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Development of Thermal Denitration to Prepare Uranium Oxide and Mixed Oxides for Nuclear Fuel Fabrication

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DEVELOPMENT OF THERMAL DENITRATION TO PREPARE URANIUM OXIDE
AND MIXED OXIDES FOR NUCLEAR FUEL FABRICATION

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ABSTRACT

The status and experimental development of thermal denitration in fuel conversion processes are described and reviewed. The nitrate solutions of uranium and plutonium from fuel reprocessing must be converted into oxide particles with good ceramic properties for fuel refabrication. Studies of the chemical flowsheet conditions revealed that the presence of ammonium nitrate (NH_4NO_3) in the denitration feed greatly improved the ceramic properties of the product oxides. Uranium, uranium-thorium, and uranium-cerium oxides were prepared by continuous denitration in an 8-cm-diam rotary kiln. Tests were made with other compositions on a small scale and, with uranium oxides only, in a 16-cm-diam rotary kiln. Sinterability tests of oxides made from feed solutions containing NH_4NO_3 showed good microstructure and densities of 90 to 93% of theoretical values for uranium oxide and uranium-thorium oxides prepared by thermal denitration of metal nitrate- NH_4NO_3 solutions. For metal nitrate- HNO_3 feed solutions without NH_4NO_3 , the pellet microstructures were poor, and the pellet densities were 68 to 76% of the theoretical values. From these results without plutonium, use of the rotary kiln and NH_4NO_3 in the feed is recommended for codenitration of uranyl nitrate-plutonium nitrate solutions.

1. INTRODUCTION

Reprocessing to recover fissile materials from spent fuel elements or fuel fabrication scrap will produce purified solutions of uranyl nitrate, plutonium nitrate, or mixed metal nitrates. The final operation in the reprocessing facility will be the conversion of these solutions to oxide powders with acceptable ceramic properties for fabrication of nuclear fuel pellets. Coconversion of uranium and plutonium (U-Pu), with no separation of free Pu, provides a safeguard against the diversion of Pu. Coconversion

can, in theory, reduce the number of process operations and also insure a more uniform composition as compared to separate preparation of UO_2 and PuO_2 . Development of coconversion processes is part of the Advanced Fuel Recycle Program directed by the Oak Ridge National Laboratory. As part of this program, an evaluation of coconversion process alternatives has been completed and reported.¹ Three alternatives were selected for more detailed evaluations, including definitions of research and development requirements. Development studies for these coconversion processes have been in progress and have been reported.^{2,3,4} Direct thermal codenitration of uranyl nitrate-plutonium nitrate solutions is one of the these selected coconversion processes.

1.1 Review of Codenitration Evaluations

In order to establish the research and development studies needed for application of codenitration, evaluations of both processes and equipment are required. The results of these comparisons are reviewed in this section; more detailed discussions may be found in the report for the evaluation study.¹

In considering conversion processes, direct codenitration was the first choice because it had many important strengths and few weaknesses as compared to the alternatives (Table 1).¹ None of the processes had been adequately demonstrated with U-Pu, therefore, this was not significant for process selection, but it does indicate an important development need. The questionable ceramic quality of the product, however, is an important weakness. Thermal denitration of uranyl nitrate and subsequent reduction gives uranium oxide (UO_2) of low surface area and reactivity, which sinters poorly compared to UO_2 from precipitation conversion processes. Extensive grinding, slugging, and other powder treatments have given good results for denitration products, but all large-scale production of UO_2 pellet fuels has been with precipitation products. Limited results indicate much better ceramic properties for plutonium oxide (PuO_2) from thermal denitration products than those for UO_2 . While the difference is not proven, the PuO_2 from denitration also appears to have better ceramic properties than PuO_2 from peroxide or hydroxide precipitations.

Table 1. Codenitration process evaluation

Strengths	Weaknesses
Simple, straightforward process	Questionable ceramic quality of product
No change in Pu-U ratio during processing	Undemonstrated on U-Pu system
Few pieces of failure-prone equipment	
Minimum remote operability and remote maintenance problems	
Process off-gases and wastes friendly	
Low in-process holdup (relatively simple accountability)	
Kilns demonstrated at scale in U service	
Safest of three processes (no peroxide or ammonia)	
No chemicals added (for process as evaluated)	

Source: Table 1 from *Processing Alternatives for Uranium-Plutonium Conversion*, NEDG-21951, by R. J. Sloat, et al., General Electric Company, San Jose, Calif. (1978).

Eight different types of denitration equipment are compared by Sloat, et al.¹; five have been used for large-scale production with natural, depleted, or low-enrichment uranium to prepare UO_2 for further conversions to UF_6 or uranium metal. The other three were tested in development units only. Denitration with U-Pu will require criticality control and remote operation, and these requirements greatly influence the choice of equipment. Among the five demonstrated types of equipment, the continuous rotary kiln with breaker bars was selected as most promising for U-Pu codenitration.¹ The first alternative equipment type in this evaluation was a relatively novel, incompletely developed flame reactor with radio-frequency heating.

1.2 Scope of Studies

The scope of the studies reported here was partially based on these four assumptions:

1. The codenitration equipment would be of the rotary kiln type, as proposed by the program evaluation of alternatives.¹
2. Chemical flowsheet conditions should be investigated for their effects on the highly important ceramic properties of UO_2 products.
3. The only dependable evaluation of ceramic properties is sinterability tests (fabrication of pellets with specified conditions).
4. The engineering development studies, including development of equipment and procedures for a codenitration pilot plant, would be done without plutonium, but the results must meet the criticality and remote operation requirements for $(\text{U-Pu})\text{O}_2$. Operation of pilot-plant scale equipment without plutonium and glovebox demonstration of the chemical flowsheet to prepare $(\text{U-Pu})\text{O}_2$ would be very desirable.

The ceramic properties of the oxide powders can be improved by jet grinding or other treatments. Therefore, representative product batches must be prepared to allow for development of these treatments, in addition to the product samples needed for sinterability tests.

2. DISCUSSION OF FUEL-PELLET AND CERAMIC PROPERTY SPECIFICATIONS

The general specifications for all nuclear reactor fuels are basically the same, although specific details may differ. The primary specification is that for fuel-pin pellets; fuel oxide powder specifications are secondary and are empirical or performance-oriented.

One set of specifications concerns the chemical composition of fuels. The final oxygen/metal ratio is adjusted by reaction with H_2 during sintering. Organic binders or lubricants may be used, since they are thermally decomposed. Otherwise, the powders must meet the same composition specifications as the pellets. For codenitration, the conversion product oxides will contain all nonvolatile impurities in the feed solution, plus any corrosion products.

A second set of specifications concerns the structure (both macro and micro) of the pellet. The powder properties and the pellet fabrication procedures must consistently give acceptable structures as free as possible from both macro and micro defects. Macro defects include cracks, laminations, noncylindrical shapes, and gross porosities. Micro defects involve grain size, microporosity, and the figure of merit for Pu homogeneity.* The pellet fabrication procedures can frequently be varied with some sacrifice of density to improve the structure. For coconversion, the U-Pu nitrate solutions can be completely homogeneous; conditions should be selected so as to minimize any separation of the uranium and plutonium during conversion.

The final set of specifications refers to the ceramic properties of the oxide powders and requires production of pellets with consistent, reproducible densities that average 89 to 93% of the theoretical densities. For the powders, the associated specification is a sinterability test that specifies the pellet density under conditions similar to production conditions. The B.E.T. surface area, the particle size, and the bulk or tap density provide useful internal checks on product quality and consistency for a given powder preparation process. Particle B.E.T. surface areas of 5 to 15 m^2/g [with 2.5 m^2/g as the lower limit after calcination and reduction to $(U-Pu)O_2$] and particle sizes (>50 wt %) below 10 μm are preferred, while low bulk densities or excessive dusting should be avoided. The B.E.T. surface area can be increased, or the particle size reduced, by jet grinding, ball milling, or similar treatments. Bulk or tap densities of $>2.5 g/cm^3$ are convenient for pellet-press feed, but lower densities may be acceptable or may be increased by pregranulating treatments.

*The figure of merit is a quantitative measure of the uniformity of U/Pu ratios as determined by a procedure and method of calculation in a fast reactor fuel specification.

A wide variety of powder treatments (e.g., grinding, screening, blending, ball-milling, calcining, addition of binders, preslugging, granulating, oxidation-reduction cycles, addition of lubricants, and addition of pore-formers) may be used to improve the ceramic properties of UO_2 and $(\text{U-Pu})\text{O}_2$ powders. If the chemical composition specifications are met, almost any oxide powder can be processed intensively to meet the other specifications. However, it is important to eliminate or greatly simplify these powder treatments for $(\text{U-Pu})\text{O}_2$ because of the cost and difficulty of performing them remotely.

2.1 Sinterability Test Procedure

A standard sinterability test procedure was selected to evaluate the ceramic properties of the products. The solids were ground to the extent necessary for complete reduction of size to -20 mesh (less than $840\text{-}\mu\text{m}$ particles). Batches of the -20-mesh solids were calcined by heating to 600°C , holding at 600°C for four hours in an Ar-4% H_2 atmosphere, and then cooling to room temperature in a CO_2 atmosphere. The calcined powder was pressed into pellets (two or three per test) at 241 MPa (35 Kpsi), sintered at 1450°C for four hours in Ar-4% H_2 (A heatup schedule of 300°C/h to 900°C , then 100°C/h to 1450°C was used.), and cooled in Ar. The green densities of the pellets were measured before sintering. Sintered pellet densities were measured by geometry and by displacement; the results were converted to a percentage of the theoretical density of that oxide composition. Whole pellets and cross sections were examined with respect to their structure (macro and micro). Microphotographs at 200X magnification were a sensitive test of structure and are used in this report to show examples of results.

The conditions most commonly used for fabrication of pellets are similar to the overall procedures of this sinterability test, but there may be important quantitative differences for individual steps. The sinterability test procedures used elsewhere may show other differences. Higher final sintering temperatures of 1700°C are common and can result in higher densities, particularly for ThO_2 . Calcine temperatures may range from 500°C to 800°C and may influence the results. Lubricants may be used on the die or added to the powder.

3. CERAMIC PROPERTIES VS CHEMICAL FLOWSHEET CONDITIONS

The preliminary part of our development study was concerned with improving ceramic properties of UO_2 by controlling the denitration flow-sheet conditions, with the expectation that these conditions could also be applied to coconversion of U-Pu. Since the U/Pu ratios are ≥ 3 , the UO_2 should be the controlling component. Limited results for plutonium indicate better ceramic properties for the PuO_2 product from denitration than from oxalate precipitation.⁵ Surface areas of 9.7 to 12.1 m^2/g and average particle sizes of 7.6 to 15.0 μm for PuO_2 prepared by denitration are near the preferred values and are much better than those of UO_2 prepared by simple denitration.

Results reported for UO_3 from denitration in a fluidized bed⁶ are typical for simple denitration. The B.E.T. surface areas and particle sizes were 0.1 m^2/g and 43 μm for UO_3 and 0.6 m^2/g and 29 μm after reduction to UO_2 . The sintered UO_2 pellet densities were 75% of theoretical density. Results for a similar material prepared at ORNL⁷ were 0.23 m^2/g and 72% sintered UO_2 pellet density. Chalder⁸ reports B.E.T. surface areas of 0.62 to 2.75 m^2/g and sintered pellet densities of 71 to 84%, but he gives no description of the sample differences. Most evaluations of UO_3 from denitration have been for conversion to UF_6 . Reactivities have generally been improved by addition of calcium or sulfate to the $\text{UO}_2(\text{NO}_3)_2$ feed. These additives are left as solids after formation of UF_6 vapor, but they are not acceptable for preparation of UO_2 pellets. Reactivities for conversion to UF_6 show little dependence on the type of denitration equipment, the flow rates of air or steam purges, or the denitration temperature. The limited discussions of the effects of these variables on other properties reveal no promising effects on ceramic properties.

The objective of our chemical flowsheet studies was to find additives for $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solutions that would produce favorable changes in the UO_3 or UO_2 products and acceptable compositions for the sintered pellets; preferably such additives would remain in solution, but precipitation and feed of slurries to the thermal decomposition might be acceptable. One concept of this type has been developed and demonstrated as the COPRECAL process for coconversion,^{1,4} in which large excess of NH_3 is added to U-Pu

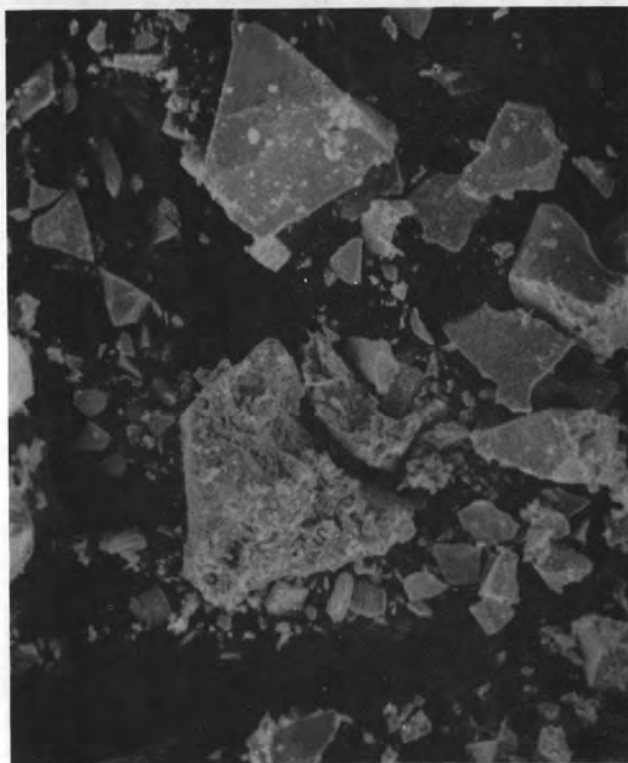
nitrate solutions to give an ADU-type precipitation, and the slurry is calcined in a fluidized bed. This process has demonstrated the preparation of $(\text{U-Pu})\text{O}_2$ with acceptable ceramic properties. Disadvantages are the coprecipitation and pumping of a mixed slurry into a remotely operated fluidized bed and the presence of NH_3 and NH_4NO_3 in the waste streams.

Ammonia, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NH_4NO_3 , $\text{H}_2\text{C}_2\text{O}_4$, $\text{N}_2\text{H}_4\text{CO}$, and H_2CO_2 were tested as additives in a series of thermal decompositions conducted in small-scale laboratory glassware; the purpose was to discover their individual effects on properties of the product oxide. The presence of NH_4NO_3 produced large and favorable changes, while urea and formate gave large, but less favorable changes, and their reactions resulted in excessive rates of reaction and/or foaming with light, fluffy solids. The visual differences with presence of NH_4NO_3 in the feed were also observed for $\text{UO}_2(\text{NO}_3)_2\text{-Th}(\text{NO}_3)_4$ solutions (Fig. 1).

The favorable effect of NH_4NO_3 on the UO_3 properties was observed both for addition of NH_4NO_3 and for addition of NH_4OH to the $\text{UO}_2(\text{NO}_3)_2$ solutions. The NH_4OH additions first neutralize any excess HNO_3 and give acid-deficient $\text{UO}_2(\text{NO}_3)_2$ solutions; further additions give partial or complete precipitation of the uranium. Some fluidized-bed UO_3 product was digested in a large excess of molten NH_4NO_3 and then calcined at a higher temperature; this also produced a favorable but smaller change in properties as compared to thermal denitration of $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ solutions. Based on these preliminary results, the thermal denitration development studies were continued, with the concentration of NH_4NO_3 in the metal nitrate feed solutions as a major process variable.

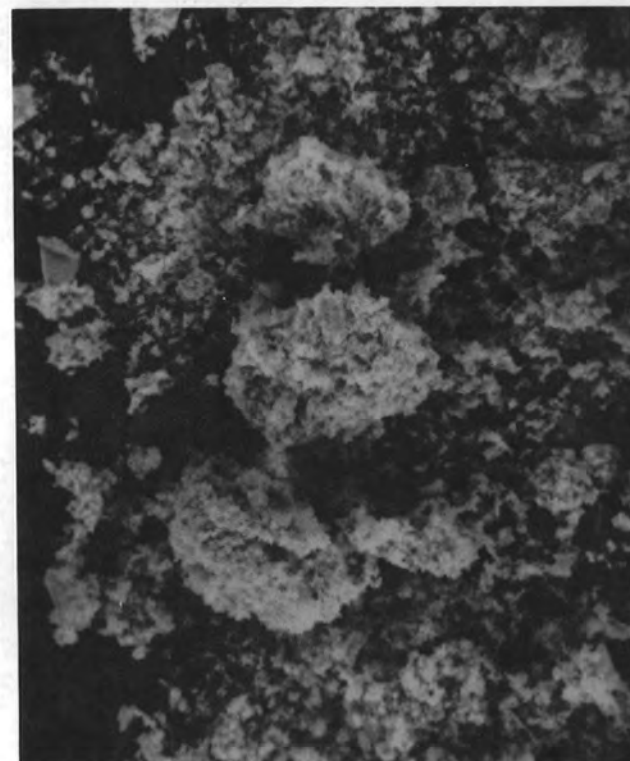
4. LABORATORY STUDIES OF $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ DECOMPOSITIONS

While rotary kilns have been routinely used for production plant conversions of $\text{UO}_2(\text{NO}_3)_2$ solutions to U_3O_8 , the proposed addition of NH_4NO_3 to the feeds has not been reported. Therefore, laboratory-scale studies were made to investigate the effects of the NH_4NO_3 . Confirming a favorable effect on ceramic properties and investigating the hazards from exothermic decomposition of NH_4NO_3 were initial priorities. Other measurements and observations were made to provide information on the process mechanisms and



← 100 μm →

U/Th = 3.0,
 $\text{NH}_4^+ = 0$;
 B.E.T SURFACE AREA = $17.5 \text{ m}^2/\text{g}$;
 BULK DENSITY = $2.3 \text{ g}/\text{cm}^3$.



← 100 μm →

U/Th = 3.0,
 $\text{NH}_4^+ / (\text{U} + \text{Th}) = 0.6 \text{ mole/mole}$;
 B.E.T. SURFACE AREA = $7.8 \text{ m}^2/\text{g}$;
 BULK DENSITY = $0.8 \text{ g}/\text{cm}^3$.

Fig. 1. Scanning electron micrograph showing effects of NH_4NO_3 on product oxide powders from batch thermal denitration of $\text{UO}_2(\text{NO}_3)_2\text{-Th}(\text{NO}_3)_4$.

the amounts and compositions of waste streams. Measurements were also made with thorium and cerium nitrates, since they are possible "stand-ins" for plutonium. Four types of investigations were made and are discussed in Sects. 4.1-4.4:

1. Feed batches were placed in a thermal oven (usually overnight) and the product solids were examined and analyzed.
2. The thermal denitration behavior was observed at intermediate stages.
3. Thermal analysis procedures were applied.
4. Batch material balance runs were made.

4.1 Oxide Properties for Batch Thermal Decompositions

Product oxide properties were observed or measured for the solid products from batch denitrations in ovens (usually at 350°C). The solutions or slurry feeds were prepared by mixing metal nitrate solutions with solid NH_4NO_3 and/or aqueous NH_4OH in lab glassware. The UO_3 product from a continuous fluidized-bed denitration of $\text{UO}_2(\text{NO}_3)_2$ solution containing no NH_4^+ is also listed for comparison (Table 2). The 100% of stoichiometric value $\text{NO}_3^-/\text{metal}$ ratios indicate solutions of metal nitrates and NH_4NO_3 . Ratios of 80% indicate acid-deficient solutions without precipitation. Ratios of 3 and 10% for thorium alone indicate two stable ThO_2 sols, as commonly used for gel-sphere processes. Other ratios of 0 and 60% show precipitation by addition of 100 and 40% of the stoichiometric amount of NH_4OH followed by thermal decomposition of the slurry.

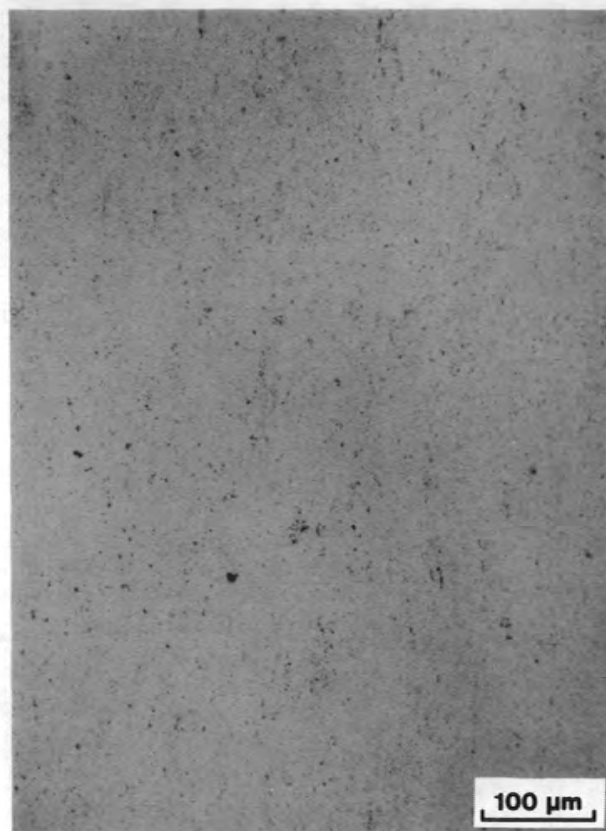
All four metal compositions used (U , $\text{U/Ce} = 3$, $\text{U/Th} = 3$, and Th) show two or three favorable effects for the presence of NH_4NO_3 in the feed (Table 2). The B.E.T. surface areas change toward the preferred range of 5 to 15 m^2/g from low values for U or U/Ce or high values for Th or U/Th . The pellet densities for a standard procedure (described in Sect. 2.1) are 15 to 21% higher when NH_4NO_3 is present, as compared to metal nitrate solutions without NH_4^+ , and the microstructure of the pellets is much better (Fig. 2). The product solids prepared with NH_4NO_3 in the feed are easily converted to fine, granular solids by shaking or stirring with a spatula, while, the metal nitrate feeds with no NH_4^+ give hard, glassy, or lava-like shards. These differences are visible in micrographs of the solids (Fig. 1). Without NH_4NO_3 in the feed, the hard, glassy, or slag-like chunks from

Table 2. Batch denitration product properties

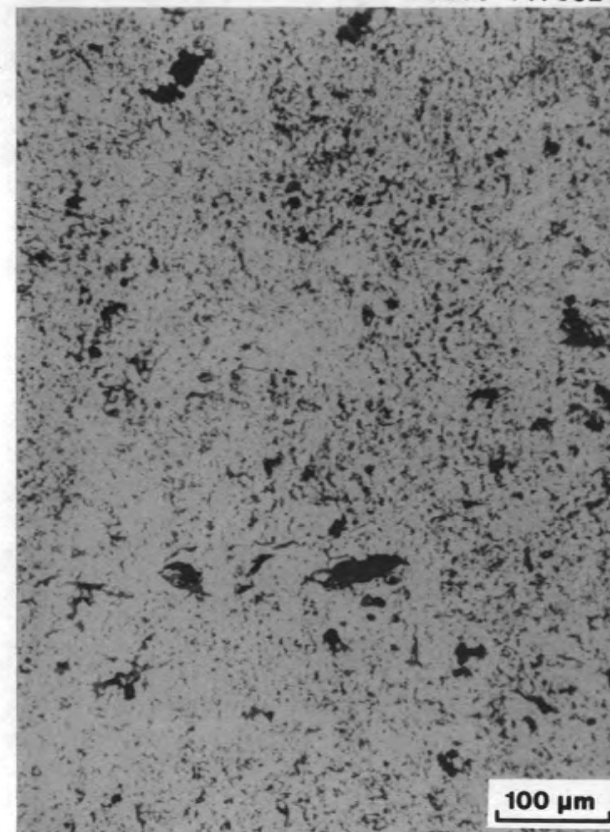
Other metals (mole/mole U)	NO_3^- /metal (% of stoichiometric) ^a	NH_4^+ /metal (mole/mole)	B.E.T. surface area (m^2/g)	Pellet density (% of theoretical)	Bulk density (g/cm^3)	Appearance of solid ^b
0	100	0	3.02	76	1.48	Hard cake
	100	2	4.91	91	0.75	Soft, easily powdered
	80	0.6			1.2	Medium hard cake
	0	2	6.85	93	0.9	Soft, foamy
0 Fluid bed denitration		0	0.23	72	4.2	Rounded, glossy
$\text{Ce} = 0.33$	100	0	0.58		0.9	Glazed, lava-like
	100	2	28.9		0.9	Soft, flaky
	0	2	1.90		1.7	Soft, easily powdered
$\text{Th} = 0.33$	100	0	17.5	68	2.3	Glazed shards
	100	2	8.32	84	0.7	Soft, easily powdered
	80	0.6	7.8		0.8	Soft, foamy
	0	2	33.4		1.5	Powder and glassy chips
$\text{Th} = 3.0$	60	0.5			1.2	Medium hard cake, foamy
$\text{Th} = \infty$	100	0	53.9		1.9	Glassy shards
(No U)	100	2	33.6	90	0.6	Very fine powder
	3	0			2.7	Very hard shards
	10	4	7.1	72	2.0	Fine powder

^aThe NO_3^- present as NH_4NO_3 is not included in this ratio.

^bVisual observations with low magnification microscope and with pressure by a spatula.



TEST: DEN-57
 $\text{NH}_4^+/\text{U} = 2.2 \text{ MOLE/MOLE}$
 $\text{NO}_3^-/\text{U} = 4.2 \text{ MOLE/MOLE}$
 B.E.T. SURFACE AREA = $4.91 \text{ m}^2/\text{g}$
 POWDER BULK DENSITY = 0.75 g/cm^3
 UO_2 PELLET DENSITY = 91% OF THEORETICAL



TEST: DEN-55
 $\text{NH}_4^+/\text{U} = 0 \text{ MOLE/MOLE}$
 $\text{NO}_3^-/\text{U} = 2.2 \text{ MOLE/MOLE}$
 B.E.T. SURFACE AREA = $3.02 \text{ m}^2/\text{g}$
 POWDER BULK DENSITY = 1.5 g/cm^3
 UO_2 PELLET DENSITY = 75% OF THEORETICAL

Fig. 2. Effects of NH_4NO_3 in $\text{UO}_2(\text{NO}_3)_2$ on pellet microstructure (polished cross-sections) for batch thermal decompositions.

batch denitrations are as large as 30,000 μm . With NH_4NO_3 in the feed, essentially all the oxide is in small particles, which may form very soft, easily dispersed agglomerates. Similar photographs for other studies of ceramic properties^{9,10} show poor sinterability for oxides with the glassy, nonrainy texture and good sinterability for the grainy texture. Higher bulk densities are convenient for pellet preparation, and the addition of NH_4NO_3 to the feed is unfavorable in this respect. A granulation or preslugging treatment may be required for the powders of low bulk density.

Overall, the results of the batch denitration tests were very encouraging. The changes in B.E.T. surface areas and pellet densities were highly favorable. More than 40 tests made with metal nitrate solutions containing NH_4NO_3 did not result in a single excessive rate of reaction or foam-over. The slurry feeds showed some splattering from the mud-like characteristics as dryness was approached, but this apparently was not caused by the decomposition of NH_4NO_3 . The soft, easily powdered solids prepared by denitration of metal nitrate solutions containing NH_4NO_3 in the feed appeared more favorable to continuous kiln operation than the hard, caked solids produced when NH_4NO_3 was not present.

4.2 Visual Observations of Thermal Decomposition Behavior

Thermal decomposition behavior of products was observed for changes in visual appearance and weight during either continuous steady heating on a hot plate or heating in an oven at constant temperatures for periods of 2 to 70 h. Solutions of metal nitrates without addition of NH_4NO_3 and with a U/Th mole ratio of 3 showed solidification at a lower temperature and lower degree of denitration than solutions with uranium alone. No other visual differences were seen, although observation was limited.

When $\text{UO}_2(\text{NO}_3)_2$ solution is heated, evolution of brown fumes begins from a syrupy, clear melt boiling at 185 to 195°C. As denitration is continued, the melt becomes thick, then a pasty mass and finally forms a glassy cake that cracks into pieces. When NH_4NO_3 is also present in the $\text{UO}_2(\text{NO}_3)_2$ solution, a yellow slurry forms at temperatures >155°C. For NH_4^+/U mole ratios of 2.0, the material formed at 180°C is relatively dry, yellow crystals. This material shows little weight loss at temperatures below

230°C and evolves white fumes at 255°C. At 280°C, the first evolution of brown fumes occurs, and the decomposition to fine UO_3 is complete at 350°C. If the yellow crystals at 180-200°C are formed into swirls, piles, or other shapes, the UO_3 after denitration shows these same shapes, indicating a lack of melting between 200 and 350°C. The weights at 190 to 230°C agree with $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, where x is 0 to 1. The weights at 270°C agree with $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$. The behavior of the mixture is distinctly different from that of either of the two separate nitrates. While $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and NH_4NO_3 are both clear melts at 180-200°C, the mixture is a crystalline yellow solid. Both NH_4NO_3 and $\text{UO}_2(\text{NO}_3)_2$ show significant thermal decomposition at 230°C, but the mixture is stable.

Several tests were made in which uranium oxides (from fluidized-bed denitration) were heated, with $\text{NH}_4\text{NO}_3/\text{U}$ mole ratios between 2 and 5. At 175°C, the mixture was a slurry of UO_3 in molten NH_4NO_3 ; at 230°C, the material was a grainy yellow solid of fairly stable weight. Decomposition occurred at lower temperatures than those for the decomposition of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$, but the final UO_3 properties were similar and were quite different from the original properties of the fluidized-bed UO_3 . The B.E.T. surface area increased from 0.23 to 2.43 m^2/g . Small amounts of brown fumes were produced, even though the starting materials were calcined UO_3 and solid NH_4NO_3 . The weights at 230°C are equivalent to $\text{UO}_3(\text{NH}_4\text{NO}_3) \cdot x\text{H}_2\text{O}$ where x is 1 to 3. The overall behavior is not as indicative of a definite, stable complex as in the case of the $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ complex.

The evolution of brown N_2O_4 fumes was used to indicate nitrate decomposition products, and boiling HCl was used to detect NH_4^+ as white NH_4Cl fumes. These observations were for samples with 0 to 109% neutralization of metal nitrate solutions with NH_4OH . Only the batch with 9% excess NH_4OH showed any ammonia fumes, and these dissipated early in the boildown. The production of N_2O_4 fumes decreased as the percentage of neutralization increased and was only a trace for the stoichiometric amount of NH_4OH . With partial neutralization, the material became a dry, yellow cake before brown fumes were evolved. For this method of observation, the decomposition of NH_4NO_3 from the mixtures did not give detectable amounts of either NH_3 or N_2O_4 .

Some of the UO_3 powders from decomposition of $\text{UO}_2(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3$ have been observed to have a reversible change between 375°C in an oven and ambient air at room temperature. The dark orange powder at 375°C slowly changes to a light yellow color, with a 3 wt % gain, in room air. This added weight is probably water and would be equivalent to 0.5 mole H_2O per mole of UO_3 .

4.3 Thermal Analyses of Samples Containing NH_4NO_3

Four samples were prepared by preliminary thermal treatment of solutions in an oven at 190°C for 70 h to remove most of the water, thus simplifying the thermal analyses. The starting solutions contained: I. $\text{UO}_2(\text{NO}_3)_2$ only, II. NH_4NO_3 only, III. $\text{UO}_2(\text{NO}_3)_2/\text{NH}_4\text{NO}_3 = 1$ mole/mole, and IV. $\text{UO}_2(\text{NO}_3)_2/\text{NH}_4\text{NO}_3 = 0.5$ mole/mole.

After 70 h at 190°C , the visual appearance and the estimated composition of the samples, calculated from weights, were as follows:

- I. A very thick, soft mass; semi-liquid or semi-solid; estimated to be 25% UO_3 -75% $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$.
- II. A clear colorless melt; about 25 wt % of NH_4NO_3 lost -- probably by slow vaporization.
- III. A hard solid, estimated to be $\text{NH}_4\text{UO}_2(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$.
- IV. Sand-like, yellow crystals estimated to be $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$.

D. A. Lee,¹¹ of Oak Ridge National Laboratory (ORNL) performed and interpreted differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and evolved-gas analysis (EGA) by mass spectrograph for these four denitration samples.

Of the three samples containing uranium, sample III had the simplest thermal analyses curves. The TGA of sample III indicated practically no decomposition until ~ 280 - 315°C when $\sim 37\%$ of the sample weight was lost by nitrate decomposition. Other observations included a gradual loss of $\sim 3\%$ between 315°C and 525°C , and the O_2 loss from UO_3 at 575°C . The total loss at 600°C was 41.7%, with 58.3% remaining, as compared to an estimate of 60%. The DTA of sample III had a simple profile with one large endotherm at 280°C ; the smaller ones were rather insignificant. The EGA mass spectrographic plots for sample III showed single large peaks at $\sim 280^\circ\text{C}$ for mass numbers 14 (N^+ from NO_3^- or NH_3), 18 (H_2O), 28 (N_2^+), 30 (NO^+ from nitrate), and 44 (N_2O^+).

The TGA of sample I showed a total weight loss of 24% at 600°C; the remaining weight was 76%, as compared to the 77% estimate for U_3O_8 . The major loss was due to nitrate decomposition at 315°C. Slight weight losses at 145°C and 190°C were probably caused by dehydration of small quantities of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ at 145°C and of $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ to $\text{UO}_2(\text{NO}_3)_2$ at 190°C. The DTA thermogram for sample I had a series of endotherms, indicating the release of decomposition products at 145, 195, 217, 240, 275, 315 (shoulder), and 555°C. These results correspond well with the TGA data. The EGA results showed very little material of mass 14 (N^+ from NO_3^- or NH_3) and mass 28 (N_2^+), but multiple or large peaks for mass numbers 30 (NO^+), 32 (O_2^+), and 46 (NO_2^+).

The TGA of sample II showed that the main decomposition occurred at ~275°C. Sample II gave a poor DTA trace, but the decomposition was complete at 275°C. The EGA results showed relatively large peaks for mass numbers 15 (NH^+), 16 (NH_2^+), 17 (NH_3^+), 18 (H_2O), and 28 (N_2^+).

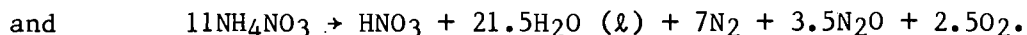
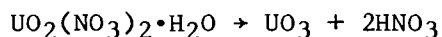
Sample IV had a weight loss at ~250°C, but the largest loss was at 315°C, with a total loss at 600°C of ~53% (47% remaining). The DTA results for sample IV indicated large NH_4NO_3 contributions (sharp endotherms at 55°C, 125°C, and 155°C). This suggests that one molecule of NH_4NO_3 in sample IV was not coordinated with UO_2^{2+} . The TGA, DTA and EGA results all indicate that sample IV decomposed like a mixture of samples III and II. This is particularly apparent for the DTA results.

The DTA and TGA results reported by Notz, for $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ crystallized from solutions,¹² agree very well with Lee's results¹¹ reviewed above. Lee also made thermal analyses for four samples having the composition: $\text{U/Th} = 3.0$; $\text{U} + \text{Th} = 1.3 \text{ M}$; and $\text{NO}_3^- = 4.2 \text{ M}$. Ammonium hydroxide solutions were added to give $\text{NH}_4^+/\text{NO}_3^-$ mole ratios of 0 (solution), 0.33 (solution), 0.66 (slurry), and 1.0 (thick slurry). The results are much more complex for these samples than for samples I to IV. However, large peaks like those seen for sample III were clearly visible for the samples with $\text{NH}_4^+/\text{NO}_3^-$ mole ratios of 0.33 and 0.66 (where $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ would be expected) and were not apparent for samples containing no NH_4OH or for samples completely neutralized with NH_4OH . Overall, the thermal analyses results gave good evidence for a $\text{NH}_4\text{NO}_3\text{-UO}_2(\text{NO}_3)_2$ complex that is thermally more stable and decomposes differently than either separate compound.

4.4 Material Balance Tests

Batch thermal decompositions were carried out in a closed system of laboratory glassware (Fig. 3) to obtain material balances. Feed solutions or slurries were heated to about 400°C in a boiling flask, and solid, liquid and gaseous products were collected and analyzed. A series of recycle tests used concentrated NH_4NO_3 solutions for feed makeup that were prepared by neutralization of the condensate with ammonia and subsequent evaporation. Continuous feed to a hot denitrator and an air purge would be expected to cause different decomposition reactions and products. Therefore, these batch results were not intended to be representative of continuous rotary kiln operation.

Results of the batch tests are reproducible and show consistent patterns (Table 3). The uranium and thorium appeared as UO_3 and ThO_2 in the solid product, with negligible carryover into the condensate. Nitrogen material balances were 89 to 112%. All of the NO_3^- in the feed, as metal nitrates or HNO_3 , appeared in the condensate as acid (HNO_3 , HNO_2). The gaseous products showed nearly one mole of N_2 and N_2O per mole of NH_4NO_3 in the feed. Gas concentrations for samples with NH_4NO_3 in the feed were typically 20% $\text{O}_2 + \text{Ar}$, 25% N_2O , and 50% N_2 . Concentration of NH_4^+ in the condensate was small for the preferred $\text{NH}_4^+/\text{NO}_3^-$ feed mole ratios of 0.5 or less. Results indicated that the mole ratio of NH_4^+ decomposed to NO_3^- decomposed was about 1.1 (Table 3), but the data were scattered badly. These analyses agree with overall reactions of:



The presence of $\text{Th}(\text{NO}_3)_4$ in the feed did not change any of the generalized results. While NO was not detected in the gaseous products, it probably was formed and was oxidized or decomposed before the gases were analyzed.

4.5 Discussion of the Effects of NH_4NO_3

Three of these four types of laboratory studies (Sects. 4.1, 4.2, 4.3) independently provide the same explanation for the thermal decompositions. When $\text{UO}_2(\text{NO}_3)_2$ and NH_4NO_3 are both present, the thermal decomposition appears to be that of a solid complex, this is distinctly different from

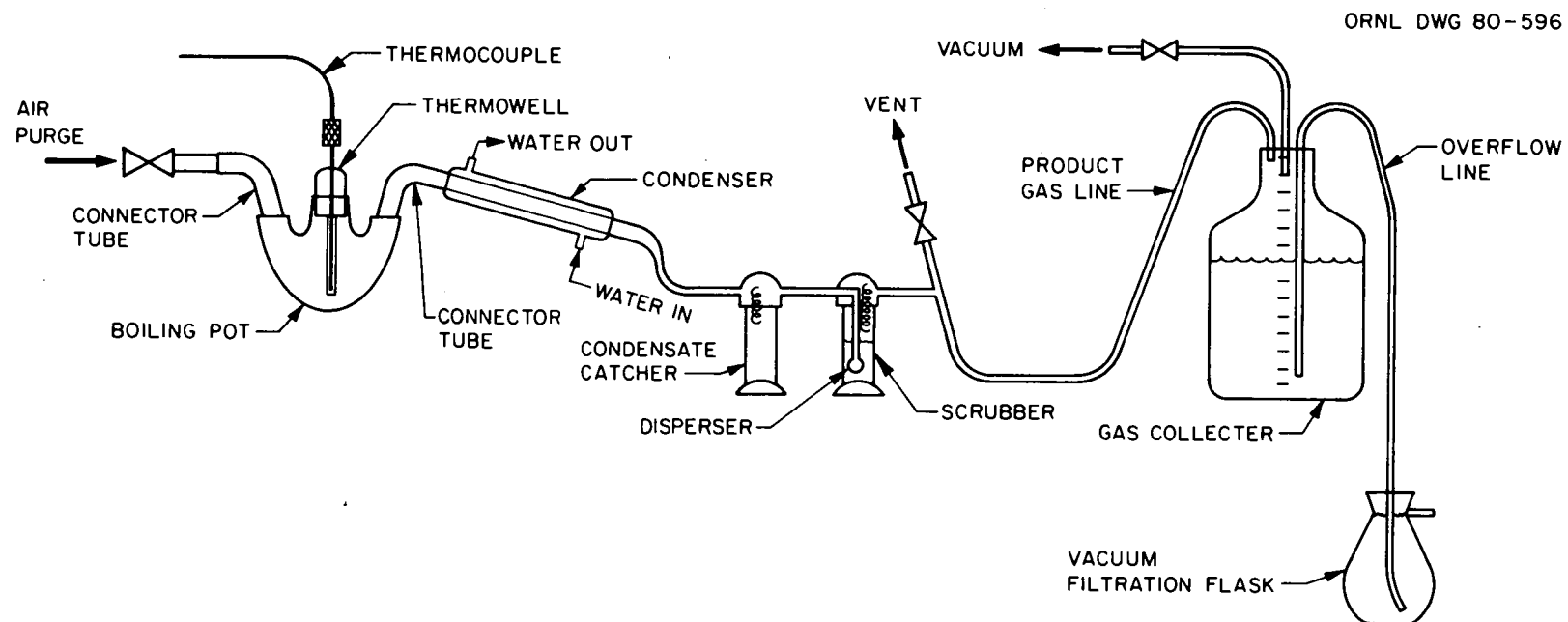


Fig. 3. Apparatus for batch thermal decomposition.

Table 3. Thermal denitration material balance results

$\text{NH}_4^+/\text{NO}_3^-$ (mole/mole)	Total $\text{NO}_3^-/(\text{Th}+\text{U})$ equivalents	Th/U (mole/mole)	Run No.	Material balances, %		Moles NH_4NO_3 in feed Moles $\text{N}_2+\text{N}_2\text{O}$ in gas	$\frac{(\text{NH}_4^+ \text{ in feed})-(\text{NH}_4^+ \text{ in cond.})}{(\text{NO}_3^- \text{ in feed})-(\text{NO}_3^- \text{ in prod.})}$ (mole/mole)	$\frac{\text{NH}_4^+ \text{ in cond.}}{\text{NH}_4^+ \text{ in feed}}$
0	1.10	0	1	94	103	0	0/0.0521	
		0.33	13	105	100	0	0/0.0620	
0.48 ^a	2.10 ^a	0	12	96	102	1.02	0.91	
0.5	1.10	0	2	112	99	0.88	1.04	0.016
	2.20	0	6	99	99	1.06	1.02	0.043
			4 ^b	b	b	b	b	b
	2.20	0.33	15	94	102	1.07	0.88	0.035
1.0	1.10	0	3	110	99	1.11	1.28	0.096
		0.33	14	100	101	1.23	1.16	0.127
	2.20	0	7	89	101	1.45	1.18	0.128
1.25	1.10	0	8	110	102	0.92	1.31	0.109

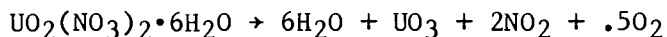
^aRecycle run by neutralization of condensate and recycle.^bGas leaked during run, causing both loss of gaseous products and in-leakage of air.

the separate decomposition of either of the two salts. For the other metal nitrates used, mixing with molten NH_4NO_3 seems to promote loss of the water of hydration, but there is less evidence for complex formation. The exothermic decomposition of the NH_4NO_3 could partially supply the heat required for the endothermic decomposition of the metal nitrates.

If the UO_3 is formed from decomposition of a solid complex, $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$, it probably has a structure retained from this complex. A better known example of this effect is the thermal decomposition of $\text{Th}(\text{C}_2\text{O}_4)_2$ solids to give ThO_2 showing the oxalate structure. The observations described in Sect. 4.2 clearly show decomposition of a solid, while both NH_4NO_3 and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decompose as molten salts. Weight measurements made with these observations and thermogravimetric measurements reviewed in Sect. 4.3 show completely different behaviors for the separate components and the mixture. After most of these data were accumulated, they were confirmed and found to agree with unpublished crystallographic and pyrolysis data.¹² For these unpublished data, carefully controlled crystallization from solutions gave $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ with a melting point of 48°C . Thermogravimetric analyses show easy loss of the hydrate water at temperatures below 100°C , loss of one NH_4NO_3 below 250°C , and decomposition of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ to UO_3 at about 300°C . The thermogravimetric results in Sect. 4.4 clearly indicate the formation of a $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ complex, while any additional NH_4NO_3 causes decomposition results similar to those for NH_4NO_3 alone.

The appearance and ceramic properties of ThO_2 undergo important changes when NH_4NO_3 is present, but information to explain these changes is not available.

The change in heat of reaction when NH_4NO_3 is added can be illustrated by the following equations:



$$\Delta H = 110 \text{ kcal/g mole U}$$



$$\Delta H = 26 \text{ kcal/g mole U}$$

Many other decomposition products are possible and are shown by thermogravimetric results. These equations are listed to show the effects of

NH_4NO_3 on the heat requirements and are not intended to indicate that they are the only or principal reactions.

If the UO_3 is formed by the decomposition of solid crystals, the properties of the solids depend on the crystallization conditions. Therefore, the rotary kiln with liquid at the feed point and a distinct region of crystallization is likely to give product properties which would not be duplicated in a fluidized bed or agitated trough where the feed is sprayed onto UO_3 solids.

4.6 Decomposition in a Microwave Oven

Decomposition tests were made by placing glass dishes containing sample solutions of different compositions in a 600-W Sharps Model R-6740 microwave oven. For some tests, the dishes were covered and surrounded by a magnesium silicate fiber insulation. Microwave exposures >30 to 60 minutes did not cause any additional weight losses. The NH_4NO_3 solutions were almost completely volatilized or decomposed (Table 4). Samples of the solid products were heated to 350°C in a standard thermal oven to determine any additional weight losses. All solids showed brown fumes in the thermal oven, indicating the decomposition of metal nitrates remaining after the microwave treatment. The results indicate ~90% denitration of $\text{UO}_2(\text{NO}_3)_2$, but little decomposition of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$, $\text{Th}(\text{NO}_3)_4$, or $\text{Ce}(\text{NO}_3)_3$ in the microwave oven (Table 4). The thermal oven at 300°C gives nearly complete decomposition of all these nitrates. Apparently, microwaves can couple with U(IV) to give severe localized overheating of uranium oxides¹³ but such overheating was not observed for the tests with nitrate feed solution. Use of microwaves severely limits the allowable construction materials. The combination of problems seemed to require detailed studies beyond the scope of our conversion program and no further tests were made.

5. ROTARY KILN TEST SYSTEM AND RESULTS

Rotary kilns (in large sizes up to 4-m-diam by 150 m long) are commonly used as process equipment, while small sizes are more difficult to fabricate and operate. The Barlett-Snow design from the C. E. Raymond Company is well known, with 16-cm-diam as the smallest standard size. For the U-Pu co-denitration, this size is excessive for convenient test system capacity and perhaps for control of criticality.

Table 4. Results for decomposition in a microwave oven

Feed solution	After microwave exposure to constant weight			Thermal oven product	
	NO_3^-/U (mole/mole)	NH_4^+/U (mole/mole)	Thermal oven loss (wt %)	Surface area (m^2/g)	Sinterability of test pellet (% T.D.) ^a
$\text{UO}_2(\text{NO}_3)_2$	0.26	0	12	3.8	71
$\text{UO}_2(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3$	2.5	0.93	38	11.1	91
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NH}_4\text{NO}_3$			35	13.1	
$\text{UO}_2(\text{NO}_3)_2 - 1/3\text{Th}(\text{NO}_3)_4 - \text{NH}_4\text{NO}_3$			43	28.4	
NH_4NO_3	Only traces of solids				

^a% T.D. = percentage of theoretical density.

An 8-cm ID rotary kiln (basically a piece of 3-in., sched. 10 I.P.S. stainless steel pipe) was fabricated and used for the development tests in this study. The pipe is mounted on steel wheels and rotates within a tube furnace around the center third of the 90-cm length. One, two, or three stainless steel rods roll freely inside the tube as "breaker bars" to crush lumps or remove solids from the tube wall. A number of different feed nozzles, weirs, breaker bars, retainers, and scrapers were tested. More detailed descriptions are given in the Appendix or wherever important to the discussion of results. The associated system and the basic kiln design are shown by Figs. 4 and 5. The need for seals was avoided by using a large flow of air to a radioactive off-gas system and by installing the test kiln inside a large fume hood. The tube angle was varied by adjustment of shims under the support frame. The system was designed to use standard fittings, glass pipe, and plastic tubing (Fig. 6) for ease of observation and modification.

Demonstration test runs for five conditions in a 16-cm-diam rotary kiln at the National Lead Company of Ohio uranium feed materials plant show good agreement with ORNL kiln test runs at similar conditions. The analyses of product oxides and the sinterability test results are also similar. The feed solutions containing NH_4NO_3 give better mechanical operation and lower concentrations of iron in the product oxides (less corrosion) as compared to feeds without NH_4NO_3 .

A reduced-scale rotary calciner of about 2-cm-diam was tested to prepare $(\text{U}, \text{Th})\text{O}_2$ and has been installed in a glove-box to prepare small samples of $(\text{U-Pu})\text{O}_2$.¹⁴

5.1 Ceramic Properties of Rotary Kiln Products

Concentration of NH_4NO_3 in the feed solution is the controlling variable for the ceramic properties of the UO_3 products. For UO_3 prepared with feed-solution NH_4^+/U mole ratios of 2.0 or 2.1, the B.E.T. surface areas were 8 to 12 m^2/g and the sinterability test pellet densities were 91 to 93% of theoretical density for a wide range of temperatures (Table 5). The presence of 1.7 M excess HNO_3 or 1.2 M acid deficiency in the feed did not change these values. The bulk densities of the powders were 0.7 to 0.9 g/cm^3 . Without NH_4^+ in the feed, the B.E.T. surface areas were 0.7 to 1.6

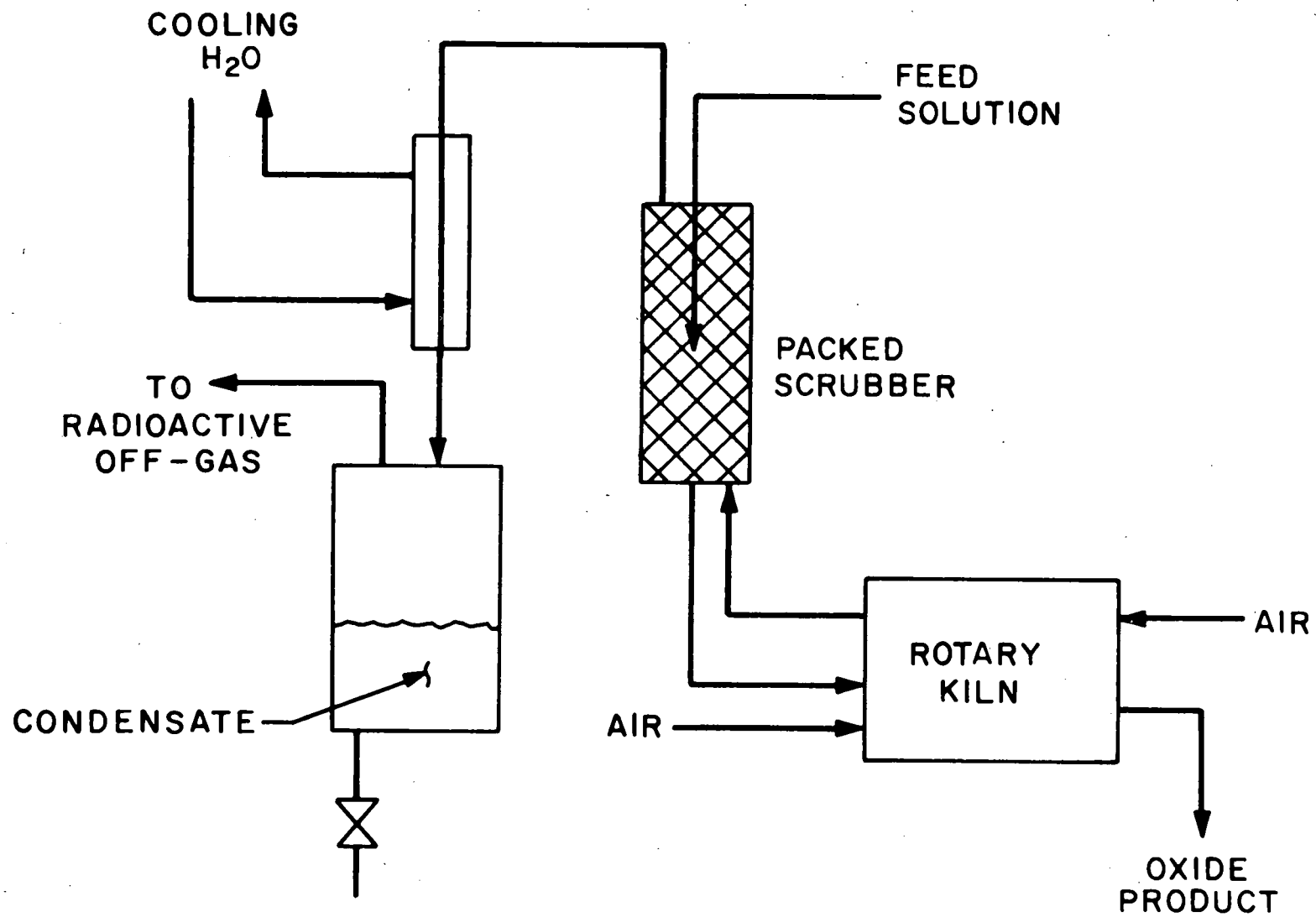


Fig. 4. Rotary kiln test system.

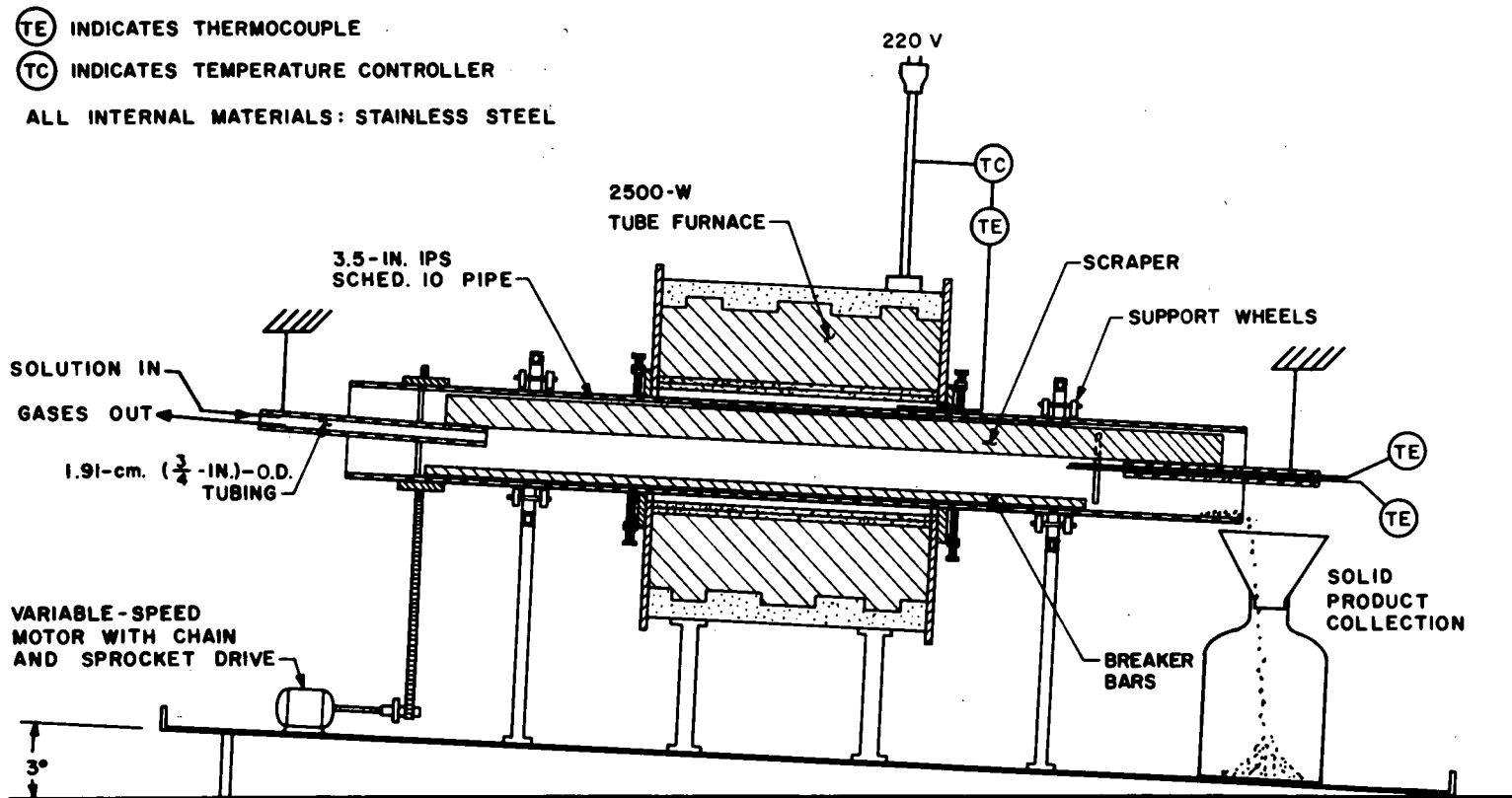


Fig. 5. Rotary kiln cross-section.

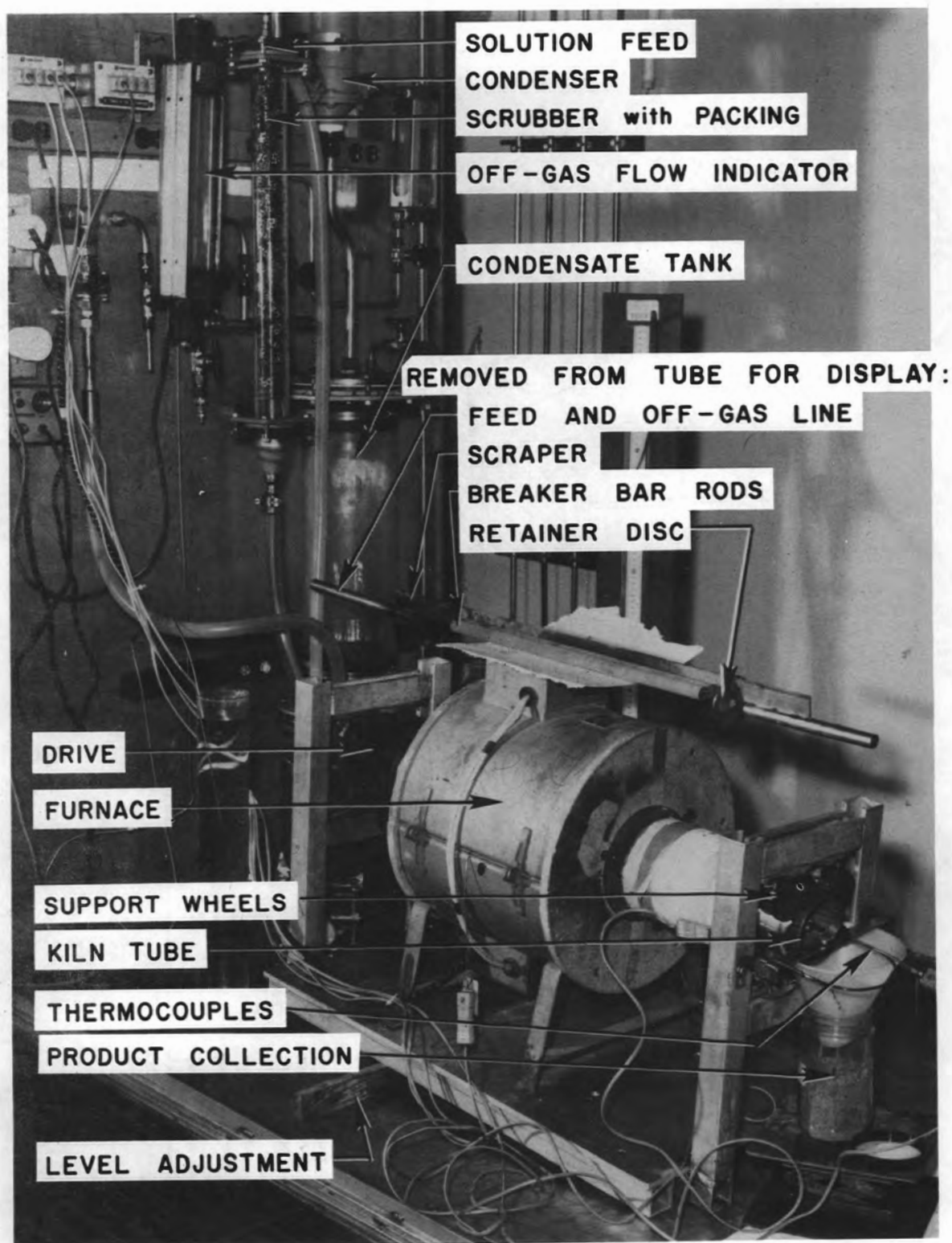


Fig. 6. The 8-cm-diam rotary kiln system.

Table 5. Rotary kiln run conditions and UO₃ product propertiesFeed solutions: UO₂(NO₃)₂, NH₄NO₃, and NH₄OH or HNO₃Feed solution rate: 11 to 14 cm³/min

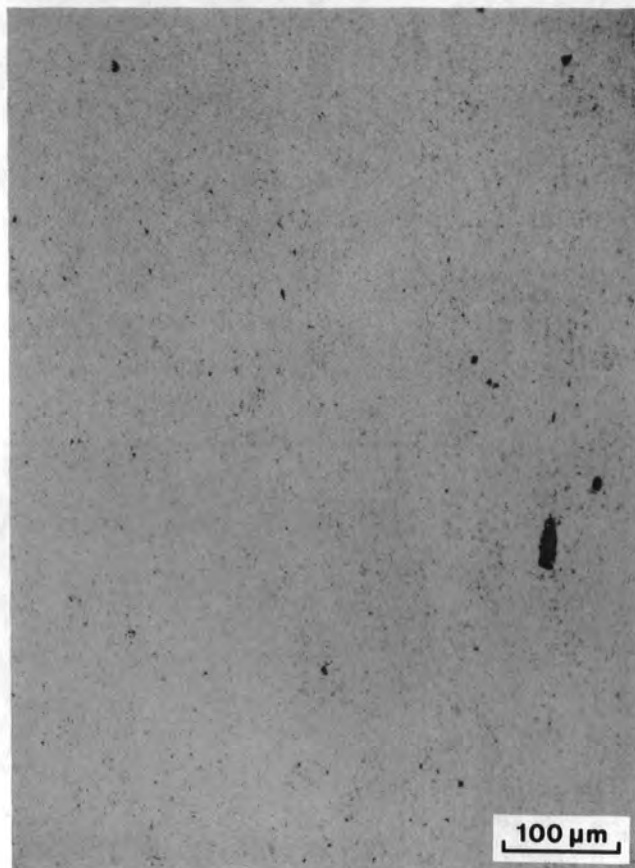
Feed concentrations			Tube temperature (°C)	Run No.	B.E.T. surface area (m ² /g)	Pellet density, (% of theoretical)	Bulk density (g/cm ³)	L.O.I. ^a (approximate) (wt %)
NH ₄ ⁺ /U (mole/mole)	U (M)	NO ₃ ⁻ /U (mole/mole)						
0	1.7	2.1	490	42	1.6		1.6	
0	1.4	2.0	500±30 ^b	14	0.89	69	2.5	2.6
0	1.4	2.0	570	7	0.68		2.0	
0.8	1.7	2.0	390±10 ^b	19	1.79	78	1.1	8
1.2	1.7	2.0	420±20 ^b	18	3.91	92	0.8	10
1.3	1.7	2.1	460-400	32	6.43	89	1.0	13
1.3	1.7	2.1	440	39	8.2	92	0.6	
1.6	1.4	0.8 ^c	470	48	6.71	85	1.2	7
2.0	1.7	1.65	490-200	26	11.3	91	0.8	
2.1	1.4	2.0	350	9C	10.2	92	0.8	7
2.0	1.7	2.0	380	13	5.0	90	0.9	16
2.0	1.7	2.1	390	37	8.68		0.8	
2.0	1.7	2.0	450	34	8.01	92	0.9	6
2.1	1.4	2.0	460	9B	10.7	92	0.8	4
2.0	1.7	2.0	490	17	8.6		0.9	5
2.0	1.7	2.0	500	35	10.03	92	0.8	3
2.1	1.4	2.0	530	12	9.2	92, 93, 92, 92	0.8	3
2.1	1.4	2.0	550	9A	11.5	93	0.8	2
2.1	1.4	2.0	570	5	10.6		0.9	
2.0	1.7	2.1	620	41	9.1	93	0.8	2
2.0	1.7	3.0	490	24	11.8	92	0.6	5
2.0	1.7	3.0	560	25	9.9		0.7	4
3.0	1.7	2.0	450	40	8.0	91	0.7	

^aL.O.I. = loss on ignition.^bTemperature cycle used to promote discharge of solids.^cSlurry feed with partial precipitation as UO₃.

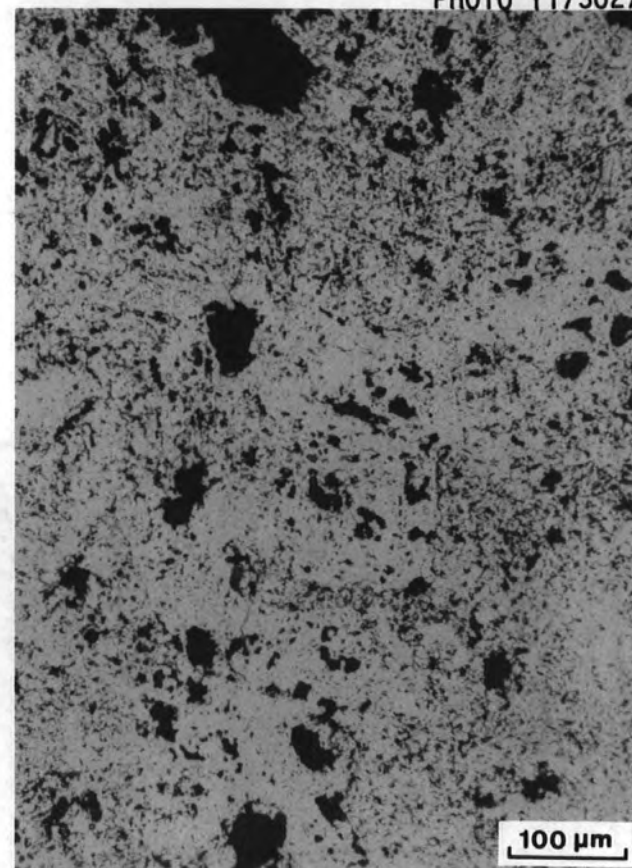
m^2/g and the pellet densities were <70% of theoretical values. The bulk densities of these UO_3 products were 1.6 to 2.5 g/cm^3 . For intermediate NH_4^+/U mole ratios of 0.8 to 1.3, the ceramic properties of the UO_3 were intermediate and variable. The kiln temperature greatly affects the NO_3^- content and the loss on ignition (LOI) to 900°C for the solid products, but does not appear to affect the ceramic properties after calcination and reduction to UO_2 at 600°C .

The effects of process variables can be illustrated by different types of photographs of the sinterability test pellets. The improvement in ceramic properties resulting from the addition of NH_4NO_3 is most clearly shown by simple cross sections at 200-fold magnification (Fig. 7). The changes are also shown by photographs of the whole pellets (Fig. 8). The kiln temperature has no significant effects on the microstructure or on pellet density at these sinterability test conditions. Figure 9 shows the etched cross sections of pellets for three denitration temperatures, and Fig. 10 shows the three different types of microphotographs for a higher denitration temperature. If the $\text{NH}_4^+/\text{U} \geq 1.6$ mole/mole, the microstructures were good for a wide range of NO_3^-/U mole ratios for excess HNO_3 , for acid-deficient $\text{UO}_2(\text{NO}_3)_2$, and for a slurry feed from addition of NH_4OH to give precipitated uranium oxides and NH_4NO_3 (Fig. 11). While the microstructures were good, all of these conditions gave other, undesirable, results. The pellet density was distinctly lower for the slurry feed; the acid-deficient feed and the slurry feed both deposited solids in the scrubber and formed harder deposits in the kiln. The feed containing excess HNO_3 resulted in a higher iron content (corrosion) for the UO_3 product.

These results are in good agreement with those for ceramic properties from batch denitrations in laboratory glassware. For solutions without NH_4^+ , the B.E.T. surface areas of UO_3 prepared by continuous denitration in the rotary kiln are distinctly lower than those of UO_3 prepared in the lab glassware tests; even lower surface areas of 0.1 or $0.2 \text{ m}^2/\text{g}$ result from continuous denitration in fluidized beds. The deposition of molten salt on denitrated solids may cause this to occur. The rotary kiln probably has an intermediate amount of this layering or coating effect as compared to batch and fluidized-bed denitrations. The difference in basic particles is shown by SEM micrographs of three rotary-kiln products (Fig. 12). With NH_4NO_3 in the feed, all the product oxides are small particles;



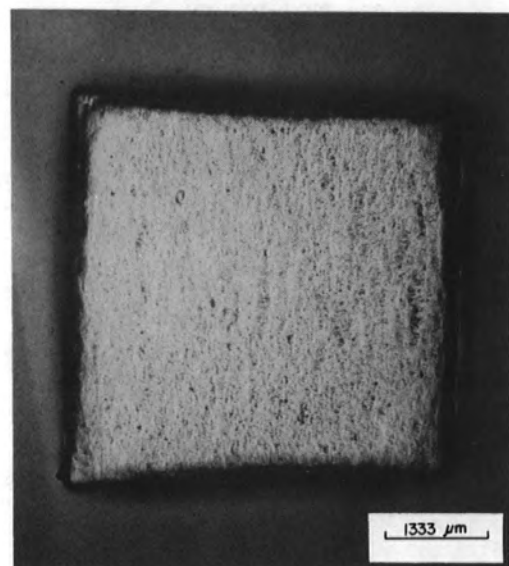
TEST: ROT-12
 $\text{NH}_4^+/\text{U} = 2.1$ MOLE/MOLE
 KILN TEMPERATURE = 530°C
 B.E.T. SURFACE AREA = $9.24 \text{ m}^2/\text{g}$
 POWDER BULK DENSITY = $0.79 \text{ g}/\text{cm}^3$
 UO_2 PELLET DENSITY = 92% OF THEORETICAL



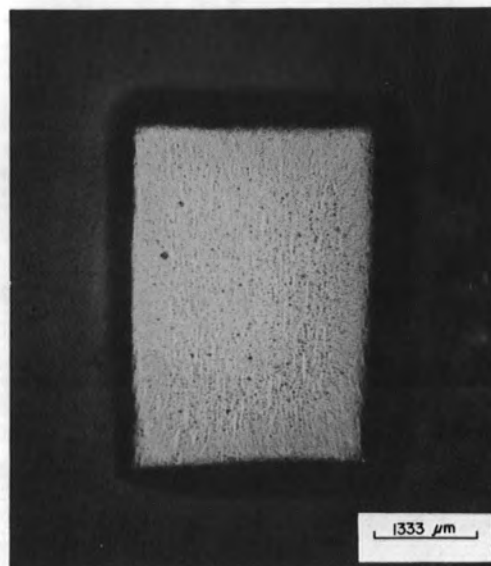
TEST: ROT-14
 $\text{NH}_4^+/\text{U} = 0$ MOLE/MOLE
 KILN TEMPERATURE = 500°C
 B.E.T. SURFACE AREA = $0.89 \text{ m}^2/\text{g}$
 POWDER BULK DENSITY = $2.5 \text{ g}/\text{cm}^3$
 UO_2 PELLET DENSITY = 69% OF THEORETICAL

Fig. 7. Effects of NH_4NO_3 in $\text{UO}_2(\text{NO}_3)_2$ on pellet microstructure (polished cross sections) for continuous rotary kiln denitration.

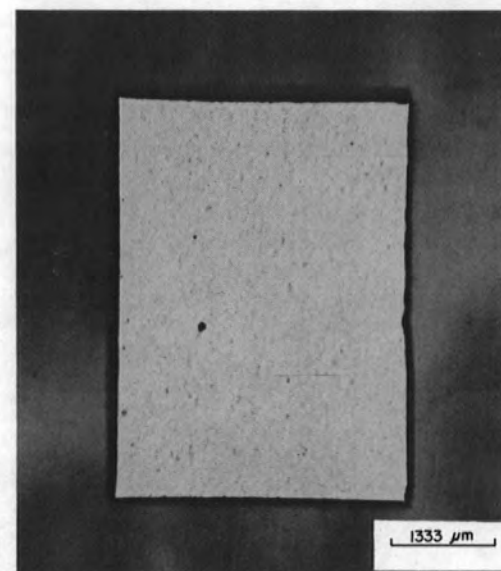
Y-176919



78.2% T. D.
ROT-19
 $\text{NH}_4^+/\text{U}=0.8$ MOLE/MOLE
SURFACE AREA: $1.79 \text{ M}^2/\text{g}$



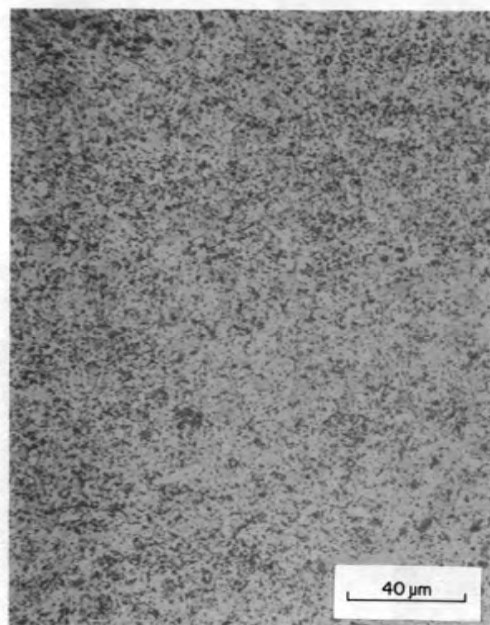
88.5% T. D.
ROT-32
 $\text{NH}_4^+/\text{U}=1.3$ MOLE/MOLE
SURFACE AREA: $6.43 \text{ M}^2/\text{g}$



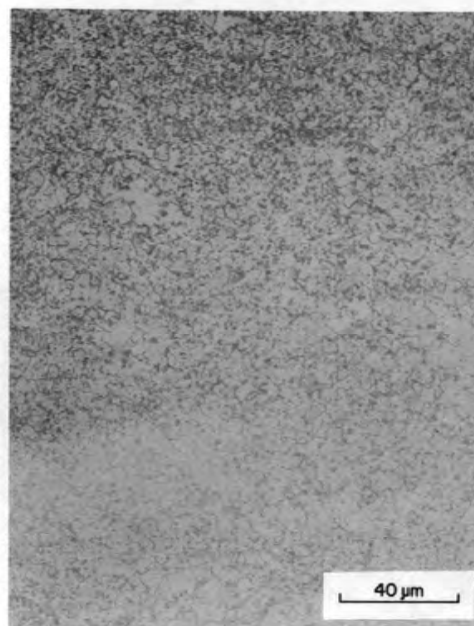
91.6% T. D.
ROT-12
 $\text{NH}_4^+/\text{U}=2.1$ MOLE/MOLE
SURFACE AREA: $9.24 \text{ M}^2/\text{g}$

Fig. 8. Photographs of UO_2 pellets (polished cross sections) for three NH_4^+/U ratios in feed.

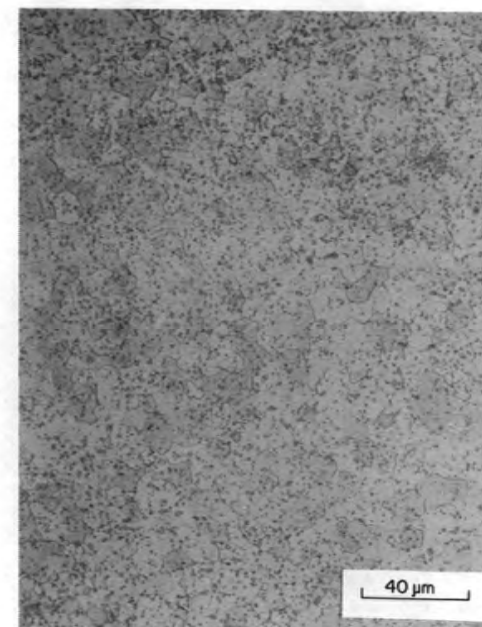
($\text{NH}_4^+/\text{U} = 2.0$ or 2.1 mole/mole in feed)



ROT-13
380°C
SURFACE AREA: $5.0 \text{ M}^2/\text{g}$
90.5% T. D.



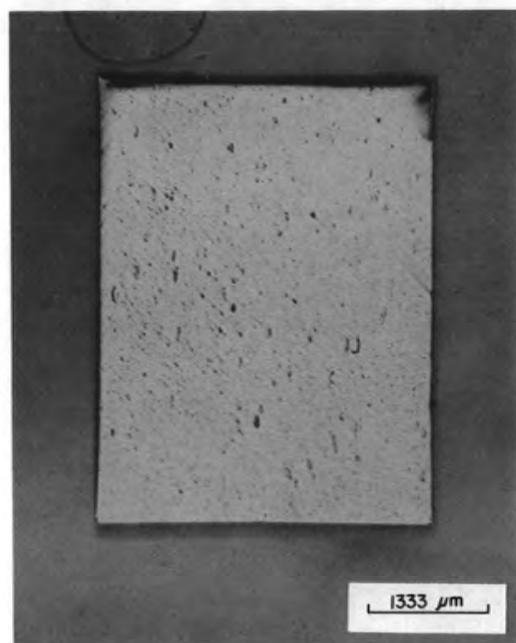
ROT-34
450°C
SURFACE AREA: $8.0 \text{ M}^2/\text{g}$
92.4% T. D.



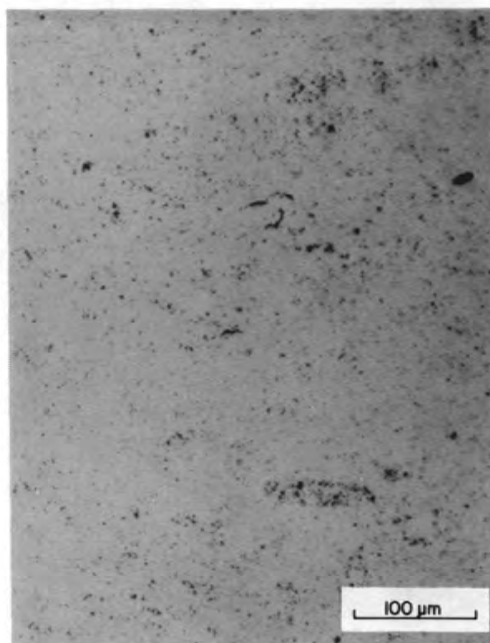
ROT-12
530°C
SURFACE AREA: $9.2 \text{ M}^2/\text{g}$
92.0% T. D.

Fig. 9. Microstructure of UO_2 pellets (etched cross-sections) for three denitration temperatures.

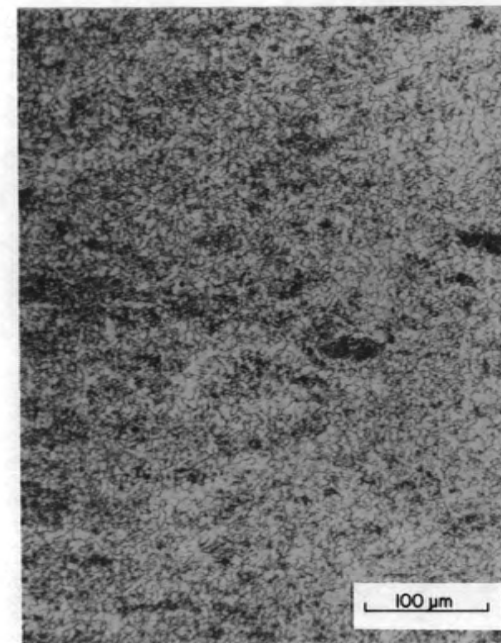
Y-176921



PELLET (15X)



200X

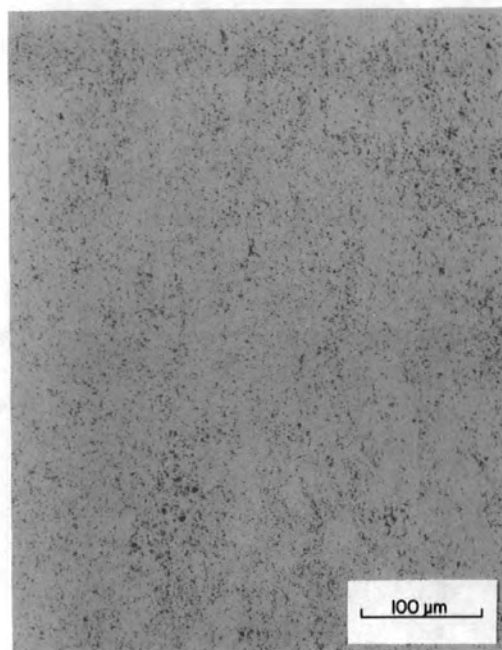


ETCHED (200X)

$\text{NH}_4^+/\text{U}=2.0$ MOLE/MOLE; 620°C TUBE TEMPERATURE
SURFACE AREA: $9.1 \text{ m}^2/\text{g}$; PELLET DENSITY: 93.5% T. D.

Fig. 10. Microstructure of a sintered UO_2 pellet (polished cross sections) from rotary kiln run (ROT) 41.

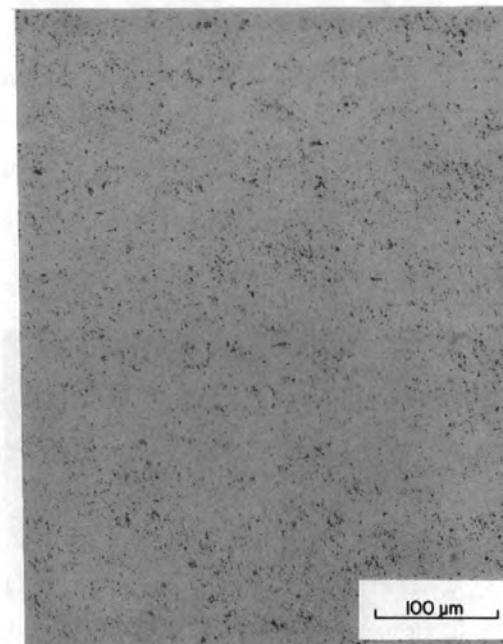
($\text{NH}_4^+/\text{U} = 1.6 - 2.0$ mole/mole in feed)



ADU SLURRY FEED
ROT-48
84.5% T. D.
SURFACE AREA: $6.71 \text{ m}^2/\text{g}$

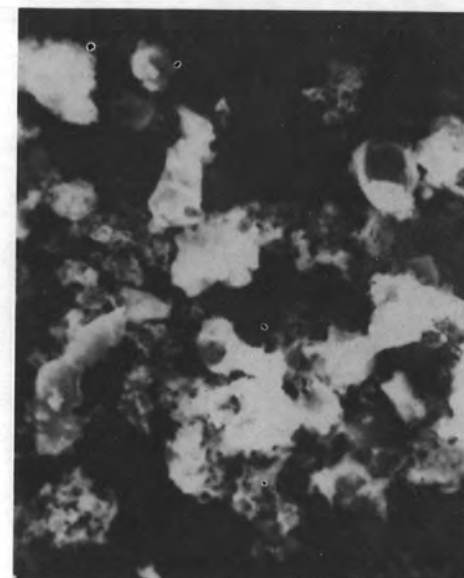
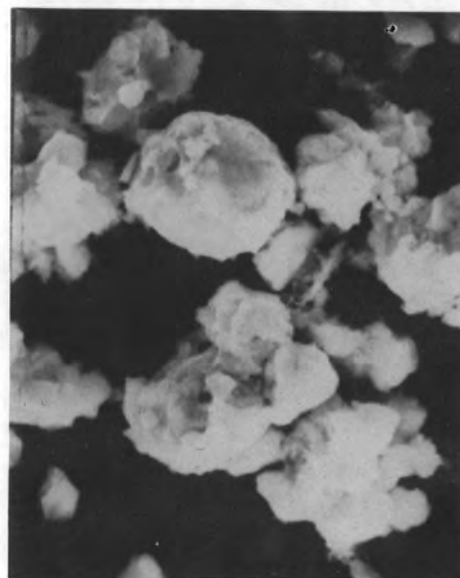


ACID-DEFICIENT $\text{UO}_2(\text{NO}_3)_2$
ROT-35
92.4% T. D.
SURFACE AREA: $10.0 \text{ m}^2/\text{g}$



$\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$
ROT-24
91.7% T. D.
SURFACE AREA: $11.8 \text{ m}^2/\text{g}$

Fig. 11. Microstructure of UO_2 pellets (polished cross sections) at several acid-deficiencies of feed.



1 μ m
SCALE

34

UO₃ (ROT-34)
NH₄⁺/U=2.0 mol/mol
in feed Solution
B.E.T. Surface Area = 8.01 $\frac{m^2}{g}$

UO₃ (ROT-42)
NH₄⁺ = 0 in feed Solution
B.E.T.
Surface Area = 1.6 $\frac{m^2}{g}$

(UTh)O_x (ROT-36)
NH₄⁺/(U+Th)=2.0 mol/mol
in feed Solution
B.E.T. Surface Area = 13.68 $\frac{m^2}{g}$

Fig. 12. Scanning electron microscope micrographs of dispersed oxide particles in rotary kiln products.

without NH_4NO_3 , the fused or slag-like particles are generally much larger (up to 10,000 μm). Figure 12 shows only the smallest particles for run 42. Since the fluidized-bed and agitated-trough denitrators operate with liquid feed sprayed onto hot UO_3 particles, they might not achieve the full favorable effects of NH_4NO_3 in the feed.

During studies of the solids-discharge behavior (Sect. 5.2), tests were made with slow accumulation of material in the rotary kiln tube and with erratic fluctuations of discharge rate. Slow accumulations in the tube (i.e., discharge rates lower than the feed rates) had little effect on ceramic properties, but large fluctuations of discharge rate produced poor properties.

Oxide products other than UO_3 were prepared and analyzed with feed solutions containing NH_4NO_3 . Chemical and colloidal behavior of $\text{Th}(\text{NO}_3)_4$ is similar to that of $\text{Pu}(\text{NO}_3)_4$, so thorium was used as a substitute for plutonium in U-Pu mixtures. It is claimed that $\text{Ce}(\text{NO}_3)_3$ provides a better simulation of the Pu-nitrate thermal decomposition¹⁵, and one rotary kiln test was made with a mole ratio of $\text{U/Ce} = 3.0$. Thorium oxide is an important nuclear fuel material, and the results for some thermal denitrations of $\text{Th}(\text{NO}_3)_4\text{-NH}_4\text{NO}_3$ are included. All the mixed-oxide products from metal nitrate- NH_4NO_3 feed solutions gave good sinterability test results and B.E.T. surface areas near or in the preferred range of 5 to 15 m^2/g (Table 6); the microstructures are also good (Fig. 13). The ThO_2 product had a higher B.E.T. surface area, but good sinterability. These results are better than those for ThO_2 prepared either by precipitation with ammonia or by simpler thermal denitration of a $\text{Th}(\text{NO}_2)_4$ solution containing no NH_4NO_3 . Thermal decompositions of slurry feeds prepared by addition of NH_4OH to the metal nitrate solutions gave poorer results.

Particle size analyses by a Micromeritics Sedigraph determined that all uranium oxides and mixed oxides from denitration in the rotary kiln with feed solutions having mole ratios $\text{NH}_4\text{NO}_3/\text{metal} = 2$ have good particle size distributions. For these products, >99 wt % of particles are smaller than 12 μm , with average diameters (weight basis) of 2.5 to 3.6 μm (Table 7). Calcination in Ar-H_2 at 600°C to reduce the uranium oxides to UO_2 has little effect on the particle size distributions. For $\text{UO}_2(\text{NO}_3)_2$ feed solution without NH_4NO_3 , a large fraction of the material is not dispersable to <60 μm and the <60 μm fraction has average diameters of 5 to 7 μm .

Table 6. Rotary kiln mixed oxide properties for feed solutions containing NH_4NO_3

Feed solution rate: 11 to 14 cm^3/min

Nominal feed composition	U/Th or U/Ce (mole/mole)	NH_4^+ /metal (mole/mole)	Tube temperature ($^{\circ}\text{C}$)	Run No.	B.E.T. surface area (m^2/g)	Pellet density, (% of theoretical)	Powder bulk density (g/cm^3)
UO_3		2.0	450	34	8.0	92	0.85
		2.0	500	35	10.0	92	0.63
		2.0	620	41	9.1	93	0.64
$\text{UO}_3\text{-ThO}_2$	3.0	2.0	430	36	13.7	90.5	0.71
	3.0	2.0	500	44	15.6	91.5	0.5
$\text{UO}_3\text{-ThO}_2$ (slurry feed)	3.0	3.5	440	47	12.3	80	1.1
$\text{UO}_3\text{-ThO}_2$ (slurry feed)	3.0	3.0	460	46	17.0	81	2.1
$\text{UO}_3\text{-CeO}_2$	3.0	2.0	460	43	6.0	85	0.65
ThO_2	0	5.0	α	DEN-62	33.6	90	0.6
	0	2.0	540	52	23.6	83	0.70
	0	5.0	550	51	25.8	85	0.75

α Batch denitration with oven at about 350°C .

Table 7. Particle size distributions for rotary kiln products

Size analyses: By Micromeritics SediGraph 5000/GB
Dispersion: 5 minutes in ultrasonic bath with Daxad-23 surfactant

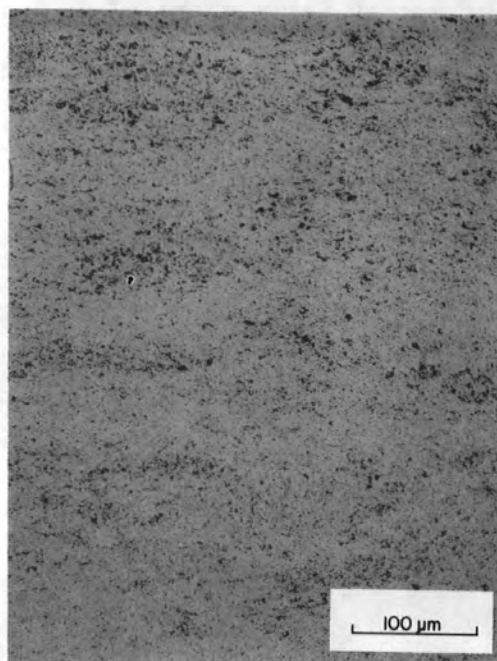
Composition NH ₄ NO ₃ /(U + Th + Ce) in feed, mole/mole	(U,Ce)O ₂	(U,Th)O ₂	UO ₂	UO ₂	UO ₂	UO ₃	UO ₃
Sample treatment	2.0	2.0	2.0	2.0	2.0	2.0	0
	Calcined	Calcined	Calcined	Calcined	Calcined	Kiln product	Kiln product
Assumed density, g/cm ³	10.3	10.8	10.96	10.96	10.96	7.3	7.3
Kiln temperature, °C	460	500	460	620	450	450	605
Batch No.	43	44	NLO-A2	41	34	34	NLO-B2
Particle size distributions, wt % ^b	<i>Particle sizes, μm</i>						
98	9.0	11.0	8.5	11.0	11.0	7.0	42 ^a
90	6.5	7.9	6.0	7.9	7.4	4.8	27 ^a
80	5.4	6.3	4.9	6.4	5.8	3.8	19 ^a
70	4.7	5.1	4.2	5.3	4.8	3.3	14 ^a
60	3.9	4.4	3.3	4.6	3.8	2.8	10 ^a
50	3.0	3.2	2.5	3.6	2.6	2.5	7
40	2.0	2.0	1.9	2.4	1.7	2.1	5 ^a

^aLarge fraction of this product without NH₄NO₃ in feed is not dispersable and is not included in size analyses result.

^bWt % of particles that are smaller than particle sizes listed in right-hand columns.



ROT-44
 $(U,Th)O_2$, $U/Th=3$
SURFACE AREA: $11.4 \text{ M}^2/\text{g}$
91.5% T. D.



ROT-43
 $(U,Ce)O_2$, $U/Ce=3$
SURFACE AREA: $6.0 \text{ M}^2/\text{g}$
83.5% T. D.



ROT-51
 ThO_2
SURFACE AREA: $25.8 \text{ M}^2/\text{g}$
85.5% T. D.

Fig. 13. Pellet microstructures (polished cross-sections) for three compositions, NH_4NO_3 in feed solutions.

Oxide products from both the rotary kiln and batch tests were examined by x-ray diffraction. The UO_3 products from denitration with NH_4NO_3 in the feed were more crystalline than those without NH_4NO_3 or those from ammonium diuranate (ADU) precipitation, but the results did not show any unique or reproducible form of UO_3 . The $\text{UO}_3\text{-H}_2\text{O-NH}_3$ system is quite complex and difficult to study by x-ray diffraction.

Pacific Northwest Laboratories conducted pellet fabrication studies with UO_3 from the ORNL kiln and the first results show very good agreement with the ORNL sinterability test results. All samples with the modified chemical flowsheet (NH_4NO_3 in the feed solution) gave pellets with 90 to 98% of theoretical density and good microstructure. Samples without NH_4NO_3 in the feed solution gave 75 to 82% of theoretical density. Four test kiln products containing thorium or cerium (possible stand-ins for plutonium) gave 91 to 97% of theoretical density. Higher sintering temperatures of 1700°C result in higher densities than for the ORNL sinterability tests. Two larger batches of UO_3 product using the modified chemical flowsheet were sent to Hanford Engineering Development Laboratory (HEDL) for pilot plant evaluation of pellet fabrication.

5.2 Demonstration Tests in a 16-cm-diam Rotary Kiln

Four U.S. Department of Energy (DOE) plant sites have used Bartlett-Snow 6.5-in. (16-cm) diameter rotary calciners for conversion of $\text{UO}_2(\text{NO}_3)_2$ solutions to U_3O_8 . The size, capacity, and easy change-over between batches are particularly suited to scrap recovery for low enrichments of uranium. The U_3O_8 has good properties for conversion to UF_6 for return to gaseous diffusion cascades. Information on these rotary kilns has not been published, and three of the plant sites were visited to discuss the equipment and procedures with operating personnel (see Appendix).

The rotary kilns at the three sites visited have demonstrated good long-term durability and reasonable maintenance, but each site has developed different operating procedures, primarily to control difficulties from a caking or "dough" stage of the denitration process. All these units are operated at 900°C in the tube to prepare U_3O_8 . For procedures at two of the sites, the operators believed the 900°C temperatures were necessary and did not believe their systems would satisfactorily prepare UO_3 at 450 to 600°C .

At the third site, the equipment had been modified to use a positive mechanical scraper inside the tube, and the chemical flowsheet was changed by using NH_3 to neutralize excess HNO_3 in the feed solution,¹⁶ primarily to reduce corrosion and thus meet product specifications for Cr in the U_3O_8 . Lower density and softer lumps for the U_3O_8 product were noticed, but other changes in product properties were not measured. This system appeared much more promising for UO_3 preparation than did the other two systems. Since addition of NH_3 was a routine part of this procedure, operation with a controlled concentration of NH_4NO_3 did not require any changes in equipment or procedures. Demonstration runs were requested by purchase order and were made with $\text{UO}_2(\text{NO}_3)_2$ solution at three temperatures and with $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ solution at two temperatures.

The demonstration tests by NLO (National Lead of Ohio) used a $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solution of enriched uranium (3.5% ^{235}U). Additional acid was added and the HNO_3 was then neutralized with NH_3 to a calculated mole ratio of $\text{NH}_4^+/\text{U} = 2.0$. Chemical analysis after neutralization shows 0.58 M U , 1.25 M NH_4^+ , and a pH of 2.5. This feed was denitrated to UO_3 with excellent mechanical operation for tests at $605 \pm 10^\circ\text{C}$ and $460 \pm 10^\circ\text{C}$ inside the kiln. The feed without NH_3 neutralization (0.61 M U , 1.10 M HNO_3) was denitrated to U_3O_8 or UO_3 with only minor mechanical difficulties for tests at $750 \pm 10^\circ\text{C}$, $605 \pm 10^\circ\text{C}$, and $445 \pm 20^\circ\text{C}$. The sound of the mechanical scraper and drive indicated a much heavier loading or resistance without NH_4NO_3 . Samples of solutions and product oxides were shipped to ORNL for analysis and comparison with the small test kiln results. The run conditions and analyses for the product oxides are presented in Tables 8 and 9. The sinterability test pellets show 93.0% of theoretical density for the NH_4^+/U ratio of 2.0 mole/mole and 67.0 to 68.5% of theoretical density for $\text{NH}_4^+/\text{U} = 0$. The microstructures of the sinterability test pellets are good for a mole ratio $\text{NH}_4^+/\text{U} = 2.0$ in the feed solution and poor for solutions with no NH_4^+ (Fig. 14). For the products prepared without NH_4^+ in the feed, the surface areas are higher and the microstructures better than for UO_3 prepared by denitration in a fluidized bed (Fig. 14).

The throughput for the ORNL demonstration runs was 3.0 kg/h of uranium oxides or 2.5 kg/h of U. For a mole ratio of $\text{NH}_4^+/\text{U} = 2.0$ the rotary kiln capacity is ~ 5 kg/h of U or 6 kg/h of uranium oxides. At NLO, 70 to 90%

Table 8. Solution analyses and run conditions for rotary kiln demonstration tests by National Lead of Ohio

Kiln: 16-cm-ID, 65-cm furnace length
Product rate: 3.0 kg/h of uranium oxides

Test No.	Tube temperature (°C)	Feed solution composition			Scrubber exit composition		
		NH_4^+/U (mole ratio)	NO_3^-/U^a (mole ratio)	Fe (ppm U)	NH_4^+/U (mole ratio)	NO_3^-/U^a (mole ratio)	Fe (ppm U)
A-1	605	2.0	2.0	130	2.0	1.6	100
A-2	460	2.1	1.9	150	2.2	2.0	120
B-1	750	0	3.9	90	0	5.2	4600
B-2	605	0	4.0	80	0	8.6	2200
B-3	445	0	3.9	-	0	8.7	1500

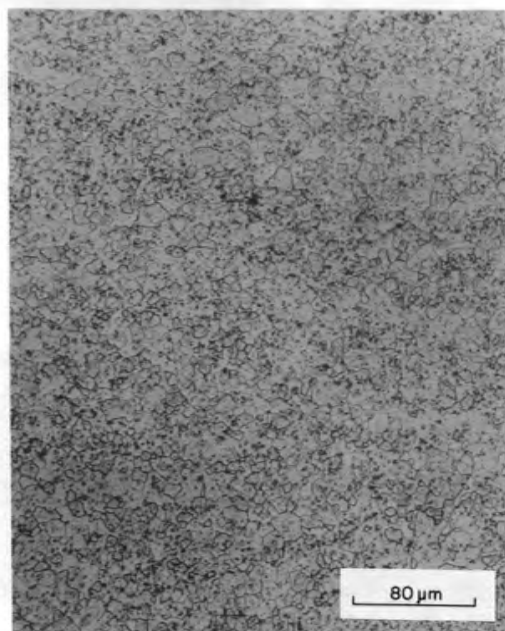
^a NO_3^- present as NH_4NO_3 not included; <2 indicates acid deficient; >2 indicates excess HNO_3 .

Table 9. Oxide product properties for rotary kiln demonstration tests by National Lead of Ohio

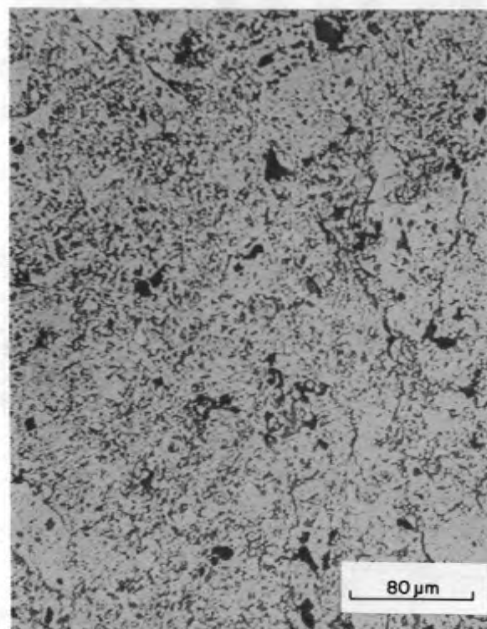
Test No.	Test pellet sinterability (% of T.D.) ^a	B.E.T. surface area (m^2/g)	Loss on ignition (wt %)	Fe (ppm U)	NH_4^+ (wt %)	NO_3^- (wt %)	Bulk density (g/cm^3)
A-1	93.0	7.23	1.20	700	0.03	0.21	0.82
A-2	93.5	6.30	5.96	700	0.05	3.20	0.70
B-1	67.0	0.92	0.42	3500	0.03	0.26	1.79
B-2	68.5	1.46	3.48	2000	0.04	2.80	1.78
B-3	68.0	0.70	2.57	4600	0.05	0.58	1.93

^aT.D. = theoretical density.

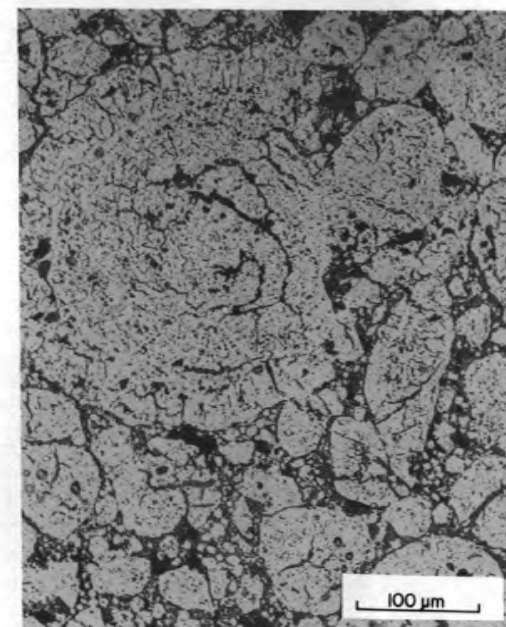
Y-176917



ROTARY KILN (NLO-A2)
 $\text{NH}_4^+/\text{U}=2.1$ MOLE/MOLE IN FEED
460°C
SURFACE AREA: $6.30 \text{ m}^2/\text{g}$
93.4% T. D.



ROTARY KILN (NLO-B2)
No NH_4^+
605°C
SURFACE AREA: $1.46 \text{ m}^2/\text{g}$
68.5% T. D.



FLUIDIZED BED (CU-13)
No NH_4^+
350°C
SURFACE AREA: $0.23 \text{ m}^2/\text{g}$
72.0% T. D.

Fig. 14. Microstructure of UO_2 pellets (polished cross sections) from three continuous denitration demonstration run products.

of the water is removed in the evaporator, and the feed rate is limited by the evaporator capacity. The feed can be evaporated to a higher uranium concentration if the excess HNO_3 is neutralized with NH_3 . The acid is recycled in the scrubber and the U concentration must be limited to avoid formation of solids in the scrubber. The NH_4NO_3 is decomposed to products that do not recycle in the scrubber, thus allowing higher uranium concentrations without solids formation. The highest solution flow rate into the kiln (calculated from uranium concentrations) was $120 \text{ cm}^3/\text{min}$. A recommended maximum design capacity for other sizes of kilns is $0.03 \text{ cm}^3/\text{min}$ of solution per cm^2 of heated tube wall. The maximum concentration going into a scrubber should be $\sim 6 \text{ N } \text{UO}_2(\text{NO}_3)_2 + \text{HNO}_3$, or 3 M U if no excess HNO_3 is present. From these criteria, a capacity of 100 kg/d of U + Pu would be practical in a rotary kiln of 10-cm-ID and 130-cm heated length.

The NLO Bartlett-Snow rotary calciner has a 90-cm furnace length and a 16-cm-ID tube, providing $\sim 4500 \text{ cm}^2$ of heated surface. The total chamber length, including the stationary end-sections, is $\sim 3.3 \text{ m}$. The alloy tubes are cast in sections and assembled to give kilns of different length.

The NLO and ORNL rotary kilns use similar thermocouple locations:

1. The tube temperature is measured by a thermocouple on the centerline, with the end located one-third into the heated length from the powder discharge end.
2. The furnace temperature is measured by thermocouples located in the air space between the heater elements and the rotating tube. This furnace temperature is 80 to 150°C higher than the tube temperature for normal operation, but the difference can be much larger if solids accumulate on the wall.

The NLO temperature recorder charts show cycles of ± 10 to $\pm 20^\circ\text{C}$ for the tube temperatures and $\pm 50^\circ\text{C}$ for the furnace temperatures.

A dilute $\text{UO}_2(\text{NO}_3)_2$ solution containing excess HNO_3 is the most common feed to the NLO kiln. Excess HNO_3 is neutralized by addition of NH_3 to a selected pH (usually $\text{pH} = 2.0$); this is done batchwise with circulation by a centrifugal pump for mixing and in-line pH elements for control. The most frequent maintenance requirement is replacement of a broken scraper, but operation to prepare UO_3 at 600°C instead of U_3O_8 at 900°C should

reduce or eliminate this type of failure. The turbo-film evaporator and the off-gas blower also require some maintenance.

5.3 Solids Discharge Behavior

Steady-state discharge of solids was demonstrated for a majority of test runs in the 8-cm-ID kiln. Several conditions were shown to contribute to accumulation of solids on the kiln walls. For the small test kiln, the size of the breaker bars is limited, and they were not dependable for removing solids under accumulation-prone conditions. A full-length stationary scraper mounted ~ 1 to 2 mm from the tube wall was effective, without any overloading of the low torque drive motor, when the feed contained the standard NH_4^+/U mole ratio of 2. The harder cakes produced without NH_4NO_3 in the feed or for the slurry feeds are more difficult to remove, requiring a more rugged scraper and tube drive. The demonstration run results (Sect. 5.2) with, and without, NH_4NO_3 in the feed confirmed these observations.

Large accumulations of solids tended to result for the following three conditions. The lower NH_4^+/U mole ratios resulted in solids accumulations when first tested. Tests with mole ratios of 0, 0.8, and 1.2 were continued by imposing a 560 to 660°C temperature cycle on the furnace to maintain a fluctuating rate of product discharge. A mole ratio of 1.1 produced continuous accumulation, but a ratio of 1.3 was used with no difficulty after the full-length scraper was installed. One test with acid-deficient feed equivalent to $\text{UO}_2(\text{OH})_{0.35}(\text{NO}_3)_{1.65} \cdot 2\text{NH}_4\text{NO}_3$ in solution gave precipitation in the feed off-gas scrubber and a very large accumulation of solids within the heated length of the kiln. Excessive heat transfer to the feed point from high furnace temperatures or by large full-length breaker bars causes caking on the walls, which is detrimental to solids discharge. Presence of liquid rather than solids at the feed point is desirable and the operating conditions, including the feed flow rate, should be selected to maintain this condition.

Use of sixty 1.9-cm-diam balls in place of breaker bars gave the poorest solids discharge of any arrangement tested. Operation without breaker bars produced rounded lumps of inadequately heated solids with chemical composition of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$, even though the tube centerline temperature was

Table 10. Solids discharge behavior for rotary kiln test runs

Mechanical features		NH ₄ ⁺ /U (mole/mole)	Furnace temperature (°C)	Run No.	Overall	Holdup (g)	Details
Scraper bar	Breaker rods						
None	Full length 1.27-cm-D, four	0	650	7	Unacceptable		Short run time
		1.1	690	6	Poor	>300	Short run time
		2.1	690	5	Good		Short run time
	Full length 1.27-cm-D, three	0	620±50 ^a	14	Adequate	600	Temp. cycle required
		2.0	710	22	Unacceptable	600	Various product solids
		2.1	650	12	Adequate	450	Varying product rates
		2.0	610	21	Very good	300	New retainer plate
		2.0	530	13	Good	550	Large solids holdup
	Full L, 1.91-cm-D, three	2.0	570	10	Good		Short run time
	Full L, 1.91-cm-D, two	2.0	590	11	Poor	400	Poor heat transfer
Short 0.3 × 3.1 × 18. cm	None	2.0	640	28	Poor	>600	Inadequate heat transfer
	1.9 cm-D balls, sixty	4.0	610	33	Unacceptable	>1000	
	Full L, 1.27-cm-D, three	2.0	620	23	Good	300	
	Full L, 1.91-cm-D, one	2.0	630	27	Poor	500	Discharge rate 0 at end
	Short L, 1.27-cm-D, three	2.0	640	29	Very good	450	
		2.0	570	30	Adequate	400	
Full 0.16 × 1.27 × 60. cm	Full L, 1.27-cm-D, three	1.3	580	32	Very good	250	
		2.0	580	31	Excellent	200	
Full 0.3 × 3 × 80. cm	Full L, 1.27-cm-D, three	0.8	630±30 ^a	19	Very poor	550	
		1.2	610±25 ^a	18	Poor	500	
		2.0	580±30 ^a	20	Good	500	8.5 h U feed
	Short L, 1.94-cm-D, two	0	490	42	Poor		Scraper weld broke
		1.3	590	39	Very good	700	
		2.0	730	41	Excellent	250	
		2.0	650	35	Excellent	200	
		2.0	590	34	Excellent	150	
		2.0	530	37	Excellent	200	
		3.0	590	40	Excellent	200	
		2.0	660	44	Excellent	200	U/Th = 3.0
		2.0	580	36	Excellent	200	U/Th = 3.0
		2.0	590	43	Excellent	150	U/Ce = 3.0
		3.0	590	46	Adequate	250	U, Th slurry feed, ADU type precipitate, U/Th = 3.0
		3.5	600	47	Adequate	250	

^a Temperature cycle imposed to give fluctuating solids discharge.

520°C. Breaker bars appear necessary to assure good heat transfer to the solids. The product discharge results are summarized in Table 10.

5.4 Results from the Off-Gas System

The feed and off-gas system were installed to allow practical operation of the ORNL rotary kiln with depleted uranium and were not intended to meet the requirements for plutonium or for a pilot plant. The test kiln system had two important limitations on operating conditions. The control of vapor flow through the open tube ends required a large air flow, which limited the average holdup times in the off-gas system and resulted in high scrubber gas/liquid flow ratios. The radioactive off-gas system has a limited vacuum, requiring low pressure drops through the scrubber.

The off-gases were exhausted through a packed scrubber column, then through the tubes of a water-cooled, shell-and-tube heat exchanger (Fig. 6). Condensate was collected in a 15-cm-I.D. tank, with discharge of gases through a rotameter to a radioactive off-gas system. A limited range of gas flow was used, since excessive flows caused trapping of feed solution in the 1.8-cm-I.D. line between the scrubber and rotary kiln and low flows allowed fume losses from the open ends of the kiln.

Uranium concentration in the condensate was reduced from ~ 25 g/L with no scrubber to less than 1 g/L for about 12-cm of coarse (5/8-in. Pall ring) packing. Lower values should be obtained from use of more efficient scrubbers.

The condensate concentration of NH_4^+ depended on the NH_4^+/U mole ratio in the feed and on the tube temperature (Table 11). This concentration could probably be reduced by more efficient scrubbing, but lower concentrations would be unnecessary if the condensate is neutralized with ammonia and recycled as proposed in Sect. 6.

The acid content in the condensate was 30 to 60% of the metal nitrate and HNO_3 concentrations of the feed. This is distinctly different from the batch material balance tests (Sect. 4.4), where the values were near 100%. The continuous kiln seems to give more NO and also more complete decomposition to N_2 and O_2 . Water material balances were calculated for a few runs and were $98 \pm 4\%$, assuming saturated off-gas without entrainment of liquid H_2O .

Table 11. Rotary kiln run conditions and some effluent analyses

Feed concentrations		Scrubber packed length (cm)	Tube temperature (°C)	ROT test No.	Condensate concentrations			Solid product Fe ^a (ppm)
NH ₄ ⁺ /U (mole/mole)	NO ₃ ⁻ /U (mole/mole)				NH ₄ ⁺ (ppm)	U (ppm)	H ⁺ (mole/mole U)	
0	2.0	0	570	7		25,000	0.44	
0	2.0	12	500	14	16	532	1.10	408
0	2.1	50	490	42	40	478	1.84	93
0.8	2.0	12	390	19	23	1,240	0.86	
1.1	2.0	0	580	6		23,200	0.18	
1.2	2.0	12	420	18	163	1,590	0.82	
1.3	2.1	50	440	39	750	1,670	0.88	
2.0	1.65	50	490	26			0.51	126
2.0	2.0	0	570	5	370	26,200	0.30	
2.0	2.0	12	380	13	3,344	689	1.00	130
2.0	2.0	12	440	21	2,810	796	1.08	129
2.0	2.0	12	530	12	1,342	567	0.90	88
2.0	2.1	50	390	37	4,389	974	1.21	
2.0	2.1	50	450	34	2,540	832	1.10	149
2.0	2.1	50	500	35	1,569	1,150	1.10	141
2.0	2.1	50	620	41	2,210	1,610	0.96	92
2.0	3.0	50	490	24	4,380	935	1.79	190
2.0	3.0	50	560	25	3,470	862	1.49	211
3.0	2.1	50	450	40	9,840	932	1.26	85

^aFe in UO₂(NO₃)₂ feed solution is equivalent to 150 ppm Fe in products.

The off-gas system holdup time and conditions do not allow much reoxidation of NO to NO₂. The requirements for such off-gases have been studied elsewhere,^{17,18} but results for a kiln with seals and a low in-leakage of air would be different. While our test kiln results do not represent pilot plant conditions, no additional experimental information is needed for pilot plant design.

The gas flow from the condensate tank to the radioactive off-gas system was sampled in two ways. Analyses on a volume basis averaged 1.71% N₂O, 19.62% Ar + O₂ and 78.83% N₂. This off-gas is ~ 90 vol % purge air, and the N₂O concentration agrees with batch material balance results. Gas flow through paper filters showed very low particulate losses of uranium and NH₄⁺; the alpha radioactivity on the filters after 20 and 60 min of flow was not measurable. Chemical analyses and estimated flow volumes indicated losses of less than 10⁻²% U and 0.1% NH₄⁺ based on the kiln feed. The demonstration runs (Sect. 5.2) with a more efficient scrubber showed 10 ppm U and 100 ppm NH₄⁺ in the condensate samples. These are 0.1 to 0.01 of the concentrations found for the ORNL rotary kiln condensate.

5.5 Mechanical Operation, Corrosion, and Capacity

Mechanical operation (other than the solids discharge behavior discussed in Sect. 5.2) and corrosion results for the rotary kiln system have been surprisingly good. The system was designed for ease of fabrication, using store-stock items or surplus components. The only significant mechanical changes from the original design were variations in breaker bars, scrapers, and retainer rings to modify the solids discharge performance.

For the UO₂(NO₃)₂-NH₄NO₃ feed solution, the product UO₃ shows the same iron content (90 to 150 ppm) as the UO₂(NO₃)₂ feed solutions or as UO₃ from denitrations of the same solution in glassware. For 1.7 M excess HNO₃, or for no NH₄NO₃ in the feed, the Fe content of product UO₃ was 200 to 400 ppm (Table 8).

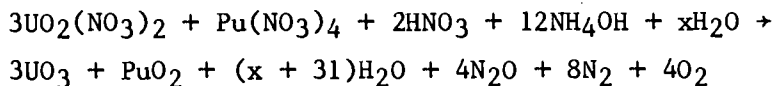
The low-torque drive motor was selected for mechanical safety, but it stalled during only three runs with a scraper in the tube and NH₄⁺/U mole ratios <2 in the feed. The motor is a Cole-Parmer Co., No. 4555G, gear motor rated for 5 in.-lbs torque at 0-150 rpm. The sprockets give a 3.3 torque multiplication. The most common tube rotation has been 16 rpm. A heavier gear motor was used for ROT-49 and later tests.

A run was made to determine the maximum capacity of the 8-cm-ID test kiln (90-cm total length, 30-cm heated length). The capacity is limited by the furnace, which is rated as 2500 W at 230 V and is estimated to operate at 2000 W. For a feed solution of $2.03 \text{ M } \text{UO}_2(\text{NO}_3)_2$ - $4.1 \text{ M } \text{NH}_4\text{NO}_3$, the capacity limits are 800 g/h UO_3 at 475°C tube temperature and 760 g/h UO_3 for a 525°C tube temperature. Operation was good at both temperatures, and this diameter tube could probably operate at much higher capacities by using a longer heated length and a larger furnace. A recommended design capacity from these results and from the demonstration runs in the 16-cm-diam kiln is $0.03 \text{ cm}^3/\text{min}$ of feed solution per cm^2 of heated kiln wall. The breaker bars are necessary to provide good heat transfer to the solids.

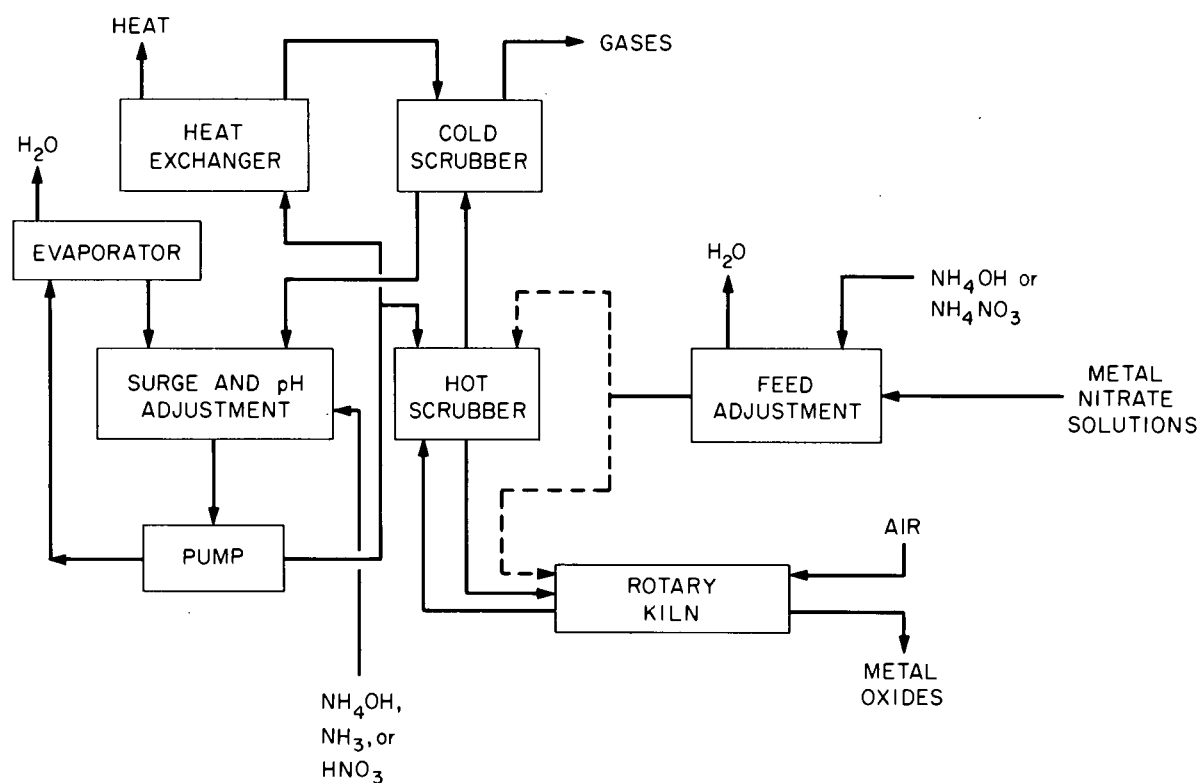
6. WASTE HANDLING AND PROPOSED FLOWSHEET CONDITIONS

The off-gases from the denitration will be similar to and compatible with those from other reprocessing plant operations such as the dissolvers. Use of the feed for a liquid-gas scrubber can provide excellent removal of particulate solids and return them to the denitrator. The technology for treatment and recovery of the nitrogen oxides has been well developed for reprocessing plants,^{17,18} but the negligible concentrations of radioactive iodine and other fission products in the denitration off-gases simplifies treatments.

Although concentrated HNO_3 could be recovered for use elsewhere, it is more practical to neutralize it with ammonia and thus produce the NH_4NO_3 required. If this were done, the HNO_3 flow would be zero and the only waste streams would be noncondensable gases and water from the evaporator (Fig. 15). The cold scrubber system would include the necessary holdup and treatments for NO_x oxidation or reduction. The net overall reaction would be:



Operations needed to separate the solid, H_2O , and noncondensable gaseous products are well developed and easily applied. Since the surge liquid would be neutralized and HNO_3 concentrations moderate, corrosion problems for waste handling should be mild.



HOT SCRUBBER RETURNS METALS AND NH_4^+ TO KILN

COLD SCRUBBER REMOVES NO_x FOR $x \geq 1$ (NOT N_2O)

EXCESS HEAT REMOVED FROM SCRUB LIQUID

NH_4^+ ADDED TO FEED ADJUSTMENT AND/OR FOR SURGE TANK pH ADJUSTMENT

Fig. 15. Proposed schematic flowsheet for codenitration.

7. RESULTS AND CONCLUSIONS

Development studies made without plutonium were directed toward use of rotary kilns for codenitration of U-Pu nitrates. Direct denitration and use of rotary kilns are the recommended selections from an evaluation of coconversion alternatives.¹ Chemical and equipment flowsheet variables were studied for preparation of uranium oxides and mixed oxides (excluding plutonium).

The ceramic properties of the product oxides were greatly improved by modification of the chemical flowsheet conditions. Small-scale, batch thermal decompositions showed that presence of NH_4NO_3 in the feed gave large, favorable changes in the solid product properties compared to those from $\text{UO}_2(\text{NO}_3)_2$ solutions without NH_4NO_3 . Based on these scouting tests, batch and continuous denitration studies were made with the concentration of NH_4NO_3 in the feed as a major process variable.

The principal criteria for the ceramic properties of product oxides are the density and microstructure of oxide pellets fabricated by a standard "sinterability test" procedure. For UO_3 from either the batch or the continuous tests, the usual denitration conditions gave sintered densities of 68 to 70% of theoretical and poor microstructures. The modified conditions, with NH_4NO_3 in the feed, consistently gave 92 or 93% of theoretical density and good microstructures. The B.E.T. surface areas for continuous denitrations were 0.7 to 1.6 m^2/g without, and 8 to 12 m^2/g with, the NH_4NO_3 in the feed. Large improvements in pellet densities and more favorable B.E.T. surface areas were also seen for uranium-thorium oxides with a mole ratio of $\text{U}/\text{Th} = 3$ when NH_4NO_3 is in the $\text{UO}_2(\text{NO}_3)_2\text{-Th}(\text{NO}_3)_4$ feed solution. Particle size distributions for UO_3 , UO_2 , or mixed oxides with NH_4^+ / metal mole ratios of two in the feed show >99% of particles are smaller than 12 μm with mean diameters of 2.5 to 3.6 μm (weight basis).

The favorable effect of the NH_4NO_3 is believed to result from decomposition of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ as a solid, whereas the $\text{UO}_2(\text{NO}_3)_2$ (without NH_4NO_3) decomposes as a molten salt. Results from thermal analyses (TGA, DTA) of a $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ mixture are not the same as a combination of results from analyses of the two separate salts. Visual observations of thermal decomposition behavior also show these differences. Batch material balance runs

indicate that the NH_4NO_3 decomposes completely to N_2 , O_2 , N_2O , and H_2O , while the metal nitrates yield higher oxides of nitrogen.

Some other favorable results of test kiln operations decrease the significance of possible problems. For example, with $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ feed solutions, the product UO_3 had the same iron content (90 to 150 ppm) as the feed solution, whereas with excess acid or no NH_4NO_3 in the feed, the UO_3 product iron content was 200 to 400 ppm. Also, with an off-gas scrubber using a short length of coarse packing to contact the feed solution and the off-gas, the condensate contained less than 0.1% of the uranium and less than 1% of the NH_4^+ present in the feed. A simple, integrated process flowsheet would neutralize the condensate with NH_3 and concentrate it to supply NH_4NO_3 to the kiln. The only process wastes would then be the H_2O removed during the condensate concentration and the O_2 , N_2 , N_2O , and unrecovered NO in the off-gases.

A rotary kiln test unit of 8-cm-ID and 90-cm length was designed, fabricated, and operated for more than fifty test runs to prepare UO_3 or mixed oxides. The amount of NH_4NO_3 in the feed is the controlling variable for the ceramic properties of the UO_3 product. Most tests were made with $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ solutions having mole ratios of $\text{NH}_4/\text{U} = 2$. Equally favorable results were obtained for NH_4/U mole ratios as low as 1.2 mole/mole, but ratios less than 1.2 gave variable results. The temperatures inside the kiln (350 to 620°C) greatly affected NO_3^- content or the loss on ignition (LOI) to 900°C for the solid products, but did not affect the ceramic properties after calcination and reduction to UO_2 at 600°C.

Steady-state discharge of solids from the rotary kiln was demonstrated for a majority of the test runs. The solution feeds containing NH_4NO_3 give soft oxides of lower densities that discharge easily. The $\text{UO}_2(\text{NO}_3)_2$ solutions without NH_4NO_3 and the slurry feeds form hard cakes; they would require a rugged mechanical scraper to assure dependable discharge of UO_3 solids.

Demonstration test runs in a 16-cm-diam rotary kiln at the NLO uranium feed materials plant show good agreement with ORNL kiln runs at similar conditions. At our modified flowsheet conditions and kiln temperatures of 605 or 460°C, the B.E.T. surface areas are 7.23 and 6.30 m^2/g , respectively, with test pellet densities of 93.0 and 93.5% of theoretical density. For unmodified conditions at 750, 605, and 445°C, the B.E.T. surface areas

are 0.70 to 1.46 m²/g and the test pellets are 68% of theoretical density. The modified flowsheet gave better mechanical operation and lower concentrations of iron in the product oxides (less corrosion).

Studies of the improved denitration process are continuing with development of optimum pellet fabrication procedures and operation of a rotary kiln in a glove box to prepare (U-Pu)O₂.

8. ACKNOWLEDGEMENTS

The experimental work in the Chemical Technology Division was done with the assistance of D. F. Peishel and C. L. Stephenson. Thermal analyses were done by D. A. Lee of the Analytical Chemistry Division. Program supervision and coordination were by A. D. Ryon, R. E. Norman, and D. J. Crouse. K. J. Notz supplied helpful unpublished data and advice.

Demonstration tests at the National Lead of Ohio plant were supervised by M. G. Mendel. Information on rotary kiln operation at uranium feed materials plants was collected with the assistance of F. E. Harrington and T. M. Scott.

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APPENDIX

Kiln Assembly Details

The rotary kiln furnace is mounted on a stand fabricated from aluminum plate and an adjustable unistrut frame (Figs. 5 and 6). The rotating tube is supported by two pairs of steel-wheel roller skates bolted to the adjustable frame. All connections to the kiln are flexible and the angle of the tube to the horizontal is adjusted by shims between the stand and the floor. The thermocouples inside the tube, the feed nozzle, and the scraper bar are fixed to the frame and supported by adjustable brackets at the open ends of the tube. At the high or liquid feed end of the kiln tube, a washer of 2.54-cm ID is seal-welded inside the tube, 7.6 cm from the open end. The stationary feed tube is usually positioned to discharge liquid feed 2.5 cm inside this washer or dam. The breaker-bars are retained by a dam with holes or slots for solids discharge 15 cm from the lower end of the tube. Initially, this dam was locked to the tube with set screws and rotated with the tube. When a full length scraper bar was installed, this retainer was made a part of the stationary scraper bar assembly with ~0.3-cm clearance to the tube wall. The rotating tube is positioned axially by an external ring which rides between the wheels of one pair of roller skates. The drive sprocket is welded to a ring of 3.5-in. sched. 40 pipe which slips over the tube and is locked with set screws. The drive motor is mounted on the stand.

The scrubber packing is supported by a coarse grid inside 5-cm-ID Pyrex pipe. The condenser is a shell and tube heat exchange (0.4 m^2) with cooling water on the shell side. The gas flow rate to a radioactive off-gas system is indicated by a rotameter. This measurement has poor accuracy as a result of liquid collecting in the rotameter and "bounce" or rapid variations of the float position. Condensate is collected in Pyrex pipe, 15-cm-ID by 60 cm in length.

The feed is pumped by a variable-speed peristaltic tubing pump, and discharges through 0.25-in.-OD tubing into the scrubber packing. The feed rate is limited by the heat rating of the furnace to about $15 \text{ cm}^3/\text{min}$, depending on the furnace temperature for water feed or $\text{UO}_2(\text{NO}_3)_2$ solution

feed. For $\text{UO}_2(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3$ solution, the NH_4NO_3 decomposes exothermically to produce gases; feed rates up to $23 \text{ cm}^3/\text{min}$ were used without difficulty.

The heat input to the rotary kiln was controlled by one of three procedures. Control from the thermocouple inside the tube to an on-off controller for the furnace gave significant temperature cycles of 20 to 50°C because of the lag between the furnace temperature and the tube temperature. Manual adjustment of a variac in the furnace power supply completely eliminated cycling effects but allowed slow drifts in temperature depending on gas flow rates, solids coating inside the tube, and other factors. Control from a thermocouple located between the furnace elements and the tube provided excellent control of the furnace temperature, but a variable difference between the temperatures of the furnace and the tube thermocouple. This last procedure was most commonly used with adjustments of the set point to change the tube temperatures. Thermal reflector washers were locked to the rotating tube, one at each end of the furnace, to reduce the heat losses (Fig. 5). The temperature difference between the furnace and the tube was sensitive to the spacing between those rotating washers and the stationary furnace end, and the gap varied from light contact to $\sim 0.3 \text{ mm}$, depending on the thermal expansion of the tube. The initial aluminum thermal reflector discs were held with set screws, and the differences in thermal expansion allowed them to loosen and move on the tube during temperature changes. The design shown in the kiln description, with stainless steel discs and bolts, remained in position much better.

Edited Trip Report on Rotary Kilns (March 4, 1980)

TO: Distribution

FROM: F. E. Harrington and P. A. Haas

SUBJECT: Trip Report: Visit to Goodyear (Portsmouth, Ohio) and
National Lead Co. of Ohio (Fernald, Ohio) to Discuss Rotary
Calciner Denitrations

A rotary kiln type of continuous denitration equipment is proposed for conversion of uranyl nitrate-plutonium nitrate solutions to (U,Pu)O₂ oxides for pellet preparation. This selection of equipment type is based on the routine use of such units for uranium at four DOE plants. The procedures used and the experiences differ greatly and the information has not been published. This trip was made to obtain information from two of these sites. The attached list "Questions Concerning Rotary Kiln Denitrator Operation" was reviewed at both sites. Some information from an earlier discussion at the ORGDP with N. G. McRea (574-9009) is also mentioned.

(1) Goodyear Atomic Corporation--2/27/80--Portsmouth

The purpose of the visit was to obtain first-hand information on their rotary kiln calciner operations. We met with John Vournazos (FTS 975-4444), Carl Worthington (975-4445), and Walter Miller (area foreman). The plant has three old, gas-fired units in the Recovery Area and one electric unit in the UF₆ section (feed is UNH). At the time of our visit, no units were in operation and the Recovery Area apparently has not operated much recently. (At the ORGDP, only scrap of $\geq 2\%$ ²³⁵U is worth recovering, and this probably also applies at Portsmouth.)

The major points evolving from the discussion and tour were:

1. The metal-metal grease seal is adequate.
2. Maintenance of chain drive (undersized) and instrumentation is a major problem.
3. The tube is ultrasonically inspected for any thinning; tube life has been ~5 years.
4. The 16-cm-ID tube is considered safe for highest enrichment (>90%) because of the rods in the tube, the overflow at the air inlet on the product end, and the limited volume of the feed tank. The tube cannot be filled with solution.

5. Reducing the kiln temperature causes caking or formation of a "doughnut" of gummy material, but quantitative information on temperature limitations was not available.
6. All the units operate as rod mills with stainless steel rods (four, 3/4 in. diam) and about 1/2 in./ft slope. The electric unit has ~3 in. slope in 7-1/2 foot length.
7. There has been no experience with use of the product for pellet preparation, with other denitration equipment, or with operation of the rotary kiln to prepare UO_3 .
8. The production rate is 10 kg/(shift), and the only product is U_3O_8 .
9. They consistently prepare a fine U_3O_8 powder using round 1.9-cm-diam stainless steel rods in the kilns and high ($>1600^\circ F$) furnace temperatures.
10. The only product compositions of concern to them are the isotopic and the residual NO_3^- and H_2O in the U_3O_8 . They have a scrubber operated hot with Raschig ring packing. Brown fumes are present in the off-gases leaving the scrubber, but they have no information on off-gas compositions or scrubber liquid composition.
11. Analysis of the product, particularly for iron, will be obtained from John Murrel (975-2182) and forwarded to us (by Carl Worthington).
12. When assays are changed, the unit is run until all loose powder is in the product can.
13. The three gas-fired units will be replaced by two electric units in the coming year.
14. Specifications and costs for new electric rotary kilns will be obtained from Steve Wethington (975-2842) and forwarded to us.
15. Questions 15 to 21 on demonstration runs were not discussed at Portsmouth as we did not expect to request demonstration runs from them. They did not offer any comments.

The Goodyear area is similar to the Recovery Area at K-25. The Bartlett Snow Kilns were identical to those at K-25 when purchased but operations have evolved differently, with Goodyear feeding uranyl nitrate solution to the kiln and K-25 inserting a drum dryer before the kiln for feed of solids by a screw feeder.

(2) National Lead of Ohio (NLO)--2/28/80--Fernald, Ohio

We met with M. G. Mendel (FTS 774-8735), Carl Polson, and Frank Neblett and toured the facility. It is currently processing UNH solution from the Savannah River Plant. The as-received feed is partially neutralized and then concentrated to ~700 gU/L in a wiped-film evaporator (called a Turbo-film at NLO) with ~1 ft² heat transfer surface using 150 psi steam. The calciner was in operation producing ~5.5 lb U (as U₃O₈)/h — as high as 10 lbs/h have been achieved — the limit is the "turbo-film" evaporator capacity. The partial neutralization is performed batchwise by addition of anhydrous NH₃ to recirculating UNH at the pump suction until pH = 2. The pH is measured by a standard in-line electrode of the type we used for the resin loading system.

The electrically heated rotary kiln was operating with 1750°F temperature at the heating element and 1650°F for the atmosphere inside the kiln. The NH₃ addition results in the elimination of the "dough" stage although the original use was to reduce chromium in the product. The feed solution passes through a packed scrubber column, countercurrent to the off-gas. The kiln contains a lawn-mower reel type scraper and is served by a cam-operated knocker on each end. The inlet metal-metal seals are backed up by teflon bellows through which the feed line enters the kiln. The scraper shaft-seals are of a type used for centrifugal pump shafts.

The major points evolving from the discussion and tour were:

1. Seals are not an important problem.
2. The scraper requires replacement every two months.
3. Heating element failure is their major maintenance problem.
Bearings on the turbo-film evaporator require periodic replacement, and the blower used for off-gas flow requires maintenance.
4. The bulls-eyes at both bottom of the scrubber and at the discharge end of the kiln are very helpful in checking satisfactory operation.
5. The NH₃ addition is the most important procedure for elimination of caking. The NH₃ addition and use of the scraper began at the same time. The knockers were added slightly later as scheduled, but were not needed after the NH₃ addition and scraper were used.
6. Current operation is reliable, producing low-chromium product containing ~0.25% H₂O and <0.1% NO₃⁻.

7. They have not prepared any products other than U_3O_8 for storage or conversion to UF_6 .
8. The product is mostly fine; the few small lumps are soft and easily broken up (density 1.1 to 1.2).
9. Run-out at the end of a batch includes a water wash-through of the turbo-film evaporator into the calciner.
10. Product concentrations other than H_2O and NO_3^- are not determined.
11. Special checks have revealed no NH_3 (or NH_4NO_3) in off-gas (after the scrubber).
12. There is essentially no uranium loss in overheads.
13. The nitrate decomposition products and the off-gas composition are not known, other than the absence of NH_3 or NH_4NO_3 .

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