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THE CONTINUOUS PRODUCTION OF URANIUM TRIOXIDE

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the Continuous Production of Uranium Trioxide

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Introduction

Uranium trioxide is an important intermediate in the production of high purity uranium metal as conducted in such plants as that operated for the AEC by Mallinckrodt Chemical Works at Weldon Spring, Missouri. Currently this step consists of the thermal decomposition of a uranyl nitrate hydrate in gas fired, stirred, stainless-steel pots. The pots are filled with the molten salt, heated and stirred until uranium trioxide is formed according to equation (1).

Where n is usually between 3 and 4.

The warm UO_3 powder is then removed from the pot by a vacuum transfer system and the cycle is repeated. A large number of pots is used and each repeats the cycle several times a day.

The desirability of a continuous method is suggested by difficulties inherent in the present process. The material is heat sensitive during denitration, so that poor agitation and overheating may result in the formation of large amounts of undesirable U_3O_8 . The resulting batch-to-batch variations in the product are apparently responsible for a number of operating difficulties in subsequent steps. In addition, the possible exposure of the operators to uranium oxide dust presents a formidable potential health problem.

The experimental program described here had as its objective the development of a low-cost continuous process for the production of a uniform uranium trioxide from purified uranyl nitrate solution. The work was done in the pilot plant of the Mallinckrodt Uranium Division under contract to the Atomic Energy Commission.

The fluidized bed technique was selected for several reasons:

1. The highly turbulent mixing of solids in such a bed insures uniform temperature with consequent ease of temperature control.
2. The good heat transfer characteristics and the utility of internal heating surfaces permit high production capacity in economically-sized equipment.
3. A fluidized bed delivers a free-flowing product of high bulk density suitable for subsequent process steps.
4. A fluidized bed is a closed system with no moving parts and thus would minimize the possibility of personnel exposure to dust.

In this process the molten uranyl nitrate hydrate is continuously atomized into a heated fluidized bed of uranium trioxide particles where evaporation and thermal decomposition occur. The resulting solid UO_3 product is withdrawn continuously.

The use of a fluidized bed for the thermal decomposition of uranyl nitrate was first investigated by Argonne National Laboratory⁽¹⁾ using a six-inch diameter reactor. Heat was supplied by tubular electrical heaters set in grooves in the reactor wall, the bed was fluidized with air, and the uranyl nitrate solution was introduced through a two fluid atomizing spray nozzle in the reactor wall. Production rates as high as 100 pounds UO_3 per hour per square foot of cross sectional area were achieved.

Since the production rate is limited by the heat input ability of the reactor, a different heating technique was required to achieve high production rates in a larger reactor, as the surface-to-volume ratio decreases with larger reactor diameter. The use of internal heat transfer surface was therefore studied in the present work.

The first ten-inch diameter fluidized bed reactor built in the Mallinckrodt pilot plant used the Argonne principles except that heat was applied to the bed internally as well as externally.⁽²⁾⁽³⁾ There were 70, one-half inch diameter by one foot long electrical heaters protruding through the gas distribution plate into the reaction bed. Several months of operating experience with this unit provided information for the design of an improved ten-inch diameter unit.

The principal difficulty experienced was with the electric heaters. Any misoperation or instability in fluidization caused high heater-element surface temperatures, resulting in the formation of U_3O_8 and frequent burn out of the heaters. A more readily controlled means of heat input was therefore sought.

Equipment Description

The present reactor, shown in Figure 1, consists of a ten-inch diameter type 347 stainless steel pipe, six feet long, with a twenty-inch diameter disengaging section located on top of the reactor and a fluidizing gas distribution plate flanged to the bottom.

Thirty, one and one-quarter inch diameter bubble-cap-type distributors are provided in this plate with a one-inch diameter bayonet heater passing through each bubble-cap and extending three feet into the reaction bed. Figure 2 shows

a detail of one of these bubble-caps. Fluidizing air from the supply chamber below the distributor plate passes through the annular space between the bubble-cap and the bayonet heater and then into the reaction bed through three holes equally spaced around the riser just under the cap.

Heat is supplied to the reaction bed by molten heat transfer salt (45% sodium nitrite, 55% potassium nitrate) circulating through the bayonet heaters. As seen in Figure 1, the hot salt enters a supply chamber directly below the fluidizing gas chamber and passes through the annular space between the one-inch diameter outer tube and the 5/8-inch diameter inner tube, then returning through the inner tube and out the discharge chamber below the supply chamber.

Molten uranyl nitrate hydrate is sprayed into the reaction bed through a two fluid atomizing nozzle mounted six inches above the tops of the heaters. A section of this nozzle is shown in Figure 3. The molten uranyl nitrate passes through the central orifice and is atomized by air flowing through the annular orifice. The nozzle is installed with the tip flush with the inside of the reactor wall.

Figure 4 shows the fluidized bed unit with its auxiliary equipment. Fluidizing air is metered through an electrical preheater to the gas distributor supply chamber. The molten uranyl nitrate hydrate is tapped from a recycle loop and metered through a rotameter to the spray nozzle. Air for atomization is also metered by a rotameter.

The heat transfer salt is heated by electrical immersion heaters in a large steel pot and pumped to the reactor by a vertically mounted, submerged centrifugal pump, driven by a 7.5 horsepower D.C. motor. The speed of the motor is controlled by the reactor temperature in the spray zone.

The UO_3 product overflows from the reactor through a two-inch diameter pipe, four and one-half feet from the bottom of the bed, through a surge hopper and a rotary valve into a packaging station. The off-gases leave the reactor through a two-inch pipe at the top of the disengaging section and pass through a cyclone separator to a scrubber; dust removed by the cyclone falls into a hopper whence it returns to the reactor through a rotary valve.

Operating Conditions

The operating conditions selected for the experimental investigation are summarized in Table I. The reactor has been operated at temperatures ranging from 600°F to 800°F . Operation of the unit below 600°F has been prevented by condensation of the reaction gases in the off-gas piping and wet powder plugging the fines refeed system. Operation at temperatures above 800°F restricted the capacity of the unit, since for safety reasons the temperature of the heat transfer salt was limited to 1000°F .

Preheated air was used as the fluidizing medium at flow rates ranging from 16.5 to 20 standard cubic feet per minute. The flow rate was varied with the bed temperature to maintain a constant fluidizing gas velocity at the bottom of the reactor.

The uranyl nitrate was fed to the reactor in concentrations ranging from five pounds of uranium per gallon to the molten uranyl nitrate trihydrate containing approximately twelve pounds of uranium per gallon. The initial experimental work was done using an aqueous solution of uranyl nitrate with a freezing point of 70°F (about 5 lbs. U/gal) to simplify the handling and metering equipment. Even though the handling and metering problems with molten uranyl nitrate

hexahydrate (which freezes at 140°F) and uranyl nitrate trihydrate (which freezes at 230°F) are more complex, later work was done using the high feed concentrations to take advantage of the higher productivity and the decrease in the quantity of reaction gases.

A single atomizing nozzle was used to introduce the feed liquor into the reaction bed. The liquid feed rate through the nozzle was varied between 6 and 13.5 gallons per hour using atomizing air flows ranging from 0.8 to 3.6 standard CFM at 10 to 60 PSIG.

Production rates of 50 to 150 pounds UO_3 per hour have been attained in this unit; the lower rates with dilute aqueous feed concentrations and the higher rates with the molten uranyl nitrate hydrates. At rates higher than 150 pounds per hour, quantities of uranyl nitrate were carried out of the reaction bed which resulted in clogging of the off-gas system.

There is an abrupt change in fluidizing velocity at the top of the heater tubes resulting from the sudden increase in free cross section area. The average superficial velocity of the fluidizing gas in the heater zone is 1.7 ft/sec and drops to a value of 1.25 ft/sec in the spray zone. Under the operating conditions employed, the gases evolved in the reaction are approximately equal in volume to the fluidizing gas, however, and since most of the reaction probably occurs in the spray zone, there is a net increase in total gas velocity above the heater tubes. Thus, the restricted free area in the bottom section causes high gas velocity promoting good heat transfer, while the expansion of area in the spray zone prevents gas velocity high enough to cause severe elutriation.

TABLE I

Fluidized Bed Operating Conditions

<u>Run Number</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Reactor Temperature, °F	810	705	735	600	630	625	615	635	595	600
Fluidizing Air Flow Rate, Standard CFM	16.5	18	18	20	20	20	20	20	20	20
Uranyl Nitrate Feed Concentration, lbs. U/gal	7.7	6.8	6.8	6.8	5.0	5.0	10.0	10.0	12.0	11.5
Uranyl Nitrate Feed Rate, gal/hr	6.7	6.0	9.4	6.0	9.1	13.5	7.8	8.4	9.7	11
Atomizing Air Flow, Standard CFM	1.5	1.5	0.8	0.8	1.5	0.8	1.0	1.3	3.6	0.8
Atomizing Air Pressure, psig	60	35	50	10	30	35	50	50	50	55
Production Rate, lbs. UO ₃ /hr	63	50	78	50	57	80	95	100	140	150

800 210

Results

The uranium trioxide product was a free-flowing granular material made up of essentially spherical particles, visually similar to those produced in the continuous trough calciner described by Szulinski.⁽⁵⁾ The assay of the product averaged 99.0 percent UO_3 with residual nitrate and water content consistently less than one percent. There was no evidence of the intermediate oxide, U_3O_8 , formation in any of the runs.

The reactor operating conditions had a pronounced effect on the particle size of the product. Figure 5 shows the effect of the operating temperature on the average particle diameter. The average particle size produced at 700°F was 2-1/2 times greater than that produced at 600°F. At an operating temperature of 800°F the average particle size of the product continued to increase until loss of fluidization occurred. This temperature effect on the particle size is not yet fully understood, but it may be postulated that, since at a given superficial fluidizing velocity there is a higher bed void fraction at higher temperature, there are fewer solid particles on which the liquid droplets may collect, thus causing more rapid growth and hence larger particles.

Figure 6 shows the effect of the nozzle operation on the average particle size of the product. As the ratio of the volume of atomizing air to volume of liquid feed through the nozzle is decreased, the average particle size of the product increases. This observation suggests that the particle size of the product is related to the degree of atomization at the nozzle.

Both the feed liquor concentration and flow rate seem to affect the particle size of the product, probably because they affect the volume of gas generated and hence the quality of fluidization in the spray zone. The average particle size of the product was correlated with the total gas flow in the spray zone and the operating temperature as shown in Figure 7. The temperature used in this empirical correlation is in the form of a denitration driving force. These data suggest that increased turbulence and attrition occurring at the higher gas flows result in a smaller average particle size in the product.

The product had a high bulk density, ranging from 3.5 gms/cc to 4.3 gms/cc depending on the production rate as shown in Figure 8. It should be pointed out that the data employed to develop this curve were not obtained at a constant feed concentration, since during operation at the higher rates a considerably higher feed concentration was employed than at the lower rates. The higher rates and/or feed concentrations may result in increased voids within the particles and consequently a lower bulk density. Particle size distributions were almost identical at different production rates in a number of cases, indicating that the distribution is not a factor in the bulk density change.

Photomicrographs of the particles produced at a low feed concentration and rate and at the high feed concentration and rate are shown in Figure 9. Apparently the mechanism of particle formation is different at the two conditions. The laminar particle formed during a run using a dilute aqueous feed at a low production rate suggests that the atomized liquid droplets deposit on the fluidized solid particles prior to decomposing. In the case of the highly concentrated feed liquor at high rates it appears that the mechanism changed to

primarily one of agglomeration of the liquid droplets or fine solid particles since no laminations are visible.

The heat input to the fluidized bed ranged from approximately 72,000 BTU/hr to 160,000 BTU/hr. Table II shows the apparent overall heat transfer coefficients for the runs made at a nominal 600°F operating temperature. These data indicate that the heat transfer improves with increasing production rate with the exception of the anomalous result reported for Run Number 7. A comparison of the overall coefficient between 600°F and 700°F operating temperature at equivalent production rates is shown in Table III.

Since the purity requirements for uranium products are very high, any corrosion of the fluidized bed unit would be of serious concern in the denitration reaction. Iron pickup in these runs has consistently been less than 20 PPM, however, and is not considered significant.

Conclusions

A fluid bed reactor has been demonstrated to be a reliable and flexible device for continuously producing UO_3 from uranyl nitrate.

Internal heat transfer tubes occupying one-third of the reactor cross section permitted a production rate of 300 pounds of UO_3 per hour per square foot of bed cross section and should allow direct scale-up to commercial-scale dimensions.

Chemical purity of the product UO_3 was excellent, and its physical properties could be controlled by variation of operating conditions.

TABLE II

Fluidized Bed Heat Transfer Data
At the Nominal 600°F Operating Temperature

<u>Run Number</u>	<u>Heat Flux</u> <u>BTU/hr·ft²</u>	<u>T_s-T_b</u> [*] <u>°F</u>	<u>U</u> <u>BTU/hr·ft²·°F</u>	<u>Production Rate</u> <u>lbs. UO₃/hr</u>
4	3000	180	17	50
5	4600	190	24	57
6	6900	275	25	80
7	4500	85	53	95
8	5500	140	39	100
9	5300	130	41	140
10	6000	145	41	150

* T_s = Average Molten Salt Temperature.

T_b = Average Fluid Bed Temperature.

TABLE III

Fluidized Bed Heat Transfer Data
At 600°F and 700°F Operating Temperatures

<u>Run Number</u>	<u>Heat Flux</u> <u>BTU/hr·ft²</u>	<u>T_s-T_b</u> [*] <u>°F</u>	<u>U</u> <u>BTU/hr·ft²·°F</u>	<u>Operating</u> <u>Bed Temp. °F</u>	<u>Product</u> <u>Rate lbs/hr</u>
2	3200	230	14	700	50
4	3000	180	17	600	50
3	5000	280	18	700	78
6	6900	275	25	600	80

* T_s = Average Molten Salt Temperature.

T_b = Average Fluid Bed Temperature.

References

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FIGURE 1
**FLUID BED
REACTOR**

FIGURE 2

DISTRIBUTION PLATE DETAIL

FIGURE 3
FEED NOZZLE

FIGURE 4

FLUID BED DENITRATOR

Figure 5

Effect Of Operating Temperature
On The UO_3 Particle Size

Figure 6

Effect Of Atomizing Air To Feed
Liquor Volume Ratio On The UO_3 Particle Size

Figure 7

Effect Of Total Gas Flow And Operating
Temperature On The UO_3 Particle Size

Figure 8

Effect Of Production Rate
On The Product Bulk Density

(a) Agglomerate particles, 100 x

(b) Laminar particle, 100 x

Figure 9. Fluid Bed UO_3