maintain a steam pressure of 10 to 12 psig. Hydrogen was metered through a rotameter from a bank of cylinders. The uranium hexafluoride was fed from a cylinder mounted on a scale and was introduced initially through an orifice (0.029-inch diameter) in the end of a tube extending about one-quarter inch into the bed. Considerable difficulty was encountered due to plugging of the orifice by solids, so the orifice was subsequently replaced with an open quarter-inch tube. A nitrogen purge was also maintained in the feed line. A thermal flow meter was used to indicate the uranium hexafluoride rate, which was manually controlled by a needle valve. The entire feed system was traced with electrical resistance-heating wire.

The uranium dioxide starting bed (1000 to 1200 grams) gave a static height of about eight inches. Nitrogen was used to fluidize the bed while it was being heated to the operating temperature. Steam and hydrogen in a mole ratio of two-to-one were introduced shortly before the uranium hexafluoride was started. The nitrogen flow was then cut off except for purges. A superficial gas velocity at column conditions of 0.5 ft/sec was used initially but was increased to 0.75 as the denser oxide and larger particles were produced. The off-gas, containing excess steam and hydrogen, hydrofluoric acid, and nitrogen, was cooled and partially condensed, and then passed through a condensate collector which absorbed most of the uncondensed hydrofluoric acid.

Product was withdrawn from the bed at approximately one-hour intervals through a side-entering tap into evacuated sampling tubes. As particle growth became evident, the product was withdrawn from the bottom of the column. This permitted withdrawal of a coarser fraction. The uranium hexafluoride and steam feeds were shut off for about one minute during these latter withdrawals. The tests were terminated by shutting off the uranium hexafluoride supply and purging the line with nitrogen. The reactor was purged for an additional five-minute period with steam and hydrogen.

The majority of the runs were of 2 to 3-hour duration and the longest was 4.75 hours. The uranium hexafluoride feed rate ranged from 1.4 to 10.9 g/min. The steam and hydrogen excesses ranged from 200 to 1500 per cent.

V. RESULTS AND DISCUSSION

At the outset of this work there were two main questions: first, would the conversion of the hexafluoride to the dioxide occur in the gas phase resulting in the formation of excessive fines; and second, would the reaction rates be sufficiently high to prevent the loss of uranium as the hexafluoride in the exit gas? The initial experiments gave positive results on both counts: negligible fines were formed and negligible amounts of uranium were found in the off-gas condensate trap. The conversion takes place primarily on the surface of the fluidized solids to form a dense, nonporous material. The deposited material is shown in Figures 3a and 3b, which are photomicrographs (45X) of cross-sectioned particles. Portions of the starting bed have been almost completely displaced, as evidenced by the growth rings of the newly produced dioxide. The raspberry-like appearance of the coating may be characteristic of the conversion reaction.

A. Conversion to Dioxide

The operating conditions and analytical results are summarized in Table 1. Over 95 per cent conversion was achieved with 300 per cent reactant excess at a "hex" feed rate of 5.7 g/min. This rate is equivalent to

Table 1

SUMMARY OF OPERATING CONDITIONS AND RESULTS OF FLUID-BED CONVERSION OF URANIUM HEXAFLUORIDE TO URANIUM DIOXIDE

Equipment	- 1½-inch-diameter Monel column
Bed Temperature	- 575 to 625 C
Fluidizing Gas Velocity	- 0.5 and 0.75 ft/sec
Starting Bed	- ~1000 g UO ₂ (static height ~8 in.)

Run No.	UF ₆ Rate (g/min)	Run Duration (min)	Reactants Excess (%)	Results	
				Conversion ^b (%UO ₂)	Residual Fluoride (%)
7A	5.7	120	300	99.4	0.08
8	1.4	180	1500	99.3	0.09
13	5.2	150	600	97.6	0.29
14	6.2	165	450	97.6	0.29
15	6.7	165	375 ^a	78.3 ^c	0.05 ^c
16	8.2	255	335	95.9	0.50
17	10.9	190	230 ^a	62.6	4.61
18	7.2	285	240 ^a	57.0	5.30

^aSome fines formation

^bConversion is based on the U⁺⁴, U^{total} and residual fluoride analyses, assuming the constituents are only UO₂F₂ and UO₂. Calculations indicate the UF₄ content is low or negligible.

^cThese analyses indicate U₃O₈ was formed.

Figure 3a

PHOTOMICROGRAPH OF URANIUM DIOXIDE PARTICLES
PREPARED IN FLUID-BED CONVERSION OF URANIUM
HEXAFLUORIDE

Run 14, - 60, +100 mesh size, 45X

Figure 3b

PHOTOMICROGRAPH OF URANIUM DIOXIDE PARTICLES
PREPARED IN FLUID-BED CONVERSION OF URANIUM
HEXAFLUORIDE

Run 14, -40, +60 mesh size, 45X

about 54 lb uranium per hr per cubic foot of static bed volume (or about 36 lb uranium per hr per square foot of reactor cross section). The residual fluoride varied from 0.08 to 0.50 per cent. The fluoride content was significantly reduced from 0.3 to 0.01 per cent during a high-temperature (1700 C) sintering experiment conducted in a hydrogen atmosphere. The analytical results of Run 15, indicating the formation of U_3O_8 with a low residual fluoride content, were rechecked and verified. Inadequate fluidization during the latter part of this run may have resulted in abnormal conditions producing U_3O_8 . The highest "hex" feed rate used was 10.9 g/min, which is equivalent to 103 lb uranium per hr per cubic foot static bed volume. In this run the reactant excess (steam and hydrogen) was only 230 per cent and the resulting conversion to dioxide was about 65 per cent complete.

B. Powder Properties

During the first few runs there was little evidence of particle growth in the bed. Apparently, the starting dioxide powder, prepared by steam pyrohydrolysis of uranium tetrafluoride, had a relatively high porosity which diminished as the "hex" entered the pores and was converted to dioxide. Surface-area measurements (Table 2) show a small decrease from that of the starting material, but these data are too preliminary for correlation. Subsequent Runs 14 and 15 showed definite trends of particle growth (see Figure 4). A light grinding was necessary in some cases to prepare a suitable particle-size distribution for the subsequent run. Microscopic examination indicated that growth was due to deposition of product uranium dioxide on individual particles of the bed, rather than to any aggregation of particles. Fines formation was associated with poor conversion in the runs made with high "hex" feed rate and low excess of reactants, indicating that gas-phase reaction had occurred as opposed to reaction on the surface of the fluidized particles. In these cases, such as for Run 18, particle-size distribution became somewhat stabilized (see Figure 4). Longer runs are necessary to confirm these size-distribution trends.

The tapped bulk density of the dioxide used in the initial tests was about 3.9 g/cc. Product densities tended to level off near 4.5 g/cc, but values as high as 5.0 g/cc were obtained in some runs. These high bulk densities may make this material particularly desirable for potential fuel elements using tamped uranium dioxide powders.⁽⁴⁾ A xylene-displacement density (see Table 2) on the powder product gave 9.9 g/cc, which is about 90 per cent of theoretical. Material containing appreciable quantities of fluoride (indicating poor conversion) showed much lower values by this method (7.5 and 7.9 g/cc).

A single sintering experiment on Run 13 product (97.6 per cent conversion) produced pellets with a density near 8 g/cc. Better sinterability can very likely be achieved by milling the uranium dioxide or by an oxidation-reduction treatment.

Table 2

PHYSICAL PROPERTIES OF PROCESS MATERIALS FROM FLUID-BED
CONVERSION OF URANIUM HEXAFLUORIDE TO URANIUM DIOXIDE

Run No.	Material	Conversion (% UO_2)	Density (g/cc)		Surface Area (sq m/g)
			Xylene Displacement	Bulk $\frac{\text{Untapped}}{\text{Tapped}}$	
-	Starting UF_4^a	-	6.4	$\frac{3.0}{3.2}$	0.39
1	UO_2 Pyrohydrolysis Product ^a	49.6	7.9	$\frac{3.3}{3.6}$	-
5	UO_2 Pyrohydrolysis Product ^a	99.3	-	$\frac{3.5}{3.9}$	0.98
8	UO_2 from UF_6 Conversion	99.3	-	$\frac{4.2}{4.4}$	0.59
14	UO_2 from UF_6 Conversion	97.6	9.9	$\frac{4.4}{4.5}$	0.90
18	UO_2 from UF_6 Conversion	57.0	7.5	$\frac{4.0}{4.3}$	-

^aThe original UO_2 bed was prepared from UF_4 by pyrohydrolysis; the material from Runs 1 and 5 are products of this operation.

Figure 4

AVERAGE PARTICLE SIZE VARIATION DURING
FLUID-BED CONVERSION OF URANIUM
HEXAFLUORIDE TO URANIUM DIOXIDE

C. Uranium Tetrafluoride Pyrohydrolyses

A number of batch uranium tetrafluoride-steam pyrohydrolysis runs were made as an operating shakedown of the equipment and, also, because of some interest in the particular process application itself. The operating conditions and analytical results of the runs appear in Table 3. The uranium tetrafluoride was a mixture of products from the fluid-bed hydrofluorination of refined uranium dioxide. Runs were of such duration as to permit four stoichiometric equivalents of steam to contact the fluoride. Intermediate bed samples were taken half-way through the run.

Table 3

BATCH FLUID-BED PYROHYDROLYSIS OF URANIUM TETRAFLUORIDE

Equipment:	1 $\frac{1}{2}$ -inch-diameter Monel column
Bed Material:	UF ₄ from fluid-bed hydrofluorination of refined UO ₂
Fluidizing Gas Velocity:	~0.75 ft/sec
Steam Excess:	300%

Run No.	Charge (g)	Temp (C)	Duration of Run (hr)	Residual Fluoride	
				Intermediate Sample ^a (w/o)	Final Sample (w/o)
1	500	500-550	0.67	-	12.2
4	750	500	1.25	15.4	2.65
3	750	600	1.75	9.66	0.30
5	800	650-675	1.50	3.26	0.18

^aAfter steam excess of 100 per cent.

A pronounced increase in the rate of reaction was observed at higher temperature. Residual fluoride contents of 0.30 and 0.18 per cent were obtained at temperatures of 600 and 650 to 675 C, respectively. The reaction time had a pronounced effect on the results. For the same steam excess, the residual fluoride content decreased from 12.2 per cent to 2.65 per cent when the reaction time was doubled in runs made at 500 C. The uranium dioxide products did not appear to be very reactive, e.g., in discharging the bed, no temperature rise was noted due to reaction with air.

D. Corrosion

Spectrochemical analysis of the product from one of the early runs (7A) showed little contamination (50 ppm nickel and 30 ppm copper) from the Monel in the bed reaction zone. Other metallic impurities were of the same order of magnitude, implying little corrosion in this zone. Corrosion test coupons will be installed in larger reactors in both the bed zone and disengaging section to gain additional information on desirable materials of construction for this process.

VI. CONCLUSION

A continuous, one-step fluid-bed process for the conversion of uranium hexafluoride to uranium dioxide using steam and hydrogen as reactants has been demonstrated in a series of experiments in a $1\frac{1}{2}$ -inch-diameter Monel reactor. Reactant excesses of 300 to 600 per cent for steam and hydrogen, and a temperature of 600 C gave greater than 95 per cent conversion to dioxide. Bulk density of the powder product was 4.5 to 5.0 g/cc, with absolute particle densities near 10.0 g/cc.

Residual fluoride contents as low as 0.08 per cent were achieved for the process. Significant reduction of the fluoride content is obtained during high-temperature (1700 C) sintering with resultant values as low as 0.01 per cent. Specifications for fluoride in reactor-grade dioxide have not been set, but analysis of material made commercially from uranium hexafluoride gave about 0.002 per cent fluoride.

The process appears very attractive due to its simplicity and potential low cost. It utilizes the excellent advantages of fluid beds, viz., good temperature control, large surface area for reaction and controlled mobility of solids. Planned scale-up to 3-inch and 6-inch-diameter reactors will more easily demonstrate the effects of process variables such as temperature, reactant excess and "hex" feed rate. This will also permit the incorporation of corrosion specimens.

In addition to the production of uranium dioxide for possible applications as nuclear fuel, the process offers a means of recovering the fluoride as hydrofluoric acid from the large quantities of depleted uranium hexafluoride now being stored. In this case high conversion to uranium dioxide would not be important, but a low steam excess would be desirable in order to produce a high assay hydrofluoric acid.

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