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COMPARISON OF A FLUIDIZED-BED AND AN AGITATED-TROUGH CHEMICAL REACTOR FOR PRODUCING ThO_2 FROM $Th(NO_3)_4$

S. D. Clinton

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CHEMICAL TECHNOLOGY DIVISION

Unit Operations Section

COMPARISON OF A FLUIDIZED-BED AND AN AGITATED-TROUGH CHEMICAL REACTOR FOR PRODUCING ThO_2 FROM $Th(NO_3)_4$

S. D. Clinton

Date Issued

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ABSTRACT

The continuous conversion of $Th(NO_3)_4$ solution to form 100- to 500-μ-dia ThO_2 particles was tested in both a fluidized bed and an agitated trough. Neither method was feasible for producing dense high-strength ThO_2 spheres. Instead of depositing uniform oxide layers on the hot surface of the bed particles, the $Th(NO_3)_4$ decomposed to form loosely bound ThO_2 agglomerates.

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1.0 SUMMARY

In 10 runs in fluidized-bed denitration equipment, aqueous and methanol solutions of $Th(NO_3)_4$ were sprayed into a fluidized bed containing either sintered ThO_2 agglomerates or classified sea sand. The $Th(NO_3)_4$ feed concentration was varied between 1.5 and 2.5 M and the superficial fluidizing air velocity between 0.6 and 1.3 ft/sec at bed temperatures between 400 and 700°C. The yield of fines was high in all runs, and bed caking was a problem in every run except that with a bed temperature of 700°C. In a single run an aqueous solution of $UO_2(NO_3)_2$ was denitrated in a fluidized sand bed at 390°C. The yield of UO_2 fines was low, and no caking was observed in the bed.

An agitated-trough denitrator was operated over a temperature range 150-300°C in an effort to denitrate and coat ThO_2 on a bed of either ThO_2 or sand. The problem of bed caking was minimized in the agitated trough, but the yield of oxide fines was not reduced in the trough compared to the fluidized bed. The trough agitator blades moving at a maximum velocity of 1.85 ft/sec prevented caking in the trough calciner, but probably increased the rate of attrition.

In an attempt to find a possible feed additive that would aid ThO_2 particle growth, a run was made by pumping aqueous $Al(NO_3)_3$ into an agitated sand bed at 425°C. The yield of Al_2O_3 fines was low enough to indicate that a mixture of aluminum and thorium nitrates might be denitrated in an agitated bed to form a cohesive oxide product. The results of the studies did not indicate that either the fluidized bed or the agitated trough is feasible for producing dense high-strength ThO_2 spheres in the size range 100-500 μ. Operating conditions for spray-calcining thorium nitrate in an agitated bed of solids and obtaining oxide particle growth is evidently more critical and difficult to attain than the conditions for similarly calcining uranium nitrate. The thorium denitration reaction appears to deposit oxide agglomerates (size range 20-30 μ) on the existing bed particles which can be removed by attrition within the bed. One possible explanation for this denitration behavior is that after the aqueous nitrate coats the hot surface of the bed particle, the thorium nitrate decomposition reaction is initiated before all the water can be driven from the nitrate. The water vapor escaping from the relatively thin two-phase layer of oxide and nitrate might result in a porous, low-strength thorium oxide product such as was produced experimentally.

2.0 INTRODUCTION

Studies with the fluidized and agitated beds were made to produce dense, spherically shaped ThO_2 particles in the size range of 100-500 μ. The primary interest in this size oxide was for studies of a heavy- or light-water fluidized-bed nuclear reactor blanket.

Results reported for denitration of uranyl or aluminum nitrate gas-fluidized and mechanically agitated beds indicated the possibility of obtaining an oxide product with the desired properties by spraying thorium nitrate solution into a high-temperature fluidized bed of ThO_2 particles.

A gas-fluidized bed was used to convert aluminum nitrate liquid wastes into free-flowing solids by spraying the liquid into the bed.[1] Similarly, uranyl nitrate solution was sprayed into a gas-fluidized and a mechanically agitated bed of UO_3 to produce dense spherical oxide particles of a desirable size.[2-4]

This report presents the results of the thorium denitration runs in both the fluidized- and agitated-bed equipment. The controlling variables for producing a dense cohesive oxide were believed to be the bed temperature and feed concentration, and the effects of these variables were investigated over the range 400-700°C and 1.5-2.5 M $Th(NO_3)_4$ for the fluidized bed and 150-300°C and 1-2 M $Th(NO_3)_4$ for the agitated trough.

The agitated-trough calciner was borrowed from the Y-12 plant, where it had been used to produce UO_3 from uranyl nitrate solution. The assistance of George Marrow in obtaining the trough calciner is acknowledged. The design features and initial startup of equipment used for this study of the fluidized-bed denitration of thorium nitrate were previously reported.[5]

3.0 FLUIDIZED BED DENITRATION STUDIES

3.1 Process Flowsheet

The principal part of the fluidized-bed denitration flowsheet was the chemical reactor which contained the fluidized bed (Figure 3.1). The reactor was constructed from a 3-in.-dia Inconel pipe with a 6-in.-long section of Inconel pipe at the top to permit some of the entrained solids to fall back into the bed.

The main fluidizing gas (all gas streams entering the reactor were air) was metered into the bottom of the reactor through a 1/8-in.-thick, sintered stainless steel gas distributor plate with mean pore size openings of 65 μ. The gas flowed up through the fluid bed and through four Micrometallic bayonet-type filters (mean pore size 10 μ). It was periodically necessary to reverse the air flow through one of the four filters with the filter blowback gas to avoid plugging by oxide fines.

The liquid nitrate feed was pumped through a Hills-McCanna metering pump to a gas atomizing spray nozzle. The nozzle was obtained from Spraying Systems Company and consisted of fluid nozzle 2850 and air nozzle 64-5. Solids for the initial fluidized bed entered the reactor from the solids feed tank.

Heavy oxide particles at the bottom of the reactor fell through a 0.5-in.-dia line to a conical classifier. The smaller of these particles were entrained by the classifier gas and returned to the bed in the vicinity of the spray nozzle. Theoretically the rate of the classifier gas could be controlled to allow the larger or desired particle size to fall into the product tank.

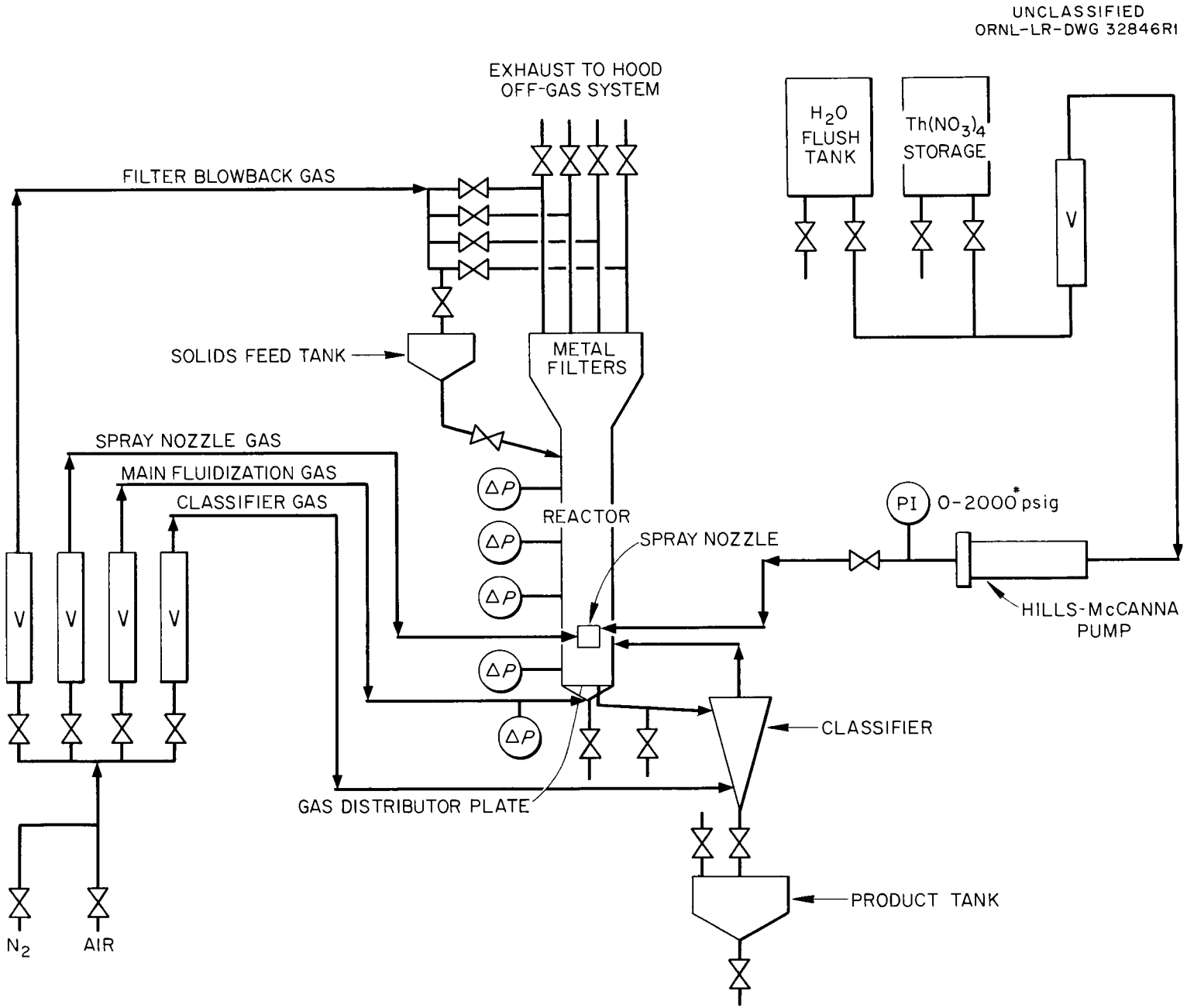


Fig. 3.1. Process flowsheet for the fluidized-bed denitration of thorium nitrate.

The reactor and main fluidizing gas were heated by means of Thermoshell Electric heating elements. These elements were resistance coils embedded in a ceramic block of semicylindrical shape.

3.2 Experimental Procedures and Results

During the operation of the fluidized bed, seven runs were made by spraying aqueous and methanol solutions of 1.5 M $Th(NO_3)_4$ into a fluidized ThO_2 bed, using a superficial fluidizing air velocity of 0.6 to 0.8 ft/sec at temperatures between 550 and 600°C (originally reported in monthly reports[6-8]). The main problem was partial caking of the ThO_2 bed. The ThO_2 for the starting bed material consisted of irregular sintered agglomerates which were not easily fluidized, and the poor fluidizing properties of the ThO_2 increased the probability of cake formation within the bed.

The last four fluidized-bed runs were made by spraying aqueous $Th(NO_3)_4$ or $UO_2(NO_3)_2$ solutions into an initial bed of classified sea sand (originally reported in monthly reports[9-11])(Table 3.1). The operating time of each run was about 8 hr with a liquid feed rate of 1 liter/hr. Caking of the bed occurred below the spray nozzle in runs T-9 and T-10. The bed remained fluidized during runs T-8 and T-11 (the latter run with $UO_2(NO_3)_2$ feed was made to duplicate results reported by Argonne National Laboratory[3]). There was a high yield of ThO_2 fines in all three of the $Th(NO_3)_4$ aqueous feed runs as indicated by a rapid buildup of the pressure drop across the metallic bayonet filters (to a maximum of 10-15 in. Hg). The yield of UO_3 fines in run T-11 was sufficiently low to maintain a minimum pressure drop across the metallic filters (3-8 in. Hg).

Effect of Temperature. During runs T-8, 9, and 10 the amount of nitrate remaining in the ThO_2 product increased approximately linearly with decreasing temperature, ranging from 0.06 wt % nitrate at 700°C to 0.51 wt % at 400°C (Table 3.1). A large percentage of ThO_2 fines (less than 20 μ) was formed in the fluidized bed at 700°C, and it was theorized that the nitrate was decomposing before a stable liquid coating could be formed on the individual bed

Table 3.1. Operating Conditions and Product Nitrate Content for Fluidized-bed Denitrations

Run	Concentration of Aqueous Feed	Bed Temp, °C	Superficial Fluidizing Air Velocity, ft/sec	NO_3 in Product, wt %
T-8	1.8 M $Th(NO_3)_4$	700	0.8	0.06
T-9	2.5 M $Th(NO_3)_4$	500	0.8	0.34
T-10	2.5 M $Th(NO_3)_4$	400	1.3	0.51
T-11	2.5 M $UO_2(NO_3)_2$	390	1.3	0.26

particles. In an effort to slow down the thorium denitration reaction, the bed temperature was decreased for subsequent runs. The problem of ThO_2 fines formation, however, continued at operating bed temperatures down to 400°C.

A cake formed in the bed below the spray nozzle during the thorium denitration runs at temperatures between 400 and 600°C. When the bed was properly fluidized, the temperature gradient from the bottom to the top of the bed was between +5 and +10°C. As the fluidized bed developed a cake, the temperature at the top of the bed underwent a sudden decrease of 50 to 150°C. The thorium denitration run (T-8) at 700°C and the uranyl nitrate run (T-11) at 390°C were the only runs with the fluidized-bed equipment in which bed caking was not a problem.

Using a thermogravimetric balance apparatus, the decomposition of $Th(NO_3)_4$ has been studied between the temperatures of 200 and 700°C.[12] Above 200°C the nitrate decomposes readily to the oxide; however, the reaction rate becomes significantly slower when the decomposition reaches 90% of completion. In order to carry the reaction to completion with a minimum bed holdup time (approximately 1 hr), a bed temperature between 600 and 700°C appeared desirable. Data from Argonne on the denitration of uranyl nitrate in a fluidized bed indicate that the percentage of coarse particles in the bed increases with increasing temperature.[3]

Effect of Feed Concentration and Composition. In the attempts to grow dense spherical ThO_2 particles, the thorium nitrate feed concentration was varied from 1.5 to 2.5 M (45 to 65 wt % $Th(NO_3)_4$). Under the thorium denitration conditions studied, however, the variation of the feed concentration had no apparent effect on the particle growth. Argonne, in their denitration studies of uranyl nitrate in a fluidized bed, reported that essentially no particle size growth occurred when the nitrate feed concentration was 70 wt % $UO_2(NO_3)_2 \cdot 6\ H_2O$ (55 wt % $UO_2(NO_3)_2$); but at feed concentrations of 80 wt % $UO_2(NO_3)_2 \cdot 6\ H_2O$ (63 wt % $UO_2(NO_3)_2$ or higher, particle growth did occur.[13]

The thorium nitrate feed was sprayed into the fluidized bed as a methanol solution during runs T-3 through T-7. The purpose of the methanol was to supply heat by oxidation at the point of denitration and thus decrease the problem of bed caking encountered in runs T-1 and 2 with an aqueous nitrate feed. Although the bed caking was decreased, the yield of ThO_2 fines was high, presumably because of thorium salt denitration in the methanol flame instead of on the surface of the hot ThO_2 particles. In subsequent runs the nitrate was sprayed into the bed as an aqueous solution in order to delay the decomposition until a liquid nitrate coating could be formed on the bed particles.

Effect of Bed Material. One of the major problems in the denitration runs was finding a suitable material for the initial fluidized bed. For the first seven runs the starting bed material was ThO_2 screen-classified between 50 and 150 μ. These individual oxide particles were irregular sintered agglomerates, which were not easily fluidized and consequently increased the probability of cake formation. In an effort to maintain fluidization the starting bed material for the last four runs was screen-classified sea sand (100 to 250 μ).

During the early stages of a run, the presence of the sand bed was definitely beneficial in maintaining proper fluidization, compared to the irregularly shaped ThO_2. Due to attrition the sand may have contributed to the high yield of ThO_2 fines in runs T-8, 9, and 10; however, this effect was not observed in the uranium denitration run.

Effect of Fluidizing-gas Velocity. Air was used as the fluidizing gas. In a glass mockup of the equipment at room temperature, air velocities between 0.1 and 0.3 ft/sec were sufficient to fluidize a bed of ThO_2 particles in the size range 50-150 μ. During the denitration runs the fluidizing air velocity (calculated at the bed temperature) was varied between 0.6 and 1.3 ft/sec. At a bed temperature of 700°C, fluidization was maintained with an air velocity of 0.8 ft/sec. However, with the same fluidizing velocity, caking occurred in the bed at 500°C (run T-9). In run T-10 increasing the air velocity to 1.3 ft/sec at 400°C had no effect in keeping the bed fluidized but instead had the adverse effect of causing a more rapid buildup of the pressure drop across the bayonet filters at the top of the reactor (blowback of each of the filters at intervals of 5 to 10 min was necessary). With a 1.3 ft/sec fluidizing velocity in the uranium denitration run at 390°C, fluidization was maintained throughout the run, and the pressure-drop across the bayonet filters was kept below a maximum of 8 in. Hg at blowback intervals of 30 min.

Effect of Gas Distributor Plate. A sintered stainless steel plate was more satisfactory than a perforated plate for distributing the fluidizing air and supporting the bed solids. The originally designed gas distributor plate was machined from a 16-gage Inconel sheet with 3/64-in. holes drilled on 1/8-in. centers. When fluidizing air was metered to the bed, this plate proved to be an inadequate support for the bed solids, since ThO_2 particles (50 to 150 μ) leaked through the distributor, filling the dead space at the bottom of the reactor. A gas-distributor bed-support plate machined from a 1/8-in.-thick Micrometallic porous stainless steel sheet with mean pore openings of 65 μ was used satisfactorily in the denitration runs succeeding run T-2.

Effect of Varying Bed Height. Observations in tests made in a glass mockup of the equipment indicated that the initial bed length should extend several inches above the spray nozzle in order to obtain a more dense phase of solid particles at the nitrate feed injection nozzle. The spray nozzle was located 11 in. above the gas distributor and bed support plate, and in runs T-3, 4, 5, and 6 the top of the fluidized bed extended approximately 2-in. above the spray nozzle. In an effort to minimize the amount of bed dispersion due to the spray nozzle air and to increase the probability of particle growth, the top of the fluidized bed was maintained at least 5 in. above the spray nozzle in all the denitration runs following run T-6. At this distance the bed height/diameter ratio (before fluidization) was approximately 5, and the fluidization probably consisted of "slugging" and violent turbulence.

Effect of Changing Spray Nozzles. The nitrate feeding nozzle that caused the least operating difficulties was obtained from Spraying Systems Company and consisted of fluid nozzle 2850 and air nozzle 64-5 (liquid is

siphoned through the nozzle by the atomizing air). Several denitration runs were made with fluid nozzle 2850 and air nozzle 73160 (liquid must be supplied under pressure). However, this atomizing nozzle assembly plugged frequently and was generally unsatisfactory. During most of the runs the pressure drop across the atomizing nozzle was maintained between 10 and 15 psi at a liquid feed rate of approximately 17 ml/min.

3.3 Oxide Product Formed in Fluidized Bed

The oxide particles produced in runs T-8 and T-11 were screen-classified and the resulting size fractions analyzed for SiO_2 and ThO_2 or UO_3 (Table 3.2). Sea sand classified between 100 and 250 μ was used as the starting bed

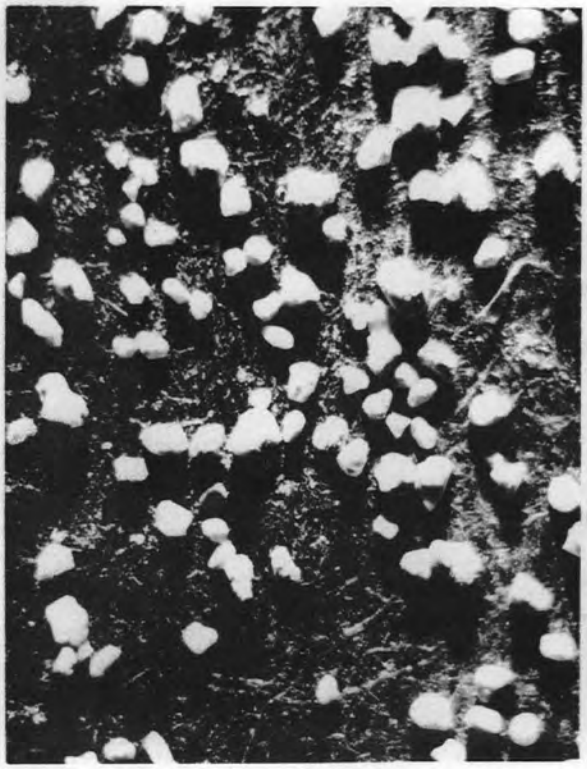
Table 3.2 Product of Fluidized-bed Denitration Runs T-8 and T-11

Particle Size, μ	Run T-8 Wt % of Bed	Wt % of ThO_2 in Bed	Wt % of SiO_2 in Bed	Run T-11 Wt % of Bed	Wt % of UO_3 in Bed	Wt % of SiO_2 in Bed
< 53	4.9	7.6	0.1	4.0	6.0	0.3
53 to 150	21.8	24.0	18.3	9.7	11.3	6.6
151 to 250	37.1	23.0	61.3	38.6	32.4	50.0
250 to 500	14.2	18.5	6.9	29.6	30.5	28.0
501 to 840	8.3	10.5	4.2	8.7	9.8	6.9
> 840	13.7	16.4	9.2	9.4	10.0	8.2

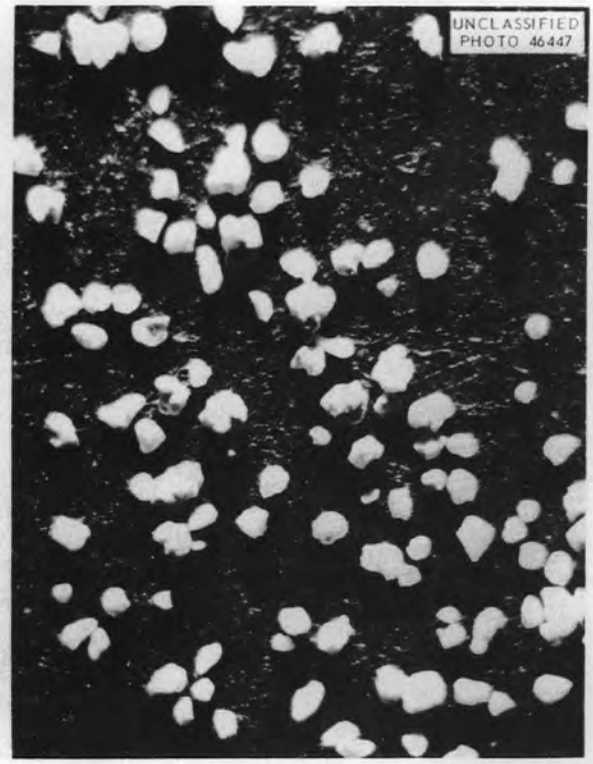
material in these two runs. Photomicrographs were made of the classified product from runs T-8 and T-11 (Figures 3.2, 3.3, and 3.4). Sample A-UO_3 and C-ThO_2 were classified to between 250 and 500 μ, and sample B-ThO_2 was classified to between 500 and 840 μ. Each figure contains three photomicrographs showing the particles as removed from the fluidized bed, after washing with H_2O, and after sectioning to show the internal structure.

Observations of the sectioned samples indicated that the UO_3 coating on the sand particles was more dense and homogeneous than the ThO_2 coating. Due to the poor light contrast between ThO_2 and sand, the makeup of the ThO_2 particles is not shown particularly clearly in the cross-sectioned photomicrographs. However, visual observation of the sectioned samples showed the sand to be covered with small, loosely bound ThO_2 agglomerates. In contrast, the UO_3 appeared to form a continuous coating around the sand particles which was not easily removed by attrition.

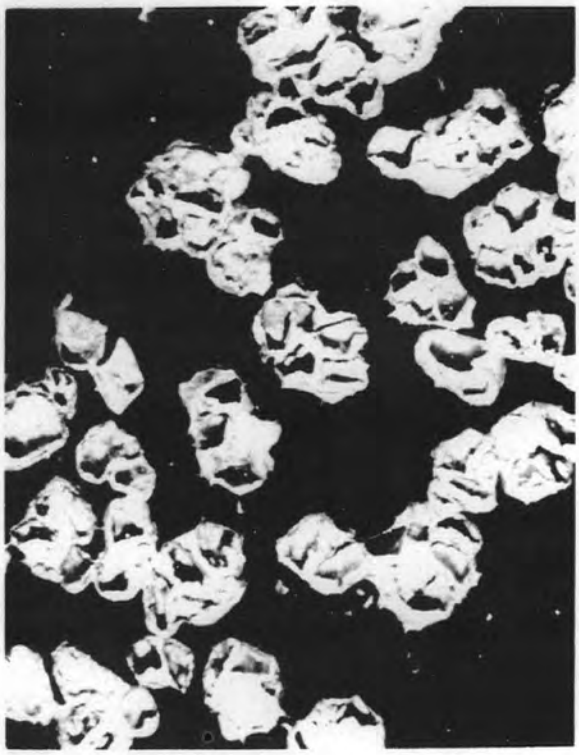
Particle size analyses (determined by neutron activation and sedimentation) on the product from run T-8 also indicated the presence of loosely bound ThO_2 agglomerates. The average particle size of ThO_2 in sample C (screen-classified to between 250 and 500 μ) was 35 μ using aqueous 0.001 M $Na_4P_2O_7$ as a dispersing agent.



A-UO_3 MAGNIFICATION 15X



A-UO_3 (WASHED WITH H_2O) MAGNIFICATION 15X

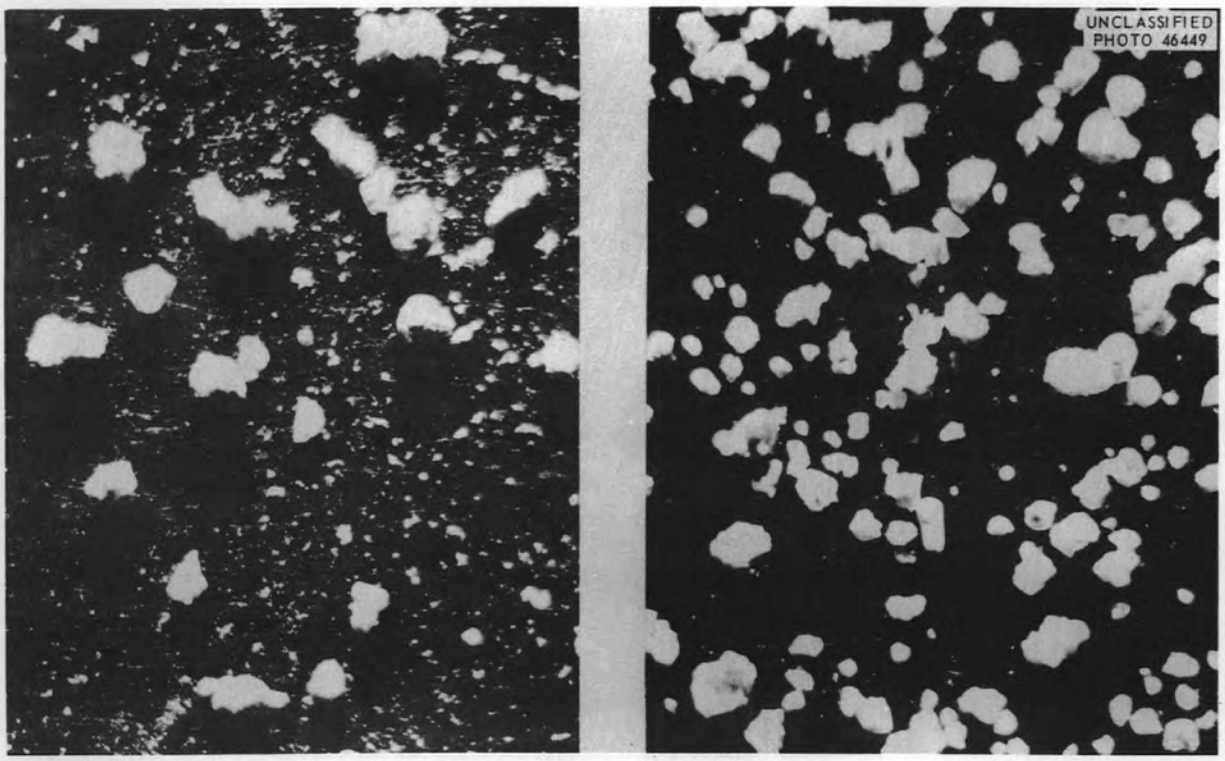


A-UO_3 (CROSS SECTION) MAGNIFICATION 34X

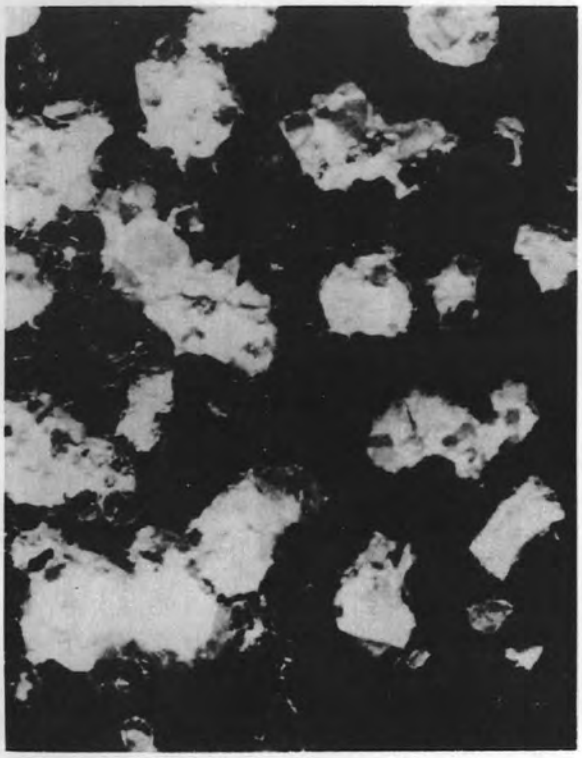
CONDITIONS

AQUEOUS FEED 2.5 *M* $UO_2(NO_3)_2$
BED TEMPERATURE: 390°C
PARTICLES SCREEN CLASSIFIED
BETWEEN 250 AND 500 microns

Fig. 3.4. Photomicrographs of particles from denitration of $Th(NO_3)_4$ on a fluidized sand bed.



C-ThO_2 MAGNIFICATION 15X C-ThO_2 (WASHED WITH H_2O) MAGNIFICATION 15X

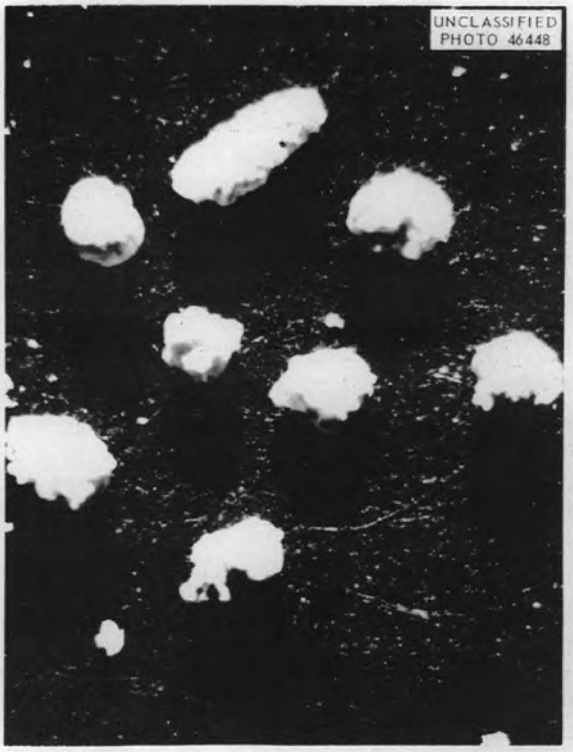


C-ThO_2 (CROSS SECTION) MAGNIFICATION 34X

CONDITIONS
AQUEOUS FEED 1.8 *M* $Th(NO_3)_4$
BED TEMPERATURE: 700°C
PARTICLES SCREEN CLASSIFIED
BETWEEN 250 AND 500 microns

Fig. 3.3. Photomicrographs of particles from denitration of $Th(NO_3)_4$ on a fluidized salt bed.

B - ThO_2 MAGNIFICATION 15 X



B - ThO_2 (WASHED WITH H_2O) MAGNIFICATION 15 X

B - ThO_2 (CROSS SECTION) MAGNIFICATION 34 X

CONDITIONS
AQUEOUS FEED 1.8 *M* $Th(NO_3)_4$
BED TEMPERATURE: 700°C
PARTICLES SCREEN CLASSIFIED
BETWEEN 500 AND 840 microns

Fig. 3.2. Photomicrographs of particles from denitration of $UO_2(NO_3)_2$ on a fluidized sand bed.

The classifier section at the bottom of the fluidized bed reactor (Figure 3.1) was of little value in these studies as a means of separating fine and coarse particles. Only the two runs T-8 and T-11 were completed in which the 0.5-in. Schedule 40 classifier line did not become plugged.

4.0 AGITATED-TROUGH DENITRATION STUDIES

4.1 Process Flowsheet

The operation of the agitated-trough denitration equipment was free of major complexities, as illustrated by the process flowsheet (Figure 4.1). The aqueous thorium nitrate feed was pumped to the electrically heated agitated trough by a Hills-McCanna metering pump, and the liquid entered the bed of agitated solids through a steam-jacketed tube (i.d. 1/16 in.). This nitrate feed line extended about 1 in. below the centerline of the agitator shaft (driven by a 1-hp Varidrive motor).

After coating the hot surface of the particles in the agitated bed, the nitrate was decomposed to the oxide. As the oxide particles increased in size and number, a fraction of the bed solids overflowed through an opening in the trough (Figure 4.2) and fell into a product receiver. The trough was maintained at a vacuum of 4-5 in. H_2O, and the product receiver vessel was vented to the atmosphere in order to sweep out the nitrate decomposition gases and steam.

The gases resulting from evaporation and denitration were conducted through a 2-in.-dia stainless steel line to a 6-in.-dia glass column packed with 3/4-in. rings. The ThO_2 fines entrained in the off-gas from the agitated trough were wetted and removed by water sprayed into the top of the glass column. A large percentage of the NO_2 gas dissolved in the water, and the resulting slurry, was pumped from the bottom of the glass column to a storage drum. The undissolved gases were exhausted to the hood off-gas system through a vacuum cleaner and filter.

4.2 Experimental Procedure and Results

Six runs were made in the agitated-trough calciner in an attempt to form an oxide product consisting of dense spherical particles (originally reported in monthly reports[11, 14, 15]). In the first four runs aqueous thorium nitrate solution was pumped into an agitated bed of solids at a rate of 25-30 ml/min. The bed temperature in the vicinity of the nitrate feed line was varied from 300 down to 150°C, and the temperature gradient of the bed from the nitrate feed line to the product removal port was approximately 100°C at an agitator speed of 85 rpm. There was no bed caking in the trough; however, the yield of ThO_2 fines was high (as indicated by the oxide slurry concentration in the packed scrubber solution), and a dense ThO_2 product was not obtained.

The major objective of the fifth and sixth agitated-trough runs was to find a possible nitrate feed additive which would aid ThO_2 particle growth. In the fifth run aqueous 2 M aluminum nitrate was pumped into an agitated bed

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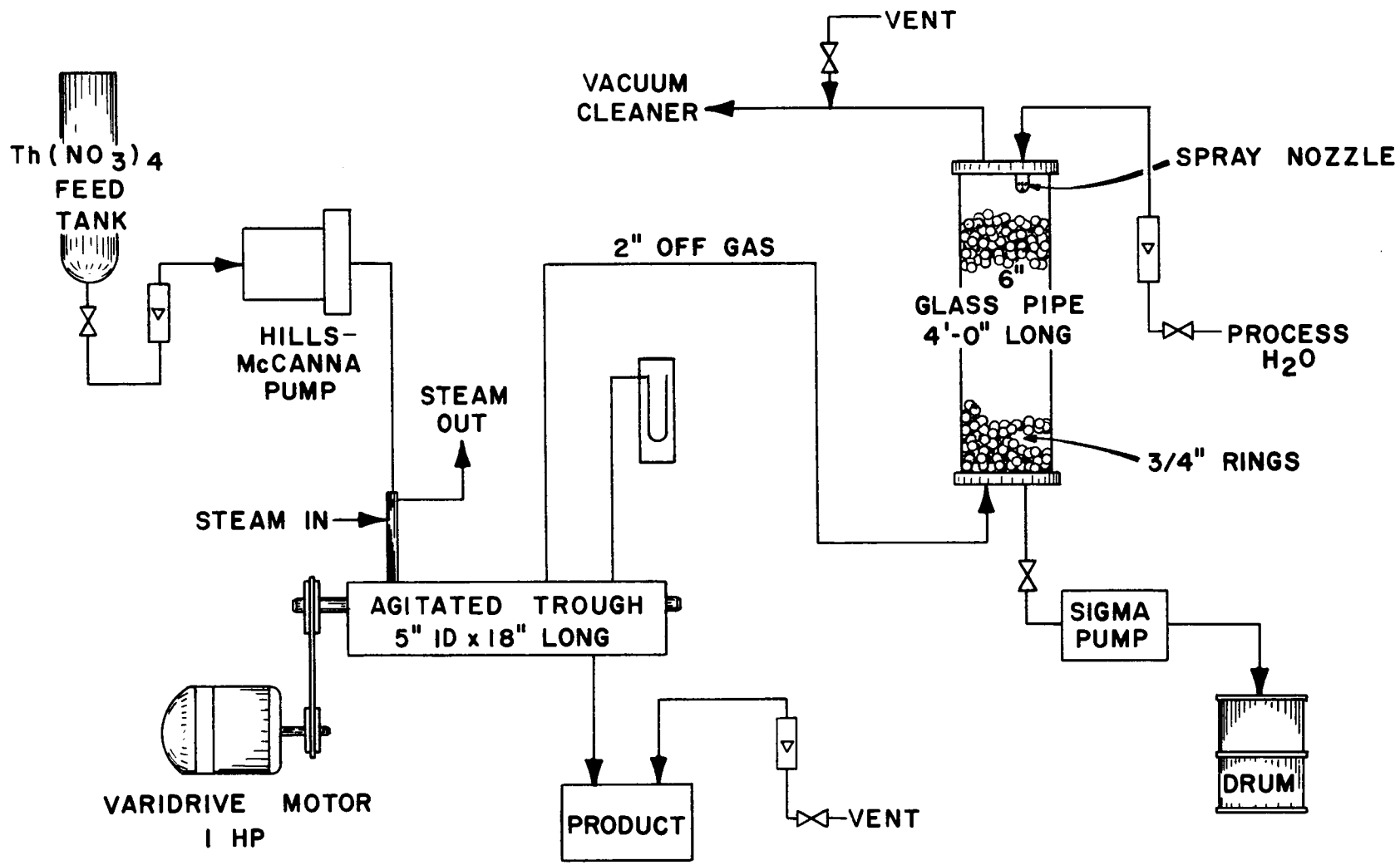

Fig. 4.1. Agitated trough calciner for denitration studies.

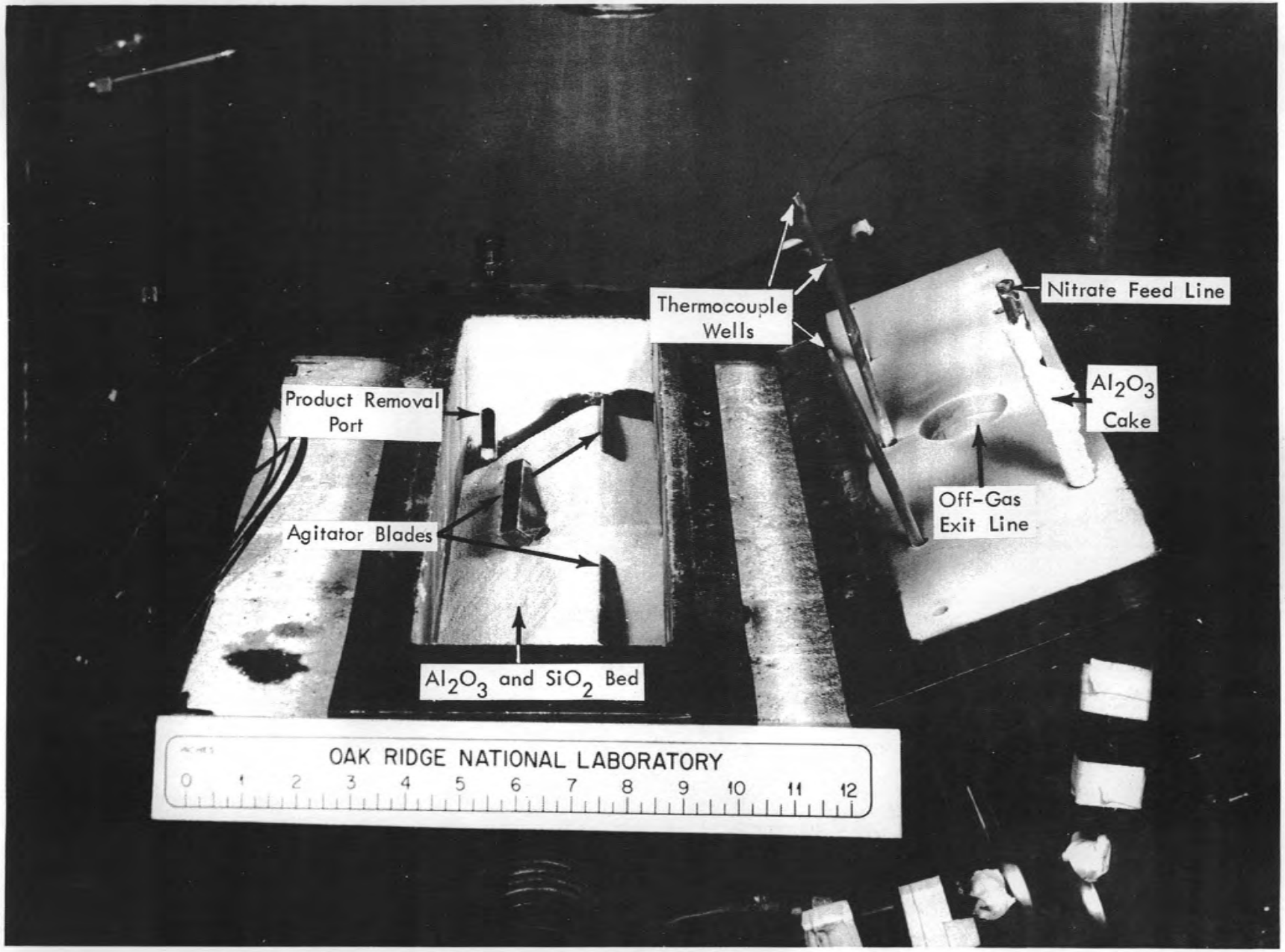

Fig. 4.2. Interior view of the agitated trough after pumping of $Al(NO_3)_4$ into a SiO_2 Bed.

of sand at an average bed temperature of 450°C. The sixth run was a continuation of run 5 except that the nitrate feed was an aqueous solution containing 0.8 M thorium nitrate and 1.4 M aluminum nitrate (which is denitrated to oxide containing 25 wt % Al_2O_3 and 75 wt % ThO_2).

In run 5 there was no indication of Al_2O_3 fines collecting in the off-gas column. However, the off-gas scrubber solution was white with oxide fines in run 6.

Effect of Trough Temperature. With the objective of slowing down the thorium denitration reaction, the bed temperature in the vicinity of the agitated-trough nitrate feed line was maintained at 300°C in the first run and decreased by 50°C increments in the subsequent three runs. During the first four runs the packed glass column in the off-gas system was white with ThO_2 fines (less than 20 μ). Evidently the formation of these fines was more dependent on the process by which thorium nitrate decomposed than on the bed temperature.

The temperature gradient along the length of the agitated bed was approximately 100°C as compared to 10°C along the length of the fluidized bed. Apparently the effective heat transfer coefficient in the agitated bed was considerably lower than in the fluidized bed. The only solids caking that occurred in any of the agitated-trough runs was on the nitrate feed line (Figure 4.2).

Effect of Feed Concentration and Composition. In the first four runs a 1 M and a 2 M thorium nitrate aqueous solution were fed to the agitated bed. Neither nitrate concentration had any apparent effect on oxide particle growth.

In an effort to find a possible feed additive that would form a cohesive oxide product, the aqueous nitrate feed for run 6 contained 0.8 M thorium nitrate and 1.4 M aluminum nitrate. At an average bed temperature of 450°C the aluminum oxide did not act as a binder for the thorium oxide and the quantity of oxide fines entrained in the off-gas was of the same order as that obtained in runs 1-4. Efforts to obtain a satisfactory second constituent for the nitrate feed were discontinued after run 6 because of the uncertainties in considering mixed thorium oxides for a specific breeding application such as an aqueous fluidized-bed nuclear reactor blanket.

Effect of Initial Trough Contents. The bed material for the first agitated trough run was ThO_2 of a size <50 μ (larger material was not readily available). The bulk of the ThO_2 in the trough at the end of the first run was in the size range 300-800 μ, but the individual particles were very porous. A material balance on the thorium indicated that some of the initial bed material had been entrained in the off-gas (Sect. 4.3).

As a possibly better starting material, sea sand was used in all subsequent runs. With the exception of run 5, in which aqueous 2 M aluminum nitrate was fed to the trough, the thorium oxide growth on the sand particles was very slight and did not approach that obtained in run 1 with the ThO_2 bed. Appar-

ently the sea sand had a significant effect on the attrition rate of the loosely bound ThO_2 coating. This effect was not noted in run 5 with Al_2O_3 or in the fluidized bed run T-11 with UO_3.

4.3 Oxide Product Formed in Agitated Trough

The thorium denitration runs in the agitated-trough calciner were characterized by a porous ThO_2 product and a high yield of oxide fines. Material balances on the thorium and aluminum best describe the results of the agitated-trough denitration runs (Table 4.1). In run 1 essentially 100% of

Table 4.1 Material Balances on Oxides Formed in Agitated-trough Denitration Runs

Runs	Nitrate Feed	Initial Bed Material	Initial Bed wt, lb	Wt of Oxided Added to Bed, lb	Wt of Product Removed, lb	Final Bed Wt, lb	Wt[a] Loss, lb
1	$Th(NO_3)_4$	ThO_2	20.0	5.3	0.0	19.4	5.9
2-4	$Th(NO_3)_4$	SiO_2	14.2	17.2	5.2	17.1	9.1
5	$Al(NO_3)_3$	SiO_2	13.6	4.9	4.2	13.9	0.4

[a]By entrainment with off-gas.

the ThO_2 fed to the trough as nitrate was apparently entrained in the off-gas. A cumulative material balance on runs 2, 3, and 4 indicates 53% ThO_2 loss to the off-gas. The improved operation of the agitated-trough denitrator with aluminum nitrate feed is shown by the material balance on run 5 in which only 8% of the Al_2O_3 was not recovered in the trough and product receiver. The addition of aluminum nitrate to the thorium nitrate feed in run 6 (25 wt % Al_2O_3) evidently did not improve the cohesiveness of the oxide product since the quantity of fines entrained in the off-gas was similar to that obtained in the first four runs.

During the agitated-trough runs the velocity in the off-gas line was between 1 and 2 ft/sec. Assuming Stokes' Law and steam at 150°C, the size of the oxide particles that would be entrained in the off-gas is less than 30 to 42 μ for ThO_2 and less than 46 to 65 μ for Al_2O_3.

For any chemical system the entrainment losses from the agitated trough would probably be appreciable, and consequently a method for returning a portion of these fines to the trough as subsequent seed material would be necessary. Probably metallic filters using an automatic air blowback system would be a satisfactory means of conserving the oxide fines created in the trough.

5.0 REFERENCES

1. E. S. Grimmett, "Calcination of Aluminum-Type Reactor Fuel Wastes in a Fluidized Bed," IDO-14416 (Aug. 1, 1957).

2. R. G. Geier, "Continuous Calcination Equipment for Converting UNH to UO_3," HW-49652 A (April 12, 1957).

3. A. A. Jonke, N. M. Levitz, D. J. Petkus, and R. G. Taecker, "Fluidized Bed Process for the Production of Uranium Tetrafluoride (Green Salt) from Uranyl Nitrate," ANL-5363 (December 1954).

4. M. J. Szulinski, "Development of an Agitated Trough Continuous Calciner," Chem. Engr. Prog., 53: 586-9 (1957).

5. H. L. List, "HRP—Preliminary Studies of the Fluidized Bed Denitration of Thorium Nitrate," ORNL CF-58-9-35 (Sept. 30, 1958).

6. Unit Operations Section September Monthly Progress Report, ORNL CF-58-9-62.

7. Ibid., October, ORNL CF-58-10-90.

8. Ibid., November, ORNL CF-58-11-93.

9. Ibid., December, ORNL CF-58-12-35.

10. Ibid., January, ORNL CF-59-1-74.

11. Ibid., February, ORNL CF-59-2-45.

12. W. E. Johnson, "Quarterly Progress Report for the Period Ending August 31, 1957," WCAP-668.

13. S. Lawroski, "Chemical Engineering Division—Summary Report: January, February, and March, 1955," ANL-5422, pp 96-97.

14. Unit Operations Section March Monthly Progress Report, ORNL CF-59-3-61.

15. Ibid., April, ORNL CF-59-4-47.

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