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PILOT-PLANT PREPARATION BY FLAME PROCESSES
OF 1-MICRON SPHERICAL THORIA PARTICLES
FOR HOMOGENEOUS REACTOR SLURRIES

C. C. Haws, Jr.
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OAK RIDGE NATIONAL LABORATORY
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UNION CARBIDE CORPORATION
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CHEMICAL TECHNOLOGY DIVISION

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Date Issued

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ABSTRACT

Spheroidal thoria and thoria-urania particles of about 1 μ average diameter were prepared in a one-step process by flame decomposition from thorium nitrate and from mixtures of thorium and uranium nitrates.

Aluminum nitrate (equivalent to 0.5 to 10 wt % alumina) was included with both systems to obtain spheroidization. A reflected oxygen-hydrocarbon flame was used and particle temperatures above 2000°C were necessary.

In aqueous slurries of density 2.0, at conditions planned for nuclear reactor blankets, these particles consistently gave low values for yield stress (about 0.02 lb/ft²), modulus of rigidity (less than 3.0 centipoise), and corrosion (type 347 stainless steel; less than 1 mil/year in standard pump-loop test). Particle degradation in long-term pumping tests was negligible. Attempts to raise the average particle diameter to above 5 μ were only partially successful. Alumina-free spheroidal thoria particles were prepared using thoria sol feeds, but these materials were not satisfactory.

Most experimental runs were made in 4-in.-ID reflectors with feed rates of 0.5 kg of thorium per hour; rates of up to 1.5 kg of thorium per hour were used, and product samples weighing up to 31 kg were collected. The operating procedures developed would permit operation on a production scale, but the normal 40% yield would require recycle of the 60% of coarse, agglomerated oxides.

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1. INTRODUCTION

A process for preparing the "ideal" slurry for use in homogeneous reactors is described. Spheroidal particles of either thorium or thorium-uranium oxides can be prepared by this method. The one step process consists in spraying solutions of thorium nitrate, or thorium and uranium nitrates where desired, into a high-temperature reflected flame. Aluminum nitrate was added to lower the melting point of either system sufficiently to allow melting of the oxides in the flame. The process was developed according to principles, and small quantities (about 300 g) were prepared for analytical evaluation. A single large batch (31 kg) was prepared for testing in engineering-scale equipment.

The breeding of U^{233} from thorium was an important long-range goal of the thermal breeder, or homogeneous reactor, program. A thoria slurry (1000 g per kilogram of D_2O) was to be pumped through the blanket region of the reactor for this demonstration. Nuclear requirements and this high slurry density demanded a slurry of exceptional properties. A thoria slurry composed of spheroidal particles about $1\ \mu$ in diameter, possessing hard, polished surfaces should offer the exceptional properties needed. It was postulated that such particles could be obtained by suspending discrete thoria particles in a very high-temperature flame, thereby fire polishing them.

1.1 Historical Account of the Production of Slurry Particles

Classical slurry development work has been based upon controlled precipitation, followed by tray firing.^{1,2} Thoria slurries produced by this method were satisfactory for reactor-component testing, and several

tons of such material were prepared. These materials, however, were still not ideal because of their basic particle shape (a platelet) and a high yield stress that resulted primarily from the shape. Attempts were made to produce a "mixed oxide" slurry, that is, a slurry in which the particles contain both thorium and uranium oxides. These slurries were prepared by sorbing uranium onto the surface of a conventional thoria slurry and then tray firing the resulting powder. Such mixed oxide slurries were unsatisfactory.

There was other past and contemporary work of interest to the flame studies. Some of this work was directed toward the production of a slurry for reactor applications, while other work simply sought conversion of thorium and/or uranium salts from one form to another by flame treatment.

The first attempt to produce a slurry for reactor use by the flame decomposition of thorium and uranium nitrates was made by Hansen and Minturn.³ The particles obtained from this test were small, ranging from a few tenths of a micron down to about 60 mμ in diameter, and the temperature attained by the particles was far below that desired in the present flame work. An electron-micrograph showed that both fragmentary and spheroidal particles were obtained in these tests, but it is suspected that the spheroidal particles obtained were the "bubbles" frequently encountered in spray-drier operations. These bubbles are mechanically weak and incompletely denitrated. A later evaluation of the slurry properties of the material collected from this firing showed that the material agglomerated.⁴

The flame conversion of thorium, or uranium, from one chemical form to another has been practiced in certain operations for a number of years.

One of the earliest to be applied was the burning of uranium hexafluoride with gaseous hydrogen to form uranium tetrafluoride. Two units were constructed to flame decompose kilogram quantities of uranyl nitrate to uranium oxides. These operations showed that the degree of oxidation could be controlled by regulating the amount of air supplied to the flame and that a flame process could be operated without significant material losses.^{5,6}

In another interesting approach to the problem, the Houdry Process Corporation passed an aqueous thoria sol through a fine capillary into an organic medium.⁷ The sol beads, dehydrated by the organic liquid, were collected, dried, and calcined. The yield of beads of less than 10 μ size was extremely low, and repeated attempts to increase the yield of smaller beads were unsuccessful. Another sol approach, examined briefly by Kleinstaub and Pearson, yielded frangible beads that disintegrated under simulated reactor pumping conditions.^{8,9}

1.2 Purpose of Present Work

The first objective of the work was to investigate the hypothesis that spheroidal particles of thoria, or thoria-urania, could be prepared in high-temperature reflected flames. A second objective was the preparation of a sufficient quantity of material (more than 25 kg) to permit dynamic out-of-pile testing. Continuous operation for periods up to 24 hr and a closed material balance were also to be demonstrated. These objectives were met and problems expected for any future scaling up of operations were defined. An economic study of the process in the present or in larger-scale operations was never intended.

The circulating-blanket-slurry concept of the aqueous homogeneous reactor has been abandoned. There is, therefore, no justification for continuing this work with present objectives. Should future applications arise for a powder prepared as described here, operations can easily be resumed from the present developmental state.

1.3 Acknowledgments

The authors acknowledge the assistance of Mr. T. E. Willmarth, who provided the many photomicrographs needed in this study. Much of the work was done by Mr. V. L. Fowler, and many useful suggestions were offered by Messrs. W. E. Unger and K. O. Johnsson. Engineering tests of the products were made by Mr. S. A. Reed and co-workers of the Reactor Division.

2. DESCRIPTION OF THE PROCESS AND EQUIPMENT

2.1 Basis of the Process

In the flame calcination process, 1- to 3- μ -diam spherical particles of thorium oxide, or thorium-uranium oxides, are prepared by aspirating solutions of thermally decomposable salts of these metals into a high-temperature reflected flame. The exhaust gases are cooled and the product (spherical particles) collected in a spray cooler placed in series with the combustion chamber. The equipment used in the flame denitration portion of this work is shown in Figs. 1 and 2.

2.2 Feed Materials and Feeding Equipment

Methanol was the most commonly used solvent for the TNT (thorium nitrate tetrahydrate) or TNT-UNH (uranyl nitrate hexahydrate) feed solutions, although water was found satisfactory in the latter part of the

study. Aluminum nitrate nanohydrate (ANN) was added to all feed solutions to obtain spheroidization at available flame temperatures. Use of BeO and SiO₂ as a substitute for alumina was tested in scouting experiments. The BeO was added as Be(NO₃)₂ and the SiO₂ as tetraethyl orthosilicate. While high concentrations of TNT (600 g/liter in methanol or 1200 g/liter in water) could be used, values roughly one-half these were used for easier pumping (see Appendix, Tables A2 and A3). The solutions were fed to the burner by means of a Hills-McCannameter pump. The feed rate was determined from changes in the level of the solution in a Pyrex pipe (2-in. or 4-in. diam) used as a feed tank.

Dry thoria powders and thoria slurried in methanol were also used as feed materials in early attempts to obtain fire polished particles. In these tests in which a dry powder feed was used, the powders were suspended in one of the burner gases and carried by the gas into the flame. The slurries were prepared by placing the thoria powder in methanol (0.003 M in oxalic acid) and stirring for several hours. The slurry was then fed to the burner by means of a centrifugal pump.

Burner gases used were oxygen-acetylene and oxygen-propane. The former was used in all the dry-powder and thoria-slurry feed experiments. The latter was the system used in most of the nitrate feed runs. Rotameters operating at constant pressure metered the mixed gases into the apparatus.

2.3 Burner-Reflector Assemblies

The burner used for feeding the methanol-thoria slurry is shown in Fig. 3. The burner vaporized the methanol and preheated the feed stream to about 200°C for injection into the flame. The reflector used for this

Fig. 1. Flame Denitration Equipment.

Fig. 2. Flame Denitration Experimental Equipment Using a Vertical Reflector.

Fig. 3. Torch for Feeding Thoria Slurries.

work was similar to the reflector described below except that its length was 9 in. and the bore was 2 in.

The aspirating burners used for most of this work are shown in Fig. 4. In both these designs the feed solution enters the combustion chamber through the central needle-orifice. Combustion gases enter through the annular area outside the needle to drive the aspirator. The design shown in Fig. 4b represents an improved design in that aspirator and peripheral burner gas flows can be independently controlled. Thus, the aspirator gases can be regulated to obtain proper atomization, while temperature is controlled by the peripheral orifices. Separate gas metering-mixing systems were provided for each set of orifices. A further advantage of the second design was the virtual elimination by the peripheral jets of deposits of solids on the inner walls of the reflector.

The 24-in.-long reflector tube was assembled from two 12-in.-long tubes of dense, stabilized zirconium oxide (Fig. 5). The inner diameter of the tubes was 4 in., and the outer diameter was 6 in. Insulation consisted of one course of insulating grade, No. 3 standard arch brick. Stabilized zirconia mortar was used in setting the brick, and the outside of the brick was heavily plastered with common magnesia mortar. Several layers of aluminum foil were wrapped around the furnace exterior and tied in place with wire. The configuration of this reflector is admittedly not the optimum indicated by the calculations later discussed, a more desirable length being 4 ft. The configuration used was dictated by the necessity of carrying out operations within a standard 6-ft laboratory fume hood (Fig. 2).

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Fig. 4. Burners Used with Methanol-Nitrate Feed Solutions.

Fig. 5. Reflector Design.

The base plate upon which the reflector rested, and the cover plate which supported the burners, required water cooling. Three thermocouples (Pt vs Pt-10% Rh) were placed in contact with the outer wall of the zirconia reflector tube, and a single sighting port was cut through the wall into the combustion chamber in order to accomodate an optical pyrometer. The entire reflector assembly was mounted on rollers that operated on rails which guided the assembly so that it could be moved into and out of position over the inlet to the product collection system. This movement was necessary to permit periodic cleaning of the product collection system.

2.4 The Product-Collection System

The product collection system consisted of a spray cooler and a domestic vacuum cleaner (Fig. 1). The latter provided the necessary downdraft for the reflector and the spray chamber. In cooling the reflector exhaust gases, the spray chamber collected about 90% of the entering suspended particles. The sharp turn in the line entering the spray cooler permitted smaller (hence, desirable) particles to pass through, but forced the larger particles to fall into the agglomerate trap. Classification of the product to obtain the desired size range was therefore not necessary. A cyclone was mounted on the exhaust of the spray tower to remove entrained water droplets. Room air was admitted to the inlet of the cyclone to prevent condensation of water as the gases passed through the remainder of the system. Air sampling (Millipore) filters were mounted at the inlet and exit of the vacuum cleaner for collecting samples of any particles reaching these points. Rotameters were placed in series with these filters so that the dust loadings of gases entering and leaving the vacuum cleaner could be calculated. A

1/2-in.-thick boiler-plate box, open at the rear, was built around the vacuum cleaner in case unburned exhaust gases exploded inside the cleaner. The gases leaving the vacuum cleaner were filtered through a conventional Chemical Warfare Service hot-gas disposal system.

3. THEORETICAL CONSIDERATIONS

3.1 Operating-Temperature Requirements

A thoria temperature of at least 1500°C appears necessary in the preparation of thoria particles if the product is to be suitable for slurry use in a homogeneous reactor. The heat required to convert droplets of thorium nitrate solution to satisfactory thoria particles is the sum of the heats of solvent evaporation and denitration and the sensible heat required to raise the resultant thoria particles and gaseous by-products to the final desired temperature. Calculations indicated that reflectors operating at more than 1500°C and times of 0.01 to 0.06 sec would be required for sufficient heat to be transferred to a 10- to 100-μ-diam droplet in order to convert the TNT to thoria of the desired properties. Calculations of particle temperatures vs time indicated that the process rate is controlled by the rate of transfer of radiant heat from the walls of the reaction vessel, through the gas of the flame, to the particle surface rather than by the rate of conductive heat transfer from the surface to the center of the particle. Most of the heat added is used to evaporate the solvent. Since the large volume (and surface) and the high heat absorptivity of the solutions, compared with those of the particles, result in high heat transfer rates in terms of unit amounts of thoria produced, the times for solvent evaporation and for raising the temperature to 1500°C are of about the same magnitude.

The exactness of the results given here is limited by uncertainties in operating conditions and by the incomplete knowledge of the thermal properties of thorium oxide at high temperatures. Therefore, the calculations were made by simplified methods, which indicate ranges rather than exact values.

3.2 Equilibrium Temperatures of the Particles

The particles exchange radiant energy with H_2O , CO_2 , and CO in the gas and with the reflector wall or surroundings. At an equilibrium temperature, the net amount of heat transfer will be zero. A system adequate for estimating the relative importance of the gas and particle temperatures is a particle in the center of a spherical mass of radiating gas surrounded by an absorbing-radiating-reflecting wall. The emissivities, ϵ , of CO_2 and H_2O are (where P_w is the partial pressure of CO_2 and H_2O , and L is thickness of radiating gas):¹⁰

$P_w L$, ft·atm	ϵ for CO_2		ϵ for H_2O	
	1000°C	1500°C	1000°C	1500°C
0.05	0.052	0.032	0.025	0.013
0.10	0.070	0.045	0.045	0.025
0.50	0.12	0.081	0.130	0.090
2	0.18	0.13	0.26	0.18

The $P_w L$ term represents the effective blanket of radiating gas around the particle in terms of partial pressure of CO , CO_2 , and H_2O and the effective thickness. Therefore, values of ϵ_G would be 0.02 minimum if the reflector is small and 0.2 maximum if the reflector is large. At temperature equilibrium, the emissivity of the thorium will be about 0.6 and that of the reflector wall about 0.8. The gas either absorbs or transmits without reflection.

The gas radiates with an emissivity ϵ_G and absorbs black-body radiation passing through it with an absorptivity ϵ'_G , which can be assumed equal to ϵ_G . Since ϵ_G and ϵ'_G are small, the reflector wall and the thoria can be considered to be gray bodies absorbing and radiating with $\epsilon = \epsilon' = 1 - \epsilon_G$.

$$\left(\frac{q}{A}\right)_{GS} + \left(\frac{q}{A}\right)_{RS} = 0 = 1730\epsilon_G \left[\left(\frac{T_S}{1000}\right)^4 - \left(\frac{T_G}{1000}\right)^4 \right] + 1730(1 - \epsilon_G) \left[\left(\frac{T_S}{1000}\right)^4 - \left(\frac{T_R}{1000}\right)^4 \right], \quad (1)$$

$$\left(\frac{T_S}{1000}\right)^4 - \epsilon_G \left(\frac{T_G}{1000}\right)^4 - (1 - \epsilon_G) \left(\frac{T_R}{1000}\right)^4 = 0, \quad (1a)$$

$$T_S^4 = \epsilon_G T_G^4 + (1 - \epsilon_G) T_R^4, \quad (1b)$$

$$\left(\frac{T_S}{T_G}\right)^4 = \epsilon_G + (1 - \epsilon_G) \left(\frac{T_R}{T_G}\right)^4. \quad (1c)$$

These equations were used to calculate particle-vs-reflector temperatures, with the gas emissivity as a parameter (Fig. 6). The results show that a reflector at the desired calcination temperature is necessary to attain the particle temperatures desired in flame calcination. Without a reflector, the particles reach maximum temperatures of only 40 to 60% of the absolute flame temperature. This results from the low emissivity of gases compared with that of the particles at temperatures above 1500°C. That is to say, heat is lost from the particle to the surroundings more effectively than it is transmitted from the gas to the particle.

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Fig. 6. Equilibrium Temperature for ThO_2 Particles in a Flame. "Gray" ThO_2 particles and reflector. For a hydrocarbon fuel gas, $\epsilon_G = 0.02$ is a practical minimum and 0.2 is a practical maximum.

3.3 Heat Transfer Rates

The use of the spherical geometry with the origin at the particle center, results in relatively simple equations for heat conduction:

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad 0 \leq r < R, \quad (2)$$

where T = temperature,

α = is thermal diffusivity = $k/\rho c_p$,

t = time,

r = radial position in the particle,

R = radius of the particle.

Substitution of $U = Tr$ reduces the equations and boundary conditions for U and r to those for flow of heat in a slab of thickness R and surface temperatures 0 and $\phi(t)$:

$$\frac{\partial U}{\partial t} = \alpha \frac{\partial^2 U}{\partial r^2} \quad 0 \leq r < R, \quad (3)$$

where $U = 0$ when $r = 0$,

$U = R\phi(t)$ when $r = R$ and $\phi(t)$ is the surface temperature of the particle,

$U = rf(r)$ when $t = 0$ if $f(r)$ is the initial (zero time) temperature distribution.

3.3.1 Rate of Conduction within Particles

For thoria particles with diameters of 1 to 200 μ ($R = 0.5$ to 100 μ), conduction within the particles would give center temperatures within a few percent of a constant surface temperature in less than 10^{-6} sec. Times of 0.01 sec are not required until the particle diameter becomes 200 μ or larger (Fig. 7).

The times required for conduction within the oxide particles are obtained from the solutions¹¹ to Eq. 2 for constant surface temperature and zero initial temperature, the boundary conditions being $\phi(t) = T_S$, $U = R\phi(t) = RT_S$, $f(r) = 0$:

$$T = T_S + \frac{2RT_S}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} \exp \frac{-\alpha n^2 \pi^2 t}{R^2}, \quad (4)$$

$$T_r = 0 = T_S + 2T_S \sum_{n=1}^{\infty} (-1)^n \exp \frac{-\alpha n^2 \pi^2 t}{R^2}. \quad (5)$$

If the surface temperature is constant, conduction within the particle is controlling, and the change in the temperature of the center of the particle with time indicates the time required for conduction within the

particle. Equation 5 can be written

$$\left[\frac{T(t)}{T_S} \right]_{r=0} = 1 - 2 \exp \left(\frac{-\alpha \pi^2 t}{R^2} \right) + 2 \exp \left(\frac{-4\alpha \pi^2 t}{R^2} \right) - 2 \exp \left(\frac{-9\alpha \pi^2 t}{R^2} \right) + \dots \quad (6)$$

Values calculated from Eq. (6) are plotted in Fig. 7.

Fig. 7. Center Temperatures of ThO_2 Particles vs Time for a Constant Surface Temperature, T_S , $T_0 = 0$; $\alpha \pi^2 = 5 \times 10^6 \mu^2/\text{sec}$.

3.3.2 Rate of Radiation to Particle Surface

The times for heat transfer from the walls of the reactor to the surfaces of thorium particles up to 5μ in diameter are 0.001 to 0.01 sec (Fig. 8), compared with the 10^{-7} to 10^{-5} sec for heat transfer by conduction within the particle. If the particle is so small that the internal temperature gradient is negligible, the boundary conditions are

$$f(r) = T_0 = T_{t=0} ,$$

$$k \frac{\partial T}{\partial r} + h (T - T_R) = 0 \quad \text{or} \quad \frac{\partial T}{\partial r} + C(T - T_R) = 0, \quad (7)$$

where T = the temperature at zero time,

k = the thermal conductivity of the particle,

h = the heat transfer coefficient of the surface film,

$C = h/k$,

T_R = the reflector temperature.

Fig. 8. ThO_2 Particle Temperatures vs Time; Rate of Heat Transfer to Particle Surface Controlling. $C = 75 \text{ ft}^{-1}$; $\alpha = 0.5 \times 10^{-6} \text{ m}^2/\text{sec}$.

The solution of Eq. (2) which involves the roots of the transcendental equation

$$\beta R \cot \beta R + RC - 1 = 0 \quad (8)$$

is:¹¹

$$\frac{T_R - T}{T_R - T_0} = \frac{2C}{r} \sum_{n=1}^{\infty} \frac{R^2 \beta_n^2 + (RC - 1)^2}{\beta_n^2 [R\beta_n^2 + RC(RC - 1)]} \exp(-\alpha \beta_n^2 t) \sin R\beta_n \sin r\beta_n. \quad (9)$$

With $CR \ll 1$, the terms for n greater than 1 are insignificant, and $\beta_1 = (3C/R)^{0.5}$. Then $\beta_1 R$ and $\beta_1 r$ are small so that $\sin \beta_1 R \approx \beta_1 R$ and $\sin \beta_1 r \approx \beta_1 r$, and the solution reduces to

$$(T_R - T)/(T_R - T_0) = \exp(-3\alpha C t/R). \quad (10)$$

This solution implies a uniform particle temperature and is therefore a measure of the rate of heat transfer to the particle surface. If the rate of heat transfer to the particle surface is not controlling, $CR = h(R/k)$ will not be small compared to unity. Since values of h will be in the range 20 to 2000 $\text{Btu hr}^{-1} \text{ft}^{-2} \text{ } ^\circ\text{F}^{-1}$, and since the value of k used is greater than 1 $\text{Btu hr}^{-1} \text{ft}^{-2} \text{ } ^\circ\text{F}^{-1}$, values of CR will be $0.6 \times 10^{-4} d$ to $6 \times 10^{-4} d$, where d is the particle diameters in microns. Thus the assumption of $CR \ll 1$ is justified for particles up to 10 μ in diameter and would cause only small errors for $d = 100 \mu$.

A fictitious film coefficient for radiation, h_r , can be estimated from

$$h_r = \frac{\frac{T_R^4}{1000} - \frac{T_S^4}{1000}}{T_R - T_S} 1730\epsilon, \quad (11)$$

when ϵ is the emissivity of the material of the particle. Values of h_r are between 40 and 70 for $T_R = 3000^\circ\text{R}$ (1400°C) and between 80 and 175 $\text{Btu hr}^{-1} \text{ft}^{-2} \text{ } ^\circ\text{F}^{-1}$ for $T_R = 4000^\circ\text{R}$ (1950°C). These values of h_r are 10 times higher than the convective film coefficients to be expected for thorium particles suspended in the gas stream. Therefore an average value of C would be $h/k = 75 \text{ ft}^{-1} = 250 \times 10^{-6} \mu^{-1}$.

For the above value of C , $R = d/2$ and $\alpha = 0.5 \times 10^6 \mu^2/\text{sec}$, the simplified equation becomes

$$(T_R - T)/(T_R - T_o) = \exp(-750t/d). \quad (12)$$

These values calculated from Eq. (12) are plotted in Fig. 8.

3.3.3 Rate of Solvent Evaporation

The calculations presented for heat transfer during the calcination of oxide particles do not apply to solvent evaporation and thermal denitration at relatively low temperatures. The same analysis made for particles will show that the temperature gradients for convective heat transfer within the drops are negligible. Any mixing within the liquid drop will further decrease the gradients. The varying heat capacity and shape of the drop during solvent evaporation make the application of Eq. (9) impractical. However, the times necessary for radiant heat transfer to the surface of the particle may be calculated from the heat requirements per unit weight of oxide and heat transfer rate q from the radiation equation.

$$q = 1730A\epsilon(T_R/1000)^4, \quad (13)$$

where A is the particle surface area. The liquid temperature is enough lower than the reflector surface or gas temperature to make T_S^4 negligible compared to T_R^4 . Since the particle is essentially surrounded by reflector and gas, ϵ in Eq. (13) is the particle absorptivity, which can be assumed to be the same as the particle emissivity, at the temperature of the reflector.

For an aqueous solution of thorium nitrate of concentration equivalent to 100 g of ThO_2 per liter and with drop sizes to give a final thoria

particle diameter d , the initial rate of heat transfer is calculated as follows:

$$A = \frac{3}{pr} = \frac{6}{0.1 \times d \times 10^4 \times 930} \left(\frac{0.1}{10} \right)^{1/3} = \frac{140}{d} \frac{\text{ft}^2}{\text{g ThO}_2}.$$

At 3000°R with $\epsilon = 0.90$ for aqueous solution:

$$q = 1730 \left(\frac{140}{d} \right) (0.90) \left(\frac{3000}{1000} \right)^4 = \frac{17.5 \times 10^6}{d} \frac{\text{Btu}}{\text{hr} \cdot \text{g ThO}_2}.$$

As the dehydration nears completion, and for denitration, since $A = \left(\frac{20}{d} \right) (\text{ft}^2/\text{g ThO}_2)$,

$$q = 1730 \left(\frac{20}{d} \right) (0.90) \left(\frac{3000}{1000} \right)^4 = \frac{2.5 \times 10^6}{d} \frac{\text{Btu}}{\text{hr} \cdot \text{g ThO}_2}.$$

A logarithmic mean average rate of heat transfer is

$$q = \frac{(17.5 - 2.5) \times 10^6}{d \ln (17.5/2.5)} = \frac{7.7 \times 10^6}{d} \frac{\text{Btu}}{\text{hr} \cdot \text{g ThO}_2}.$$

After the dehydration and denitration are complete,

$$q = 1730 \left(\frac{6.7}{d} \right) (0.35) \left(\frac{3000}{1000} \right)^4 = 330,000 \frac{\text{Btu}}{\text{hr} \cdot \text{g ThO}_2}.$$

Values of $U = q/A\Delta T$ are about $60 \text{ Btu hr}^{-1} \text{ ft}^{-2} \text{ }^\circ\text{F}^{-1}$ for the above situations; these are much higher than the film coefficients expected for convective and conductive heat transfer to small particles suspended in a gas. For gas temperatures below 1000°C , convective heat transfer would become significant because of the rapidly decreasing radiation rates.

For the evaporation of water,

$$qt = (5 \text{ g H}_2\text{O/g ThO}_2)(2.4 \text{ Btu/g H}_2\text{O}) = 12 \text{ Btu/g ThO}_2.$$

Note that this amount is inversely proportional to concentration of the feed solution.

For the denitration of $\text{Th}(\text{NO}_3)_4$,

$$qt = (120,000 \text{ cal/mole Th})(1 \text{ mole}/264 \text{ g ThO}_2)(1 \text{ Btu}/252 \text{ cal}) = 1.80 \text{ Btu/g ThO}_2.$$

For raising the temperature of the ThO_2 to 1500°C ,

$$qt = (0.080 \text{ cal/g} \cdot ^\circ\text{C})(1500^\circ\text{C})(1 \text{ Btu}/252 \text{ cal}) = 0.5 \text{ Btu/g ThO}_2.$$

The time t required for radiant transfer of the required amounts of heat is equal to qt/q . For the evaporation of water,

$$t = (12 \times 3600d)/7.7 \times 10^6 = 5.6 \times 10^{-3}d \text{ sec.}$$

For denitration,

$$t = (1.80 \times 3600d)/2.5 \times 10^6 = 2.6 \times 10^{-3}d \text{ sec.}$$

For raising the temperature of the ThO_2 to 1500°C ,

$$t = (0.5 \times 3600d)/0.33 \times 10^6 = 5.5 \times 10^{-3}d \text{ sec.}$$

This calculation for raising the ThO_2 temperature is much less exact than the method of Eq. (10) and Fig. 8. It is interesting to note that the agreement is good. For $d = 1 \mu$, $t = 5.5 \times 10^{-3}$ sec as calculated from qt/g . This gives a value of $(T - T_o)/(T_R - T_o) = 0.98$, as shown on Fig. 8.

When methyl alcohol is the solvent, the heat of vaporization is much smaller, and combustion of the alcohol probably results in increased heat transfer to the drop surface. Calculations of the same type as for the evaporation of H_2O would give for the evaporation of methyl alcohol:

$$qt = (7 \text{ g CH}_3\text{OH/g ThO}_2)(1 \text{ Btu/g CH}_3\text{OH}) = 7 \text{ Btu/g ThO}_2$$

$$t = qt/q = (7 \times 3600d)/7.7 \times 10^6 = 3.3 \times 10^{-3}d \text{ sec.}$$

3.3.4 Reflector Heat Losses

Calculations were made in order to determine the magnitude and relative importance of the following heat losses: (a) by radiation out of the reflector ends, (b) by conduction through the vertical surfaces of the insulation, (c) by conduction through the horizontal surfaces of the insulation, and (d) to bring the feed solvent and salts to the calcination

temperatures. For small (2-in.-ID) reflectors, these tend to have the following decreasing orders of magnitude: (c), (b), (a), and (d). For water feed solutions to 6-in.-ID reflectors, the order changes to (d), (a), (b), and (c). The heat losses to the reflector ends can be approximated by radiation with emissivity of unity, the same as for a small hole in a closed chamber. The losses through the reflector walls are controlled by conduction, while those to the solvent and gaseous flame products are determined by their heat capacities. For a constant fuel and solvent loading per unit cross section area, the percentage heat losses are proportional to q/R_1^2 , where q is the rate of heat loss and R_1 is the inside radius of the reflector. The first approximations for the heat losses in terms of the reflector wall temperature T , the reflector outside radius R_2 , the length L , and reflector conductivity k , gave:

(a) for losses to the open ends,

$$\% \text{ loss} \propto \frac{q}{R_1^2} \propto T^4;$$

(b + c) for losses through the insulation,

$$\% \text{ loss} \propto \frac{q}{R_1^2} \propto \frac{kLT}{R_1^2 \ln \frac{R_2}{R_1}};$$

(d) and for vaporizing the solvent,

$$\% \text{ loss} \propto \frac{q}{R_1^2} = \text{constant}.$$

For heating the gaseous solvent and the flame products:

$$\% \text{ of heat} \propto \frac{q}{R_1^2} \propto (a + bT)T,$$

and $bT < 0.5a$.

Relationships of the above type along with heat balances can be used to calculate reflector temperatures.

An insulation thickness of about 1.5 ft appears optimal because the effectiveness of greater thicknesses is largely offset by the convective heat losses from the greater surface area of the insulation. Reflector temperature distributions were calculated for several configurations and operating conditions, using better approximations than those listed above (Fig. 9). The actual temperature distributions observed on the reflector agreed with these calculated values.

Fig. 9. Typical Reflector Temperature Distributions.

3.3.5 Conclusions Regarding the Rate Calculations

Calculations of particle-temperature-vs-time relations for the flame denitration—calcination method of preparing thorium dioxide from thorium nitrate solutions indicated that the times required for heat transfer are controlled by the rate of radiant heat transfer to particle surfaces instead of by conductive heat transfer within particles. Most of the heat added is necessary to evaporate the water or methyl alcohol feed solvent. Since the larger volume (and larger surface) and the higher absorptivity of the solutions, compared with those same properties for the thorium particles result in high heat transfer rates in terms of unit amounts of thorium produced, the times for solvent evaporation and calcination are of about the same magnitude. Total times of 0.01 to 0.06 sec were calculated for the heat transfer necessary to convert feed solution droplets to ThO_2 particles 1 to 5 μ in diameter, calcined at 1500°C . These times may be used to estimate reflector dimensions. Combinations of acceptable gas velocities, acceptable dust loadings, and times required for heat transfer indicated reflector lengths between 1 and 6 ft and capacities of 5 to 20 kg of thorium per hour per square foot of cross sectional area. For pilot-plant production of thorium or mixed thorium-uranium oxides the dimensions would be 4 ft length and 6 in. ID, giving a capacity of about 2 kg of thorium per hour.

3.4 Reflector Materials and Construction

Many variables must be considered in the selection of refractory materials for high-temperature applications. The choices for this study were limited by the combination of extreme temperatures and oxidizing conditions. Of the refractory oxides considered for this application,

only three had a high enough melting point and sufficient oxidation resistance. These were magnesia, stabilized zirconia, and thoria. Magnesia sublimes rapidly at the expected furnace temperatures and is not recommended for service above 1600°C (Table 1). Thoria has a high melting point, but experience and performance data on thoria refractories are limited. Thoria is more expensive than stabilized zirconia and not as readily available. Stabilized zirconia suffers a weakness common to many refractories; that is, contact with dissimilar refractories at high temperatures is disastrous. This weakness was easily met in furnace design by assuring that only zirconia to zirconia high-temperature contacts occurred. This design feature was met in the reflectors built for this study (Fig. 4).

Table 1. Properties of Refractory Oxides

Material	Formula	Fusion	Temperature Limits (°C)	
			Maximum ^a Duty	Reflector ^b Service
Alumina	Al ₂ O ₃	2000	1950	1800
Magnesia	MgO	2700	2200	1600
Urania	UO ₂	2877	2000	
Stabilized zirconia	ZrO ₂ (plus a stabilizer)	2550	2400	2000+
Thoria	ThO ₂	3300	2800	

^aLiterature values for commercial refractories.

^bEstimated reflector temperatures.

While awaiting delivery of the zirconia tubing and arch brick for construction of the large reflector used in the latter portion of this study, furnaces for temporary use were built, and both graphite and

magnesium oxide were used for the reflector tube. Neither of these materials was satisfactory. The graphite burnt out in about 2 hr, and the operating temperature was so high that even a small error in controlling the furnace fused the magnesia reflector. The reflector materials used in each run are tabulated with run data in the Appendix.

3.5 Fuels and Flame Temperatures

Fuel gases considered (Table 2) for use in this study were limited to gaseous hydrocarbons because of their ease of handling, availability, and low cost. Of these, propane gas with oxygen was most convenient and was used for most of this study. Natural gas—oxygen gives essentially the same flame temperature (Table 2) and would be used in larger operations. The propane-oxygen flame proved adequate for flame denitration. The acetylene flame was used in all tests in which thoria particles were injected directly into the flame and, in early denitration runs, in order to study the effect of the highest possible flame temperatures.

Table 2. Maximum Flame Temperature for Some Common Gaseous Fuels (1 atm)

Fuel System	Temperature (°C)	Literature Reference
Acetylene-oxygen	3137	12
Acetylene-air	2320	13
Hydrogen-oxygen	2657	12
Hydrogen-air	2045	14
Carbon monoxide-oxygen	2925	14
Carbon monoxide-air	2097	12
Natural gas (1025 Btu)-oxygen	2930	14
Natural gas (1025 Btu)-air	1927	12

3.6 Glassing Agents

The possibility of producing spheroidal thorium and uranium was not altogether as hopeless as the data of Tables 1 and 2 might indicate. First, there was the possibility that it would not be necessary to reach the fusion point. A temperature between the sintering temperature (about 1800°C) and the fusion point might be adequate. Second, the fusion point measurements had been made on the massive pieces of extremely high purity oxides. Very small particles (1 μ) and, in particular, sharp curves or projections from these particles could be expected to fuse at lower temperatures than massive pieces. Further, the trace impurities could be expected to lower the melting point sharply. Therefore, it was reasoned that particles of these oxides might be spheroidized if a favorable combination of these factors existed.

The controlled addition of a selected impurity (glassing agent) to the thorium and/or uranium was an attractive possibility for producing microspheroids. Thorium has the highest melting point of all oxides (about 3300°C), with uranium melting (2880°C) only a few hundred degrees lower (Table 3). Further, the melting points of thorium-uranium mixtures fall on essentially a straight line between the two melting points. From all the above considerations, the flame preparation of microspheroids of either of these oxides, or any combination of these oxides, would probably require a glassing agent. Thus, the addition of any of the common oxides would effectively lower the melting points of the oxides of either of these two elements.

Table 3. Melting Points of Thoria and Urania¹⁵

Thoria (wt %)	Urania (wt %)	Melting Point (°C)
100	0	3300
75	25	3230
50	50	3110
25	50	2940
0	100	2877

The element whose oxide is to be used thusly, however, must have (1) a low thermal neutron cross section, (2) a chemical form which will decompose thermally to the oxide, and (3) be stable in the high-temperature (about 280°) aqueous blanket region. Some suitable chemical form of the element must also be mutually soluble in a given solvent with its intended decomposable thorium or uranium salt. Another possibility was the sorption of a glassing agent on the surface of the particles in the slurry and then flame-firing the slurry. This latter possibility was not thoroughly investigated.

Examination indicated that three oxides might be suitable glassing agents. These oxides were alumina, beryllia, and silica. Alumina appeared to be ideal because of its low cross section, its stability in high-temperature water, and its existence as a common, thermally decomposable salt (the nitrate). Because of its low cross section, an alumina concentration of 1 wt % is equivalent to a neutron loss of only about 0.2%. The aluminum nitrate would be mutually soluble with either thorium or uranium nitrate in all proportions in a wide variety of solvents. The melting points for

thoria-alumina and urania-alumina show that alumina has a marked effect on the melting points in these systems. The effect of alumina on the thoria melting point is precipitous in concentrations below 20 mol %; the melting point is about 2200°C at 20 mol %.¹⁶ The same effect is observed for urania-alumina but is not as dramatic; 20 mol % alumina lowers the urania melting point only to about 2300°C.¹⁷ In either case, however, these compositions melt at temperatures available in a reflected flame and offered the possibility of producing spheroidal particles.

No data were found for the effect of silica addition to thoria or urania in less than 20 mol % concentrations. Some data, however, showed that 70 mol % ThO₂—30 mol % SiO₂ melts at about 2300°C, and 50 mol % UO₂ 50 mol % SiO₂ melts at about 2200°C.¹⁸ Thus, comparable melting point depressions are achieved only at the expense of considerably higher impurity concentration. Silica also exhibits undesirable behavior traits in high-temperature water, apparently dissolving to a limited extent in hot water and then later precipitating onto equipment surfaces. For these reasons silica offered less promise as a glassing agent than alumina, and it received only a cursory examination. The silica used in these experiments was added to the feed solutions as tetraethyl orthosilicate.

Instead of parasitically absorbing neutrons as the two oxides mentioned above, beryllia would result in neutron multiplication by the $n,2n$ reaction. Thus, insofar as neutron economy alone is concerned, any beryllia concentration could be used. The addition of beryllia to urania lowers the melting point slowly from about 2880°C down to a eutectic at about 2100°C at about 65 mol % BeO.¹⁹ The thoria-beryllia system has a minimum melting point of about 2400°C. Toxicity is the overriding disadvantage of beryllia,

and for this reason only a single beryllia firing (60 mol % BeO—40 mol % ThO₂) was made. The beryllia was added to the feed solution as beryllium nitrate.

No such information was available on the ternary oxide system (ThO₂-UO₂-Al₂O₃) upon which the bulk of the work of this study was done. The crystalline species present in the microspheroids produced by flame denitration are not known.

4. DEVELOPMENT OF THE PROCESS AND THE EQUIPMENT

4.1 Procedures for Feeding Solutions, Slurries, or Powders

A methanol or aqueous solution of thorium nitrate was found to be the preferred feed to the flame calciner in preference to two other feeds tested: dry thoria powder and a slurry of thoria in an organic liquid. A solution feed can be pumped and metered, and it also offers the unique advantage of a one-step conversion from a metal nitrate solution to an oxide product. Further, mixed oxides can be produced from decomposable salts that can be dissolved in a common solvent, and other elements can be included, for example, palladium and molybdenum salts for forming PdO and MoO₃ for the catalytic recombination of radiolytic hydrogen and oxygen produced in the nuclear reactor. The disadvantage of solution feed is the lower temperatures attainable because of the heat required to evaporate the solvent, to decompose the nitrate, and to bring the gaseous decomposition products to flame temperature. The chief problems were thought to be the design of an atomizing nozzle capable of producing extremely small droplets in a narrow size range and also capable of giving high yields of product.

Both the dry-powder and slurry-feeding systems offered the advantages inherent in feeding a presized (classified) powder. The powder considered, however, was expensive, as it was already a reactor grade powder prepared for slurry use. A dry powder would provide the highest possible temperature, but complete dispersion and adequate metering of the feed was extremely difficult. The principal disadvantage of the slurry method was a lower potential flame temperature than the dry feed, due to the liquid and the cost of providing the classified powder to make up the feed.

4.1.1 Solution Feeding

With solution feed, 100- to 300-g quantities of thoria in a 1- to 3- μ -diam range were produced in 25 to 35% yield—a yield adequate for the purpose of this study but not suitable in a production operation. The remainder of the material collected in the agglomerate trap (Fig. 1). Methanol or aqueous solutions of concentrations up to 2.0 M handled well.

The 25 to 35% yield was obtained with a burner similar in design to commercial spray-atomizer nozzles. It had a single, aspirating, centrally located feed jet, and peripheral burners (Fig. 4b). In the last model tested, the center feed jet was so located and the piping to it so arranged that it could be fed and driven independently of the burners. This modification eliminated the buildup of solids inside the top of the reflector, which was a problem with an earlier model in which the jet and burners were fixed in relation to each other. Oxypropane fuel was used, with a reducing flame (5 to 10% deficient in oxygen) to ensure combustion to carbon monoxide and water. This eliminated flashbacks, which had been a problem with oxyacetylene fuel. The first burner tested

had a central hypodermic needle (0.013 in. in diameter) for the liquid, and four peripheral gas-burner ports (Fig. 4a). The subdivision of the inlet feed stream was adequate to produce powders in the desired particle-size range, but the product yield was only 10%. Oxyacetylene fuel was used.

The solutions were fed by a Hills-McCanna metering pump. A smooth, continuous feed could not be sustained at feed rates at the lowest range of this pump (10 to 30 ml/min). A higher feed rate would have permitted the pump to operate smoothly, but the cooling capacity of the spray-column system limited the feed rates. The gases were measured by a constant-pressure rotameter in the mixing stream.

4.1.2 Slurry Feeding

A methanol-thoria slurry, prepared by adding oxalic acid (0.003 M) as a dispersing agent and stirring for 8 hr, remained dispersed through a high-temperature calcination. Passing the feed slurry stream through an ultrasonically energized chamber also gave an excellent dispersion,²⁰ but this method is less flexible and more expensive than the use of oxalic acid as a dispersing agent.

In the torch design most satisfactory for firing a slurry feed, the oxygen and acetylene were premixed in the handle section of a standard acetylene torch before entering the heated chamber (Fig. 3). The methanol was vaporized, and the entire gaseous mixture carrying the suspended particles was preheated to 150 to 175°C at the burner orifice. The temperature at the orifice was controlled by regulating the steam pressure in the heating annulus. The flange on the burner end was mounted in direct

contact with the end of the reflector tube in order to retard the inleakage of air. The flange picked up heat from this contact, as well as from "seeing" the hot surface of the reflector. The flange temperature was controlled to between 150 and 200°C by passing air through the coil on the rear surface.

Slurries were fed from a high-resistance bypass loop driven by a centrifugal pump. A stream off the bypass was passed into the burner.

4.1.3 Dry-Powder Feeding

No method was found that would give a sustained feed of pure, dry thoria or thorium oxalate powder to a flame, and the product that was formed was not comparable with the product of slurry feeding or denitration.

A thoria powder calcined at 650°C or higher and stored in a dry box pours freely at first, but after several pourings small agglomerates (about 0.2 cm in diameter) are produced, even while in the dry atmosphere. If the container is shaken, about half the thoria forms these agglomerates, and the other half settles into a hard putty-like mass in the bottom, packing to such a density that cutting with a spatula point is difficult. Thoria suspended in a gas stream quickly coats the walls of the pipe, tube, or orifice through which it is passed, plugging the opening. If suspended in a gas jet long enough and at a high enough dust loading, agglomerates form which, though weak, cannot be dispersed. Thorium oxalate shows the same behavior but to an even higher degree. The use of screw conveyors or vibrating feeders is thus completely impractical, and hopper storage is unsuitable because of a packing-bridging effect in the bottom outlet.

Surface-treating agents used by the ceramics industry in dry-powder handling operations did not improve the thoria properties. Because of the thoria dust hazard, they were not applied by dry ball milling but by treating the thoria powders with solutions of the agents and drying. A mixture of thoria and lubricating-grade graphite powder that was dry-ball-milled was fed for 4 hr, but the flow was gusty. With all other powders the flow could be maintained for only a few minutes.

Three commercial flame-spraying guns were tested for powder feeding capability. One was equipped with a vibrating feed cartridge on top, while a second had an aspirating attachment that used compressed fuel gas to carry the powder into the flame. Neither of these devices fed thoria for more than a few seconds under any conditions tested. The third gun had a better-designed feeding system, including a pressurized feed hopper, a variable-speed feed screw, and an aspirating jet that dispersed the powders in the oxygen stream.²¹ All potential points of dust-escape from the feed hopper and its nozzles were back-pressured with oxygen, and the whole was covered by a hood that could be made airtight with minor modifications. This third spray gun fed the graphited thoria but would not feed untreated thoria. The first two nozzles burned an oxyacetylene mixture, while the third burned oxyhydrogen.

Suspending the thoria dust above an ultrasonically energized metal diaphragm and then picking up the dispersed particles by an oxygen stream gave excellent dispersions for the thoria entrained in the oxygen. However, about half the powder formed balls or settled into a putty-like mass in the bottom of the container. An overnight contact of a sample of the balls with a 2-r/hr P^{32} source in an attempt to discharge the static charge that held the balls together had no effect.

4.2 Reflector Temperatures

The dimensions of the reflector were dictated by the necessity of enclosing the entire burner-reflector assembly in a standard laboratory hood (Fig. 2). The design was, therefore, not efficient from either a fuel-consumption or an attained-temperature basis.

The confinement within the hood sharply limited efforts to measure either reflector or exhaust gas temperatures. The temperatures referred to in all tabulated data were taken from a Pt vs Pt—10% Ru thermocouple in contact with the outer wall of the zirconia reflector tube. Further, this thermocouple was located at the midpoint along the length of the tube. From heat-flux measurements, temperatures were estimated to be about 600°C higher than the thermocouple readings. Optical pyrometer readings taken through the sighting port ranged from 1700 to 1900°C. A carbon electrode held in the exhaust end of the reflector gave optical pyrometer readings of 1900°C when corrected for radiation losses. A single trial-and-error flame-temperature calculation was made with standard thermodynamic data.²² This calculation, using data from the run (No. 19) in which pure thoria particles were rounded, yielded a theoretical flame temperature of 2500°C.

It is estimated from the above consideration that reflector and flame temperatures used in this work exceeded 2000°C.

5. EVALUATION OF FLAME-CALCINATION PRODUCTS

5.1 Products of Methanol-Solution Feeds

Summarizing, thoria and mixed oxide powders were prepared by flame denitration. These powders were spheroidized when a glassing agent was

used, and the desired slurry properties were obtained. Powders containing no glassing agent were also prepared but their properties were not satisfactory.

5.1.1 Properties of Thoria-Urania-Alumina Products

Mixed oxide powders prepared by flame denitration and containing 1 to 10 wt % of alumina met or exceeded all specifications for a reactor grade-slurry. Mole ratios (U/Th) of 0.04 and 0.08 were used interchangeably without apparent effect. Product particles were spherical (Fig. 10), and surface areas were 2 to 3 times the theoretical minimum value (Table 4). The yield stress is estimated to be one-sixth, or even as low as one-tenth, that of tray-fired ThO_2 (Fig. 11), a particular advantage (Sec 9.1.4). Modulus of rigidity values were good, consistently below 3.0 centipoise vs a reactor specification of 4.0. In toroid tests, significant changes in particle size or surface area occurred in only one run (run 63). Electron micrograph comparison of the run-72 product before and after toroid circulation showed no change in particle shape (Fig. 12). Two corrosion rates were high (runs 66 and 69).

The results of both toroid and dynamic tests in a pump loop of a slurry with a U/Th ratio of 0.04 also were favorable (Table 5). The 31 kg of mixed oxide used for this loop test was obtained by combining the products of two extended runs, that is, 76 and 82 (Table 4). Corrosion rates were very low, being comparable to or better than the best pilot-plant (tray-calcined) thorium oxide slurries.²³ The yield stress doubled during the test but still remained below the maximum value specified for reactor service of 0.1 lb/ft^2 . It is not known whether the yield stress

PEM No. 2128-3

(a) Run 63; U/Th = 0.08; 2.5 wt % Al_2O_3 ; 1500°C;
mean diameter = 1.7 μ .

PEM No. 2250-2

(b) Run 70; U/Th = 0.08; 5.0 wt % Al_2O_3 ; 1500°C;
mean diameter = 1.4 μ .

Fig. 10. Typical Photomicrographs of Thoria-Urania Containing
2.5 and 5 wt % Alumina.

Table 4. Physical Properties of Flame-calcined Thorium-Uranium Oxides
Containing Alumina: Before and After Toroid Test

Flame calcination conditions: U/Th mole ratio = 0.08 for runs 62 to 73
0.04 for runs 76 to 82

Flame: oxypropane
Solvent: methanol
Reflector: MgO for runs 62 to 73
ZrO₂ for runs 76 to 82

Toroid test conditions: Overpressure gas: oxygen
Temperature: 280°C
Circulation rate: 26 fps
Duration of run: 300 hr
Concentration: 500 g solids per kg D₂O

Run No.	Nominal wt % Alumina	Reflector Temp. (°C)	Avg Particle Size (μ)		Surface Area (m ² /g)			Yield Stress (lb/ft ²)	Modulus of Rigidity (cp) ^b	Rate of Corrosion SS 347 (mpy)
			Before	After	Theo. min.	Measured Before	After			
62	5	1550	1.5		0.42	2.0		0.02	1.2	
63	2.5	1530	1.7		0.37	2.4		< 0.005	1.8	
63T ^a			2.1	1.8		2.3	6.2			1.3
66		1520	2.0		0.31	2.6		0.03	1.6	
66T ^a			1.6	1.5		2.5	3.0			4.8
69	10	1500	1.6		0.39	3.1		0.05	2.2	
69T ^a			1.5	1.5		2.9	3.6			5.8
70	5	1500	1.4		0.44	1.4		< 0.02	1.6	
72T ^a			1.1	1.4		1.7	2.4			2.4
73T ^a			1.4	1.1		1.8	2.5			2.7
76	2.5	1600	1.5		0.42	2.0		0.03	1.3	
76T ^a			1.2	2.0		-	3.0			1.6
77T ^a			1.5	1.5		1.6	2.1			3.0
82	2.5	1500	1.3		0.47	1.3		0.03	1.1	
82T ^a			1.3	1.4		-	1.7			0.2

^aToroid test results.

^bCentipoise.

Fig. 11. Yield-stress Values for Spherical Thoria-Urania-Alumina, Compared with Tray-Calcined ThO₂ (see Appendix, 9.1.4 for Nomenclature).³⁰

PEM No. 2253-2

PEM No. 2575

Fig. 12. Photomicrographs of Thoria-Urania-Alumina Particles Before and After Toriod Tests. (a) Before tests, and (b) after tests.

had attained a constant value or not at the end of the test, but all other properties had.²³ The test was terminated after 240 hr because of a pump failure which was not related to the slurry properties. The products are considered representative of production-scale operations since they were prepared in two separate periods of continuous operation, each covering several days.

Table 5. 100A Slurry-Loop Test of Flame Denitrated Thoria-Urania-Alumina

Conditions: Temperature: 250°C
Duration: 239.8 hr
Overpressure gas: oxygen
Slurry pH: 8.2 to 6.1
Slurry concentration: 457 g ThO₂ per kg H₂O
U/Th mole ratio = 0.04 (product of runs 76 and 82)

Physical Properties			
		<u>Before the Run</u>	<u>After the Run</u>
Average particle size, μ		1.3	1.2
Surface area, m ² /g		1.3	1.4
Yield stress, lb/ft ² (ref a)		0.027	0.07
Attack Rates (347 SS, mpy) ^b			
<u>Coupons</u>		<u>Loop Piping</u>	<u>Pump Impeller</u>
<u>(20 fps)</u>	<u>(40 fps)</u>	<u>(6-7 fps)</u>	<u>(Zircaloy II)</u>
0.1	0.9	0.2 avg	1.2

^aThis yield stress is referred to 1359 g of ThO₂ per kg of H₂O.

^bFor comparison, standard toroid test velocity is 26 fps.

5.1.2 Properties of Thoria-Alumina Products

Thoria that contained 0.5 to 5 wt % alumina (Table 6) was spheroidized (Figs. 13 and 14) and exhibited uniformly good physical properties. Surface areas were between 2 and 3 times the theoretical minimum. Yield stresses

PEM No. 2427-3

(a) Run 78; 1.0 wt % Al_2O_3 ; 1550°C; mean diameter, < 1.3 μ.

PEM No. 2251-5

(b) Run 71; 5 wt % Al_2O_3 ; 1450°C; mean diameter, 1.0 μ.

Fig. 13. Photomicrographs of Thoria-Alumina Particles of 1.0 and 5.0 wt % Al_2O_3 .

PEM-3037-2

(a) Run 112; 1600°C; feed of 920 g/liter of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and 8.3 g/liter of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in CH_3OH ; product of 1.0 μ mean diameter and 1.8 m^2/g surface area.

PEM-3056-3

(b) Run 116; 1625°C; feed of 600 g/liter of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in CH_3OH ; product of 0.9 μ mean diameter and 3.6 m^2/g surface area.

Fig. 14. The Effect of 0.5 w/o Al_2O_3 in ThO_2 Flame Denitration at 1600-1625°C.

were low, compared with the maximum acceptable value, 0.1 lb/ft². The modulus of rigidity was also favorable when compared with its maximum acceptable value of 4.0 centipoises. Electron micrographs of the run-71 product indicated a particle size greater than the 1.6 μ indicated by sedimentation analysis. Toroid results showed this material to be satisfactory (Table 7).

Table 6. Physical Properties of Flame Denitrated Thoria-Alumina Powders

Run No.	Nominal wt % Alumina	Reflector Temp. (°C)	Avg Particle Size (μ)	Surface Area (m ² /g)		Yield Stress ^a (lb/ft ²)	Modulus of Rigidity (centipoise)
				Actual	Theor. Min.		
71	5	1450	1.0	1.3	0.62	0.03	2.6
78	1	1550	1.6	1.4	0.44	<0.02	1.6
112 ^b	0.5	1600	1.0	1.8	0.62	<0.02	1.6
116	0	1625	0.9	3.6	0.69	<0.02	1.2

^a Measured at a slurry density of 2.0 g/cc, equivalent to 1120 g of ThO₂ per kg H₂O.

^b H₂O as feed solvent instead of methanol.

While these limited tests cannot be considered conclusive, the results indicate a performance equal to that of the mixed oxides.

Table 7. Toroid Test Results for a Thoria-Alumina Powder

Conditions: Run 71 Product of 5 wt % Al₂O₃
 Overpressure gas: oxygen
 Temperature: 280°C
 Circulation rate: 26 fps
 Duration of run: 300 hr
 Concentration: 500 g of solids per kg of D₂O

Avg Particle Size (μ)		Surface Area (m ² /g)		Corrosion Rate of 347 SS (mpy)
Before	After	Before	After	
1.1	2.0	1.3	1.8	2.2

5.1.3 Properties of Urania-Alumina Products

Urania with 1 and 5 wt % alumina showed no spheroidizing of the particles, according to electron micrography (Fig. 15). The lack of spheroidization and the presence of large numbers of both very large and extremely small particles make this an undesirable product. The surface area of the two samples was high, as was the yield stress (Table 8), although the latter was indeterminate because of the poor fluid properties of these samples.

Table 8. Exploratory Firings of Oxides of Incidental Interest

Run No.	Product Composition (wt %)				Reflector Temp (°C)	Surface Area (m ² /g)	Mean Diam (μ)	Slurry Yield Stress (lb/ft ²)
	ThO ₂	UO _x	Al ₂ O ₃	SiO ₂				
84	95			5	1200 ^a	1.5	1.2	<0.02
85	99			1	1200 ^a	4.0	1.0	<0.02
86		95		5	1500	6.2	1.2	<0.02
87		99		1	1500	6.1	1.0	<0.1
88		95	5		1500	7.4	0.6	>0.1 ^b
89		99	1		1500	8.5	0.6	>0.1 ^b
90	90	5		5	1500	1.9	1.2	<0.02

^aFaulty thermocouple led to operation at this temperature level.

^bUncertain values. Difficult to handle in analytical test equipment.

5.1.4 Properties of Silica-Containing Products

The thoria-silica (runs 84 and 85) and urania-thoria-silica (run 90, Fig. 16) combinations produced spheroidal particles. Urania-silica products (runs 86 and 87) were not spheroidal and had poor fluid properties similar

PEM No. 2620-2

(a) Run 89; 1 wt % Al_2O_3 ; 1500°C ; mean diameter, about 0.6μ .

PEM No. 2619-1

(b) Run 88; 5 wt % Al_2O_3 ; 1500°C ; mean diameter, 0.6μ .

Fig. 15. Photomicrographs of Urania-Alumina Particles of Flame Denitration.

PEM No. 2569-1

(a) Run 84; 95 wt % ThO_2 -5 wt % SiO_2 ; 1200°C;
mean diameter, 1.2 μ .

PEM No. 2621-3

(b) Run 90; 90 wt % ThO_2 -5 wt % UO_x -5 wt %
 SiO_2 ; 1530°C; mean diameter, 1.2 μ .

Fig. 16. Photomicrographs of Thoria-Urania-Silica Products
of Flame Denitration.

to those of the urania-alumina slurries (Fig. 15). Surface areas and yield stresses of the thoria materials were low except for the unexplained high value ($4.0 \text{ m}^2/\text{g}$) for the surface area in run 85. In toroid runs with products containing SiO_2 , the silica coated the test specimens with a hard, tenacious silica coat, and in most cases gelation occurred.²⁴

5.1.5 Properties of Thoria-Beryllia Product

A flame-calcined thoria (98 wt %)—beryllia (2 wt %) product was composed of small spheroidal particles, as shown by electron micrography (Fig. 17) but could not be further evaluated because of the small quantity of sample. This sample was fired at 1475°C , and the average particle size was 0.6μ .

5.1.6 Properties of Oxides with no Glassing Agent

Samples of UO_x , ThO_2 , and $\text{UO}_x\text{-ThO}_2$ (where $x = 2.5$ to 2.9) prepared by flame denitration were fragmented, had high surface areas (about ten times the theoretical minimum), high yield stresses, and showed mild corrosive attack. The properties, particularly surface area, appeared to be insensitive to firing (reflector) temperature. The results (Tables 9 and 10, Fig 14b) are representative of those for pure thoria, urania, or thoria-urania.

Table 9. Physical Properties of Flame Denitrated Thoria-Urania Powders

U/Th ratio = 0.08

Run No.	Reflector Temp. ($^\circ\text{C}$)	Avg Particle Size (μ)	Surface Area (m^2/g)		Yield Stress (lb/ft^2)
			Theor. Min.	Actual	
35	1400	1.1	0.56	5.8	
36	1300	1.5		5.5	
37	1450	2.5	0.25	4.8	
38	1580	1.2	0.51	4.9	
39	1550	0.9	0.69	5.9	0.275
40	1560	14		7.8	0.8 ^a

^aThis sample agglomerated badly, making both size and yield-stress analyses difficult, possibly meaningless.

Fig. 17. Shadowgraph of BeO-ThO_2 Particulates Produced by Flame Denitration. Conditions: temperature outer reflector wall 1475°C ; 60 mole % BeO (2 wt %); 40 mole % ThO_2 (98 wt %).

Table 10. Results of Toroid Tests of Thoria-Urania Powders

Conditions: Oxygen overpressure
Circulation: 300 hr
Flow velocity: 26 fps
Temperature: 280°C

Run No.	Avg Particle Size (μ)		Surface Area (m^2/g)		Corrosion Rate of 347 SS (mpy)
	Pre-run	Post run	Pre-run	Post run	
35	1.0	1.2	5.9	14.2	3
36	1.5	1.3	5.6	7.4	7
38	1.2	1.2	5.3	6.7	2.8

The ThO_2 product of run 116, which was made at the highest temperature (1625°C) obtainable in the equipment used, had a yield stress of $<0.02 \text{ lb/ft}^2$ even though no glassing agent was used. However, no appreciable percentage of the particles were spheroids (Fig. 14b). The surface area was $3.6 \text{ m}^2/g$, five times the theoretical minimum, and the modulus of rigidity was 1.2 centipoises. The particle size indicated by sedimentation analysis was 0.9μ , but electron micrographs indicated much smaller particles.

5.1.7 Properties of Oxides Plus Recombination Catalysts

Mixed oxides were prepared with palladium nitrate and molybdenum nitrate added to the nitrate feed solutions in order to introduce an H_2-O_2 recombination catalyst into the product. The reflector temperatures were reduced to avoid complete volatilization of the Pd or Mo oxides. The standard-product analytical results show characteristics equivalent to previous thoria-urania products. About two-thirds of the molybdenum was lost, probably by volatilization, at both temperatures tested. Ninety percent of the palladium was volatilized at 1400°C, but only 10% in the 1200°C firings (Table 11).

Table 11. Retention of MoO_3 or PdO_2 as Recombination Catalysts in Flame Denitration Products

Reflector Temperature (°C)	Calculated Product Conc. from Feed (wt %)	Product Conc. by Analyses (wt %)
1200	0.53 MoO_3	0.195 MoO_3
1440	0.53 MoO_3	0.165 MoO_3
1205	0.017 PdO_2	0.0135 PdO_2
1425	0.017 PdO_2	0.0017 PdO_2

5.2 Properties of the Products of Oxide Slurry Feed

5.2.1 Effects of Low-Temperature Calcination

Yield stresses of the products of thorium oxide and thorium oxalate slurries in methanol fired at temperatures of 1100 to 1400°C were comparable with those of oxides produced by tray calcination of thorium oxalate at 1600°C (Table 12). Surface areas were higher. Toroid tests results (Table 13) showed that the flame-calcined powders were comparable to tray-calcined in dynamic behavior.²⁵

In one run with SiO_2 -coated thoria powder (run 27),²⁵ in which the SiO_2 made up 0.6% of the weight of the sample, the modulus of rigidity was appreciably lowered, but no spheroidizing of the particles was observed in the electron micrograph.

Graphite reflectors were initially used because graphite was the only material readily available at the time. Temperatures indicated by thermocouples in the wall and along the length of the graphite reflector ranged from 1400°C (at the center) to 1100°C (at the exhaust) in each run. The

reflector was insulated with 7.5 in. of uncemented insulating firebrick and had a service life of about 2 hr at temperature, sufficient only to produce the needed sample. A stabilized zirconium oxide reflector (2-in. bore, 12 in. long, 7.5 in. of insulating firebrick) and an oxyacetylene flame were used with a feed containing 0.6% SiO_2 for run 27.

Table 12. Flame-Calcined Products Fed as a Slurry Compared with a Typical Tray-Calcined Product

Conditions: Slurry: ThO_2 in methanol (200 g/liter)
 Flame: oxyacetylene
 Reflector: graphite, except as noted

Run No.	Description of Feed		Product Properties		
	Flame Calcination Feed Slurry	Avg Particle Size (μ)	Avg Particle Size (μ)	Surface Area (m^2/g)	Yield Stress (lb/ft^2)
20	Thorium oxalate ^a	1.4	1.6	2.5	
23	ThO_2 , 650°C ^b	0.86	1.1	2.5	0.25
24	ThO_2 , 650°C ^b	0.86	1.1	2.4	0.27
25	ThO_2 , 650°C ^b	0.86	1.1	3.4	0.23
27	ThO_2 , 650°C ^{b,c}		1.1	3.6	0.23
d	d	0.86	1.6	1.6	0.25-0.35

^aThis feed material represents a sample taken from a pilot-plant thorium oxalate batch later calcined by the pilot plant to produce the tray-calcined product given here as a reference.

^bThis feed material was oxalate precipitated and tray-fired to 650°C.

^cMade with ZrO_2 reflector and 0.6% SiO_2 in feed.

^dTypical tray-calcined product listed for comparison purposes.

Table 13. Toroid Test Results for Typical Slurry-Fed
Flame-Calcination Products

Run No.	Avg Particle Size (μ)		Corrosion Rate 347 SS (mpy)	Surface Area (m^2/g)	
	Pre-run	Post run		Pre-run	Post run
14 and 15 (combined)	1.2	0.8	2.6	2.8	3.6
16	1.2	1.0	2.8	2.4	3.2

5.2.2 Properties of the Product from a High-Temperature Calcination

A sample fired at a very high temperature (run 19) had $2.3\text{-}\mu$ (avg) particles, a surface area, after correction for particle size, of $1.2\text{ m}^2/\text{g}$, and a yield stress of zero.^a For comparison, the lowest yield stress values reported up to the time of this run was 0.17 lb/ft^2 for tray-calcined oxides. Electron micrographs showed a perceptible degree of spheroidizing (Fig. 18).

The slurry feed consisted of 650°C -calcined thoria, 200 g/liter in methanol that was 0.003 M in oxalic acid. The temperature could not be measured accurately, but calculations from indirect measurements indicated it to be 2200 to 2500°C . The reflector was made of stabilized ZrO_2 , 1-in. ID, 12 in. long, surrounded by insulating firebrick.

5.2.3 Properties of the Products of a Thoria-Alumina Slurry Feed

A run was made in which the irregularly shaped particles of ThO_2 —5 wt % Al_2O_3 obtained by flame denitration at 1000°C were refed as a slurry and calcined at 1600°C to give rounded particles (Fig. 19). The product

^a Although this was reported as zero, the measurement was made during the infancy of the yield stress analytical development. The yield stress of this sample may be assumed to be roughly equal to that of later spheroidal powders.

RUN NO. 19 - THORIA FEED
MATERIAL

RUN NO. 19 - FLAME CALCINED
THORIA PRODUCT

Fig. 18. Photomicrograph of Pure Thorium Particles Rounded by
Flame Calcination at about 2500°C . (a) Run 19; thorium feed material;
(b) flame-calcined product.

PEM-3004-1

(a) Run 109; 1000°C; feed of 920 g/liter of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and 83 g/liter of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O ; product of 2.2 μ mean diameter and 5.6 m^2/g surface area.

PEM-3057-4

(b) Run 113; 1600°C; feed of 200 g/liter slurry in CH_3OH of classified run-109 product; product of 1.8 μ mean diameter and 0.84 m^2/g surface area.

Fig. 19. Effects of Flame Calcination at 1600°C on Flame-Denitrated $\text{ThO}_2\text{-Al}_2\text{O}_3$ Prepared at 1000°C.

from run 109 was classified in order to avoid plugging by any large particles; this may be the cause of the decrease in particle size from 2.2 to 1.8 μ in mean diameter. The surface area of 0.84 m²/g after the 1600°C calcination was the lowest obtained for a flame-calcination product. This result shows that fusion of the ThO₂—5 wt % Al₂O₃ particles occurs in the reflected flame.

5.3 Properties of the Products of Aqueous Solution or Slurry Feeds

Because of the heat capacity of water, more fuel gas was required when aqueous feed solutions were used. For the larger, better-insulated zirconia reflector and the final torch design, temperatures were easily controlled up to the maximum practical for the stabilized-zirconia reflector material. Methanol was used for the earlier studies with smaller equipment because the extra heat loss to an aqueous feed solvent limited the temperature possible. The most economical system would depend on the relative costs of fuel gas, oxygen, and methanol.

5.3.1 Denitration Products

Eighteen denitration runs were made with aqueous feed solutions of TNT-ANN or TNT alone (Table A.4 in Appendix). The effects of changing from methanol to water as the feed solvent were not significant if the temperatures and concentrations were held constant. This was shown during studies of particle-size control (Table 15), with other typical values in Table 14. Results of toroid and loop tests also showed no significant differences from the products of methanol solution feeds.

Table 14. Effect of H₂O vs Methanol as the Flame Denitration Feed Solvent

Feed Concentrations: 300 g/liter TNT and 28 g/liter ANN to give nominal 2.5 wt % Al₂O₃ in product.

Reflector Temperatures (°C)	Feed Solvent	Average Particle Size (μ)	Surface Area (m ² /g)
1600	Methanol	1.0	1.4
1550	H ₂ O	1.1	1.5
1500	Methanol	1.5	2.2
1500	H ₂ O	1.3	1.9
1000	Methanol	1.8	3.2
1000	H ₂ O	1.9	5.4
900	Methanol	1.7	6.7
900	H ₂ O	1.6	5.3

5.3.2 Properties of the Products of Thoria-Sol Feeds

Stable thoria sols or thoria-alumina sols were used as feed materials to determine if the decomposition of the nitrates in TNT feed solutions causes the small product-particle size. Spheroidal particles were obtained even in the absence of alumina (Fig. 20). However, the particle sizes were about the same as for TNT-ANN solutions of the same thorium and aluminum molarities, and the products showed more particle degradation during toroid tests than that shown by flame-denitration products.

6. STUDIES ON THE CONTROL OF PARTICLE SIZE

Since the properties of thoria slurries are very dependent on the particle size, its control during preparation is important. Therefore the variables that might affect the mean particle diameter were studied.

PEM-3059-3

(a) Run 117; 1 *M* thorium sol calcined at 1600°C; product of 2.7 μ mean diameter and 0.90 m²/g surface area.

PEM-3058-3

(b) Run 115; 2 *M* thorium sol calcined at 1525°C; product of 4.6 μ mean diameter and 0.98 m²/g surface area.

Fig. 20. Product from Flame Calcination of Thorium Sols.

Control of the particle-size distribution would also be necessary to obtain a high yield within specified size limits. Typical size-distribution curves (by the method described in Sec 9.1.2 in the Appendix) are shown for products collected in the spray cooler (Fig. 21).

6.1 Control of Mean Diameters

The amount of thorium in the 1- μ -diam particles (a common mean diameter) was equivalent to the $\text{Th}(\text{NO}_3)_4$ in about 5- to 10- μ -diam drops of the methanol feed solution. The drop size to be expected from the atomizing nozzles was calculated to be about 30 μ , using the method of Nukiyama and Tanasawa.²⁶ In order to confirm this, the torch was removed from the system, liquid droplets sprayed in the open without flame, and samples of the droplets were collected on microscope slides. The majority of the drops collected were about 150 μ at the usual flow rates, and as small as 30 μ at high gas flow rates. Since each drop contains 100 to 10,000 times the amount of thorium in the average product particle, either the liquid drop or the solid mass split into smaller units in the flame.

Attempts to control the particle size were only partially successful; the effects of variables are listed below.

1. A significant increase in particle size was obtained for increased feed concentrations. This effect is shown most clearly for $\text{Th}(\text{NO}_3)_4$ in water feeds (Table 15), but was also noticeable for $\text{Th}(\text{NO}_3)_4$ in methanol and for thorium sols. It is postulated that the increase in particle size results from changes in the physical properties of the liquid at high concentrations rather than from the mere presence of more material per droplet.

Fig. 21. Typical Size Distribution Curves for Several Products of Denitration.

Table 15. The Effects of Operating Parameters on the Particle Size of Flame-Calcined Thoria-Alumina

Feed: Al present in same form as thorium to give 2.5 wt % alumina in product, water used as feed solvent

Atomizing gas: 2.19 SCFM of N₂, with exceptions as noted

Thorium Feed Form	Conc. (g/liter)	Reflector Temperature (°C)	Feed Rate (cc/min)	Product Mean Diam (μ)	Product Surface Areas (m ² /g)
Th(NO ₃) ₄	300	1500	7	1.3	1.9
		1550 ^a	30	1.1	1.5
		900	6	1.6	5.3
		900	30	2.0	6.1
	600	1500	6	2.1	1.3
			28	1.9	2.4
		1000	8	1.9	5.4
			33	2.9	5.7
			9	2.5	5.2
			33	2.1	6.3
	920	1500	26	1.8	1.3
			29	1.8	1.4
		1000	30	2.1	5.6
	1226	1450	27	2.0	1.7
Th(SO ₄) ₂	35	1500	30	1.1	5.3
ThO ₂ sol	264	1600 ^b	30	2.7	0.9
		1500	26	1.8	0.94
		1000	24	2.5	3.2
	528	1525 ^{a,b}	29	4.6	0.98
Th(NO ₃) ₄ ^c	300	1600 ^a	30	0.9	2.4
		1500	30	1.5	2.2
		1300 ^a	30	1.6	1.8
		1000	30	1.8	3.2
	536	1500	35	1.3	1.3
		650	35	5.0	3.8

^aThe atomizing gas in this experiment was not 2.19 SCFM of N₂; variations are not considered important.

^bThese two thoria-sol runs were without alumina in the feed-sol, and there was therefore no alumina in the product.

^cThese runs were with methanol solvent instead of water.

2. A larger particle may also be obtained by lowering the reflector temperature in the region in which the droplets are formed to 1000°C from the 1500 to 1600°C level (Table 15). Substantially lower temperatures (600°C) show no further increase in particle size.

3. The effect of the size of the entering droplet apparently has no relationship to the ultimate particle size. The about-8-cc/min feed rates gave smaller liquid drops from the atomizing nozzle than the 33-cc/min rates, but did not give significantly smaller particles.

4. The use of $\text{Th}(\text{SO}_4)_2$ solutions or thoria sols to avoid the nitrate decomposition products did not result in any significant change in the particle size of the product. Apparently the product particle size is not a result of an explosive thermal decomposition, as could be postulated for nitrate solution feeds.

5. The effects of changing from methanol to water as the solvent were not significant if conditions were controlled to give the same reflector temperatures and other similar conditions.

6.2 Discussion of Product Yields

High yields of spherical particles within specified size limits would be desirable in order to reduce the recycle of unusable products. Yields of product of 1 to 10 μ diam for the flame denitration runs at 1500°C were mostly 25 to 35% of the feed thoria. Material that collected on the furnace wall or in the trap could have been broken up in water and then classified to obtain some additional 1 to 10 μ product, but most of it was much too large for use in slurries.

A complete material balance was made for run 111. The recovery for a 24-hr run with a feed input of 14.8 kg of thorium as $\text{Th}(\text{NO}_3)_4$ crystals was 94% of the feed thorium (Table 16). Rounded product particles 1.35 μ in mean diameter were produced. All effluent streams were carefully sampled; the loss of 6% or 1 kg is larger than would be expected from analytical uncertainties. If the 16.9 kg of recovered solids were considered to be 95% ThO_2 —5% Al_2O_3 , the material balance would be over 98%. The lower percentages of thorium by analyses shown in Table 16 are believed due to incomplete drying, as shown by weight losses on ignition. The feed thorium was recovered as 40% product and 54% as furnace-wall and trap material, from which the product recovery would be low.

7. CONCLUSIONS

In a one-step process, spheroidal thoria and thoria urania particles about 1 μ in mean diameter were prepared by thermal decomposition, in a high-temperature flame, of thorium nitrate and thorium nitrate—uranyl nitrate solutions containing a glassing agent. Oxygen-hydrocarbon flames supplied the heat. These particles showed excellent properties when tested at conditions applicable to breeder blankets of aqueous homogeneous reactors. Yield stresses were 1/6 to 1/10 of those for nonspheroidal thoria of the same particle size. Particle degradation in long-term pumping tests was negligible. Corrosion rates and modulus of rigidity values were low--comparable to the best of the other thoria slurries tested.

Aluminum nitrate in the aqueous or methanol feed solutions equivalent to 0.5 to 10 wt % alumina was used to obtain spheroidization at temperatures estimated to be about 2200°C. Temperatures measured at the

Table 16: Thorium Material Balance for Run No. 111

Basis: Thorium analyses on a weight basis

Input				
Feed salt basis:				
$(36.8 \text{ kg TNT})(0.401 \text{ g Th/g salt}) = 14.75 \text{ kg Th}$				
Feed solution basis:				
$(66.14 \text{ kg solution})(0.228 \text{ g Th/g solution}) = 15.09 \text{ kg Th}$				
Output				
Location	Wt (kg)	% Th	Wt Th (kg)	% of Feed Th ^a
Product (recycle stream)	5.17	85.14	4.40	29.8
Trap	7.89	76.9	6.06	41.1
Furnace wall	2.35	82.7	1.95	13.2
Filter bags	0.90	84.3	0.76	5.2
Product (recycle holdup)	0.59	81.4	0.48	3.3
Product (recycle supernate)	192.2	0.117	0.23	1.6
Off-gas			0.001	0
Total Material Recovered, kg			13.88	94.2

^aBased on feed salt input of 14.75 kg Th.

outside of a stabilized zirconia reflector were about 1500°C for these tests. Silica, from tetraethylorthosilicate in the feed solutions, and BeO (from $\text{Be}(\text{NO}_3)_2$ in the feed solutions) also gave spheroidal thoria or thoria-urania particles. Spheroids were not obtained at these conditions for urania-alumina or urania-silica nor for products (pure thoria, pure urania, or thoria-urania) which did not contain a glassing agent.

Calculations of the rates of heat transfer and equilibrium temperatures for the flame denitration process show that 0.01 to 0.06 sec inside a reflected flame is necessary. Without a reflector, the particles reach maximum temperatures of only 40 to 60% of the absolute flame temperatures. The times required for heat transfer are controlled by the rate of radiant heat transfer to particle surfaces, not by the conductive heat transfer within particles.

Aqueous or methanol solutions of nitrate salts were easily pumped and dispersed by atomizing nozzles. A number of dry-powder feeding methods were tested for feeding dispersed thoria or thorium oxalate to a flame; none was satisfactory. A torch was developed for feeding methanol-thoria slurries that were kept in suspension by ultrasonic treatment or by making the methanol 0.003 M in oxalic acid.

Stabilized zirconia was a more satisfactory reflector material than magnesia or graphite.

The mean particle diameter of spheroidal flame-denitration products was controllable only from 0.9 to $2.1\ \mu$ when the concentration of the feed solution was the independent variable. The size of the liquid drops from the atomizing nozzle had no effect on the ultimate particle size; the average drop contained 100 to 10,000 times the amount of thorium in the

average product oxide particle. Larger, nonspheroidal particles of up to 5 μ were obtained by lowering the reflector temperature to 1000°C. Use of $\text{Th}(\text{SO}_4)_2$ solution or thoria sols as the feed liquid did not result in any large variations in particle sizes of the oxide products. Alumina-free spheroidal thoria particles were obtained when the thoria-sol feeds were used, but the amount of particle degradation during toroid tests was higher than that for thoria-alumina denitration products.

Yields of flame denitration product in the desired particle-size range (<10 μ) constituted 25 to 35% of the feed thoria for normal short runs and 40% for a longer run. About half of the feed thoria was collected as furnace-wall or trap agglomerates, from which product recovery would be small.

8. REFERENCES

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9. APPENDIX

9.1 Analytical Methods and Their Significance

The physical properties used to characterize a slurry powder are surface area, average particle size, particle shape, yield stress, crystallite size, and particle density. All these properties are measurable.

Meaningful relations between the measured property, process variables and slurry behavior exist for the first four properties listed. However, the anomalies of slurry behavior subject even these best-defined relations to wide error. Attempts to describe mathematically the relations between a physical property (or properties) and slurry behavior have yielded only approximations. Analytical data furnish a qualitative appraisal of a slurry material but are most useful when making comparisons. The most thorough attempt to relate measurable physical properties and slurry behavior is given below in the discussion on yield stress. Examination of the equation relating yield stress to physical properties will thus show the least uncertainty met.

9.1.1 Surface Area

The surface area of the slurry powder determined by the standard (Brunauer-Emmet-Teller) nitrogen adsorption method²⁷ is from 1 to 100 times that obtained by calculating an area assuming solid, smooth spheres or cubes. For particles of theoretical density, the theoretical surface area, S , in square meters per gram, is

$$S = 6/\rho d,$$

where ρ is the particle density in grams per cubic centimeter, and d is the diameter of a sphere or edge of a cube, in microns.

The surface area of a thoria powder varies inversely with the calcination temperature as shown for an average particle diameter of 1.1 to 1.4 μ (Table A-1).

Table A-1. Characteristic Properties of Fired Thoria²⁸

Final Firing Temp (°C)	Firing Time (hr)	Avg X-Ray Crystallite Size (Å)	Specific Surface Area (m ² /g)
650	24	143	25.0
1000	12	803	4.3
1600	12	2000	1.0

Thus a knowledge of surface area permits an estimate of the calcination temperature of a sample of known particle size. High calcination temperatures also provide needed mechanical strength for the slurry particle. While resistance to attrition is thus obtained, the powder bed frequently sinters, giving large particles (larger than 10 μ), which are extremely abrasive.

9.1.2 Average Particle Size

The size distribution of a powder was determined by a modification of Stokes's sedimentation technique.²⁹ The sample of thoria (urania or thoria-uranium can also be analyzed this way) is made radioactive by neutron irradiation and is then dispersed in distilled water and placed in a long, vertical glass tube (1.5 in. in diameter and 30 in. high). The gamma emission of an incremental length near the bottom of this tube is recorded as a function of time. The decrease in the rate of gamma emission thus obtained can be related by the Stokes equation to the size of the particles

remaining in suspension. Treating the data by increments, a complete particle-size distribution may be obtained. The values for average particle diameter, d_{50} , obtained by this method are on a weight basis. Results are reproducible within $\pm 0.1 \mu$ in the 1- to 3- μ range encountered in this work. As this method was used on all samples and the data are used comparatively, absolute accuracy of the method is not needed.

The particle-size distribution is customarily plotted on logarithmic probability paper, and the average particle size is used to simplify this discussion. Herein, the term "particle size" is used interchangeably with the average particle size. This simplification is adequate unless a marked departure from the usual distribution is encountered. Particle-size distributions were determined independently for product samples and for toroid or loop test samples; therefore, slightly different values are tabulated for the same materials.

The average particle size of a slurry is the most widely used of the slurry properties. The distribution of the particle sizes is also frequently useful and may be obtained directly from the plotted distribution. The rate of erosive attack of a particular slurry is directly dependent on the average particle size and concentration of the slurry. The yield stress (see below) of a slurry can also be related to its average particle size. The tendency of a slurry to form cakes or large agglomerates (balls) in engineering-test equipment may be markedly affected by the presence of small quantities of 50- to 100-A particles. These small particles result from breakage, or degradation, of larger particles in extended pumping tests and are particularly prominent for slurries of thoria that has been fired at temperatures less than 800°C.

9.1.3 Particle Shape

The shape of a particle in the size range of interest in this work is shown adequately by its silhouette on an electron micrograph. The more refined electron microscopy techniques of stereo viewing, shadowgraphs, and carbon replication were used in the early work to confirm that particles appearing round in silhouette were also round when viewed in three dimensions. Since this confirmation, silhouettes have been used exclusively.

The principal effects of particle shape, distinguishing between the spheroidal and all other shapes, are that corrosion rates and yield stresses are lower for spheroidal particles. Both the Houdry spheres and the spheroids produced in the flame work showed these improvements. Inseparably combined with the effect of particle shape in this comparison is the additional effect of a smooth, high-fired surface. However, the comparison holds for conventional high-fired particles that have comparable surface characteristics.

9.1.4 Yield Stress .

The yield stress and coefficient of rigidity of the thorium slurries (1000 g of ThO_2 per kilogram of H_2O) were determined by capillary viscometry at room temperature. With the data thus obtained, the rate of shear (y axis) is plotted against the shearing stress (x axis). The straight portion of the plot is extrapolated to intersection with the x axis. The value at the intercept is the yield stress. The slope of the line is the coefficient of rigidity

Thorium slurries are non-Newtonian, exhibiting pseudo-plastic behavior. Thomas³⁰ selected the Bingham-plastic model as the most suitable flow model for studying the rheology of thorium slurries. The coefficient of rigidity

and the yield stress are the two parameters that characterize the Bingham plastic model. The coefficient of rigidity represents the limiting value of the viscosity at high rates of shear, while the yield stress is the stress necessary to initiate flow in a non-Newtonian fluid.

Turbulent flow of the slurry must be maintained throughout the reactor system to prevent settling. Since the yield stress has a marked effect upon the critical velocity of the slurry, (i.e., the minimum velocity at which turbulent flow may be obtained), the importance of this parameter is recognized. The effect of the coefficient of rigidity on the critical velocity is comparatively small; therefore, this parameter, while important in some respects, is of less overall importance. Values of 0.1 lb/ft² and 4.0 centipoise were specified as the maximum acceptable values for these properties. These values refer to a slurry composed of 1000 g of ThO₂ per kilogram of D₂O at room temperature. This is the design concentration of the breeder blanket for the nuclear reactor.

The yield stress for conventional slurries may be related to concentration and particle size by the following equation:³⁰

$$y = K \phi^3 / D_p^{1-4},$$

where

y = yield stress in lb/ft²,

$K = (1.8^{+1.8}_{-0.8}) \times 10^2$,

ϕ = volume fraction ThO₂,

D_p = the mean particle diameter, μ .

Since the design concentration is 0.145 volume fraction thorium, a minimum mean particle diameter of 3 μ is needed to obtain the desired yield stress of 0.1 lb/ft². Classifying conventional materials to yield so large an

average particle size without having an accompanying large fraction of the erosive 10- μ (and larger) particles is difficult. Spherical slurry particles give much lower yield stress values (lower values of K) and thus give acceptable yield stresses with smaller mean particle diameters. The absence of sharp corners also lowers the erosiveness of the slurry.

The wide variation in the numerical constant of the above equation is ascribed by Thomas to important factors not considered in the equation: electrolyte effects, surface phenomena, and particle shape. The yield stress is independent of temperature up to 300°C. The coefficient of rigidity decreases with increasing temperature.

9.1.5 Crystallite Size

X-ray-diffraction line broadening is used to measure thoria crystallite sizes. Allred, Buxton, and McBride related crystallite size to surface area and calcination temperatures.³¹ General relationships were found and they were similar to those already discussed between surface area and calcination temperature (see 9.1.1 and Table A1). Large crystallites (1500 Å) are formed from small crystallites by sintering during high-temperature ($\geq 1400^\circ\text{C}$) calcination. Annealing of the slurry particle also occurs.³¹ The result is a crystallite size that approaches the size of the slurry particle. This annealed particle is highly resistant to degradation. Any significant decrease in crystallite size during a slurry-attrition test is always accompanied by particle degradation.

9.2 Engineering-Test Methods

Empirical dynamic tests give the most reliable and reproducible data available on the behavior of slurries at reactor blanket conditions.

Although these loop and toroid tests (see below) show some anomalous behavior, screening by such tests is more dependable than screening by use of the above described analytical measurements.

9.2.1 Toroid Test

The toroid test is a dynamic test devised for studying on a small scale the chemical and physical stability of slurry samples at reactor-blanket conditions. The toroid is a closed loop (doughnut) of 3/8-in. pipe about 5-1/2-in. in diameter.³² It is mounted and driven eccentrically so that the slurry sample in the toroid is swirled. Velocities in the 20- to 40-fps range are attained. A furnace encloses the toroid, and temperatures up to 300°C can be maintained within the sample. Corrosion specimens are inserted through the outer periphery of the toroid, projecting into the swirling slurry. Pressurized oxygen or hydrogen is maintained in the void space above the slurry sample in order to simulate reactor conditions.

9.2.2 Pump-Loop Tests

The pump-loop tests furnish the same physical, chemical, and corrosion data as the toroid, but since they more closely approach reactor conditions, the data are more representative of an operating system. The points of particular interest are those of extreme turbulence (e.g., produced by pump impellers), those where abrasive properties are troublesome (e.g., in canned-rotor pump bearings), and those heat transfer surfaces where caking might occur.

The apparatus for these tests is designed to circulate slurry under reactor operating conditions, lacking only the effect of a radiation field.

The equipment ranges from bench-size to full-scale models. The components (e.g., pumps and heat exchangers) of which these loops are constructed are either the same as intended for reactor construction or of the same type but suitable in size for the scale of the model in which they are installed. The results from the loop tests are currently the most reliable data available for the overall performance of a slurry.

It must be pointed out that slurry testing to date includes analytical and out-of-pile tests. These tests afford an economical though incomplete screening of prospective slurry preparations. The considerably more expensive and complex in-pile testing of many slurries will be required before the ultimate suitability of a slurry can be assured.

9.3 Detailed Tabulated Data

Conditions and results are summarized. The estimated temperatures are the indications of thermocouples in contact with the outside wall of the reflector at the midpoint. When these thermocouples indicated 1600°C , the flame temperatures were estimated to be 600°C higher. The feed rates are those of the slurries or the solutions. The gas rates were controlled to hold selected temperatures.

Table A2 shows runs with thorium slurry feeds. Table A3 shows the experimental runs with feeds of thorium nitrates and other salts in methyl alcohol solutions. Table A4 shows runs made while attempting to control the product particle size. These include runs with thorium-sol feeds and one run with a saturated $\text{Th}(\text{SO}_4)_2$ solution feed.

Table A2. Results of Slurry-Calcination Experiments for Exploring the Feasibility of the Flame-Calcining of a Powder

Feed Liquid: Methanol

Run No.	Est. Temp. (°C)	Properties of the Feed			Additives	Reflector		Analytical Results			
		Feed Rate (cc/min)	ThO ₂ Conc'n. ^a (g/liter)	Th(C ₂ O ₄) ₂ (g/liter)		Type	Size in Inches (ID x Length)	Average Particle Size (μ)	Surface Area (m ² /g)	Yield Stress (lb/ft ²)	Mod. of Rig. (centi-poise)
1		?	10		1000 ppm Na ^b	None					
2		?	10		1000 ppm Na	None					
5		~3.0	10		None	None					
6		50.0	10		None	None					
8		20.0	10		None	None					
9		~20.0	10		None	None			3.1		
14		~20.0	200		0.003 M H ₂ C ₂ O ₄ ^c	Carbon	1 x 9	1.65	2.7		
15		~20.0	200		0.003 M H ₂ C ₂ O ₄	Carbon	1 x 9	1.65	2.7	0.25	
16	~1600	~20.0	200		0.003 M H ₂ C ₂ O ₄	Carbon	1 x 9	1.05	2.5	0.21	
19	>1600	~20.0	200		0.003 M H ₂ C ₂ O ₄	Zirconia liner	1 x 12	2.6	1.2	0	
20		10.0		200.0	0.003 M H ₂ C ₂ O ₄	Carbon	2 x 13.5	2.03	2.5		
21	1100	18.0		200.0	0.003 M H ₂ C ₂ O ₄	Carbon	2 x 13.5	1.65	6.0	0.196	3.3
23	1400	17.0	200		0.003 M H ₂ C ₂ O ₄	Carbon	2 x 13.5	>1.1	2.5	0.25	3.4
24	1400	18.0	200		0.003 M H ₂ C ₂ O ₄	Carbon	2 x 13.5	<1.2	2.4	0.27	3.3
25	>1650	18.0	200		0.003 M H ₂ C ₂ O ₄ (0.5% SiO ₂)	Carbon	2 x 13.5	<1.1	3.3	0.225	
27	>2000	18.0	200		0.003 M H ₂ C ₂ O ₄ (0.6% SiO ₂)	Zirconia liner	1 x 12	<1.1	3.6	0.225	2.09

^aThe ThO₂ and Th(C₂O₄)₂ used in these experiments were obtained from the Oak Ridge National Laboratory Pilot Plant.

^bSodium was first added as glassing agent.

^cOxalic acid was added for dispensing slurry.

Table A3. Flame Denitration Experiments

Runs performed for the purpose of Process and Equipment Development. Later runs were made for product evaluation purposes.

Feed Solvent: Methanol

Run No.	Temp. (°C)	Feed Properties ^a				Reflector		Analytical Results				Remarks
		Feed Rate (cc/min)	Th(NO ₃) ₄ (g/liter)	UNH (g/liter)	Al(NO ₃) ₃ (g/liter)	Type	Size in Inches (ID x length)	Average Particle Size (μ)	Surface Area (m ² /g)	Yield Stress (lb/ft ²)	Mod. of Rigidity (centi-poise)	
28		~25.0	80.0	6.0		Carbon	2 x 13.5	~2.6	4.6			
29		~25.0	80.0	6.0		Carbon	2 x 13.5	3.4	2.2			
35	1400	16.0	80.0	6.0		Carbon	2 x 13.5	1.1	5.8			
36	1310	15-20	160.0	12.0		Carbon	2 x 13.5	1.5	5.5			
37	1480	17.5	80.0	6.0		MgO	3 x 18	~2.57	4.8			
38	1635	15.0	160.0	12.0		MgO	3 x 18	1.2	4.9			
39	>1550	17.0	160.0	12.0		MgO	3 x 18	0.9	5.9	0.275		
40	1560	15-20	160.0	12.0		MgO	3 x 18	1.4	7.8	0.80	6.84	
41	1550	17.0	160.0	12.0		MgO	3 x 18	2.7	6.5			
42	1550	20.0	160.0	12.0		MgO	3 x 18	2.7	6.3			
43	~980	20.0	160.0	12.0		MgO	3 x 18	3.1	6.7			
44	800	~25.0	160.0	12.0		MgO	3 x 18	1.8	6.9			
45	1200	~20.0	160.0	12.0		MgO	3 x 18	1.2				
46	1000	24.0	160.0	12.0		MgO	3 x 24	3.1	7.6	0.94	5.06	
47	800	24.0	160.0	12.0		MgO	3 x 24	2.4	6.5	0.45	3.08	
48	1440	20.0	160.0	12.0		MgO	3 x 24	2.4	6.2	0.80	1.63	0.53 g MoO ₃ per 100 g ThO ₂ in feed
49	1220	20.0	160.0	12.0		MgO	3 x 24	2.5	7.7	0.675	4.07	0.53 g MoO ₃ per 100 g ThO ₂ in feed
50	1425	20.0	160.0	12.0		MgO	3 x 24	2.5	7.7			174 ppm PdO ₂ in product
51	1205	21.0	160.0	12.0		MgO	3 x 24	2.3	7.8			174 ppm PdO ₂ in product
52	1425	23.0	160.0	12.0	32.0	MgO	3 x 24	1.5	2.0			
53	1405	23.0	160.0	12.0	64.0	MgO	3 x 24	1.8	5.7	0.196	3.09	
54	1405	25.0	160.0	12.0	17.6	MgO	3 x 24	1.6	3.0			
55	900	21.0	160.0	12.0		MgO	3 x 24	2.0	8.3	0.80	4.0	
57	1475	21.0	160.0	12.0	64.0	MgO	3 x 24	1.8				
59	1500	21.0		160.0		MgO	3 x 24	4.5				

^aTh(NO₃)₄ and UO₂(NO₃)₂ shown include correction for contained water.

Table A3 (continued)

Run No.	Temp. (°C)	Feed Properties ^a				Reflector		Analytical Results				Remarks
		Feed Rate (cc/min)	Th(NO ₃) ₄ (g/liter)	UNH (g/liter)	Al(NO ₃) ₃ (g/liter ³)	Type	Size in Inches (ID x length)	Average Particle Size (μ)	Surface Area (m ² /g)	Yield Stress (lb/ft ²)	Mod. of Rigidity (centi-poise)	
62	1550	25.0	160.0	12.0	32.0	MgO	3 x 24	1.7	1.8	<0.02	1.21	
63	1530	28.0	160.0	12.0	16.0	MgO	3 x 24	1.7	2.4	<0.05	1.8	
64	1545	28.0	160.0	12.0	16.0	MgO	3 x 24	<2.03				
65	1520	30.0		160.0		MgO	3 x 24					
66	1520	22.0	160.0	12.0	6.6	MgO	3 x 24	2.0	2.6	0.026	1.58	
67	1480	30.0	160.0	12.0	64.0	MgO	3 x 24					
68	1495	21.0	160.0	12.0	16.0	MgO	3 x 24	3.0	1.6	0.02	1.27	
69	1500	19.0	160.0	12.0	64.0	MgO	3 x 24	1.6	3.1	0.049	2.17	
70	1510	21.0	160.0	12.0	32.0	MgO	3 x 24	1.4	1.4	<0.02	1.62	
71	1450	20.0	160.0		29.5	MgO	3 x 24	1.0	1.3	0.026	1.65	
72	1495	22.0	320.0	24.0	64.0	MgO	3 x 24	0.9	1.7	0.02	1.45	
73	1500	21.0	160.0	12.0	32.0	MgO	3 x 24	1.1	2.1	0.06	1.74	
74A	1505	100.0	354.0	9.7	34.0	MgO	3 x 24	2.5	2.3	0.154	1.98	
74B	1500	50.0	537.0	14.6	51.0	MgO	3 x 24	3.0	1.3	0.02	1.68	
75A	855	50.0		400.0		MgO	3 x 24	1.9	4.3			
75B	1020	50.0		400.0		MgO	3 x 24	1.6	2.7			
76	1600	80.0	536.0	14.5	51.0	ZrO ₂	4 x 24	1.5	2.0	0.03	1.31	
77	1490	100.0	536.0	14.5	51.0	ZrO ₂	4 x 24	1.5	1.6	0.02	1.7	
78	1550	50.0	320.0		12.0	ZrO ₂	4 x 24	<1.3	1.4	<0.02	1.59	
80	1500	50.0	540.0	21.4		ZrO ₂	4 x 24	1.6	6.3	0.47	2.71	37 g La(NO ₃) ₃ in feed
81	1485	30.0	380.0	10.5		ZrO ₂	4 x 24	1.0	2.5	<0.02	1.72	1.0% SiO ₂ in feed as TES ^b
82	1500	~35.0	536.0	14.5	51.0	ZrO ₂	4 x 24	1.3	1.3	0.034	1.12	
83	600-700	30.0	536.0	14.5	51.0	ZrO ₂	4 x 24	5.0	3.8	~0.01	~2.5	
84	1200	39.0	552.0			ZrO ₂	4 x 24	1.2	1.5	<0.02	1.22	5% SiO ₂ in feed as TES ^b
85	1200	27.0	591.0			ZrO ₂	4 x 24	1.0	4.0	<0.02	2.10	1.0% SiO ₂ in feed as TES ^b
86	1500	~30.0		545.0		ZrO ₂	4 x 24	1.2	6.2	<0.02	1.26	5.0% SiO ₂ in feed as TES ^b
87	1505	28.0		588.0		ZrO ₂	4 x 24	1.0	6.1	<0.1	~2.5	1.0% SiO ₂ in feed as TES ^b
88	1510	33.0		508.0	92.0	ZrO ₂	4 x 24	0.60	7.4	0.1	~3.0	
89	1500	~30.0		576.0	24.0	ZrO ₂	4 x 24	~0.60	8.5	0.1	~3.0	
90	1530	~30.0	525.0	26.0		ZrO ₂	4 x 24	1.2	1.9	0.02	2.17	5% SiO ₂ in feed as TES ^b
91	1430	33.0	111.0			ZrO ₂	4 x 24	0.60				56.5 g Be(NO ₃) ₂ in feed

^b tetraethylorthosilicate

Table A4. Flame Denitration-Particle Size Studies
(Runs performed in attempts to increase product particle size)

Run No.	Temp. (°C)	Feed Properties				Atomizing Gas			Analytical			Remarks	
		Solvent	Feed Rate (cc/min)	Th(NO ₃) ₄ (g/liter)	ThO ₂ (g/liter)	Al(NO ₃) ₃ (g/liter)	Material	Flow Rate (scfm)	Relative Velocity (m/s)	Q _B /Q _E	Average Particle Size (μ)		Surface Area (m ² /g)
92-A	1300	CH ₃ OH	30	300		28	O ₂ + C ₃ H ₈	1.48	119	1400	1.6	1.8	
92-B	1300	CH ₃ OH	30	300		28	O ₂ + C ₃ H ₈	2.85	160	2690	2.0	0.92	
92-C	1600	CH ₃ OH	30	300		28	O ₂ + C ₃ H ₈	1.48	119	1400	1.0	1.4	
92-D	1600	CH ₃ OH	30	300		28	O ₂ + C ₃ H ₈	2.85	160	2690	0.9	2.4	
93	1000	CH ₃ OH	30	300		28	N ₂	1.66	120	1568	1.8	3.2	
94	1500	CH ₃ OH	30	300		28	N ₂	1.66	120	1568	1.5	2.2	
95	1550	H ₂ O	30	300		28	O ₂ + C ₃ H ₈	1.42	114	1340	1.1	1.5	
96	1500	H ₂ O	7	300		28	N ₂	2.19	130	8860	1.3	1.9	
97-A	900	H ₂ O	6	300		28	N ₂	2.19	130	10300	1.6	5.3	
97-B	900	H ₂ O	30	300		28	N ₂	2.19	130	2070	2.0	6.1	
98	900	CH ₃ OH	10	300		28	N ₂	2.19	130	6200	1.7	6.7	
99-A	1500	CH ₃ OH	30	300		28	N ₂	2.19	130	2070	1.6	2.4	
99-B	1500	H ₂ O	30	300		28	N ₂	2.19	130	2070	1.3	1.7	
100-A	600	H ₂ O	33	600		56	N ₂	2.19	130	1880	2.1	6.3	
100-B	600	H ₂ O	9	600		56	N ₂	2.19	130	6880	2.5	5.2	
101-A	1000	H ₂ O	8	600		56	N ₂	2.19	130	7750	1.9	5.4	
101-B	1000	H ₂ O	33	600		56	N ₂	2.19	130	1880	2.9	5.7	
102-A	1500	H ₂ O	28	600		56	N ₂	2.19	130	2220	1.9	2.4	
102-B	1500	H ₂ O	6	600		56	N ₂	2.19	130	10300	2.1	1.3	
103	1500	H ₂ O	30				N ₂	2.19		2070	1.1	5.3	35.0 g/liter Th(SO ₄) ₂ feed
104	1500	H ₂ O	26		264	62.5	N ₂	2.19		2380	1.8	0.94	Thoria sol feed
105	1000	H ₂ O	24		280	66.6	N ₂	2.19		2580	2.5	3.2	Thoria sol feed
106	1500	H ₂ O	26	920		83	N ₂	2.19		2380	1.8	1.3	
107	1450	H ₂ O	27	1226		110	N ₂	2.19		2295	2.0	1.7	
108	1500	H ₂ O	33		528		N ₂	2.19		1880	4.0	2.2	Thoria sol feed
109	1000	H ₂ O	30	920		83	N ₂	2.19		2070	2.1	5.6	
110	1500	H ₂ O	29	920		83	N ₂	2.19		2140	1.8	1.4	
111	1500	H ₂ O	30	920		83	Air	2.19		2070	1.35	1.1	
112	1600	H ₂ O	31	920		83	Air	2.19		2000	1.0	1.8	
113	1600	CH ₃ OH	30		190	10(Al ₂ O ₃)	O ₂ + C ₃ H ₈	2.19		2070	1.8	0.84	Slurry feed <10μ particles
114	1500	H ₂ O	29		264		O ₂ + C ₃ H ₈	2.19		2140	2.03	1.1	Thoria sol feed
115	1525	H ₂ O	29		528		O ₂ + C ₃ H ₈	2.19		2140	4.6	0.98	Thoria sol feed
116	1625	CH ₃ OH	29	600			O ₂ + C ₃ H ₈	2.19		2140	0.9	3.6	
117	1600	H ₂ O	30		264		O ₂ + C ₃ H ₈	2.19		2070	2.70	0.90	Thoria sol feed

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