~~UNCLASSIFIED~~

ANL-5363

~~CONFIDENTIAL~~

Argonne National Laboratory
FLUIDIZED-BED PROCESS FOR THE PRODUCTION
OF URANIUM TETRAFLUORIDE (GREEN SALT)
FROM URANYL NITRATE. INTERIM REPORT

by

A. A. Jonke, N. M. Levitz, E. J. Perkus,
and R. G. Taecker

~~RESTRICTED DATA~~

~~This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.~~

~~CONFIDENTIAL~~

~~UNCLASSIFIED~~

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

UNCLASSIFIED

~~CONFIDENTIAL~~

ANL-5363

Technology - Feed Materials

AEC RESEARCH AND DEVELOPMENT REPORT

ARGONNE NATIONAL LABORATORY

P. O. Box 299

Lemont, Illinois

FLUIDIZED-BED PROCESS FOR THE PRODUCTION OF URANIUM TETRAFLUORIDE (GREEN SALT) FROM URANYL NITRATE. INTERIM REPORT

by

A. A. Jonke, N. M. Levitz, E. J. Petkus,
and R. G. Taecker

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

December 30, 1954

Operated by The University of Chicago
under
Contract W-31-109-eng-38

Photostat Charge \$ 6.30 for
Access Permittees

Available from
Technical Information Service
P. O. Box 1001, Oak Ridge, Tennessee

UNCLASSIFIED

~~CONFIDENTIAL~~

UNCLASSIFIED

~~CONFIDENTIAL~~

ANL-5363

Technology - Feed Materials

ARGONNE NATIONAL
P. O. Box
Lemont, Illinois

ORY

FLUIDIZED BED PROCESS FOR THE PRODUCTION OF URANIUM
TETRAFLUORIDE (GREEN SALT) FROM URANYL NITRATE.
INTERIM REPORT

AEC RESEARCH AND DEVELOPMENT REPORT

by

A. A. Jonke, N. M. Levitz, E. J. Petkus,
and R. G. Taecker

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmission to unauthorized persons is prohibited.

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

December 30, 1954

Operated by The University of Chicago
under
Contract W-31-109-eng-38

Photostat Charge \$ 6.20 for
Access Permittees \$ 6.29
Available from
Technical Information Service
P. O. Box 1001, Oak Ridge, Tennessee

This report was prepared as a scientific account of Government-sponsored work. Neither the United States nor the Commission makes any warranty or representation as to the accuracy, completeness, or reliability of the information contained in this report, nor does it assume any liability with respect to the use of, or from reliance upon, any information, apparatus, method, or process described in this report.

UNCLASSIFIED

~~CONFIDENTIAL~~

Application of standard
provisions relating to
the extent of the
classification

CHEMICAL ENGINEERING DIVISION

CLASSIFICATION CANCELLED
DATE 3-7-60
For The Atomic Energy Commission
H. R. Cane
Chief, Declassification Branch

037128.030

~~CONFIDENTIAL~~

TABLE OF CONTENTS

	<u>Page</u>
I. SUMMARY	4
II. PROPOSED FLUIDIZED-BED PROCESS.	6
A. Fluidized-Bed Principle.....	6
B. Description of the Process	6
III. CONTINUOUS DENITRATION OF URANYL NITRATE IN A FLUIDIZED-BED.....	10
A. Preliminary Experiments	10
B. Experimental Equipment.	11
C. Operating Procedure	15
D. Run Results - General	18
E. Particle Size of Product	20
F. Effect of Bed Temperature	27
G. Effect of Feed Flowrate	29
H. Effect of Nozzle Type.....	30
I. Other Variables	31
J. Heat Transfer Coefficient	32
IV. REDUCTION AND HYDROFLUORINATION	33
A. Experimental Equipment.....	33
B. Preliminary Experiments.....	35
V. FUTURE WORK.....	37
VI. ACKNOWLEDGEMENTS	37

~~CONFIDENTIAL~~

DECLASSIFIED

553-2

~~CONFIDENTIAL~~

4

FLUIDIZED-BED PROCESS FOR THE PRODUCTION OF URANIUM
TETRAFLUORIDE (GREEN SALT) FROM URANYL NITRATE.
INTERIM REPORT

by

A. A. Jonke, N. M. Levitz, E. J. Petkus and R. J. Taecker*

I. SUMMARY

This interim report describes a proposed new processing technique for the production of uranium tetrafluoride from uranyl nitrate solution. This technique involves the application of the fluidized-bed principle for the contacting of gases with powdered solids. In addition, this report describes a new application of fluidization developed at this Laboratory and applied to the denitration of uranyl nitrate to produce uranium trioxide.

The purpose of this work is to develop a low-cost, continuous process for the denitration of uranyl nitrate hexahydrate, the reduction of uranium trioxide to uranium dioxide, and the hydrofluorination of uranium dioxide to uranium tetrafluoride. No new chemistry is involved - only the application of improved engineering techniques.

Experimental work has developed certain basic information necessary to establish the technical feasibility of a full-scale fluidized-bed process. Uranium trioxide and uranium dioxide powders can be satisfactorily fluidized over a wide range of particle sizes. A small amount of attrition and dusting occurs, but these do not constitute serious problems. Techniques for confining the dust and returning it to the fluidized bed have been developed.

A continuous process for the denitration of uranyl nitrate in a fluidized bed has been developed and thoroughly demonstrated in both bench-scale and pilot-scale equipment. The equipment is simple and compact and requires a minimum of operating attention. The product is a powder having a high bulk density and satisfactory physical and chemical properties. Production rates of 100 lbs/(hr)(sq ft) of reactor cross section have been demonstrated in many runs. Experimental work is continuing to obtain additional information of the effects of operating variables.

Bench-scale equipment has been constructed and installed for the investigation of the reduction and hydrofluorination operations in fluidized

*On loan from Kansas State College, Department of Chemical Engineering, under the Participating Institution Program.

~~CONFIDENTIAL~~

5-53-3

over

~~CONFIDENTIAL~~

5

beds. A single exploratory reduction run has been completed with encouraging results. Experimental work is now underway to determine the optimum operating conditions and to estimate the size and number of stages required for the production of specification-grade uranium tetrafluoride.

~~CONFIDENTIAL~~

DECLASSIFIED

553-4

II. PROPOSED FLUIDIZED BED PROCESS

A. Fluidized-Bed Principle¹

Fluidization may be described briefly as the phenomenon which occurs when a fluid, normally a gas, passes upward through a bed of solid particles at sufficient velocity to prevent the particles from remaining in intimate contact with one another. In this condition, each particle is surrounded by a film of fluid, and a certain degree of freedom to move is imparted to the solid particles. In the fluidized state the solid-gas phase behaves much like a liquid, having the ability to flow readily under the influence of a hydrostatic head. At high gas velocities a large percentage of the gas flows upward through the solid particles in the form of bubbles or pockets of gas, and a vigorous agitation of the solids occurs.

The use of the fluidized-bed technique has significant advantages in reactions involving a gas and a finely divided solid. These advantages may be summarized as follows:

1. The mobility of the fluidized solids permits the ready transfer of solids to and from a reaction vessel, thereby permitting continuous operation.
2. Excellent temperature control is obtainable.
3. High heat transfer coefficients are obtained between the solid particles and a heating or cooling surface, due to solids agitation.
4. High reaction rates are obtained because of the large surface area of the fluidized particles.

The fluidization principle has been widely used for the catalytic cracking of petroleum with outstanding success. Many other applications have been proposed, and a number of these have been placed in operation.

B. Description of the Process

The process for the conversion of uranyl nitrate to uranium tetrafluoride consists of three operations:

¹Lapple, C. E., Fluid and Particle Mechanics, Newark, Del., University of Delaware (1951)

DECLASSIFIED

553-5

- (1) thermal decomposition or denitration of uranyl nitrate hexahydrate to form uranium trioxide according to the reaction²

- (2) reduction of uranium trioxide with hydrogen to form uranium dioxide according to the reaction³

- (3) hydrofluorination of uranium dioxide with anhydrous hydrogen fluoride to form uranium tetrafluoride according to the reaction⁴

A flow diagram of the proposed process is shown in Figure 1. Three fluidized-bed reactors in series, one above the other, are employed. In the first reactor molten uranyl nitrate hexahydrate is atomized and fed into a fluidized bed of uranium trioxide at a temperature of approximately 350 C. The uranyl nitrate is thermally decomposed to uranium trioxide. The uranium trioxide flows by gravity from the denitration reactor into the second reactor where it is reduced by dissociated ammonia at a temperature of approximately 700 C. The uranium dioxide then overflows into the third reactor where it is converted to uranium tetrafluoride by hydrogen fluoride gas at a temperature of approximately 500 C.

The reduction and hydrofluorination reactors contain a number of fluidized beds in series, one above the other, interconnected by down-comer tubes in the manner of a sieve-plate gas absorption column. Solids flow by gravity from one stage to the next, and the reactant gas flows upward countercurrent to the solids flow.

~~As a basis for the flow diagram of Figure 1, a production rate of 10 tons per day of uranium tetrafluoride is used.~~ The requirements of liquid ammonia and hydrogen fluoride are based upon an excess of 50%. A smaller excess may be possible because of the countercurrent operation and the efficient gas-solid contacting.

²Reactor Handbook, Vol. 4, Fuel Processing, page 507.

³Katz and Rabinowitch, The Chemistry of Uranium NNES VIII-5, page 295, New York, McGraw-Hill Book Company (1951).

⁴Kuhlman, Carl W., Equilibrium Ratio of Hydrogen Fluoride and Water In The Fluorination of Uranium Dioxide at High Temperatures, MCW-118.

DECLASSIFIED 553-6

FIGURE 1
FLUIDIZED BED PROCESS FOR URANIUM TETRAFLUORIDE

55-3-7

The heat generated in the reduction and hydrofluorination steps will amount to approximately 340,000 Btu/hr. The heat required in the denitration step is approximately 800,000 Btu/hr. To remove the heat from the reduction and hydrofluorination reactors, molten salt will be pumped through cooling coils, and this heat will be supplied to the denitration reactor.

DECLASSIFIED

553-8

III. CONTINUOUS DENITRATION OF URANYL NITRATE IN A FLUIDIZED BED

The major experimental effort thus far has been expended on the development of the denitration process, since the present production technique ("pot" denitration) does not produce uranium trioxide having a particle size which is conducive to good fluidization. Moreover it was felt that a superior continuous process for denitration might be useful ~~at separations process plants, such as at Hanford and Savannah River, as well as at feed materials production plants, such as Fernald and Mallinckrodt.~~

The fluidized-bed denitration process has a number of advantages over the present batch process. Some advantages are:

- (a) Lower operating cost because of the continuous feature of the process,
- (b) Lower equipment cost because one simple piece of equipment replaces a large number of pots together with grinding, screening, and conveying equipment,
- (c) improved product due to the elimination of caking on the walls of the equipment,
- (d) lower corrosion rates because hot feed does not contact metal,
- (e) reduced health hazards because the uranium is completely confined within the equipment,
- (f) ready adaptability to remote operation or shielding, if desired, to reduce personnel exposure to residual fission product and natural uranium radiations.

Although the fluidized solids technique has been in use for a number of years in connection with processes involving gas-solid contacting, the use of a fluidized bed for the evaporation or calcination of a liquid solution has not to our knowledge been previously reported. Consequently the denitration of uranyl nitrate solution in a fluidized bed represents the development of an entirely new and useful technique which may have many additional applications in the chemical process industry.

A. Preliminary Experiments

Early exploratory experiments indicated that the problem of introducing a solution of uranyl nitrate into a bed of uranium trioxide without serious agglomeration or caking might be solved by atomizing the liquid and agitating the solid. Accordingly attention was directed toward the use

DECLASSIFIED

5-53-9

of atomizing spray nozzles in conjunction with a heated bed of fluidized solids. It was felt that the vigorous agitation of the solids, which occurs in a fluidized bed, would aid in the uniform dispersion of feed droplets throughout the bed during the denitration period. Thermal decomposition of the uranyl nitrate would occur by the rapid transfer of heat from the solid uranium trioxide particles in the bed to the finely divided droplets of feed. By this means it was hoped that caking in the bed might be avoided, and that a free-flowing, powdered uranium trioxide product could be obtained.

It was found that the arrangement and location of the spray nozzle relative to the fluidized bed were critical. For example, the location of the nozzle above the bed with the spray directed onto the surface of the fluid bed resulted in caking both in the bed and on the nozzle. Likewise, mounting the nozzle through a hole in the gas distributing plate at the bottom of the bed with the spray directed upward, also resulted in caking around the nozzle. After several other arrangements had been tested, a method was finally adopted wherein the atomizing nozzle is mounted horizontally through a hole in the side of the reaction chamber in such a way as to feed the atomized liquid directly into the vigorously agitated, fluidized uranium trioxide particles.

B. Experimental Equipment

Two sizes of equipment have been used for the development of the fluid-bed denitration process. The first is a 3-inch diameter bench-scale unit used for exploratory runs to determine the feasibility of the process and to establish the approximate operating conditions. It consists of a 3-inch diameter stainless steel pipe surmounted by a 4-inch diameter pyrex glass pipe disengaging section. The second unit is a 6-inch diameter stainless steel pilot-scale reactor, which was used for determining the optimum operating conditions and for demonstration of the process on a larger scale.

A photograph of the pilot-scale reactor prior to installation of the thermal insulation is shown in Figure 2. A schematic drawing of the apparatus is given in Figure 3.

1. Reactor

The reactor is constructed entirely of stainless steel type 304 and consists of three sections: gas dispersion chamber, reaction chamber, and disengaging section. The gas disperser and reaction chamber are 6 inches ID and the disengaging section is 12 inches ID. The overall height of the unit from bottom of gas chamber to top of disengaging section is 64 inches. The unit is installed inside of a well-ventilated hood to protect personnel and avoid contamination of the area.

553-10
DECLASSIFIED

Figure 2

Pilot-Scale Fluid Bed Denitrator

DECLASSIFIED

553-11

Figure 3

FLUIDIZED BED DENITRATION REACTOR.

DECLASSIFIED

5-3-12

The reaction chamber is provided with four openings for the installation of spray nozzles. These are located in two planes, the lower two nozzles being six inches from the bottom of the bed, and the upper nozzles 11.5 inches from the bottom of the bed. Radially the nozzles are 90 degrees apart.

The reaction chamber is heated by thirty 1000-watt tubular electric heaters set into grooves in the chamber wall. The heat transfer characteristics and the limitation on the heater sheath temperature (1500 F max) limit the maximum input to approximately 20 kw. Thermocouples are provided for measuring the temperatures at the top and bottom of the bed. Other thermocouples are used to measure off-gas temperatures, reactor wall temperature, and heater surface temperatures.

In order to provide a certain degree of automatic temperature control, five of the tubular electric heaters are actuated by an automatic controller using one of the bed thermocouples as the sensing element. The remaining heaters are manually controlled by variable transformers, in groups of six heaters to one transformer.

The weight of uranium trioxide in the fluid bed at any time is determined by measurement of the pressure drop across the bed. For this purpose pressure taps of 1/8-inch pipe are installed at the bottom of the bed and in the disengaging section.

2. Off-Gas Filter System

The disengaging section contains eight porous stainless steel bayonet-type filters for filtering dust particles from the off-gas. Each filter is 18 inches long, 3 inches wide, and 5/8 inches thick, and has a mean pore diameter of 10 microns. The filters are divided into two banks, separated by a baffle. One bank is used to filter the off-gas while the other bank is being blown back with air to remove the dust cake. To avoid condensation of moisture in the disengaging section the blowback air is preheated. Valves are provided in the off-gas lines to permit each filter to be individually blown back, thus minimizing the volume of air required.

3. Charge Hopper

The charge hopper is used to fill the reactor with uranium trioxide at the start of a run, and to recycle product to the fluidized bed. It consists of an 18-inch long by 3-inch diameter section of pyrex glass pipe, reduced to 1-inch diameter at the bottom. It is connected to the reactor through a 3/4-inch pipe containing two plug valves and a union, which permits the charge hopper to be disconnected and refilled during a run. Glass pipe is used to permit visual observation of the charge rate.

DECLASSIFIED

55-3-13

4. Product Removal

Product is removed from the bottom of the bed through a 1/2-inch pipe and plug valve. The product receiver, which consists of a 6-inch long by 4-inch diameter section of pyrex glass pipe, serves as a means of visual measurement of the amount of product withdrawn from the reactor. Removal of product from the bottom of the bed is preferred over the use of an overflow tube from the top of the bed, in order to preferentially remove any larger particles which may collect at the bottom.

The product reservoir is a 10-liter stainless steel carboy equipped with a 3/4-inch plug valve and union to connect it to the product receiver. Samples for analysis are removed from the product receiver through a 1/2-inch pipe and plug valve.

5. Air and Liquid Feed Systems

The uranyl nitrate solution is pumped to the spray nozzles from a weigh tank using Milton-Roy metering pumps. One pump is used for each nozzle, the flowrates being measured by rotameters in the lines.

The atomizing air, fluidizing air, and the filter blowback air are metered and fed under pressure. The fluidizing air and the blowback air are preheated in electrically heated copper pipes packed with stainless steel Raschig rings.

C. Operating Procedure

The range of operating conditions tested in the fluidized-bed process runs denitration is shown in Table 1. A complete set of operating data for runs made in the pilot-scale reactor is given in Table 2. The operating procedure was as follows. In starting the reactor, air was first passed through the spray nozzles in order to prevent the nozzles from plugging with solid particles from the bed. The reactor was then charged with a predetermined amount (usually 55 lbs) of uranium trioxide from a previous run. In most cases the starting bed was first screened through a 40 mesh sieve to remove coarse particles.

The flow of preheated fluidizing air was started, and the bed was brought up to the desired temperature by means of the electrical heaters. Water was then pumped through the spray nozzles at a low flow rate to check the operation of the nozzles. After a few minutes of steady operation the flow of water was stopped, and the uranyl nitrate feed solution was started. The feed rate and heat input were then adjusted to the desired values.

DECLASSIFIED

553-14

Table 1

RANGE OF OPERATING CONDITIONS TESTED IN FLUIDIZED-BED
DENITRATION RUNS

Bed Temperature, C	310 to 450
Fluidizing Air Flow rate,* ft/sec	1.3
Nozzle Air Pressure, psig	15 to 25
Nozzle Air Flowrate, cfm @ STP	0.5 to 0.8
Bed Level After Fluidization (Approx), inches	20
Feed (Uranyl Nitrate) Concentration, <u>M</u>	2.4
Feed Flowrate, ml/min	up to 235
UO ₃ Production Rate, lb/hr	up to 21
Number of Feed Nozzles	one or two
Heat Input (Approx) kw	up to 17
Run Duration, hr	up to 13.6
UO ₃ Recycle Rate, % of Production Rate	0 to 20

* Superficial velocity at bed temperature and pressure.

The flow of preheated blowback air to the off-gas filters was maintained at 2.5 cfm during operation of the reactor. As the filters became coated with dust particles the reactor pressure increased. When the pressure reached 5 psig the flow of off-gas was diverted to the clean filter bank. This operation was repeated at frequent intervals throughout the run.

In many of the runs a side stream of finely sieved uranium trioxide particles was fed into the reactor at frequent intervals to counteract the tendency for the particles of uranium trioxide in the bed to increase in size during the course of the run. (This procedure was later found to be unnecessary. See Section E1.) This recycle material consisted of product which had been screened in the size range 100 to 325 mesh. In most cases the recycle rate was 20 per cent of the uranium trioxide production rate. For simplicity the recycle material was fed periodically at intervals of 15 minutes, rather than continuously.

Product was withdrawn from the reactor at intervals of 5 to 10 minutes. The bed level, as measured by the pressure drop, was maintained approximately constant.

DECLASSIFIED 553-15

Table 2

OPERATING CONDITIONS FOR DENITRATION RUNS

Run Number	44	45	46	47	48 ⁽⁴⁾	49	50	51	52	53
Bed Temperature, C	390	385	390	390	395	390	440	350	350	310
Fluidizing Air, ft/sec ⁽¹⁾	1.2	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.2	1.3
Nozzle Air, psig	15	15	15	25	28	26	27	26	26	26
Nozzle Air, cfm @ STP ⁽⁵⁾	0.58	0.47	0.50	0.77	0.56	0.55	0.67	0.72	0.73	0.57
Bed Height, inches ⁽²⁾	13	15	17	20	13	20	20	20	20	20
Feed Concentration, M	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Feed Rate, ml/min	94	125	154	226	92	230	220	235	230	230
UO ₃ Production, lb/hr	8.5	11	14	20	8.5	21	20	21	21	21
Number Feed Nozzles	2	2	2	2	1	1	1	1	1	1
Heat Input, kw ⁽³⁾	9.6	12	14	17	9.8	16	17	16	15	15
UO ₃ Recycle Rate, %	5	15	12	20	0	20	20	20	0	0
Run Duration, hr	6.5	6.5	6.3	13.6	6.5	8.0	8.0	8.0	8.0	8.0

(1) Superficial velocity at bed temperature and pressure.

(2) Approximate bed height after fluidization.

(3) Values reported represent electrical input to heaters.

(4) Pressure-feed type nozzle used in Run 48 (See Section III H).

(5) Values reported represent air rate through each nozzle used.

5-8-3-16

Although the denitration reactor has provision for the installation of four spray nozzles, only one or two nozzles were used in the runs completed thus far. In Runs 43 through 48 two spray nozzles were used, and in Runs 49 through 53 one spray nozzle was used. The nozzles are located 6 inches above the bottom of the bed.

D. Run Results - General

1. Operability of The Reactor

Thus far the pilot-scale denitration reactor has been run a total of 85 hours during which time a total of 1370 lb of uranium trioxide were produced from uranyl nitrate solution. Most of the runs were of relatively short duration (about 8 hr). These were made to determine the effect of various operating variables on the physical and chemical characteristics of the product and to determine the effect of these variables on the operability of the process. One run (No. 47) of 13.5 hr duration was made to demonstrate operability over a longer period and to illustrate the attainment of a steady-state particle size in the product.

The last seven runs (47 thru 53) were made at a uranium trioxide production rate of approximately 20 lb/hr, which is equivalent to 100 lb(hr)(sq ft) of sectional area. This production rate is the maximum for this equipment when the feed solution is 2.4 M uranyl nitrate. Under the present conditions the feed rate is limited by the capacity of the off-gas filtering system and by the heat input to the fluidized bed. If 100 per cent uranyl nitrate hexahydrate were used as feed in place of the 2.4 M solution (approx. 70 per cent UNH), a considerable increase in production rate should be realized since less off-gas would be produced and less heat required per pound of product.

2. Product Analyses

Analyses of the product samples for the runs made at a production rate of 20 lb/hr are given in Table 3. The residual nitrate content was less than 0.6 per cent and the residual water content was less than 0.2 per cent in all cases. The bulk density was high, averaging about 4.4 g/cc tapped and about 4.1 g/cc untapped. A negligible amount of U_3O_8 was present in the product.

3. Corrosion and Erosion

Spectrographic analyses of the feed solution and of the product were made to determine if any increase occurred in the iron, nickel, and chromium contents as a result of corrosion or erosion of the stainless steel reactor. The results listed in Table 4 show that within the accuracy of the analyses (factor of two) no detectable increase in these impurities occurred in going from feed to product.

DECLASSIFIED 553-17

Table 3

RESULTS OF CHEMICAL AND PHYSICAL ANALYSES OF PRODUCT
FROM DENITRATION RUNS

Analysis	Run No.					
	47	49	50	51	52	53
UO ₃ , %	98.1	99.8	99.3	99.4	99.5	99.4
NO ₃ , %	0.40	0.50	0.41	0.43	0.53	0.50
H ₂ O, %	0.18	0.11	0.08	0.12	0.18	0.15
U ₃ O ₈ , %	0.04	0.05	0.04	0.05	0.07	0.22
Bulk Density						
Not tapped, g/cc	4.1	4.1	4.2	4.2	4.1	4.1
Tapped, g/cc	4.5	4.3	4.5	4.4	4.4	4.3

Table 4

METALLIC IMPURITIES IN FEED AND PRODUCT OF
DENITRATION RUNS

Run Number	Impurities as Per Cent of U ₃ O ₈ Content					
	Feed			Product		
	Fe	Cr	Ni	Fe	Cr	Ni
45	0.0015	0.0005	0.001	0.003	0.0005	0.001
46	0.0015	0.0005	0.001	0.003	0.0001	0.0005
47	0.005	0.0002	0.0005	0.003	0.0002	0.0005
49	-	-	-	0.004	0.0005	0.001
50	0.007	0.0005	0.001	0.003	0.0005	0.001
51	0.007	0.0005	0.001	0.005	0.0007	0.0015
52	0.01	0.0007	0.002	0.004	0.0004	0.001
53	0.007	0.0004	0.001	0.0057 ⁽¹⁾	-	-

(1) Colorimetric analysis - all other analyses by spectrograph.

553-18
DECLASSIFIED

A slight increase in the iron content of the feed solution is evident between the earliest runs and the latest (0.0015% to 0.007%). This increase is probably due to corrosion which occurs in dissolving the uranium trioxide product in nitric acid to prepare feed solution. The same uranium trioxide was re-used for many runs, and a slight amount of corrosion of the stainless steel dissolving tank is to be expected.

For the denitration process itself, a very low corrosion rate is expected, since denitration in the fluidized bed occurs as a result of contact between hot uranium trioxide and feed solution rather than contact between a hot metal surface and the feed as is the case in "pot" denitration.

No visual evidence of corrosion or erosion was apparent when the reactor interior was examined after 69 hours of operation; however, this period is too short to be conclusive.

E. Particle Size of Product

1. Necessity for Recycle of Fines

For satisfactory operation of the fluidized-bed denitration process it is important that the particle size of the uranium trioxide in the reactor remain within suitable limits. Large amounts of coarse particles or large amounts of very fine particles are undesirable. It is necessary, therefore, that both the average size and the size distribution reach a suitable equilibrium value during the initial period of operation and thereafter remain constant.

Early experience in the 3-inch diameter unit showed that the particle size of the uranium trioxide in the reactor tended to increase gradually during the course of a denitration run. In many instances the average diameter was approximately doubled after 7 hours of operation, and there appeared to be no tendency toward an approach to steady state.

To account for the growth of particles during denitration, two possible mechanisms may be hypothesized: (1) individual particles of uranium trioxide grow by contact with droplets of feed solution which decompose leaving additional uranium trioxide deposited on the original particle; and (2) clusters of uranium trioxide particles are cemented together after contact with feed droplets.

A photomicrograph of uranium trioxide particles produced in the fluid-bed reactor is shown in Figure 4. The smooth, glossy appearance of the particles tends to support the hypothesis that uranyl nitrate first coats the surface of the particles, then decomposes to uranium trioxide. The near-spherical shape of the particles is probably due to attrition causing the rough corners to abrade.

5-53-19
DECLASSIFIED

Figure 4

Uranium Trioxide Produced In Fluidized Bed Denitrator

(Magnified 94X)

DECLASSIFIED 5-53-20

In opposition to the above factors which tend to produce enlarged particles, there are probably other factors which tend to produce small particles. These include (1) attrition or abrasion resulting from the movement of the particles in the fluid bed, (2) calcination of fine feed droplets by hot gases, and (3) disintegration of particles as a result of very rapid denitration in the hot medium.

Since in the early runs a net increase in particle size occurred, it is evident that small particles were not produced at a rate sufficient to counteract the particle growth. There appeared to be, therefore, two possible courses which might be followed in the experimental work in an effort to promote the attainment of an equilibrium particle size. These were (1) investigation of operating variables in an effort to find conditions which would produce larger amounts of small particles; and (2) separation of fine particles from the product and recycling these to the fluidized bed to act as new nuclei for the deposition of uranium trioxide from the feed.

The latter method is less desirable from a process standpoint but has the advantage of an immediate solution. The recycling technique was therefore investigated first. Later it was found that by suitable adjustment of operating variables, particularly the bed temperature, the percentage of fine particles produced was increased and the necessity for recycling was eliminated. Thus Runs 44 through 51 were made with recycling and Runs 52 and 53 were made without recycling.

2. Average Particle Diameter and Size Distribution of Product

The variation in the average particle size of the uranium trioxide product during the operation of the denitration reactor is shown for a few selected runs in Figure 5. It is apparent that the particle size usually increases during the initial period of operation then reaches an equilibrium value for the remainder of the run. Since the starting bed in all cases was sieved to remove particles larger than 40 mesh, the initial increase in average particle size is primarily due to the formation of coarse particles. After several hours of operation the coarse particles are removed in the product at the same rate as they are formed in the bed, and a steady state is attained.

Moreover, it was found that not only did the average particle diameter reach a constant value, but also the particle size distribution reached a steady state after several hours of operation. In Table 5 are listed the results of sieve analyses on the uranium trioxide product samples which were taken at hourly intervals during Run 47 in which the recycling technique was used. It may be seen that the particle distribution remained essentially invariant at least during the latter half of the run. In Table 6 are listed the sieve analyses for Run 52 in which recycling was not used. Again it is apparent that the size distribution remained constant during the latter portion of the run.

DECLASSIFIED 553-21

5562

FIGURE 5

Table 5

VARIATION OF PARTICLE SIZE DISTRIBUTION DURING DENITRATION RUN 47
(20% RECYCLE)

(For run conditions see Table 2)

Sieve Number	Percentage of Each Size Range for Indicated Hourly Sample													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
+40	6.5	10.1	13.3	14.9	15.2	15.1	15.9	17.4	17.4	16.9	17.4	17.4	17.7	17.9
-40, +60	10.1	11.7	9.9	9.2	8.8	9.1	8.9	9.2	8.5	8.0	8.1	8.0	7.9	8.1
-60, +80	17.0	17.0	13.2	11.3	10.3	10.2	9.5	9.5	9.0	8.7	8.7	8.8	8.6	9.1
-80, +100	14.3	13.6	12.0	11.4	11.4	12.0	11.6	11.7	12.1	12.4	12.0	12.4	12.3	13.4
-100, +200	27.4	27.7	31.4	31.2	36.3	35.8	34.1	32.4	33.4	34.8	33.2	34.5	33.4	36.4
-200, +325	11.2	11.2	12.5	11.4	11.5	10.3	10.0	9.8	9.9	10.6	9.9	10.5	10.7	10.9
-325	13.5	8.6	7.8	10.7	6.7	7.4	9.8	9.9	9.6	8.6	10.8	8.4	9.4	4.4

553-23

Table 6

VARIATION OF PARTICLE SIZE DISTRIBUTION DURING
DENITRATION RUN 52 (NO RECYCLE)

(For run conditions see Table 2)

Sieve Number	Percentage of Each Size Range for Indicated Hourly Sample							
	1	2	3	4	5	6	7	8
+40	7.1	8.7	12.3	9.0	15.3	18.4	19.2	19.0
-40, +60	14.2	14.6	14.1	13.9	13.6	12.9	11.8	10.9
-60, +100	23.0	24.2	25.1	29.0	26.9	24.7	23.3	21.4
-100, +200	46.6	46.5	43.5	41.6	34.9	32.9	35.7	38.8
-200, +325	7.7	4.9	3.1	3.9	6.0	7.6	7.8	7.4
-325	1.4	1.0	1.8	2.6	3.4	3.6	2.1	2.6

3. Coarse Particles In the Product

The product from the fluidized-bed denitration process contains a certain percentage of coarse particles ranging in size from 40 mesh up to approximately 1/16 inch in diameter. These are probably formed by the cementing together of clusters of finer particles. The concentration of these particles in the product at steady state was found to be dependent upon the operating conditions used.

In Figure 6 is shown the variation in the percentage of coarse particles (+40 mesh) in the product samples taken at hourly intervals during Run 47. The percentage increases initially, then reaches a steady value of 17 to 18 per cent after about 8 hours of operation.

The theoretical curve in Figure 6 is based upon the equation

$$t = - \frac{W_B}{W_F} \ln \left(\frac{C_\infty - C_t}{C_\infty} \right)$$

where

t = time in hours from start of run,
 W_B = weight of UO_3 in bed in pounds,
 W_F = rate of UO_3 production in lb/hr,
 C = percentage of coarse particles in product
 (C_t at time t ; C_∞ at infinite time).

553-24-

DECLASSIFIED

PERCENTAGE OF COARSE PARTICLES (+ 40 MESH)

This equation is easily derived from a continuity balance. A plot of the above equation yields a family of curves with values of C_{∞} as a parameter. For the curve in Figure 6 the value of C_{∞} is 18 per cent. It may be seen that the experimental curve follows the theoretical curve closely. After eight hours of operation the percentage of coarse particles should be within 93 per cent of the value which would be attained at infinite time, and after 14 hours it should be within 99.5 per cent of the ultimate value.

The variation in the percentage of coarse particles with time is shown for several 8-hour runs in Figure 7. Steady state is reached after about 6 to 8 hours of operation.

F. Effect of Bed Temperature

The temperature of the fluidized bed during denitration was measured by thermocouples at two points - one at a distance of one inch below the spray nozzle and the second at a distance of 6 inches above the nozzle. The temperature at the upper point was usually only about 5C lower than the temperature below the nozzle despite the large amount of heat absorbed by the denitration process at the spray zone.

For most of the runs completed thus far a bed temperature of 400C was arbitrarily selected. To determine the optimum bed temperature, several additional runs were made at temperatures varying from 450C to 310C. Within this range the effect of temperature on the extent of denitration and dehydration was found to be small as shown in Table 7. The residual nitrate content increased from 0.41 per cent at 450C to 0.50 per cent at 310C. The residual water content increased from 0.08 per cent at 450C to 0.15 per cent at 310C.

Table 7

EFFECT OF TEMPERATURE ON THE RESIDUAL NITRATE AND WATER CONTENT OF THE PRODUCT FROM DENITRATION RUNS

Run No.	Bed Temp. (C)	Residual Nitrate (%)	Residual Water (%)
50	450	0.41	0.08
49	400	0.50	0.11
51	350	0.43	0.12
52	350	0.53	0.18
53	310	0.50	0.15

553-26

DECLASSIFIED

03400000

5-5-3-27-

The operating temperature was found to have a considerable effect on the particle size of the product as may be seen in Table 8. At the higher temperatures a larger percentage of coarse particles are formed. For example, at 450C the percentage of +40 mesh particles was 30, whereas at 310C the percentage was only 13. Moreover the percentage of fine particles (100 to 200 mesh) was over twice as large at 310C as at 450C under otherwise comparable conditions.

Table 8

EFFECT OF TEMPERATURE ON THE PARTICLE SIZE OF PRODUCT
FROM DENITRATION RUNS

Run No.	Bed Temp. (C)	UO ₃ Recycle Rate (%)	Sieve Analysis At Steady State (Percentage in each size range-mesh)			
			+40	-40, +100	-100, +200	-200
50	450	20	30	37	22	11
49	400	20	19	38	32	11
51	350	20	18	28	42	12
52	350	none	19	38	33	10
53	310	none	13	36	45	6

Because of the greater percentage of fine particles formed at the lower temperature the necessity for recycling fine particles to the fluidized bed was eliminated. Thus in Runs 52 and 53 (Table 8) a steady state particle size was attained without recycling by using bed temperatures of 350C and 310C respectively.

It is concluded that in the temperature range tested (310 to 450C) the lowest temperature is optimum. Future runs are planned to determine the effect of temperatures below 310C.

G. Effect of Feed Flowrate

The number of atomizing nozzles required for the introduction of feed into a full-scale denitration unit will depend upon the maximum feed rate possible for a single nozzle. At high flow rates a large number of feed droplets are concentrated in a narrow spray zone, thereby increasing the possibility for agglomeration or caking. The maximum feed rate per nozzle may therefore depend upon the ability of the fluidized bed to distribute the spray droplets and transfer heat to the spray zone.

553-28

DECLASSIFIED

In order to determine the effect of feed flowrate on the quality of the product, several runs were made in which the feed rates were varied from 47 ml/min per nozzle to 230 ml/min per nozzle. The results listed in Table 9 show that the percentage of coarse particles (larger than 40 mesh) in the product at steady state increased from 13.6 per cent at a feed rate of 47 ml/min per nozzle to 19.5 per cent at 230 ml/min per nozzle. Thus a definite but small increase in coarse particles results from increasing the volume of feed introduced through each nozzle. No noticeable effect on the residual nitrate or water content of the product was observed as a result of varying the feed rate.

Table 9

EFFECT OF FEED FLOWRATE ON THE PERCENTAGE OF
COARSE PARTICLES
(+40 Mesh) In Product

Bed Temperature = 400C

Two Nozzles used in Runs 44, 45, 47; one nozzle in Run 49.

For other run conditions see Table 2

Run No.	Feed Flowrate Per Nozzle ml/min	Percentage of +40 Mesh Particles at Steady State
44	47	13.6
45	63	12.6
47	113	17.9
49	230	19.5

Assuming that the highest feed rate tested (230 ml/min per nozzle) was used in a full-scale unit, approximately forty nozzles would be required to produce 10 tons of uranium trioxide per day. This number might be reduced if 100 per cent uranyl nitrate were used as feed.

H. Effect of Nozzle Type

The spray nozzles used in nearly all of the denitration runs are Spraying Systems Company pneumatic atomizing nozzles No. 1/4 JH, syphon type, with variable sized tips depending upon the flow rate to be used. For example, at 230 ml/min a No. 3 nozzle tip was used. With this type nozzle (syphon type) atomization occurs externally, that is, the air and liquid are mixed after leaving the nozzle. The spray angle is approximately 20°.

DECLASSIFIED 553-29-

In Run No. 48 a wide-angle nozzle (Spraying Systems Co. Set-up No. 16) was tested. This nozzle is a pressure-feed type, that is, liquid is supplied under pressure and atomization occurs internally (before leaving the nozzle). The nozzle is designed with six orifices drilled at an angle. The resultant spray is a combination of six individual round sprays having a spray angle of about 70° .

It was found that despite the low feed rate used (92 ml/min) the percentage of coarse particles increased steadily to 26 per cent after 6.5 hrs, at which time the run was terminated. When the nozzle was removed and examined, it was found that a small cake had formed around the nozzle. It was concluded that this type nozzle was less suitable than the syphon type.

I. Other Variables

Other variables which have not yet been completely investigated are the following

- (1) nozzle air pressure,
- (2) nozzle location, i.e. vertical distance from the bottom of the bed,
- (3) fluidizing air velocity,
- (4) feed concentration.

At present only qualitative statements concerning these variables can be made.

The nozzle air pressure effects the degree of atomization, and so might be expected to influence the particle size to some extent. In preliminary runs in the bench-scale reactor the nozzle air pressure was varied between 10 and 25 psig, but no correlation between particle size and air pressure was observed.

The location of the nozzles relative to the bottom or top of the bed is probably of minor importance. In the bench-scale unit the nozzle is located about midway between the bottom and top of the bed. In the pilot scale unit the nozzles are located about one third of the bed height from the bottom of the bed. Both arrangements were satisfactory. It is believed important that the nozzles be mounted horizontally with the tip flush with the inner wall of the reactor. This type of mounting helps to prevent caking around the nozzle.

The fluidizing air velocity has been held virtually constant in all the runs at 1.3 ft/sec calculated at the bed temperature and pressure. Preliminary runs indicated qualitatively that the percentage of coarse

DECLASSIFIED

553-30

particles in the product decreased when the fluidizing air velocity was increased. The optimum velocity will be determined in future investigations.

A feed concentration of 2.4 M uranyl nitrate (approx 70% UNH) has been used in nearly all of the runs. This concentration was chosen for convenience so that the feed solution would not have to be heated above room temperature to avoid precipitation. In future runs it is planned to alter the feed system so that 100 per cent uranyl nitrate hexahydrate can be used as feed.

J. Heat Transfer Coefficient

The heat transfer coefficient between the reactor wall and the fluidized bed is not clearly defined in this equipment because of variations in the wall temperature from point to point. Measurements of the wall temperature were made by means of two thermocouples brazed into the reactor wall in the space between the tubular electric heaters. The temperatures so measured are lower than the true average wall temperatures, but approximate corrections based on the thermal conductivity of the wall can be made. By this means the heat transfer coefficient between the wall and the bed was roughly estimated to be between 50 and 100 Btu/(hr)(ft²)(F).

In the pilot-scale reactor the heat input was limited by the rate of heat transfer between the tubular electric heaters and the reactor wall. The maximum sheath temperature of the heaters was limited to 800C. This rate of heat transfer could be increased, with corresponding increase in production rate, by bonding the heaters to the wall with sprayed metal, such as copper.

5-53-31-
DECLASSIFIED

IV. REDUCTION AND HYDROFLUORINATION

The advantages of fluidized beds as gas-solids contactors for the hydrogen reduction of uranium trioxide to uranium dioxide and for the hydrofluorination of uranium dioxide to uranium tetrafluoride were discussed previously (Section II A). However, the use of a single fluidized bed for mass transfer operations of this type has certain shortcomings, namely: (1) countercurrent contact between the gas and the solid cannot be achieved because of the mixing which occurs in a fluidized bed; (2) the residence time of the gas in the bed is relatively short; and (3) some of the solid may flow from the inlet to the outlet without adequate residence time. For these reasons a multiple-stage fluidized-bed reactor was designed and constructed to investigate the reduction and hydrofluorination operations.

A. Experimental Equipment

1. Reactor

A schematic drawing of the reactor and its associated equipment is shown in Figure 8. The reactor, which contains three stages, is similar in design to a sieve-plate gas absorption column, except that the fluidized solid replaces the liquid used in gas absorption. The solid feed enters at the top stage where a baffle causes the feed to flow to the bottom of the fluidized bed. Solid overflows from the top of the fluid bed through a downcomer which carries it to the bottom of the middle stage. In this manner solid flows downward through the reactor, eventually overflowing from the bottom stage into a hopper. The solid is fluidized by a mixture of nitrogen gas and the reactant gas, either hydrogen or anhydrous hydrofluoric acid.

The reactor and associated equipment are constructed of monel and nickel except for a few stainless steel parts which were used for expediency. The latter will be replaced before any hydrofluorination runs are made. Each stage consists of a 10-inch length of 3-inch diameter pipe, flanged at each end so that any number of stages can be connected together. The bottom of each stage is covered by a perforated plate containing one hundred 0.04-inch diameter holes (except the bottom stage which is covered by a porous metal plate). A downcomer of 5/8-inch tubing is welded to the plate. The depth of the fluidized bed on each plate is approximately equal to the height of the downcomer, which is 5 inches.

2. Gas System

The fluidizing and reactant gases are mixed and preheated before entering the bottom of the reactor. The gas flows upward through the three fluidized beds and into the disengaging section, where two porous monel filters remove the entrained dust particles. The disengaging section

DECLASSIFIED 553-32-

Figure 8

MULTIPLE-STAGE FLUID BED REACTOR.

DECLASSIFIED 553-38-

is 6 inches in diameter and 12 inches high. The off-gas from the reactor passes through a caustic scrubber for removal of hydrofluoric acid and into an air jet for dilution of hydrogen before being exhausted into the ventilating duct.

3. Solids Feed System

The solids feed system consists of a feed hopper, a gage glass, and a solids meter. The feed hopper is capable of holding about 80 lbs of uranium trioxide or uranium dioxide. The calibrated gage glass, a 6-inch length of 2-inch diameter glass pipe, serves as a means of measuring the rate of flow of solids into the reactor. The solids meter is a modified Jabsco rubber impeller pump. The impeller is revolved at low speed by a motor coupled to a Graham variable speed transmission. When revolved at a few revolutions per minute the pump performs like a vane-type solids feeder. From the feeder the solids flow through a 1/2-inch tube into the reactor. A stream of nitrogen flowing into the solids meter helps to carry the feed through the inlet tube.

4. Associated Equipment

Each stage of the reactor is heated by a 1000-watt tubular electric heater coiled around the outside wall. The reactor is insulated with 2 inches of Kaylo pipe insulation. Since both the reduction and the hydrofluorination reactions are exothermic, it will be necessary to remove heat after the reactor is in operation. Tentatively it is planned to remove portions of the insulation to control the temperature. Cooling coils may be installed later if necessary.

The temperatures of each of the fluidized beds will be measured by thermocouples inserted through a 1/4-inch inclined pipe welded into the reactor wall above the bed level. These inclined pipes also serve as pressure taps for the measurement of the pressure drop across each stage.

B. Preliminary Experiments

Since it is not possible to observe the behavior of the fluidized beds in the all-metal reactor, a mock-up was constructed from glass pipe in order to study the hydraulics of the unit and to observe the solids flow pattern. This glass model was used to test several sieve-plate designs and various sizes of downcomers, and to determine the approximate gas velocity required for fluidization.

Following these experiments one exploratory reduction run was made in the metal reactor. Each of the three stages was filled with uranium trioxide produced in the denitration reactor. Preheated nitrogen gas was used for fluidization. After the bed temperatures were brought up to 600C,

553-34-
DECLASSIFIED

the flow of hydrogen gas was started, and uranium trioxide feed was introduced at approximately 4 lbs/hr. A 100 per cent excess of hydrogen was used, and the ratio of nitrogen to hydrogen was 1.5 to 1 by volume. After six hours of operation the run was terminated and samples of the solid were collected from the product receiver and from each of the three stages. The percentages of uranium dioxide in the samples from each of these points were as follows:

top stage 18.7 per cent, middle stage 72.7 per cent,
bottom stage 73.1 per cent, final product 90.0 per cent.

These results are considered encouraging for the initial run. It is believed that considerable improvement can be obtained by using somewhat higher temperatures and more favorable ratios of hydrogen to nitrogen. Additional stages can be added to the unit, if necessary, to obtain more complete reduction.

553-35

DECLASSIFIED

~~CONFIDENTIAL~~

UNCLASSIFIED 37

V. FUTURE WORK

The investigation of operating variables in the denitration process is continuing. Future work will emphasize the use of 100 per cent uranyl nitrate as feed. Efforts will be made to increase the production capacity per spray nozzle, and to increase the capacity per unit area of reactor cross section.

In the reduction and hydrofluorination operations a series of runs will be made to demonstrate the technical feasibility of the process. Following these runs, it is planned to investigate the optimum operating conditions and the optimum equipment design. In order to optimize the process conditions certain fundamental kinetic studies may be necessary to determine whether the reactions are controlled by the rate of diffusion or by the rate of chemical reaction or both.

Future plans also include the investigation of the applications of fluidized beds to the following processes:

- (1) production of uranium hexafluoride by reaction of uranium tetrafluoride with fluorine gas,
- (2) reduction of uranium hexafluoride to uranium tetrafluoride by hydrogen.

VI. ACKNOWLEDGEMENTS

The authors wish to acknowledge the operating assistance of Mr. M. S. Jones, the assistance of the Analytical Group under Dr. R. P. Larsen, and the helpful advice of Dr. S. Lawroski and Mr. W. A. Rodger.

~~CONFIDENTIAL~~

UNCLASSIFIED

DECLASSIFIED

553-36-