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For The Atomic Energy Commission

H. F. Cansell

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SUMMARY

Slurries of Lindsay No. 8 oxide and of oxide prepared from Thorex product were irradiated at 300°C in the LITR for 115 and 288 hr, respectively, without apparent damage. A similar Thorex-product oxide slurry irradiated 6 days in the ORNL Graphite Reactor at 300°C also showed no apparent deterioration. A slurry, containing ThO_2 , U^{235} , and copper, previously irradiated in the Graphite Reactor at 300°C was recovered; it had changed from a tan to a gray-green color, indicative of reduced uranium, and contained a large fraction of lumpy material.

The addition of 0.09 m CuSO_4 alone to an Ames oxide slurry resulted in a gas recombination rate approximately 30% lower than that obtained when 0.0025 $\text{m H}_2\text{SO}_4$ was added with the copper sulfate. With oxide prepared from Thorex product by calcination of the precipitated oxalate at 650°C the combination rate was even lower. The presence of 0.03 m silver in an Ames oxide slurry combined 10 M H_2 /hr/liter at 300°C and $P_{\text{H}_2} = 500$ psi. Slurries containing silver prepared from D-16 oxide were very much more reactive, 0.02 m silver recombining 35 m H_2 /hr/liter at 270°C and the same hydrogen partial pressure. The silver-thorium mixed oxide, in contrast to the copper sulfate, apparently acts as a true heterogeneous catalyst.

In laboratory studies on the properties of oxide prepared by the thermal decomposition of oxalate precipitated from Thorex product thorium nitrate, increasing the final calcination temperature from 650 to 750, 900, and 1000°C gave more crystalline oxides, had little effect on the particle size as measured by sedimentation analyses, increased the bulk density of settled solids (after wet autoclaving at 300°C) from 1600 to 2100 g of thorium per liter, and decreased the nitrogen adsorption surface area from 35.3 to 21.9, 12.3, and 8.3 m^2/g , respectively. Autoclaving the solids in water at 300°C in the presence of 0, 200, 500, 1000, 2000, 5000, and 10,000 ppm of sulfate as thorium sulfate did not promote crystallite growth but had a pronounced affect on the bulk density of settled solids.

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The final pH's of slurry supernatants decreased more rapidly with sulfate concentration with the higher calcination temperatures.

The crystallite sizes determined by x-ray measurements and specific surface areas determined by nitrogen adsorption for oxides obtained by oxalate calcination at 650, 750, 900, and 1250°C showed a 1:1 correspondence. Sedimentation particle size analyses of oxides pumped as a slurry at high temperature or degraded dry at room temperature in a micronizer show them to reach essentially the same average size. Only a slight increase in surface area was obtained with the micronized sample, indicating that the surface areas measured by nitrogen adsorption are mainly internal and that a surface area measurement would be a comparatively insensitive one in the study of pumped slurries.

1.0 THORIUM OXIDE SLURRY IRRADIATION STUDIES

Studies to determine the effect of in-pile irradiation on the properties of thorium oxide slurries and to demonstrate slurry radiation stability have continued. Four more in-pile irradiations of pure thorium oxide slurries were carried out at 300°C, one in the graphite reactor, and three in the LITR. All slurries previously irradiated and all but two from the current series were recovered and examined. The pure thorium oxide slurries were apparently unaffected by irradiation, but slurries containing 8% U^{235} by weight of thorium were adversely affected. Studies to determine the effect of lower uranium percentages are under way. Efforts to stir a slurry during an extended irradiation period with the simple dash-pot type stirrer were unsuccessful and it has not been possible to obtain reliable measurements of the viscosity of slurries under irradiation. An improved version of the dash-pot employing a self-timing principle and a power stroke in both the up and down directions is currently under test.

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1.1 Slurry Irradiations in the LITR

Thorium oxide slurries, containing 500 g of thorium per kilogram of H_2O irradiated in the LITR, were not apparently affected by the irradiation although the stirring mechanism failed during the irradiation. One of the slurries studied was prepared with Lindsay No. 8 oxide (oxalate calcined at $900^\circ C$), irradiated but not recovered during the previous quarter; two with D-16 oxide (prepared from Thorex product by calcination at $650^\circ C$, see Sec. 3.1), and one from D-16 oxide recalcined at $900^\circ C$. All irradiations were carried out in hole C-44, flux = 3×10^{13} n/cm²/sec, at $300^\circ C$ in the dash-pot-stirred radiation bomb previously described.⁽¹⁾ All slurries were mixed before being put in the irradiation bombs, and the experimental set-ups were pretested at temperature before insertion in the reactor. The total irradiation time for the Lindsay No. 8 oxide was 115 hr and for the D-16 oxide 288 hr. The settled densities of the recovered Lindsay No. 8 and D-16 slurries were 1330 and 1500 g of thorium per liter, respectively.

1.2 Slurry Irradiations in the ORNL Graphite Reactor

A 10-ml slurry of oxide prepared from Thorex product by $650^\circ C$ calcination (D-12) (see Sec. 3.1) containing 500 g of thorium per kilogram of H_2O was irradiated for 6 days at $300^\circ C$ at a flux of 7×10^{11} n/cm²/sec. Steam pressure decreased during irradiation, indicating a leak. Approximately 2 ml of H_2O was added to the slurry when the capillary connecting the irradiation bomb to the pressure-recording system was pressurized with nitrogen. The recovered slurry contained very little water (3 to 4 ml total volume) but appeared unchanged by the irradiation after dilution. Its settled density was 1270 g of thorium per liter.

A slurry with a thorium concentration of 500 g/kg H_2O , made from 90% thorium--8% U^{235} --2% copper mixed oxide, which had been irradiated for two weeks at $300^\circ C$ in the ORNL Graphite Reactor, was recovered.

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No gas pressure in excess of steam had been observed during the irradiation, and stirring had stopped during the first 24 hr. The irradiated slurry was gray-green in color, presumably from reduced uranium, and a large fraction of the material was lumpy. In a control experiment, in which there was no irradiation, there was no stirring difficulty, and the recovered slurry was tan colored and showed no deterioration of properties. It is presumed that the reduction and crystal growth in the irradiated slurry were the result of a net accumulation of hydrogen resulting from the efficient catalytic recombination of radiolytic gas and a consumption of oxygen by other processes. Uranium reduction and crystal growth have been observed in the laboratory when a mixed oxide slurry of thorium and uranium was subjected to a hydrogen overpressure at 250°C.

1.3 Development of Facilities for Irradiation Studies

Effort is under way to develop small-scale devices, suitable for in-pile use, to study, at least qualitatively, the changes occurring in properties of slurries, primarily viscosity, while under irradiation. Extensive out-of-pile testing of the simple dash-pot-stirred irradiation bomb demonstrated its utility in measuring the changes in viscosity of water and water-glycerin mixtures as they are heated to 300°C. Consistent and reliable results have not been obtained with thorium oxide slurries, however, and it has not been possible with present bombs to successfully stir slurries containing 1000 g of thorium per kilogram of water. Modifications in both the stirrer and bomb proportions are being made which should permit operation with slurries of higher thorium concentrations.

An improved version of the dash-pot-stirred irradiation bomb for use in hole C-44 of the LITR, which uses a multicoil activation arrangement to give a power stroke in both the up and down directions and a self-timing principle for the measurement of viscosity, is currently under test with slurries. Initial tests with water and water-glycerin mixtures show the stirring rate to be very sensitive to viscosity.

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The shielded hood for use in the remote opening and handling of the radiation bombs was completed and has been used in recovering the irradiated slurries discussed above. A shielded unit for removing bombs from the LITR has been constructed for use with this facility; it permits a bomb to be removed from the reactor and transported to the hood without the use of an additional shielded carrying container.

The slurry abrasion tester is being modified for use with irradiated slurries. The metal foil used as the target has been incorporated into an evacuated pressure cell which permits the penetration time to be detected by a pressure change.

2.0 GAS RECOMBINATION STUDIES

Development of an internal catalyst to effect the recombination of the radiolytic gases expected to be produced in a thorium oxide slurry blanket has continued. A catalyst capable of recombining, with stoichiometric oxygen, 10 moles of hydrogen per hour per liter of slurry at 280°C and a hydrogen partial pressure of 500 psi is considered satisfactory. It should be chemically compatible with the slurry and have low neutron-capture characteristics.

Out-of-pile gas combination studies included additional experiments with copper sulfate, an investigation of the use of silver as a catalyst and studies with oxide prepared from Thorex product by calcination at 650°C . Results indicate that 0.01 m silver with Thorex product oxide should be more than sufficient for both TBR and HRT purposes.

The addition of 0.09 m CuSO_4 alone to an Ames oxide slurry with a thorium concentration of 660 g/kg H_2O resulted in a combination rate at 292°C and a hydrogen partial pressure of 500 psi of 14.5 moles of H_2 per hour per liter. With 0.09 m CuSO_4 -0.0025 m H_2SO_4 a slurry of oxide prepared from the Thorex product gave a recombination rate of 7.1 moles of H_2 per hour per liter (Table 1). Mole for mole, silver was catalytic-

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cally more active in oxide slurries than copper sulfate. In an Ames oxide slurry with a thorium concentration of 660 g/kg H_2O , 0.03 m silver combined 10 moles of H_2 per hour per liter of slurry at 300°C and a hydrogen partial pressure of 500 psi (Table 2). Slurries prepared from the D-16 oxide (made from Thorex product) were very much more reactive with silver present, 0.02 m silver combining 35 moles of H_2 per hour per liter at 270°C and the same hydrogen partial pressure (Table 3). Combination rates with slurries of the pure D-16 oxide alone were three times those obtained with Ames oxide under the same conditions but were still much too low for such slurries to be used without an additional catalyst (Table 4).

Experimental details and methods of analyses have been described previously.^(2,3) The specific reaction rate constant, k_π , and the rate of hydrogen combination with oxygen in moles per hour per liter listed in the tables were obtained from the observed decrease in gas pressure with time, perfect gas behavior being assumed. First order dependence of the rate on the hydrogen partial pressure and, in effect, total gas pressure has been demonstrated. Combination rates calculated in this manner do not consider gas solubility in the slurry and therefore may be 10 to 20% lower than the actual rates.

The decrease in catalytic activity of copper sulfate in the absence of added acid and the additional decrease in activity when the higher-surface-area D-16 oxide was substituted for the Ames material (Table 1) further emphasize the complex nature of the reaction when copper sulfate is used as a catalyst in a slurry. Since copper sulfate functions best as a solution catalyst, a decrease in concentration of the catalytically active ionic species occasioned by hydrolysis or surface adsorption results in a decreased gas combination rate. In the experiments on Ames oxide slurries with copper sulfate without added acid, the amount of copper in solution was less than in similar experiments with added sulfuric acid (Table 5). In addition, the increase in the SO_4/Cu ratio and the rise in pH suggest that the decrease in catalyst activity was

Table 1
Combination Rates of Stoichiometric H₂ and O₂ Mixtures in
Thorium Oxide Slurries Containing Copper Sulfate

Slurry thorium concentration: 660 g/kg H₂

Initial gas pressures: 960 psi H₂, 500 psi O₂ (at 25°C)

Oxide	Catalyst (m)	Temperature (°C)	k _π (hr ⁻¹)	H ₂ Combination Rate, P _{H2} = 500 psi (moles/hr/liter)
Ames	0.09 m CuSO ₄ + 0.0025 m H ₂ SO ₄	293	76	22
	0.09 m CuSO ₄	292	55	14.5
D-16 ^a	0.09 m CuSO ₄ + 0.0025 m H ₂ SO ₄	263	7.5	2.9
	0.09 m CuSO ₄ + 0.0025 m H ₂ SO ₄	292	23.1	7.1

^aPrepared from Thorex thorium nitrate product by oxalate precipitation and final calcination at 650°C.

Table 2
Combination Rates for Stoichiometric H₂ and O₂ Mixtures in
Ames Thorium Oxide Slurries Containing Silver

Slurry thorium concentration: 660 g/kg H₂O

Initial gas pressures: 960 psi H₂, 500 psi O₂ (at 25°C)

Silver Conc. (<u>m</u>)	Temperature (°C)	k _π (hr ⁻¹)	H ₂ Combination Rate, P _{H₂} = 500 psi (moles/hr/liter)	Final pH at 25°C
0.0019	250	1.2	0.55	5.7
	278	1.56	0.63	
	289	1.69	0.63	
0.031	265	8.8	3.7	6.2
	300	30.1	9.95	
0.08	185	26.3	15.8	6.2
	196	33.2	18.9	
	201.5	42.0	23.2	

Table 3

Combination Rates for Stoichiometric H₂ and O₂ Mixtures in
D-16^a Thorium Oxide Slurries Containing Silver

Slurry thorium concentration: 660 g/kg H₂O

Initial gas pressures: 960 psi H₂, 500 psi O₂ (at 25°C)

Silver Conc. (<u>m</u>)	Temperature (°C)	k _p (hr ⁻¹)	H ₂ Combination Rate, P _{H₂} = 500 psi (moles/hr/liter)	Final pH at 25°C
0.04	162	4.8	3.4	---
0.02	201	8.6	4.9	---
	220	10.9	5.5	6.7
	260	43.5	16.3	---
	270	96.0	34.7	---

^aPrepared from Thorex thorium nitrate product by calcination at 650°C.

Table 4

Effect of Oxide Preparation on the Combination Rate of
Stoichiometric H_2 and O_2 Mixtures in Thorium Oxide Slurries

Slurry thorium concentration: 660 g/kg H_2O

Initial gas pressures: 960 psi H_2 , 500 psi O_2 (at 25°C)

Preparation	Temperature (°C)	k_{H_2} (hr ⁻¹)	H_2 Combination Rate, $P_{H_2} = 500$ psi (moles/hr/liter)
Thorium oxalate ^a calcined at 600°C	300	0.13	0.04
Thorium oxalate calcined at 650°C (D-16)	297	0.06	0.02
Thorium oxalate calcined above 650°C (Ames)	300	0.023	0.007

^aPrepared from mantle-grade thorium nitrate.

Table 5
Chemical Properties of Ames Thorium Oxide Slurries Containing
CuSO₄ After Combination Experiments

Slurry thorium concentration: 660 g/kg H₂O
0.09 m CuSO₄

H ₂ SO ₄ Added (<u>m</u>)	Copper Adsorbed on ThO ₂ at 25°C (% of total Cu)	SO ₄ /Cu Mole Ratio in Liquid Phase	pH	
			Initial	Final
0	77.3	1.59	3.10	3.41
0.0025	71.3	1.38	2.51	3.43

associated not only with a decrease in soluble copper but also with an increase in the relative concentration of less active but soluble hydrolytic products such as $\text{Cu}(\text{HSO}_4^+)$.⁽⁴⁾ Decreases in activity associated with the use of the higher-surface-area Thorex D-16 oxide or with increasing thorium oxide concentration noted previously⁽¹⁾ are probably the result of adsorption phenomena.

The silver catalysts were prepared by heating silver carbonate with the thorium oxides at 280°C for 2-3 hr in the presence of oxygen. The slurry solids were recovered and washed with water. With the Ames oxide only about 10 to 30% of the original silver added stayed with the slurry solids. However, essentially 100% of the silver added to the D-16 oxide was adsorbed. The low silver adsorption on the Ames oxide and possibly the lower activity of silver catalysts prepared from Ames oxide may be associated with its significant sulfate impurity (7.55 mg of sulfate per gram of thorium). Almost stoichiometric amounts of sulfate and silver ions were found in the supernatants from the silver-Ames oxide catalyst preparation and combination experiments.

Prior to the use of the silver-thorium oxide in the combination runs, the silver could be leached from the solid with cold dilute nitric acid. However, after the combination experiment the silver could be removed only by heating with concentrated nitric acid, and the evolution of nitrogen oxides indicated that at least a partial reduction of the silver to the metallic state had taken place.

3.0 LABORATORY STUDIES ON THORIUM OXIDE SLURRIES

3.1 The Preparation of Thorium Oxide from Thorex Product Solution

The availability of a large quantity of pure, essentially sulfate-free thorium nitrate product solution from the Thorex process prompted its utilization in the large-scale preparation of pure thorium oxide for use in the laboratory and engineering development of a blanket

slurry.⁽⁵⁾ The method consisted in precipitation of the oxalate at 40°C by the addition of 15% excess solid oxalic acid to a 1 M solution of the Thorex product and subsequent thermal decomposition of the washed and air-dried oxalate to oxide by heating for 2 hr at 370°C, 2 hr at 520°C, and 4 hr at 650°C. More than 3000 lb of the oxide was produced in 160-lb lots.⁽⁶⁾

Previous laboratory studies with mantle-grade thorium nitrate indicated that the oxide product prepared in this way should be reasonably nonabrasive and suitable as slurry material. Additional laboratory preparation studies were carried out using the Thorex product solution as a source material, an oxalate precipitation at 40°C with 10% excess solid oxalic acid, drying the oxalate at 110°C, and a multistage calcination consisting in heating for 4 hr at 370°C and for 4 hr at 650°C. The effects on oxide and slurry properties of increasing the final calcination temperature to 750, 900, and 1000°C and of wet autoclaving the oxide products at 300°C for 22 hr in the absence and presence of added thorium sulfate were studied.

Increasing the final calcination temperature gave more crystalline oxides, decreased the nitrogen adsorption surface areas from 35.3 m²/g for the 650°C material to 21.9, 12.3, and 8.3 m²/g for 750, 900, and 1000°C materials, respectively. The bulk density of settled solids (after wet autoclaving at 300°C) increased from 1600 g of thorium per liter for 650°C to 2100 g of thorium per liter for the 1000°C material.

Autoclaving the solids in water at 300°C in the presence of 0, 200, 500, 1000, 2000, 5000, and 10,000 ppm of sulfate as thorium sulfate did not increase the crystallite size as determined by x-ray diffraction but had a marked effect on the bulk density of settled solids. Oxides calcined at 750, 900, and 1000°C gave minima in the bulk density curves between 200 and 1000 ppm of sulfate while a pronounced difference in behavior was observed with oxides prepared

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by calcination at 650°C (Fig. 1.1). The oxide prepared in the laboratory by calcination at 650°C had a much higher bulk density than the oxide prepared in the pilot plant with the final calcination at 650°C. The difference may be due to the fact that the laboratory preparation had a different calcination history. Surface areas, crystallite sizes, and chemical composition of the 650°C oxides were comparable, but the average particle size by sedimentation analyses of the laboratory preparation was 12 μ and of the pilot plant preparation, 3 μ .

The pH's of the supernatants of slurries of the oxides autoclaved at 300°C and zero sulfate concentration varied between 7.3 and 9.5. As the sulfate concentration increased, the pH of the supernatants decreased more rapidly the higher the calcination temperature and in all cases approached a final pH of 4 (Fig. 2). Autoclaving equivalent thorium sulfate solutions in the absence of solids gave lower pH's (2.3-3.65). The difference in pH's observed with different slurries are probably the result of thorium sulfate hydrolysis and variation in free acid adsorption because of differences in specific surface area and activity of the oxides. The final pH's observed are comparable to the final pH observed in loop runs. Pronounced attack on the autoclave interior surfaces occurred at 5000 to 10,000 ppm sulfate with the 1000°C oxide and in the presence of the pure thorium sulfate solutions.

The pertinent chemical composition data for the Thorex product solution, the oxalic acid used, the oxides prepared in the laboratory, and a typical pilot plant product are given in Table 6. The only significant impurity in the product oxide is barium, which is present in the Thorex product solution and will probably not be a source of trouble.

Oxide	Calcination Temp. (°C)
Ø D-16	650
● Lab prep	650
⊙ Lab prep	750
○ Lab prep	900
● Lab prep	1000

Fig. 1 Effect of Sulfate Addition on Bulk Density of Settled Thorium Oxide Solids

Fig. 2 Effect of Sulfate Addition on pH of Supernatant for Selected Thorium Oxide Slurries

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Table 6

Typical Chemical Composition Data

	Thorex Product, Thorium Nitrate	Oxalic Acid	Th-650 Thorium Oxide by 650°C Calcination	D-16 Thorium Oxide by 650°C Calcination	Th-750 Thorium Oxide by 750°C Calcination	Th-900 Thorium Oxide by 900°C Calcination
Loss on ignition			0.83	1.16	0.39	0.08
Composition						
Th (%)	24.79	---	86.83	86.82	87.30	87.40
NO ₃ ⁻ (%)	4.08	---	0.0019	< 4 ppm	0.0018	0.0018
CO ₃ ⁼ (%)	0.06	---	0.52	0.55	0.13	< .05
SO ₄ ⁼ (ppm)	10	12	<10	65	< 10	10
Cl ⁻ (ppm)	6	435	10	40	10	<10
F ⁻ (ppm)	70	---	295	25	---	---
PO ₄ ⁼ (ppm)	4	---	60	100	45	25
Fe (ppm)	33	<5	13	25	30	60
Cr (ppm)	<5	<5	<10	<10	<10	<10
Ni (ppm)	<5	<5	<10	<10	<10	<10
Pb (ppm)	<10	<10	<10	<10	<10	<10
Ba (ppm)	800	---	1800	2600	2100	2100
Cd (ppm)	45	---	90	120	105	90
Mg (ppm)	25	---	<400	300	<400	<400
Nd (ppm)	9	---	---	23	---	---
K (ppm)	<5	---	---	<10	---	---
Li (ppm)	<5	---	---	<10	---	---
Si (ppm)	<5	---	15	20	10	10

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3.2 Characterization of Oxide Products

Progress has been made toward the characterization of thorium oxide products, in particular those produced by the thermal decomposition of thorium oxalate. Nitrogen adsorption surface areas and crystallite size as determined by x-ray line broadening have been investigated as a function of calcination temperature. Thermogravimetric and CO₂ and H₂O adsorption studies have been carried out with D-16, the Thorex product oxide. Sedimentation particle size analyses have been obtained on both pilot plant and laboratory preparations and on slurries that have been pumped at elevated temperature (see Sec. 3.3). In addition, a study of the effect of oxalate precipitation temperature on the oxide characteristics has been initiated.

Nitrogen adsorption surface areas and crystallite sizes for several oxide products are listed in Table 7. In general, the surface area decreases and the crystallite size increases with increasing temperature of calcination. Close control of precipitation and calcination conditions in the large scale production of oxide from Thorex product is indicated by the marked agreement in specific surface obtained with the various lots, identified by the code letter D. Figure 3 illustrates more clearly the marked change in specific surface and crystallite size with change in calcination temperature obtained with D-16 oxide. A linear dependence for the specific surface area on the reciprocal of the absolute temperature is shown in Fig. 4. Although the theoretical significance of the relation is not clearly understood, it provides a convenient method of correlating the surface area--calcination temperature data.

There appears to be a direct correlation between the average crystallite size and the specific surface area (Fig. 5). Theoretically for a perfect cube or sphere the specific surface area is related to an edge or diameter by the equation

$$A = \frac{6}{\rho} \left(\frac{1}{D} \right)$$

Table 7

Material	Final Firing Temperature (°C)	Surface Area (m ² /g)	Ave. X-Ray Crystallite Size (Å)
ThO ₂ from formate	650 ^a	16.6	---
ThO ₂ from formate	650 ^b	22.5	---
Lindsay No. 8	900	6.6	---
Lindsay No. 11	650 ^a	13.0	261 ± 6
Lindsay No. 12 ^c	650 ^b	26.2	144 ± 5
Lindsay No. 13 ^d	650 ^b	18.0	184 ± 5
Lab Prep Th-602 ^c	650 ^e	35.3	145 ± 13
Lab Prep Th-701 ^c	750 ^e	21.9	262 ± 32
Lab Prep Th-901 ^c	900 ^e	12.3	490 ± 80
Lab Prep Th-1001 ^c	1000 ^e	8.3	953 ± 66
H5A ^c	650 ^e	31.9	---
D-10 ^c	650 ^e	31.9	---
D-15 ^c	650 ^e	35.6	---
D-15	800	17.6	
D-15	850	13.5	
D-16 ^c	650 ^e	34.7	117 ± 3
D-16 - 750 ^c	750 ^e	21.1	209 ± 6
D-16 - 900 ^c	900 ^e	7.9	465 ± 10
D-16 - 1250 ^c	1250-1300 ^e	2.0	1904 ± 129
D-17 ^c	650 ^e	35.4	---
D-18 ^c	650 ^e	36.0	---
D-19 ^c	650 ^e	33.9	---
D-20 ^c	650 ^e	35.6	---
D-21 ^c	650 ^e	35.0	---

^aSingle-stage hot furnace.

^dOxalate precipitation at 80-100°C.

^bPlaced in cold furnace.

^eMultiple-stage calcination.

^cOxalate precipitation at 40°C.

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Fig. 3 Effect of Calcination Temperature on Specific Surface Area and Crystallite Size of Thorium Oxide

A vertical strip of 15 frames showing a sequence of dot patterns that form the letters 'A', 'B', 'C', 'D', 'E', 'F', 'G', 'H', 'I', 'J', 'K', 'L', 'M', 'N', and 'O'. Each frame contains a grid of dots, with some dots being black and others white, creating the shape of each letter.

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Fig. 5 Variation in Specific Surface Area with Variations in Average Crystallite Size of Recalcined D-16 Oxide

where A is the area, ρ the density, and D the edge or diameter. The data of Fig. 5 fit an equation of the form:

$$A = \frac{6}{\rho} \left(\frac{1}{D} \right) \left(\frac{1}{E} \right)$$

where the E is a packing factor representing the relative crystallite area unavailable for nitrogen adsorption minus any roughness factor causing a deviation from the assumed perfect shape. Packing and shape factors are probably a function of the precipitation and calcination history of the oxide sample.

Figure 6 illustrates the steady state ignition loss for a typical oxide (D-16) and the steady state CO₂ and water vapor adsorption on the sample after it had been heated to 940°C. The break in the thermogravimetric curve between 600 and 700°C is probably real and indicative of a twofold process of gas desorption and an irreversible decrease in available surface. The adsorption of CO₂ and H₂O on this sample is apparently reversible, but a true zero point has not been established since it is not known to what temperature the oxide must be heated to completely degas it. Bonding energies associated with the desorption of CO₂ on the solid have been calculated from the equation

$$\frac{Q}{R} = \frac{d \ln W}{d(1/T)}$$

where Q is the isobaric heat of adsorption, R the gas constant, W the weight of adsorbed CO₂, and T the absolute temperature (see Fig. 7). Emmett gives a value of 17 Å² as the cross-sectional area for an adsorbed CO₂ molecule.⁽⁸⁾ With this value for the cross-sectional area and an estimated surface area of 6 m²/g (see Fig. 4), a monolayer of adsorbed CO₂ is calculated to contain 2.6 mg of CO₂ per gram of the ThO₂ sample under consideration.

3.3 Particulate Properties of Thorium Oxide Slurries

A study has been initiated whose object is the development of particle size concepts and methods of particle size analysis of

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Fig. 6 Thermogravimetric Properties of D-16 Oxide; CO₂ and H₂O Adsorption Curves for D-16 Recalcined at 940°C

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Fig. 7 Calculated Heats of Adsorption for CO₂ on ThO₂ Prepared by Refiring D-16 Oxide at 940°C

importance in the study of thorium oxide slurries and a determination of the effect of particle size on the characteristics of thorium oxide slurries. The results to date suggest that a sedimentation analysis⁽⁷⁾ in a dilute slurry (less than 0.5%) in the presence of a dispersing agent ($0.005 \text{ M Na}_4\text{P}_2\text{O}_7$) gives a particle size of significance in the study of thorium oxide slurries. Oxides that had been pumped as a slurry at elevated temperatures reached approximately the same average particle size as those degraded dry at room temperature in a micronizer. Preliminary results of experiments with Waring and Brookfield blenders to simulate the effect of pumping on slurry properties indicate that the observed increases in slurry viscosity are not the result of particle degradation alone.

Sedimentation particle sizes obtained with D-10 pilot plant oxide as prepared, after being pumped, and after micronizing are shown in Fig. 8. Figure 9 is a similar plot of another pilot plant product, D-16, as prepared, after being blended 2 hr in a Waring blender, and after being micronized. The degradation occasioned by mechanical handling is obvious and the effects of the three different methods used to degrade the sample are similar. The surface area of the D-10 oxide was increased by micronizing from $32.4 \text{ m}^2/\text{g}$ to only $37.9 \text{ m}^2/\text{g}$, indicating that N_2 adsorption is measuring essentially internal surface area and that little change in total surface area will be brought about by prolonged pumping in a loop system.

Several samples of D-16 oxide and D-16 oxide recalcined at 750 and 950°C were made up into slurries containing 1000 g of thorium per kilogram of H_2O . One sample of the D-16 was shaken briefly at room temperature and a second tumbled for one week at room temperature. A third sample of the D-16 oxide and slurries of the recalcined materials were blended in a Waring blender at 8°C for 2 hr. Apparent Brookfield viscosities were obtained for all the samples and for a slurry of the micronized D-16 material containing 1000 g of thorium per kilogram of H_2O (see

Legend:

- Original oxide, D-10
- D-10 oxide after being pumped 24 hr at 250°C as a 650 g Th/kg H₂O slurry (9000 ppm SO₄ and 0.24 wt. % of Na₂O·(SiO₂)_{3.25} added)
- Original oxide micronized twice

Fig. 8 Effect of Pumping and Micronizing on ThO₂ Sedimentation Particle Size

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Legend:

- Original D-16
- D-16, blended, 1000 g Th/kg H₂O, 80°C, 2 hr
- D-16, micronized, material collected in dust bag

Fig. 9 Effect of Blending and Micronizing on Thorium Oxide Sedimentation

Particle Size
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Table 8). Little increase in apparent viscosity is noted for the micronized sample over the unmicronized material despite the fact that it had been degraded from an average size of 3.1μ to 0.8μ . The blended material, on the other hand, showed a pronounced increase in apparent viscosity even though it was not degraded to as small a size. The higher temperature calcined materials showed a relatively smaller increase in viscosity on blending but were degraded to nearly the same extent as the original D-16.

3.4 Rheological Properties of Thorium Oxide Slurries

In studies on the viscosity of thorium oxide slurries it has been shown that at room temperature and constant rates of shearing strain the apparent viscosity varies by a factor of 10^3 - 10^4 depending on the electrolyte atmosphere in the slurry. It has also been shown⁽¹⁰⁾ that at room temperature and with a constant electrolyte atmosphere, the apparent viscosity varies by a factor of 10^4 as the rate of shearing strain is varied. It appeared that a measurement of viscosity of thorium oxide slurries would be useful in the characterization of various preparations of thorium oxide. Since no information is available on the viscosities of thorium oxide slurries at elevated temperatures, it also appeared desirable to be able to make measurements over a range of temperatures from ambient to 300°C .

A capillary viscometer now being used⁽¹¹⁾ to measure the viscosity of molten salts seemed to possess many desirable features. These were:

1. operation required small quantities of material,
2. with simple modifications the system could be operated at 2000 psi and 300°C , and
3. the geometry of the system permitted rigorous analysis of the data.

A stainless steel viscometer was designed (see Fig. 10), and construction

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Table 8

Effect of Pretreatment on the Viscosity of Thorium Oxide Slurries

Starting material: D-16 ThO₂, calcined at 650°C

Slurry thorium concentration: 1000 g/kg H₂O

Pretreatment	Apparent Brookfield Viscosity (cp)				Final Mean Particle Size (u)
	At 6 rpm	At 12 rpm	At 30 rpm	At 60 rpm	
Shaken by hand to disperse	600	900	680	430	3.1
Tumbled one week	700	850	580	540	3.1
Micronized dry, shaken	1500	850	700	500	0.79
Blended 2 hr	7000	4000	2500	2600	0.92
Calcined 750°C, blended 2 hr	---	2000	2000	2100	0.95
Calcined 900°C, blended 2 hr	3500	1500	900	500	1.1

- 1. PRESSURE INLETS
- 2. THERMOCOUPLE WELL
- 3. INNER RESERVOIR
- 4. OUTER RESERVOIR
- 5. CAPILLARY

Fig.40. Capillary Viscometer

is about 50% completed. In this instrument the slurry is made to flow either from the inner reservoir to the outer reservoir or vice versa under the action of a differential pressure. The differential pressure is measured by a DP cell and the equalization of pressure between the two reservoirs indicates the end of a cycle. The inner reservoir is stirred with a dash-pot stirrer and the outer with a magnetic stirrer.

The accuracy of the experimental results will depend upon the evaluation of end and kinetic effects on the capillary as well as on the effects of slippage between the particles and the fluid and slippage at the wall of the capillary. The latter effort could cause an erroneous interpretation of the data in that a Bingham plastic would appear as a pseudo-plastic if there was wall slippage.

The viscosity of ThO_2 slurries at elevated temperatures was estimated in order to choose the proper range of capillary sizes for use in the viscometer. Guth and Simha¹² have proposed the following relation for the viscosity of concentrated suspensions of solid spheres in liquids:

$$\eta_{sp} = \eta_o \left[1 + 2.5 \phi + 14.1 \phi^2 + \dots \right] \quad (1)$$

where η_{sp} = apparent viscosity of suspension
 η_o = viscosity of pure liquid
 ϕ = volume concentration of particles

The calculated viscosities of a slurry containing 1800 g of ThO_2 per kilogram of H_2O are plotted in Fig. 11 for temperatures up to 300°C . The validity of the calculated viscosity curve for ThO_2 slurry depends upon there being no interaction between ThO_2 and H_2O . At room temperature a pronounced interaction has been shown.^(7,28) However, hindered settling data taken at elevated temperatures⁽¹³⁾ show a sharp change in the viscosity-temperature relation at temperatures in the range 150 - 200°C . Therefore, for the temperature range 200 - 300°C , it is expected that the

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Fig. 11 Calculated Viscosities of Thorium Oxide Slurry (1800 g of ThO₂ per kilogram of H₂O) at Various Temperatures

(The experimentally determined viscosities of water are given for comparison.)

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viscosity of all ThO_2 slurries will be approximated by a relation similar to that of Eq. 1. At lower temperatures the viscosity is expected to be characteristic of a particular slurry preparation, and thus one of the principal uses of the viscometer will be in the study of slurries below 200°C .

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