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STUDY OF CAUSES AND PREVENTION OF
HARD CAKE FORMATION DURING OUT-
OF-PILE CIRCULATION OF AQUEOUS
THORIUM OXIDE SLURRIES

C. S. Morgan

OAK RIDGE NATIONAL LABORATORY

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Oak Ridge, Tennessee
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ABSTRACT

Occasionally, hard, intractable ThO_2 deposits have formed on surfaces of the containing system during circulation of aqueous ThO_2 slurries at high temperature. Although entire surfaces of systems have been coated with 1/4- to 1/8-in.-thick thoria deposits, cake formation is usually localized, forming preferentially in the pump impeller. Frequently, impeller deposits accelerate bearing failure. Cake formation is usually accompanied by formation of equal dense spherical aggregates 5 to 60 microns in diameter which remain suspended in the slurry. Caking and sphere forming phenomena, as investigated by tests of slurry properties in the laboratory and in a 30-gpm slurry loop, are described, as are methods for preventing caking.

Thoria cakes and spheres are believed to form by reagglomeration of small particles or fragments worn or chipped off the larger thoria particles composing the initial slurry. It is thought that small fragments are forced over each other by the shear stress into positions of minimum energy where they are held together by van der Waals' forces. Thoria solubility is not believed to be an appreciable factor in cake or sphere formation. The extent of chemical bonding in the deposits is not clear. Greatest cake-forming tendency was noted in thoria prepared by calcination of $\text{Th}(\text{C}_2\text{O}_4)_2$ at 800°C , though cakes did occur with other ThO_2 preparations. Deposits formed from oxide batches that contained particles more resistant to degradation were softer, apparently because there were fewer fine fragments. A deposition preference between different metal surfaces as well as between different velocity sections was noted.

Cake formation by fresh batches of thoria, that is, slurry in which the initial oxide particles have not been made finer by previous circulation, is prevented by any factor which reduces particle comminution. Cake formation is avoided if particles are too resistant to degradation or if they degrade rapidly to intermediate-size particles. Intermediate-size particles, 0.1 to $0.5\ \mu$, apparently do not yield fine fragments readily because of the reduced shear forces which are acting on smaller particles. Improved particle integrity can be accomplished by the method of oxide preparation, for example, the use of high calcining temperature or long digestion time.

Cake formation by fresh oxides is also prevented by the addition of small quantities of surface-active electrolytes to the slurry. Effective electrolytes tested included CrO_3 , NaAlO_2 , Na_2SiO_3 , and MoO_3 . The electrolytes are thought to be effective by means of reducing particle fragmentation.

Prevention of cake formation by slurries already containing particles in the caking-size range (e.g., a slurry composed of spheres produced during circulation) is more difficult, because agglomeration of the fine particles must be prevented. Lithium sulfate tended to reduce cake formation but was not completely effective. Other electrolyte additives tested (CrO_3 and NaAlO_2) failed to hinder cake formation during ThO_2 sphere circulation. (These spheres were "loop produced" in a previous slurry circulation experiment.) However, after extended circulation during which partial dispersion of the spheres took place, cake formation was almost absent. It is postulated that the very fine particles wearing off the spheres gradually agglomerate into particles which are too large to form cakes but so small that fine particles or fragments are not worn off readily.

Autoclaving of fresh thoria in water or dilute acids did not strengthen the particles sufficiently to prevent cake formation. Cake formation did not occur when the loop circulation temperature was reduced to 45°C . Extremely low thoria concentration did not deter cake formation. The integrity of loop-produced spheres was greatly improved by a combination of chemical and thermal treatment but was not improved sufficiently to prevent cake formation. Cake deposited in a ThO_2 -circulation system is partially destroyed by thermal cycling and can be removed by circulation of a non-caking slurry.

Particle integrity of the thoria is increased by coprecipitating small quantities of a second metal oxide with the ThO_2 . The relation of zeta potential and slurry properties frequently appears anomalous. Thoria deposition on metal plates suspended above rapidly rotating Waring Blendor blades is influenced by electrolyte additives and to a limited extent by a potential applied to the plate. The settled-bed concentration of slurries in quartz tubes at elevated temperature is sometimes influenced by electrolyte additives but varies with time at temperature.

INTRODUCTION

Aqueous thorium oxide slurries have been suggested as a means for utilizing thorium in a nuclear breeder reactor. This has led to an extensive investigation of the characteristics of thoria suspensions (rheology, heat transfer, surface chemistry, preparation, etc.). In the course of out-of-pile circulations of these slurries, it was observed that hard, intractable deposits formed on the surfaces of the circulating system; these cakes were particularly prevalent in the pump impeller. On two occasions the entire surface of the circulating system was coated with $1/8$ - to $1/4$ -in.-thick thoria deposits. The objective of this investigation, then, was

to elucidate the mechanism of cake formation and to devise methods of controlling cake build-up either by prevention of formation or by removal of cake once formed.

This report is submitted now to put on record the information obtained during investigation of cake formation and its prevention. It will be evident that certain aspects of the problem are not yet well understood. In some cases the experimental evidence is incomplete or contradictory.

General Discussion of Cake Formation

Formation of a hard ThO_2 cake has been largely limited to circulation of thoria prepared by oxalate precipitation and subsequent calcination at 800°C . Hard cake was also observed in a run in which ThO_2 spheres (prepared from a gel and calcined at 1000°C) were circulated. Selective formation of softer films has occurred with 1600°C -calcined ThO_2 and with ThO_2 - UO_2 preparations. However, circulation of 650°C -calcined thoria or of oxalate precipitated ThO_2 calcined above 800°C is not known to have ever resulted in hard cake formation.

Cake production is usually accompanied by the formation of small spheres, 10 to 60 μ in diameter, which remain suspended in the circulating stream. Like the cakes, these spheres are believed to be aggregates of small thoria particles or fragments.¹ (In this report small oxide particles obtained by degradation of initial slurry particles will usually be called fragments.) Circulation of untreated spheres results in the deposition of cake in the circulating system. The effect of treatment to increase sphere integrity and reduce the cake forming tendency will be described.

With slurries composed of thoria prepared from $\text{Th}(\text{C}_2\text{O}_4)_2$ and calcined at 800°C , cake and sphere formation occur in the first 100 hr of circulation.¹ In most cases spheres or cake were evident either within less than 50 hr or did not occur during the run; in some runs sphere formation was noted within less than 6 hr after circulation was initiated. Particle degradation occurred early in slurry circulation and usually became negligible after about 100 hr, depending on the oxide particle integrity and on the magnitude of shear forces in the system.

Early theories on the mechanism of cake formation included consideration of water loss from the slurry at the pipe wall due to boiling, of the effect of electrolyte concentration on the colloidal properties, and of particle size distribution.² A similar caking phenomena was encountered with drilling muds in the petroleum industry and was attributed to particle attrition, with the particle-size distribution going through a critical region when cake formed. It has been pointed out that a critical velocity gradient at the wall could exist which would exert sufficient force on a flocculated, loosely packed wall deposit to move the particles over each other to positions of minimum energy corresponding to a very densely packed bed.²

Acknowledgment

Many people in the Reactor Experimental Engineering Division and the Chemical Technology Division made contributions to this study. The author wishes to particularly acknowledge the contribution of R. N. Lyon and to point out that a great part of the experimental work was done by B. J. Sutton.

EXPERIMENTAL

Description of Loop, Instruments, and Principal Factors Studied

The Loop

A schematic diagram of the 30-gpm loop is shown in Fig. 1. The system was constructed of type 347 stainless steel and used a Westinghouse canned-rotor pump with a titanium impeller. A multidiameter sample barrel (MDSB), which contained three sizes of tubes in series, made possible the study of the effect of flow rate (nominal flow rates of 5, 10, and 20 fps) in a single experiment. The MDSB could be removed from the loop and opened lengthwise to allow close inspection of oxide deposits. Flow in the 1-in. pipe, of which most of the system was composed, was nominally 13 fps. The circulating volume was approximately 12.5 liters.

Fig. 1. Schematic Drawing of 30-gpm Slurry Loop.

Flow in the slurry stream was monitored by a venturi; temperatures were determined by skin thermocouples. The system temperature was regulated by varying the heat input to strip heaters. During all runs an oxygen overpressure was maintained. Oxygen content of the slurries was not determined, but sufficient oxygen for oxide film formation on metal surfaces was always present.

Heat Transfer Coefficients

A copper-disk heat transfer meter was used in the 30-gpm loop to detect cake formation. This disk used a nickel-plated surface at the slurry interface and, while similar in design to that in the 200B loop,³ used a Calrod heater at the outer periphery instead of water cooling. The heat flow was computed from the thermocouple readings at various depths from the surface. Because the exact position in the disk which the thermocouple readings represent was difficult to ascertain, the heat transfer coefficients must be considered as qualitative. However, changes in heat transfer coefficients should be accurate, and results on the detection of thoria films were good.

The data indicated a definite difference in reading between two sides of the heat meter in one run. Subsequent examination of the disk when the loop was opened showed that one side had an approximately 1-mil-thick deposit, while the deposit on the other side was 2 mils in thickness. The difference in heat transfer coefficient was sufficient to account for the difference in film thicknesses if the conductivity of the cake is assumed to be 0.3 Btu/ft.²°F·hr.

A summary of each run is given in Table 1. All runs were made with slurry concentration of 400 to 500 g of Th per kg of H₂O and at 275°C, unless otherwise mentioned. Loop pressure was about 1600 psi in each run except for the low temperature run (30A-11).

Cake Hardness

No satisfactory method of measuring thoria cake hardness has been developed. Pieces of cake are characterized by the cake resuspension index determination (CRI) (see Appendix), which gives a value related to ease of

Table 1. Summary of 30A Loop Runs

Run No.	Oxide Batch	Pretreatment or Special Circulating Conditions	Results
30A-1	L0-20	None	Cake and sphere formation
30A-2	Std. Slurry Sphere	Treated to increase integrity	Cake formation
30A-3	L0-44-100	None	No cake or sphere formation except film in 5-fps section and few small spheres
30A-4	L0-20	Autoclaved in H ₂ O	Cake and sphere formation
30A-5	L0-20	Autoclaved in dil H ₂ SO ₄	Cake and sphere formation
30A-6	L0-20	Treatment in Waring Blendor	No cake or sphere formation
30A-7	L0-44-100	Autoclaved in H ₂ O	No cake or sphere formation except soft film in 5-fps section
30A-8	L0-20	Treatment in Waring Blendor	No cake or sphere formation
30A-10	L0-20	Circulating concentration very low	No cake, only few small spheres
30A-11	L0-20	Low-temperature circulation	No cake or sphere formation
30A-12	L0-20	Circulation at 48°C	No cake or sphere formation except a soft film in the 5-fps section which probably formed at 275°C
30A-13	L0-20	Autoclaved in dil HNO ₃	Cake and sphere formation
30A-14	L0-20	Intermediate concentration	Sphere formation and thin film in 5- and 10-fps section
30A-15	L0-20	CrO ₃ (350 ppm/ThO ₂)	No cake, some small spheres
30A-16	L0-20	Low concentration	Film and very small quantity of cake on impeller

Table 1. Continued

Run No.	Oxide Batch	Pretreatment or Special Circulating Conditions	Results
30A-17	Run 38, 2 hr	None	A few small spheres formed, but disappeared before end of run; no cake or film formation except thin film in 5-fps section
30A-18	Run 38, 4 hr	None	No cake; some small sphere formation; film in 5-fps section
30A-19	200A - 16 Spheres	None	Cake, sphere size increased; inner layer of cake was white or cream colored while the outer layer was reddish brown, as was the color of part of the spheres
30A-20	LO-20	Treatment in Waring Blendor; test of cake removal	The impeller and MDSB were returned to the loop after run 30A-19 without disturbing ThO ₂ deposits; loop opened after 24 hr, cake still present; loop closed and run 65 additional hr; all deposits gone from impeller except film on face; 10-fps section nearly clear of deposits; 5-fps section still 75% covered with deposits
30A-21	200A - 16 Spheres	None	Cake and film formation; some sphere dispersion evident
30A-22	DT-8-1600°C	None	Loop put together without disturbing deposits from run 30A-21; after 23.3-hr circulation, only small amount of ThO ₂ remained in impeller; 20- and 10-fps sections were clear; 5-fps section contained some original ThO ₂ film;

Table 1. Continued

Run No.	Oxide Batch	Pretreatment or Special Circulating Conditions	Results
			there were some soft deposits of 1600°C-oxide over the original film
30A-23	200A - 16 Spheres	CrO ₃ (500 ppm/ThO ₂)	Small deposits of cake and thin film; some sphere dispersion evident
30A-25	LO-20	Low concentration, 52 to 11 g Th/kg H ₂ O	Cake and sphere formation
30A-26	200A - 16 Spheres	CrO ₃ (1500 ppm/ThO ₂)	Small quantities of film and cake
30A-27	Run 38, 2 hr	Autoclaved in dil H ₂ SO ₄	No cake, some small spheres; 5-fps section - unusually white film - thin film in Cu disk (low corrosion)
30A-29	LO-20	None	Cake and sphere formation
30A-30	200A - 16 Spheres (from run 30A-26)	CrO ₃ (3000 ppm)	Small amount of cake; film formation
30A-31	200A - 16 Spheres (from run 30A-30)	CrO ₃ (10,000 ppm)	No cake; a very thin film on 5-fps section
30A-32	200A - 16 Spheres (from run 30A-31)	CrO ₃ (10,000 ppm, continuation of 30A-31)	No hard cake; film deposit in the 5-fps section
30A-33	200A - 16 Spheres	CrO ₃ (12,000 ppm/ThO ₂)	Cake and film formation
30A-34	Run 38 - 4 hr	Partially deionized	No hard cake or sphere formation; film in 5-fps section
30A-35	200A - 17 Spheres	NaAlO ₂ (5,000 ppm/ThO ₂)	Cake and film formation

Table 1. Continued

Run No.	Oxide Batch	Pretreatment or Special Circulating Conditions	Results
30A-36	200A - 17 Spheres (from run 30A-35)	NaAlO ₂ (10,000 ppm/ThO ₂)	Small quantity of cake and film
30A-37	MO-51	None	After 114 hr circulation, the 10-fps section (SS) was covered with ThO ₂ -UO ₂ deposit; small, very thin film on 5-fps section (Cu); 10-fps section (Cu), small quantity of film; 20-fps section (Ni), covered with brown deposit; 30A-37-B after 300 hr - no cake; 5-fps section (Ni), thin film
30A-38	DT-23-1600°C	None	After 101-hr circulation, there was a very thin film on 10-fps section (SS and Cu section); 30A-38-B after 300 hr, very thin film in 20-fps section and 10-fps section; no cake or film in impeller
30A-39	MO-51	None	Cakes and films similar to 30A-37, although oxide deposition pattern in the MDSB was altered
30A-40	MO-51	Treatment in Waring Blendor	Cake and film formation
30A-41	200A - 17 Spheres DT-23	50 wt % mixture of caking and noncaking oxides	Reduced cake formation
30A-42	200A - 17 Spheres	Li ₂ SO ₄ (2000 to 7000 ppm)	Very slight film formation
30A-43	200A - 17 Spheres	Li ₂ SO ₄ (1000 ppm)	Small amounts of cake and film

resuspension of the cake in water. A "cake tester" was used to measure the thickness of the thorium films deposited in the MDSB. The cake tester consisted of a steel rod tapered to a dull point on one end. A dial gauge (marked in tenths of mils) was read when the point came in contact with the film, as indicated by a drop in resistance from near infinity to 10 - 50 ohms. The dial gauge was read again when the point touched the metal surface under the oxide film, as indicated by a resistance drop to 1 or 2 ohms. This gave film thickness with a precision of ± 0.3 mil. The cake tester also gave a qualitative indication of relative film hardness by the weight required to force the pointer through the oxide film as the pointer was rotated back and forth through a small arc.

Particle Size

Electron microscopy and sedimentation measurements (both done by the Analytical Chemistry Division) were used to determine particle size of fresh oxide batches and of redispersed thorium cakes. However, the uncertainty of the extent of redispersion always clouded the meaning of the particle-size distribution obtained for cakes.

RESULTS AND DISCUSSION

Mechanism of Thorium Cake Formation - Slurry Circulation Studies

Formation of hard thorium cakes is known to depend upon generation of small fragments by attrition of larger particles.¹ The fragments (order of magnitude, 200 A) then deposit on surfaces and can build into hard, thick cakes. Slurry circulation tests were made by using thorium batch LO-20 (one of a number of the pilot plant preparations which formed cakes and spheres) to determine the effect of oxide treatment and flow perturbation on cake formation. Although there is no clear differentiation, experiments described in this section were directed principally to elucidation of the mechanism of cake formation.

Theory of Cake Formation

The hypothesis that hard ThO_2 cake forms when suitably sized oxide particles are pushed over each other into positions of minimum energy has been advanced by Lyon.⁴ In the positions of close contact, particles are held together by van der Waals' forces. When the shear forces at the wall exceed some value which is a function of the particular slurry, no cake can form because of the limited strength of the strongest possible aggregate. Under such conditions it may still be possible for aggregates within the stream to compact and grow into spheres which approach a uniform size dependent on the slurry and flow conditions. In the remainder of this paper the term "spheres" refers, unless otherwise defined, to such aggregates which were formed either during the run under discussion or in a previous slurry circulation experiment. Deposition of thoria in the MDSB of the 30-gpm loop during circulation of a cake-forming oxide tends to confirm this theory. In run 30A-4, with slurry composed of LO-20 oxide which had been autoclaved in water for 36 hr at 300°C , thick films or cakes were deposited on the MDSB surfaces exposed to nominal fluid velocities of 5 and 10 fps. The metal surface of the section exposed to slurry having a velocity of 20 fps was perfectly clean. The film in the 10-fps section, covering approximately 60% of the surface, had a glossy appearance and was comparatively difficult to remove. The film in the 5-fps section covered the entire surface, was dull appearing, and washed away easily with a bristle brush. The inner surface of the MDSB after this run is shown in Fig. 2. Apparently, in the 20-fps section the shear force associated with

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Fig. 2. One Side of Multidiameter Sample Barrel After Run 30A-4. The MDSB is of two-part construction so that it can be opened for inspection after a run.

the high fluid velocity was too great to permit slurry fragments to adhere to the pipe wall, while in the 5-fps section the low shear forces did not force particles into very low energy positions, resulting in a soft film.

Influence of Aggregate Size on Cake Formation

The effect upon cake and sphere formation of reduced initial oxide particle size was tested by blending LO-20 thoria (using a Waring Blendor) until the mean particle-size was reduced from $3.0\ \mu$ to $0.9\ \mu$. Circulation of slurry composed of this oxide (run 30A-6) did not result in cake or sphere formation (except for a few small spheres formed initially and which subsequently disappeared). A repeat run under similar conditions gave identical results: no cake or sphere formation.

A comparison of electron micrographs (Figs. 3 and 4) of slurry of the 2-hr sample from run 30A-6 (Waring-Blendor treated LO-20) with that of the 2-hr sample from run 30A-1 (fresh LO-20 ThO_2) shows that the ratio of large particles ($>0.5\ \mu$) to intermediate particles (range 0.1 to $0.5\ \mu$) was much higher for untreated thoria. Since untreated LO-20 thoria formed cakes and spheres in all runs, it appears that smaller particles do not degrade as readily as larger particles into the extremely fine fragments thought to be necessary for cake or sphere formation.

Results of circulation of ThO_2 batch LO-44-100 (prepared without appreciable digestion time of the thorium oxalate in the mother liquor and fired at 800°C for 2 hr) in run 30A-3 were identical with those obtained for Waring-Blendor treated LO-20 — no cake and only a few spheres early in the run. The electron micrograph of a sample taken 2 hr after start of the run (Fig. 5) shows, as did those from circulation of Waring-Blendor treated LO-20, a lower ratio of large to intermediate or small particles than that of the 2-hr sample from untreated LO-20.

Failure of Pretreatment by Autoclaving to Prevent Cake Formation

It has been observed that if a cake forms during the circulation of fresh thoria, it forms early in the run. Thus the possibility existed that the high-temperature aqueous treatment of the slurry in the first part of the run strengthened the particles so that delayed cake formation did not occur. To test this possibility, several circulation experiments were made in which slurry composed of LO-20 thoria was tested for caking tendency after autoclave treatment. The following table describes the autoclave treatment and the results of subsequent loop circulation.

Fig. 3. Electron Micrograph of Waring Blendor Treated Thoria
(Batch IO-20) After 2 hr of Loop Circulation. 20,000X. Reduced 15%.

Fig. 4. Electron Micrograph of Fresh Thoria (Batch LO-20) After 2 hr of Loop Circulation. 20,000X. Reduced 14.5%.

Fig. 5. Electron Micrograph of Thoria (Batch IO-44-100) After 2 hr of Loop Circulation. 20,000X. Reduced 15%.

<u>ThO₂</u> <u>Batch</u>	<u>Autoclave</u>				<u>Results in Loop</u>
	<u>Medium</u>	<u>Temp.</u> <u>(°C)</u>	<u>Time</u> <u>(hr)</u>	<u>Run No.</u>	
L0-20	H ₂ O	300	36	30A-4	Cakes and spheres
L0-20	800 ppm H ₂ SO ₄ (based on thoria)	300	36	30A-5	Cakes and spheres
L0-20	3200 ppm HNO ₃ (based on thoria)	300	36	30A-13	Cakes and spheres

Loop circulation showed that the autoclaving had no effect on cake formation, which is possibly the most sensitive test for change in the thoria particle structure. This would appear to rule out any solubility effect on particle integrity or other hydrothermal effects during short pumping times as an explanation for the absence of delayed cake formation. The arrangement of very fine fragments into aggregates by shear forces in the stream is a possible time-dependent factor controlling cake formation. A second possible time-dependent factor is the fragment surface state during circulation. This perhaps should be considered unimportant because of the fact that circulation of thoria spheres results in cake formation regardless of the extent of prior circulation. There is further discussion of these points in a subsequent section on sphere circulation.

It is interesting to note that the cake resuspension index (CRI) of the L0-20 oxide after autoclaving in 3200 ppm HNO₃ (based on thoria present) was zero, which indicates that cake formation would not occur. Actually, small batches of L0-20 had been autoclaved with lesser quantities of HNO₃, and the CRI had gradually declined with increasing acid concentration until it reached zero. The fact that the autoclaved thoria caked suggests that the electrical double-layer repulsion caused by the HNO₃ reduced particle degradation during Waring Blendor treatment at room temperature but that this surface active effect was negligible at elevated temperatures. A decrease of the surface active effect with increased temperature is normally to be expected,⁵ but in many cases the addition of an electrolyte has prevented cake formation during circulation of a fresh oxide at elevated temperatures.

Effect of Circulation Temperature on Cake Formation

Cake formation during circulation of thorium slurries has usually been in the temperature range of 200 to 300°C. To study the effect of temperature on cake formation, a slurry of LO-20 thorium was circulated at 45°C (run 30A-11). Cake formation did not occur, and only a few small spheres (5 to 10 μ in diameter) developed. It is not clear whether caking was prevented by the increased effectiveness of the electrical double layer at low temperature,⁵ possibly in conjunction with increased hydrophilic properties of particle surfaces at lower temperatures, or by the changed water viscosity. During this low-temperature run, corrosion was extremely low.

After 270 hr of circulation at 45°C, the temperature was increased to 275°C, and circulation was continued an additional 170 hr. Size of the few small spheres present increased nominally for about 20 hr. Spheres then slowly decreased in size and were not evident at the end of the run. Cake formation did not occur.

Attempts to Prepare Caking Oxides

Two small batches of thorium were prepared by the pilot plant, following as nearly as possible the procedure used in producing the early LO-oxide series, several of which caked. The time of digestion of the thorium oxalate in the mother liquor is thought to be the determining factor in whether LO oxides caked or not.⁶ Batch LO-44-100 had zero digestion time following the oxalate-precipitation step (CRI of 7), while batches run 38 - 2 hr and 4 hr (referring to firing time at 800°C) - were digested for 1 hr and had a CRI of 6. These oxides were circulated as received, after autoclaving and partial deionization (runs 30A-3, 7, 17, 27, and 34). In each run, small spheres formed initially but did not grow. There was no hard cake formation, but in each case a thin, relatively soft ThO₂ film formed in the 5-fps section of the MDSB.

It is believed that the failure of the non- or short-digested oxides with CRI values in the caking range to form hard cakes emphasizes the narrow bounds into which the extent and rapidity of particle degradation must fall if hard cakes are to form. It can be added that there was no significant difference between the chemical analyses of cake-forming and noncake-forming oxides (Table 2).

Table 2. Comparison of Chemical Analyses of
Caking and Noncaking ThO₂ Batches

Component	Caking ThO ₂		Noncaking ThO ₂	
	LO-12	LO-14	LO-2A	LO-7
Concentration of Thorium (wt %)				
Th	87.3	87.6	87.2	87.2
Concentrations of Minor Components (ppm)				
Fe	<5	6	12	<5
Ni	<5	<5	<5	<5
Cr	<5	<5	<5	<5
Cl	<10	30	40	10
Na	120	200	50	320
K	<50	<100	60	<50
Ca	<50	<100	30	430
SO ₄	<100	<100	<100	160
CO ₃	2200	1100	1600	1600
Si	<10	-	<5	<10
PO ₄	<20	<20	<20	<20
Mg	20	<5	<9	41
Al	40	<10	170	20
Pb	<20	-	<20	10

Studies for Preventing Cake Formation by Oxides Composed of Fragments
Already Reduced to Cake-Forming Size: Effect of Added Electrolytes

Slurry circulation tests were made in order to determine the effectiveness of added electrolytes in preventing cake formation by slurries in

which the particles are already dispersed or broken into fragments of suitable size for cake formation. Such tests are of interest because of the possible in-pile degradation of oxide particles which are resistant in out-of-pile tests. However, the principal reason for such tests was that they offered another avenue of gaining knowledge of the factors involved in cake formation.

Thoria spheres produced during loop circulation appear to be agglomerates of caking-size particles. During circulation, particles wearing off the spheres can reagglomerate on metal surfaces to form cakes. Thus, loop-produced spheres are a source of caking-size particles and were circulated to determine the influence of Li_2SO_4 , CrO_3 , and NaAlO_2 on cake formation.

Spheres were circulated in a series of runs in the 30-gpm loop, with CrO_3 additions of 500, 1500, 3000, and 10,000 ppm based on ThO_2 (runs 30A-23, 26, 31, and 33). Fresh spheres (made during circulation of a slurry and then transferred to the loop for this test) were used in the 500-ppm and 1500-ppm run; the succeeding two runs used the spheres from the 1500-ppm run. In the three lower-concentration runs, cake formation occurred approximately as expected in the absence of CrO_3 addition. In the 10,000-ppm run there was no cake in the pump impeller and only a thin film in the 5-fps section of the MDSB. This result does not give a definitive answer as to whether CrO_3 can prevent cake formation. It was observed in the first run that part of the spheres became dispersed into fine particles, and in runs where the charge consisted of previously pumped oxide the sphere dispersion became extensive. During the 10,000-ppm run, more than 50% of the oxide appeared to be fines rather than spheres. Also, another run with fresh spheres and 12,000 ppm of CrO_3 (run 30A-33; CrO_3 addition increased from 10,000 ppm to compensate for CrO_4^{--} from corrosion which was present in prior run) resulted in hard cake formation.

Circulation of spheres with added NaAlO_2 (runs 30A-35 and 36) resulted in formation of hard cake.

Discussion of Behavior of Thoria Fragments During Circulation

These results represent reasonably conclusive evidence that electrical double layers produced by ions from CrO_3 or NaAlO_2 cannot prevent cake

formation during slurry circulation at 275°C when sufficient fragments of cake-forming size are present. However, they suggest that the caking tendency of a slurry becomes reduced if there are not sufficient small fragments available. Results of low-concentration runs described later indicate that the ratio of cake-forming particles to other particles is the important factor.

Two possibilities suffice to account for the unavailability of sufficient fine fragments after extended sphere circulation. The first possibility is that as fragments wear off the spheres, part of them are reformed into small- or intermediate-size aggregates which continue to circulate as slurry particles. The second possibility is that the shear forces acting on these small aggregates are not strong enough to cause sufficient spalling of fragments to make a caking slurry.

Particle- or fragment-size data and electron micrographs of samples withdrawn during the circulation of spheres or partially dispersed spheres must be examined in light of the fact that the extent of dispersion or of agglomeration during preparation of the sample slides is not known. This prevents a conclusive proof or disproof of the above-mentioned possibilities on the basis of experimental results now available. The correlation of fresh-oxide caking behavior with particle-size distribution after a 2-hr circulation, as described earlier, tends to support the second possibility mentioned above. Furthermore, during circulation of a low-fired oxide, the particle-size reduction stops after about 200 hr, suggesting that fragments are redepositing to make agglomerates which do not break down rapidly, even during dispersion for particle-size measurement.

The extent to which CrO_3 in the circulation stream influenced the dispersion of spheres and subsequent formation of smaller aggregates is not clear. Partial sphere dispersion has been noted in a number of loop runs in which no electrolytes were added. The flow pattern in the circulating system may be important. Spheres have appeared to hold up much longer in the larger 200A loop than in the 30-gpm loop.

Circulation of thoria with Li_2SO_4 added gave more positive indications of electrolyte-produced deterrent effect on cake formation and is discussed in a subsequent section.

Absence of Solubility Effect in Thoria Cake Formation

The following observations are advanced to indicate the improbability of an appreciable contribution to ThO_2 cake formation by solubility processes.

1. Autoclaving of fresh thoria batches at 300°C in water had no effect on cake formation in subsequent circulation. An appreciable ThO_2 solubility effect would have been expected to result in more solid, stronger particles, which would not have readily formed cakes.

2. Crystal growth in thoria samples during aqueous circulation at elevated temperatures has never been detected at Oak Ridge National Laboratory.

3. No evidence of hard cake formation has been found in oxides allowed to stand in water at high temperatures in autoclaves or in stagnant portions of circulating loops.

4. The argument could be advanced that the increased solubility of fresh surfaces formed by particle degradation is responsible for cake formation and therefore would not be detected in any static test. However, circulation of loop-produced spheres results in cake formation, and, in this case, the particles forming the cake are thought to be worn off the spheres, and the formation of fresh thoria surfaces is not involved.

5. Small quantities (a few hundred ppm) of electrolytes will prevent cake formation. It is not expected that there would be an effect on thoria solubility except for a solubility increase with certain acids.

6. Cake deposition in the slurry-circulation loops is dependent on the slurry flow pattern and occurs on pipe sides and tops as well as bottoms. It is also an experimental fact that slurry velocity sharply influences the hardness of the cake deposits.

7. The density of cakes formed in circulating systems is always substantially higher than densities obtained in settled beds.

The last five points, while not disallowing a solubility effect in cake formation, tend to relegate any solution effect to a position of minor importance.

Bonding in Cakes and Spheres

Forces holding thorium particles together when cakes and spheres are formed are thought to be predominantly van der Waals' forces. However, as previously pointed out by the author,¹ the dividing line between chemical bonding and van der Waals' bonding is nebulous and it is possible that chemical bonding contributes appreciably to cake strength. A quantitative measure of the extent of chemical bonding has not yet been obtained. It may be mentioned however that thorium spheres and cakes are largely dispersed by immersing them in hot nitric or hydrochloric acid, followed by dilution with water until the right ion concentration is reached. Gentle stirring is required. That such mild treatment separates particles rules out extensive bonding through solubility or sintering processes. The fact that hot acid treatment is required (spheres and cakes were never dispersed simply by addition of a dispersing agent) for dispersion suggests that some chemical bonding is present. As limited sintering of high-melting-point materials apparently can occur near room temperature,⁷ slight sintering in compacted ThO_2 particles would be a reasonable expectation. It has been observed, as described later, that thorium cakes disintegrate when flooded with water after thorough drying. However, the tendency to disintegrate is reduced if the drying temperature is above 150°C , indicating that a limited chemical bonding through sintering processes occurs in the absence of water. Impurities on particle surfaces may contribute substantially in forming these chemical bonds.

Loop Studies with Oxides Resistant to Particle Comminution

After a slurry of $\text{ThO}_2\text{-UO}_2$ calcined at 1050°C , and with a CRI of zero, formed a cake (CRI = 3) on the surface of the heat transfer disk in the 200B loop,⁸ studies of deposition by a similar $\text{ThO}_2\text{-UO}_2$ slurry were made in the 30-gpm loop. Half of each velocity section of one side of the MDSB was plated with copper and half with nickel, thus providing three different metal surfaces for oxide to deposit on in each section. A water cooler was added to a 1-in.-long section of the loop 1-in. piping to determine if oxide plated preferentially on lower-temperature surfaces.

Oxide Batch MO-51. - Oxide batch MO-51 $\text{ThO}_2\text{-UO}_2$ (U/Th atom ratio = 0.098; mean particle size = $2\ \mu$; $\sigma = 1.5$; surface area = $1.1\ \text{m}^2$; firing temperature, 1050°C) was circulated for 114 hr (run 30A-37). Examination of the MDSB revealed $\text{ThO}_2\text{-UO}_2$ deposits 1.3 mils thick over 60% of the stainless steel section of the 10-fps section. The nickel half of the 20-fps section was covered with a deposit of similar thickness. There were thin, small-area deposits in the copper part of the 5-, 10-, and 20-fps sections. Deposits in the cooled section of the 1-in. pipe were similar to those in thermally undisturbed 1-in. pipe. Surface roughness in the MDSB (the 10-fps section is rougher than the 20- or 5-fps sections) may have influenced oxide deposition; however, the roughness factor in each section was practically the same in each 30-gpm-loop run, and the pattern of oxide deposits has varied from run to run. No variation of oxide deposition with MDSB side occurred until one side was plated with copper or nickel. Figure 6 shows deposits in the MDSB after run 30A-37.

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Fig. 6. Deposits in Multidiameter Sample Barrel After Loop Circulation of $\text{ThO}_2\text{-9\% UO}_2$ (Run 30-A-37).

The MDSB was returned to the loop, and circulation continued to a total time of 300 hr. Examination then showed that there were no deposits in the MDSB except for a very thin film (too thin to measure) on the nickel in the 5-fps section. This film extended $1/2$ in. downstream on the copper. There were no deposits in the pump, which was opened after 300 hr.

1600°C-Fired Thoria. - Thoria calcined at 1600°C was circulated (30A-38) to determine if there was a preferential deposition of this oxide on certain metal surfaces, as was found with mixed thorium-uranium oxide. After 101 hr of circulation, the MDSB was examined. There was a thin thoria deposit on the stainless steel and copper (estimated 0.5-mil thickness) in the 10-fps section. There were no deposits on the nickel or on any surface in the 5- or 20-fps section. However, there was a deposit in

the 1-in. pipe (nominal velocity, 13 fps) resembling that in the 10-fps section.

Circulation was resumed for an additional 200 hr after which there was an oxide film too thin to measure (estimated 0.1 to 0.3 mil) covering the entire 20-fps section (all nickel and copper plating had worn away) and covering about 50% of the 10-fps section, with no preference for different metal (actually metal oxide) surface. This film did not wash away in a stream of water but was easily removed with a touch of the sponge. There was no thoria film in the 5-fps section. A thin thoria film with circular striations was visible in parts of the 1-in. piping. There was no difference in appearance of the surface of the cooled section and pipe on either side. No deposits were found in the impeller.

Near the end of run 30A-38 the heat transfer coefficient at the copper disk declined from about 3800 to about 2500 Btu/hr.ft².°F over a period of 50 hr. The heat transfer then began to increase and in 20 hr had returned to 3700. The run was then shut down and the disk was observed to have no thoria film on it. This apparently represents a period during which slight changes in slurry properties caused thoria to deposit on the disk and then to be removed. No change in circulating conditions was evident from loop instruments.

Discussion of Results. - The deposition of films by oxide batches that contained particles more resistant to degradation seems to follow the caking behavior of 800°C-calcined thoria in that deposits form during initial circulation. Also, size of the particles in the redispersed films is smaller than that of the circulating slurry. Films tend to form early in the run, presumably because fines generated by attrition of irregularly shaped particles are then most plentiful. It is believed that the film-forming mechanism for these oxides is essentially the same as that proposed by Lyon for 800°C-calcined thoria. The films have usually been softer, apparently reflecting the reduced number of very small particles available. Slurry deposition is influenced by the affinity of the metal surface as well as by the velocity.

Circulation of Thoria Spheres Treated to Prevent Caking

Spheres offer some potential advantages, such as low yield stress, as a means for achieving a satisfactory aqueous slurry. Untreated spheres produced in a loop invariably result in cake formation when circulated. For this reason, 15- μ loop spheres were treated to increase particle integrity. These spheres, treatment of which is described under the section on laboratory investigations, were circulated in the 30-gpm loop to evaluate sphere integrity and to observe their circulation characteristics. Molybdenum trioxide, which has prevented cake or sphere formation by fresh oxides, was added. Spheres remained in suspension nicely during the 273-hr run (run 30A-2). Particle-size analysis indicated almost no sphere disintegration, but inspection at the end of the run revealed that sufficient fines were worn off to cause a small quantity of hard cake to form in the pump impeller. Corrosion during the run was extremely mild (0.5 mil/year) compared with that for the circulation of 800°C-fired material under similar conditions in the 30-gpm loop. Weight loss by the titanium pump impeller was negligible.

Effect of Low-Concentrations of Thoria on Cake Formation

Circulation in 200- and 100-gpm loop runs had demonstrated that cakes formed readily in the concentration range of 500 to 1000 g of Th per kg of H₂O. Three runs (30A-14, 16, and 25) were made to determine if cake formation was inhibited by very low thoria concentrations. In run 30A-25, the oxide concentration ranged from 52 to 11 g of Th per kg of H₂O. Cake formation occurred, and the sphere development pattern, as exhibited by periodic samples, was similar to that of 500 g of Th per kg of H₂O runs. This seems to demonstrate conclusively that cake formation will occur at very low concentration and suggests that degradation due to particle-particle interaction is of secondary importance.

A Note on Colored Thoria Spheres

During circulation of spheres in run 30A-19, described below, microscopy showed that reddish-brown spheres were developing, and, by the end of the run, they were more numerous than the cream-colored spheres charged to

the loop. The red spheres averaged larger than cream-colored spheres by about $4\ \mu$ (diameters of $19\ \mu$ and $23\ \mu$, respectively, for larger spheres). There were almost no spheres of intermediate color. Red spheres were crushed and the fragments examined. The red color was uniformly distributed throughout the mass. Why fine fragments which are colored tend to aggregate along "color lines" and build uniformly colored spheres is not known.

Removal of Thoria Cakes

Circulation of Noncaking Slurry to Remove Caked Deposits

Tests were made in the 30-gpm loop to determine the ease of removal of hard cakes by circulating a noncaking thoria slurry.

In run 30A-19, a slurry composed of 200A-16 spheres was circulated for 239 hr to deposit a thin ThO_2 film in the 10-fps section (estimated 0.5 mil) and the 5-fps section (estimated 1.5-mil thickness). The impeller had a 1/16- to 1/8-in.-thick hard cake in the vanes, and the weep holes were half full. Oxide film covered part of the impeller face. After examination, the system was closed without allowing the cake to dry and then loaded with slurry from 30A-8, a Waring Blendor treated, 800°C -calcined batch of ThO_2 , to a concentration of about 400 g of ThO_2 per kg of H_2O . After 24 hr of circulation, examination of the loop showed that only a small fraction of the cake had been removed. The slurry circulation was then continued for an additional 65 hr (run 30A-20) and the loop examined again. About 95% of the deposit in the 10-fps section was removed, but most of the film in the 5-fps section remained. All cake had been removed from the impeller vanes and weep holes. Some of the film on the impeller face remained.

Thoria deposits were then replaced by further circulation of spheres, and a run was made with fresh 1600°C -calcined thoria in the scavenging slurry. A point of interest is that a few spheres left from the sphere run and circulated with the 1600°C -fired oxide appeared to grow about $4\ \mu$ larger (from an average size for larger spheres of 17.3 to a new average of $21.8\ \mu$). The circulation was continued for only 23.3 hr, followed by

examination of the loop. Film which had been in the 20-fps section after the preceding sphere run was gone, as was film in the 10-fps section. The area of the 5-fps section covered with oxide film was reduced. The original 800°C-fired oxide film remaining in the 5-fps section was covered with a coating of 1600°C-fired oxide which appeared to have been brushed on. The films did not wash away in a stream of water, but a soft stroke of the sponge removed the 1600°C-fired oxide, while moderate scrubbing with the sponge removed the underlying oxide film. The two oxide batches were easily distinguished in the film by color, because of the differing amounts of iron that they had picked up from corrosion and erosion of the stainless steel.

In the pump impeller a small amount of deposit remained in the vanes and weep holes and on the impeller face. The amount remaining indicated that continued removal at the same rate would have cleared the vanes and weep holes in a few more hours of circulation. The unpumped 1600°C-calcined ThO_2 was more effective, as expected, in removing cake deposits than previously pumped 800°C-fired material.

Disintegration of Thoria Cakes by Water or Dilute Solutions of Electrolytes

Pieces of hard cake produced during slurry circulation in loops are partially disintegrated by flooding with water or dilute electrolyte after thoroughly drying.¹ Chunks of cake break into smaller pieces usually within 10 sec after addition of the liquid. The extent of disintegration is a function of the compactness or extent of bonding in the cake, which varies substantially even for pieces of cake from the same run. Twenty-four to 48 hr is usually sufficient drying time to achieve extensive disintegration, but the tendency of the cake to disintegrate slowly increases as drying is continued. Best results were obtained with a drying temperature of 90 to 150°C; higher drying temperatures were deleterious to disintegration. A number of electrolyte solutions were tested, but the significance of variation of results with different electrolytes, different electrolyte concentration, and with pure water was obscured by variation in the cake from piece to piece.

Cake disintegration by flooding with water was used successfully to remove cake after two runs in a 100-gpm loop. Extensive dismantling was

avoided by drying the loop overnight with a hot air current and then flooding with tap water in one case and with 0.1 N H_2SO_4 in the other case. In each case the cake disintegrated into small pieces, which were washed out. The principal failing of this method of cake removal is that thorium deposits in the form of thin films (less than 1/16 to 1/22 in. thick) are usually not removed by it. Also, unusually hard, vitreous cakes underwent only limited disintegration.

Application of Thermal Stresses to Remove Caked Deposits

During circulation of spheres containing 3000 ppm of CrO_3 , the loop was put through three thermal cycles between room temperature and 275°C. Thorium that was deposited in the 5-fps section and in the copper heat-transfer disk showed abrupt breaks, with some layers thicker than others, indicating that parts of the deposits had broken off under thermal stresses. The cake in the copper disk is seen in Fig. 7.

Fig. 7. Heat Transfer Disk from 30-gpm Loop After Run 30A-30. Breaking off of cake deposits during thermal cycling is evident.

Prevention of Cake Formation

Digestion of Thorium Oxalate

Some thoria preparations have formed cakes while other similarly produced batches did not. During early experience with cake formation there was no oxide property or measurement by which to distinguish a caking batch from a noncaking one. Differences in ionic impurities were not thought to be significant, because no consistent difference of ion concentration between caking or noncaking oxide batches were detected. Table 2 gives the chemical analyses of oxide batches LO-14, LO-12, LO-7, and LO-2A, of which LO-14 and LO-12 were cake-forming batches while LO-2A and LO-7 never formed ThO_2 deposits.

It was found that an indication of the caking potential of fresh batches of thoria calcined at 800°C is given by a measure of particle integrity during agitation. Such a measure is obtained by determining the cake resuspension index (CRI) which is described in the Appendix. If the CRI of a batch was below about 4, the material would not form cakes or spheres. For example, the CRI of the nonsphere forming batch LO-7 was zero after 70 min of Waring Blendor treatment, whereas the CRI's of the cake-forming batches LO-20 and LO-23 were around 7 after the same Waring Blendor time.

Laboratory tests showed that the integrity of thoria particle as measured by the CRI is dependent upon the digestion time, that is, the time that the freshly precipitated $\text{Th}(\text{C}_2\text{O}_4)_2$ is allowed to contact the mother liquor. The following table gives CRI values as a function of digestion time for ThO_2 batches similarly precipitated and calcined at 800°C .

<u>Digestion Time (hr)</u>	<u>50% Size After Waring Blendor Treatment (μ)</u>	<u>Time in Waring Blendor (hr)</u>	<u>CRI</u>
0	0.7	1.16	7
1	0.6	1.16	5.7
6		1.16	1
16	0.9	1.16	0
48	1.0	1.16	0
112		5	0

Neither the surface area nor crystallite size of the resulting thoria was greatly affected by digestion time. However, $\text{Th}(\text{C}_2\text{O}_4)_2$ which was digested for 48 hr and then filtered and dried at 120°C had a nitrogen adsorption surface area of $4.6 \text{ m}^2/\text{g}$, as compared with $12.7 \text{ m}^2/\text{g}$ for $\text{Th}(\text{C}_2\text{O}_4)_2$ which was not digested. Water-vapor adsorption measurements at Rice Institute indicate that pore volume (pores of 10 and 75 Å radius) was greater for oxides made from undigested thorium oxalate than for oxides made from 48-hr digested oxalates.⁹

Since CRI values indicate a marked increase in particle integrity as a function of digestion time, it seems probable that the important difference between caking and noncaking ThO_2 batches which had no known difference in preparation was the time that the $\text{Th}(\text{C}_2\text{O}_4)_2$ was allowed to stand in the supernatant liquid. Initially these data were not recorded during oxide preparation. In any event, it was found that thoria prepared with digestion did not form cakes or spheres.

Another possible variation in batch to batch oxide preparation is firing temperature. Overheating could possibly have occurred due to combustion of $\text{Th}(\text{C}_2\text{O}_4)_2$. However, extensive tests of ThO_2 prepared by the pilot plant with firing temperatures from about 700 to 900°C showed the CRI to be insensitive to small variation of calcination temperature.

High Calcination Temperature

An effective method of thoria preparation which prevents cake formation is use of high calcination temperature.⁴ Oxide calcined at 1600°C has not formed hard cakes in any of a large number of circulation tests. The CRI of high-fired oxides is always zero. Crystallite size in 1600°C -calcined material is in excess of 2000 Å, which means that crystal degradation would be required for normal, hard cake formation. Many of the particles composing the cake are around 200 Å. No instance of ThO_2 crystal degradation during slurry circulation in large systems has been detected.

Effect of Electrolytes on Caking of Thoria

Effect on Previously Uncirculated Thoria. — Runs in 100-gpm loops demonstrated that the addition of small quantities of substances acting as

electrolytes under loop conditions would prevent cake formation during circulation of a fresh batch of thoria.¹⁰ One run (30A-15) in the 30-gpm loop showed that 350 ppm of CrO_3 (based on ThO_2 present) would prevent cake formation by LO-20 thoria. This run was made because chromates are always generated during circulation of slurry under an oxygen overpressure in a stainless steel system. Most electrolytes tested have prevented cake formation. A few have failed, for example, HNO_3 and Na_2SO_4 .¹¹ This failure possibly resulted from insufficient ion adsorption of from almost equal adsorption potential of the ThO_2 for each ion.

The actual mechanism of cake prevention by small quantities of electrolyte during circulation of a fresh thoria batch is not certain. It is assumed that the electrolyte contributes to formation of a stronger electrical double layer which in turn influences particle degradation characteristics. In run 30A-15, small spheres (up to $12\ \mu$) formed early in the run but did not grow and slowly became smaller and less numerous. This suggests that the small fragments could form aggregates (spheres or cakes) but that not enough fine fragments were produced to build either many or large spheres or cakes. It appears that the primary effect of the electrolyte is to influence particle degradation so as to reduce the number of cake-forming fragments rather than prevent reagglomeration of fragments once formed. As mentioned earlier, cake formation by spheres containing caking-size fragments is not prevented by low electrolyte concentrations.

Deterrent Effect of Li_2SO_4 on Caking of Slurries Containing Caking-Size Fragments. - Slurry in quartz tubes was maintained in dispersed suspension at elevated temperatures by addition of Li_2SO_4 . The maximum temperature used was 250°C . The dispersing effect was marked over a wide Li_2SO_4 concentration range of 500 to 20,000 ppm (based on ThO_2 present; ThO_2 concentration approximately 250 g of Th per kg of H_2O). Flocculation had not occurred in a slurry of small particles after more than two weeks at 250°C . As no other electrolyte tested in these studies exhibited a strong dispersing capacity at 250°C , loop tests (runs 30A-42 and 43) were made by circulating fresh spheres with added Li_2SO_4 . The runs were made at 250°C rather than 275°C so as to correspond with the temperature used in the quartz-tube studies. Previous runs had demonstrated that untreated

spheres caked readily in the 200 to 300°C range and that addition of CrO_3 , NaAlO_2 , or MoO_3 did not prevent cake formation. In the first run, the initial Li_2SO_4 concentration of 2000 ppm (based on ThO_2 concentration of about 400 g of Th per kg of H_2O) was increased to 3000 ppm after 50 hr and to 7000 ppm after about 170 hr. During circulation there was no difficulty that suggested cake formation. Examination of the loop after the run showed that there was no deposits in the impeller vanes or weep holes. Such deposits had always occurred in prior sphere circulations runs. The MDSB had no deposits in the 10- or 20-fps sections. There was a thin, soft thoria film covering the entire 5-fps section (stainless steel, copper, and nickel surfaces). The film, too thin to measure, was in two layers, the upper of which peeled off in some places on drying.

A second run under similar conditions but with 800 ppm of Li_2SO_4 resulted in small quantities of oxide cake in the impeller vanes and weep holes as well as a thicker film in the 5-fps section of the MDSB. Film in the 5-fps section was again layered, possibly due to disturbance by a loop shutdown to repair a leak and also due to the resultant shift in Li_2SO_4 concentration.

These circulation tests demonstrated that Li_2SO_4 is partially effective in preventing thoria cake formation, being the most effective electrolyte tested in this respect. The layered film in the 5-fps section of run 30A-42 suggests that oxide deposition occurred after additional Li_2SO_4 was added to the loop.

Room-temperature determination of zeta potentials of thoria with added Li_2SO_4 gave the results shown below. Similar ζ determinations with CrO_3 added are included for comparison.

Concentration of Additive (ppm)	Zeta Potentials (mv)	
	<u>Li_2SO_4</u>	<u>CrO_3</u>
0	-94	-94
500	-195	-65
1,000	-156	-59
5,000	-146	-39
20,000	-90	-23
500 Li_2SO_4 , 500 CrO_3	-180	

These ζ values are the highest (absolute values) obtained for ThO_2 in Homogeneous Reactor Project studies. It will be noted that the presence of added ions (500 ppm of CrO_3) did not materially decrease the ζ potential. The effectiveness of Li_2SO_4 in increasing it and in reducing thoria cake formation is possibly due in part to the fact that Li^+ ions are highly hydrated. The SO_4^{--} ions are absorbed on the oxide surface, and the counter ion layer is composed largely of Li^+ ions. The tendency of Li^+ to hydrate may enhance the electrical double layer repulsion between particles by making the counter ion layer more resistant to compression.

A strongly adsorbed water layer could theoretically exert a steric effect on particle-particle agglomeration. These studies do not enable one to discern whether such an effect is operable in addition to the electrical double layer repulsion. The author does not know of a case in an inorganic system in which a clear-cut differentiation has shown an appreciable water-layer steric effect.

Laboratory Investigation of ThO_2 Properties Related to Cake Formation

Slurry and oxide batch properties have been studied in so far as seemed useful with respect to caking problems by a number of tests that could be run in the laboratory. Studies of sphere growth in stirred systems and particle integrity studies by CRI determination have been reported.¹ Some additional investigations which have proved interesting are discussed below.

Thoria Deposition on Metal Surfaces During Agitation

A measure of the caking tendency of a slurry is obtained by determining deposition on a metal plate suspended above the blade in a Waring Blender.¹² Batch LO-12 ThO_2 , a batch which had a CRI of 6 and which formed cakes in loop circulation, gave thicker deposits than LO-7 ThO_2 , a non-caking oxide batch with a CRI = 0.

The deposition of LO-12, a cake-forming preparation, was strongly influenced by the addition of NaAlO_2 , as shown in Table 3 and Fig. 8. With

Table 3. Oxide Deposition on Metal Plates
Suspended above Waring Blendor Blades

Oxide Batch	Additive or Potential (wt % or mv)	Results	
		Wt Gain (g)	Metal-Plate Appearance
LO-12 (800°C)	None	0.06	Thin - medium film
LO-12	0.11 NaAlO ₂	0.04	
LO-12	0.22 NaAlO ₂	0.01	
LO-12	0.44 NaAlO ₂	0.00	Extremely thin film visible
LO-12	3.52 NaAlO ₂	0.00	Very clean appearance
LO-7 (800°C)	None	0.0062	Film visible, some spots bare
LO-7	0.11 NaAlO ₂	0.0020	
LO-7	0.22 NaAlO ₂	0.0007	Film perceptible
LO-7	0.44 NaAlO ₂	0.0004	Film still perceptible
LO-12	0.014 H ₂ SO ₄		Film thicker than for case of no additive
LO-12	0.028 H ₂ SO ₄		Film slightly thicker than with 0.014% H ₂ SO ₄
LO-12	0.11 H ₂ SO ₄	0.06	Film about same as for case of no additive
LO-12	0.28 H ₂ SO ₄	0.0029	
1600°C ThO ₂	None		Film definitely visible
200B-3B Drain (ThO ₂ - 8% UO ₂ ; circulated several hundred hr)	None	Wt % ranged 0.0087 to 0.0161 g for several tests	
200B-3B Drain	+90 mv	0.0087	
200B-3B Drain	-90 mv	0.0077	
200B-3B Drain	+190 mv	0.0092	
200B-3B Drain	-190 mv	0.0071	
200B-3B Drain	+500 mv	0.0119	
200B-3B Drain	-500 mv	0.0073	
200B-3B Drain	+5000 mv	0.0084	
200B-3B Drain	-5000 mv	0.0070

Fig. 8. Influence of NaAlO_2 on the Deposition of Thoria (Batch IO-12) on Plates Suspended Above Waring Blendor Blades.

no additives present, a heavy thoria film formed on the surface of the plate; however, with increasing NaAlO_2 content of the slurry, the film thickness steadily declined and had almost vanished at 0.44 wt % NaAlO_2 . The influence of NaAlO_2 in preventing the film formation was not altered by nine days of autoclaving at 300°C . Deposition of LO-7 thoria similarly decreased with increasing NaAlO_2 content. With addition of H_2SO_4 , there was a slight increase in film thickness at extremely low acid concentration (0.028 wt % H_2SO_4 , based on ThO_2 present); however, film thickness began to decline with larger acid additions.

Behavior of slurry containing $\text{ThO}_2\text{-UO}_2$ (8% U) suggested that electrical potentials developed by electrokinetic action, galvanic action, or that thermal effects may have influenced oxide film formation in the 200B loop⁸ and in the 30-gpm loop. The effect of an applied potential on a metal disk suspended above the Waring Blendor blade was tested by applying

a constant dc voltage to the disk and to a conductor suspended in the slurry. Oxide films formed with a pumped $\text{ThO}_2\text{-UO}_2$ slurry (200B-3B drain) at a concentration of 300 g of ThO_2 per kg of H_2O did not show a consistent correlation with potential applied to the metal plate. No effect on oxide deposition was noted with the use of copper or nickel surfaces rather than stainless steel plates. The only strain of consistency in the results was a consistent decrease in weight of the oxide film during deposition on a negatively charged plate following a test with a positive potential of the same magnitude (Table 3). This was expected because the slurry particles had a negative ζ potential.

High-Temperature Slurry Studies in Quartz Tubes: Settled-Bed Concentration and Extent of Dispersion

Studies in heated quartz tubes (6-mm ID) showed that between 150 and 250°C that slurries composed of small particles (mean particle size less than about 4 μ) would cease to flow as the rocking tube was heated. Slurry concentrations of approximately 400 g of ThO_2 per kg of H_2O and higher were used. Plug formation marked the point at which the slurry became a rigid floc, with the dispersing medium trapped in its interstices.

Influence of Electrolytes on Settled-Bed Concentrations. — In subsequent studies made to determine the influence of surface active agents on the behavior of thorium slurries, the oxide concentration was reduced so that nonflowable flocs did not form (below about 300 g of Th per kg of H_2O). Settled-bed concentrations were determined as a function of electrolyte concentration and temperature. Portions of slurry from run 30A-32 consisting largely of dispersed spheres were treated with $\text{Ba}(\text{NO}_3)_2$ and with LiNO_3 . It is seen in Fig. 9 that the settled-bed concentration of the thorium containing LiNO_3 is less than that containing $\text{Ba}(\text{NO}_3)_2$. The lithium ion is highly hydrated, while Ba^{++} is much less hydrated. It is possible that a hydrophilic shell surrounds the particles of the slurry containing Li^+ and holds them apart. However, the extent of flocculation exerts a much greater influence on settled-bed concentration and may be the principal factor in the concentration differences.

The settled-bed concentrations shown in Fig. 9 were determined over a period of 24 to 48 hr after the tube was put in the rocking bomb. It was found that if slurry containing Li^+ or Ba^{++} ions or no additive remained at elevated temperature for several days that the settled-bed densities (after agitation and settling) increased, indicating that the slurry was settling from a more disperse state.

Slurry Dispersion at High Temperatures. - A slurry composed of thoria spheres (run 200A-17) which had been treated in the Waring Blendor until

Fig. 9. Settled-Bed Concentration of a Pumped Slurry. Sealed quartz tubes, 6 mm in diameter, were used in determining the settled-bed concentrations.

most of the spheres were dispersed to fine particles was rocked in a quartz tube at a concentration of about 250 g of ThO_2 per kg of H_2O . It also contained 20,000 ppm of LiNO_3 (based on ThO_2). The temperature was raised slowly until at about 200°C the slurry turned to well-formed, large (0.2 to 0.5 mm) spheres. At 250°C an estimated 98% of the oxide had been converted to spheres. Microscopy showed that the spheres were ellipitical and appeared to have a rather low density. Hand-shaking of the tube (at room temperature) caused dispersion. When the tube was returned to the rocker and the temperature raised, spheres reformed. However, after thorough dispersion in an ultrasonic-energy bath spheres could not be formed again.

Several tubes of spheres were prepared from the Waring Blendor blended slurry. If the temperature was reduced below 200°C while the quartz tubes were being rocked, the spheres begin to disperse, with very extensive dispersion occurring around 140°C . Spheres formed in slurry containing 1500, 20,000, and 60,000 ppm of LiNO_3 but did not form in slurry containing 20,000 ppm of CrO_3 .

With one exception, slurries treated with LiNO_3 or $\text{Ba}(\text{NO}_3)_2$ always appeared flocculated at temperatures above 175°C , irrespective of their low-temperature state. One slurry, consisting of oxide from run 30A-32 and containing 27,000 ppm of LiNO_3 (based on ThO_2 present), was flocculated initially even at low temperature but after about six days at 250°C became well dispersed at low temperatures and maintained partial dispersion at 250°C .

Lithium sulfate exhibited the greatest dispersing power at high temperature of the electrolytes tested. All slurries treated with 500 to 20,000 ppm of Li_2SO_4 was dispersed up to the 250°C limit of the tests. In a long test, slurry remained dispersed for more than two weeks, at which time it became partially coagulated.

It is interesting to note that with Li_2SO_4 -treated slurries, as well as occasionally with untreated or LiNO_3 -treated slurries, dispersion became evident or increased in extent at a given temperature after the slurry had been at a 250°C for a number of hours or days. The reason for increased dispersion after high-temperature treatment is not known. A possible explanation is that ion interaction adjusts the ion concentration to a value

that gives a more powerful electrical double layer repulsion. Generation of silicate ions may be a factor.

Addition of Na_2SO_4 also produced slurry dispersion at 250°C , but the extent of dispersion appeared to be less than with Li_2SO_4 . A long test, however, indicated that the dispersion effect of Na_2SO_4 was maintained at least as long as that of Li_2SO_4 . Trilithium phosphate also produced excellent slurry dispersion at 250°C , but, after a few days at temperature, large portions of the slurry coagulated to form a gel-like precipitate.

Improvement of Sphere Integrity by Flux Sintering

Loop-produced spheres, as described earlier, form cakes quickly during loop circulation unless subjected to prior treatment. Simple high-temperature treatment was not satisfactory, because large clinkers formed.¹³ Combinations of chemical and heat treatment were tested to increase sphere structural strength. A treatment which gave favorable results consisted of a one-pass extraction with hot nitric acid followed by the addition of a solution containing $\text{Th}(\text{NO}_3)_4$ in excess of what could be adsorbed on the sphere surfaces. The $\text{Th}(\text{NO}_3)_2$ solution was decanted and NH_4OH added. The slurry was then filtered and dried. Calcination was carried out at 1300°C , overnight. The added $\text{Th}(\text{OH})_4$ may have acted to promote sintering of particles in the sphere. Spheres treated in this manner had a weight loss of 3.4%, as indicated by a special test of sphere integrity. The test consisted first in Waring "Blending" 3 g of spheres in 200 ml of water for one hour. The slurry was then poured into a 250-ml graduate and the suspension level brought to 230 ml by addition of water containing a dispersing agent. The slurry was shaken and allowed to settle 5 min; then, the upper volume of about 70 ml was drawn off through a special stopcock and analyzed for thorium. Thorium indicated by this analysis was taken as degraded thorium. Table 4 gives some typical values. Note that treatments similar to the above but using $\text{Pb}(\text{NO}_3)_2$ gave about the same results in increasing sphere integrity. The spheres actually circulated in the loop (run 30A-2) had a loss of 7.5% in the sphere-integrity test, showing that the treatment was not as well handled on a large batch of spheres. Feeding spheres through an acetylene-oxygen flame did not give adequate improvement

Table 4. Sphere Disintegration Tests

Slurry Tested	Treatment	Firing Conditions		Disintegration
		Temperature (°C)	Time (hr)	
Standard*	No treatment			70
Standard	HNO ₃ - Th(NO ₃) ₄ - NH ₄ H	1300	13	3.4
Standard	HNO ₃	1600	4	2.1
Houdry spheres	No treatment			1.5
Houdry spheres	Th(NO ₃) ₄	1300	21	1.0
Standard	HNO ₃ - Pb(NO ₃) ₂ - NH ₄ OH	1300		3.1
Standard	No chemical treatment	1300	21	4.6
"Cubes"	No treatment			2.5

* Size of standard slurry spheres (loop produced) was about 17 μ .

of integrity, while an attempt to pass spheres through an electric arc also gave unsatisfactory change of integrity.

Consideration of Zeta Potential Influence on Thoria Slurry Behavior

The theory of lyophobic dispersion assumes an electrical double layer which produces a potential gradient around particles in an aqueous suspension.¹⁴ In stable lyophobic suspensions, the repulsion resulting from the electrical double layer is sufficient to prevent agglomeration of the suspended particles even though the agglomerated system would be in a lower energy state. Thermodynamically unstable suspensions can sometimes be maintained for years. In the literature there is general agreement that an electrical potential greater than about 30 mv is usually sufficient to maintain dispersion of a colloidal system. The electrical potential of particles can be determined by electrokinetic measurements. These measurements yield a zeta potential which, while not representing the actual charge on the particle surface, represents the part of the charge which would be expected to be effective in causing particle-particle repulsion.

Extensive measurement of ThO₂ zeta potentials has been carried out at the Atomic Energy Research Establishment in Great Britain.¹⁵ The influence

of different ions and ion concentrations on the zeta potential of irradiated and nonirradiated thoria were determined. At the Pennsylvania Advanced Reactor project, a correlation was found between zeta potential and deposition of oxide films on metal plates suspended above the Waring Blendor blades.¹²

For the Homogeneous Reactor Project, the electrophoretic method of zeta potential determination has been adapted by the Analytical Section.¹⁸ All the zeta potentials discussed in this paper were determined by the Analytical Chemistry Division.

The zeta potential of slurry particles which have been circulated in loops under oxygen overpressure is always negative, with magnitude usually in the range of 50 to 100 mv. Despite the high zeta potentials, circulated slurries are usually highly flocculated. It is known that increased concentration and agitation are prime factors in promoting aggregation of dispersed systems.¹⁷ To test if dispersion would be present in pumped slurries of very low concentration and sufficiently fine particles, dilute pumped slurry composed of dispersed spheres (30A-32 drain) was further dispersed in the ultrasonic bath. After a settling period the slurry still in suspension was poured off and further dispersed. This procedure was repeated, yielding a very dilute colloidal suspension. However, after about 1 hr the suspension had flocculated and partly settled out. Oxide particles from this suspension were found still to have a high negative zeta potential of -60 mv. A possible reason for this apparent discrepancy is that small oxide particles which aggregate actually have rather low zeta potential. When the aggregate forms, the charge on the surface of the small particles migrates to the surface of the large floc giving it a higher zeta potential, which is reflected in the measurement (suggested by Professor E. Matijewic, Clarkson College, Potsdam, New York).

Aggregation in the secondary minimum offers a possible explanation for flocculation of particles with high zeta potential. The secondary minimum results from interaction of the electrical double layer repulsion and the van der Waals' attraction between two particles. More rapid decay of the repulsion forces with distance from the surface permits particles to be held together but with a gap between them. Verwey and Overbeek estimate

that the secondary minimum can be a significant factor for particles in the size range covered by thorium slurries.¹⁸ The depth of the secondary minimum may be several kT . D. M. Eissenberg has observed thorium slurry behavior to occasionally fit expectations of flocculation in the secondary minimum. However, no definite verification of appreciable influence of the secondary minimum on thorium slurries has been established.

It has also been observed that slurries with particles of near zero zeta potential occasionally remained dispersed. There is no explanation for this behavior within the generally accepted concepts of lyophobic suspensions with which the author is familiar.

Fresh slurry batches have different zeta potentials but no correlation of zeta potential with caking tendency has been detected.

Properties of ThO_2 that Contains a Coprecipitated Oxide

Study of slurry caking phenomena emphasized the importance of particle integrity. Raising the calcination temperature, at least to a certain point, increases particle integrity. For a given calcination temperature, it was thought that additives which lowered the sintering temperature would aid in forming particles more resistant to degradation. One additive which lowers the sintering temperature when present in small proportions is alumina.¹⁹ Other additives studied were the oxides of Si, Pb, Zr, and Mg. Mixed oxides (thorium plus added oxide) with the above-mentioned additives were prepared by coprecipitation (either as oxalates or hydroxides), filtration, and stepwise firing to $800^\circ C$. The following table gives results for the oxides containing Al, Pb, or Si. Precipitation in each case was with ammonium hydroxide. The precipitate was digested 50 hr, and, subsequently, 5-hr Waring Blendor treatment was used in determining the CRI.

<u>Additive</u> <u>(mole fraction)</u>	<u>CRI</u>
None	6
Si, 0.1	4.6
Al, 0.1	2
Pb, 0.1	1

The following table gives the results for ZrO_2 addition via coprecipitation as oxalate. In this case all precipitates were digested for about 4 hr, and the CRI was determined after 70-min Waring Blendor treatment of the ignited oxides.

<u>ZrO_2 (mole %)</u>	<u>CRI</u>
0	4
5	1
5 (fired at 1000°C)	0
10	0.5
25	0

Results for the MgO -addition experiment were unfavorable with respect to particle integrity.

A series of 12 samples covering the entire composition range of the systems $\text{ThO}_2\text{-Al}_2\text{O}_3$ and $\text{ThO}_2\text{-PbO}_x$ were prepared. Data on these samples is reported in Tables 5 and 6. Notice that particle integrity as indicated by CRI determinations was improved by the additive only in the low-concentration range. Mutual protection against crystallization, which was exhibited in both systems, would no doubt have been more evident for a lower calcination temperature.

From the data available, it appears that ZrO_2 is the most promising additive in increasing particle integrity. The CRI method of particle integrity determination reports a room-temperature result. It does not necessarily follow that a definite improvement in particle integrity under loop or reactor conditions can be obtained by the use of coprecipitated additives, but it appears promising.

Brief Study of Adsorption from Solution at Elevated Temperature

Studies were made of ion adsorption from solution by 800°C -calcined thorium (batch LO-23), using a stainless steel autoclave. The extent of adsorption was determined by chemical analysis of samples drawn from the solution, assuming that the missing ions had been adsorbed. Results were

Table 5. Properties of Thoria-Alumina Samples

Sample No.*	Composition of Mixed Oxides (mole %)		Surface Area (m ² /g)	Wt Loss on Heating from 30 - 1000°C (mg/g)	CRI**	Zeta Potential (mv)	ThO ₂ Crystallite Size (Å)
	Th	Al					
PTA-1	100	0	15.3	26	2	0	125
PTA-2	95	5	24.0	43	2	-78	87
PTA-3	90	10	25.9	45	1	-33	73
PTA-4	80	20	18.0	41	0	-39	59
PTA-5	70	30	26.4	49	1	+23	56
PTA-6	60	40	13.0	37	0	+21	51
PTA-7	50	50	32.2	65	0.5	+39	54
PTA-8	40	60	31.1	95	2	+43	54
PTA-9	30	70	61.5	120	5.6	+39	54
PTA-10	20	80	79.0	141	2.8	+39	57
PTA-11	10	90	87.5	153	1	-67	55
PTA-12	0	100	138.0	215	0	+59	-

*These samples were prepared by coprecipitation of mixed nitrates with NH₄OH, with 5-hr digestion. All samples fired stepwise to 800°C.

**CRI values determined with 70-min Waring Blendor treatment.

disappointing in that with the small quantities adsorbed, the chemical analyses were not sufficiently accurate to produce adsorption isotherms suitable for thermodynamic calculations. Adsorption of Na₂SO₄ indicated that the thoria surface had a greater affinity for sulfate than for Na⁺ ions in the temperature range 100 to 275°C. Adsorption of NaAlO₂ showed that over a wide range of adsorbate concentration the amount of AlO₂⁻ adsorption increased in going from 100 to 150°C and fell below the 100°C

Table 6. Properties of Thoria-Lead Oxide Samples

Sample No.*	Mole %		Surface Area (m ² /g)	CRI**	ThO ₂ Crystallite Size (Å)
	Th	Pb			
PTL-1	100	0	10.9	6.5	192
PTL-2	95	5	12.0	3	135
PTL-3	90	10	15.3	6.5	109
PTL-4	80	20	24.0	8.6	70
PTL-5	70	30	31.3	8	74
PTL-6	60	40	35.7	7	68
PTL-7	50	50	23.3	9.5	65
PTL-8	40	60	24.0	3	65
PTL-9	30	70	16.0	5.5	59
PTL-10	20	80	5.0	8	67
PTL-11	10	90	0.5	6	—

* Samples prepared by precipitation of the mixed nitrates with oxalic acid. Digestion time was 30 min. All samples fired at 800°C.

** Seventy-minute Waring Blendor treatment used in CRI determinations.

adsorption level at 250°C. These changes in amounts of adsorption with temperature probably reflected changes in the ion species being adsorbed. More extensive studies of ion adsorption on thoria have been carried out at the University of Utah through the utilization of infrared adsorption techniques.²⁰

CONCLUSIONS

1. Formation of hard cakes during thoria circulation is prevented if the slurry particles are sufficiently resistant to degradation. Particles

with high resistance to degradation are obtained by high calcination temperatures or by long digestion of the oxalate precipitate prior to calcining. Small quantities of electrolytes functioning as surface active agents will also prevent cake formation in fresh thoria batches by affecting particle degradation.

2. Thoria deposition patterns during the circulation of cake-forming batches of 800°C-fired oxide support Lyon's theory that cakes are formed when small particles are pushed over each other into positions of minimum energy, where they are held together by van der Waals' forces.

3. Solubility of ThO_2 does not contribute appreciably to cake formation with thoria slurries. The extent of chemical bonding in cakes is not known.

4. The behavior of oxides which are more resistant to degradation (1600°C-fired ThO_2 , $\text{ThO}_2 - 8\% \text{UO}_2$) appears to follow a similar process, but films which they form are softer due to less particle degradation.

5. Surfaces of different metals (container materials) exert differing affinities for oxide particles during slurry circulation.

6. Initial oxide particle size is important in determining whether hard cake will form. Rapid breakup of large particles will inhibit cake formation, apparently because very fine particles necessary for hard cake formation are not readily worn off the intermediate-size particles.

7. While cake formation is prevented by electrolytes when particle degradation must occur, it is not inhibited by most electrolytes when caking-size particles are already present. Lithium sulfate addition to slurry composed of cake-forming size particles reduces cake formation but is not completely effective in preventing it.

8. Prolonged circulation of loop-produced spheres reduces or eliminates their caking tendency. Apparently, fragments from the spheres slowly agglomerate into small particles which are too large for cake formation, but not large enough for fines to wear off rapidly enough to produce cake formation. This process of avoiding cake formation may occur to some extent in all oxide circulation.

9. Autoclaving of a caking oxide in dilute acid did not change the particle structure sufficiently to prevent cake formation. The absence of

an autoclaving effect emphasizes the probable importance of very-fine-particle agglomeration on the leveling out of slurry particle size after initial degradation and on the reduced caking tendency after initial circulation.

10. The most important slurry property to control is particle size, which is dependent on particle integrity. Particle surface state and particle shape are important also but in general will tend to reach a condition predetermined by status of the circulation system and, thus, are not subject to close control. Preparations of ThO_2 with a coprecipitated oxide should be tested for particle integrity under loop conditions. The importance of determining the influence of radiation on particle integrity cannot be overemphasized.

11. The fraction of fine particles required for cake formation should be more clearly determined by circulating a slurry composed of loop-produced spheres mixed with different weight fractions of a noncaking oxide.

12. Treatment of loop-produced thoria spheres resulted in reasonable particle integrity, and further improvement can probably be obtained, but circulation of spheres of size greater than about $10\ \mu$ without cake formation is questionable. However, the stability of treated loop-produced spheres and the greater stability of the best spheres produced from gels (made by the Houdry Process Corporation) are suggestive that, out-of-pile at least, spheres of sufficient integrity for the less rigorous stresses of a fluidized bed operation are available.

13. Oxide deposition is a function of slurry velocity and should be further investigated by the use of a variable frequency source to broaden the circulation conditions covered.

14. The influence on slurry properties of the degree to which the thoria particle surface is hydrophilic and how to control this factor is little understood, and further study could prove valuable.

REFERENCES

1. C. S. Morgan, Status Report on ThO₂ Caking Studies, ORNL CF-57-9-102 (Sept. 26, 1957).
2. D. G. Thomas, Further Information on the Cake Formed During Slurry Test 200A-3, ORNL CF-56-4-120 (Apr. 30, 1956).
3. I. Spiewak et al., HRP Quar. Prog. Rep. Jan. 31, 1959, ORNL-2272, p 61.
4. R. N. Lyon, The Choice in Thorium Oxide Slurries for the Prevention of Caking in Circulating Systems, ORNL CF-57-4-77 (Apr. 22, 1957).
5. C. S. Morgan, Influence of Surface Active Agents on ThO₂ Slurries, ORNL CF-58-7-56 (July 15, 1958).
6. P. R. Kasten et al., HRP Quar. Prog. Rep. Jan. 31, 1958, ORNL-2493, p 43.
7. F. N. Rhines, Trans. Am. Inst. Mining, Met. Engrs. 166, 474 (1946).
8. I. Spiewak et al., HRP Quar. Prog. Rep. Oct. 31, 1959, ORNL-2879, p 65.
9. A. L. Draper and W. O. Milligan, Structure and Surface Chemistry of Thorium Oxide, Summary Report to Union Carbide Nuclear Company, Sub-contract Number 1201 (Sept. 1, 1959).
10. R. B. Korsmeyer et al., HRP Quar. Prog. Rep. Jan. 31, 1958, ORNL-2561, p 109.
11. E. L. Compere et al., HRP Quar. Prog. Rep. Jan. 31, 1957, ORNL-2272, p 91.
12. A. Biancheria, personal communication.
13. D. G. Thomas, personal communication.
14. H. R. Kruyt, Colloid Science, vol I, chap. 2, Elsevier, Amsterdam, 1949.
15. D. J. O'Connor, The Ion Exchange and Ion Adsorption Properties of Neutron Irradiated Thoria, AERE C/R 1767 (Mar. 2, 1956); D. J. O'Connor, AERE C/M 230, RCTC.
16. C. M. Boyd, H. P. House, and O. Menis, Micro-Electrophoretic Determination of the Zeta Potential of Thorium Oxide, ORNL-2836 (Nov. 10, 1959).
17. I. Reich and R. D. Vold, J. Phy. Chem. 63, 1497 (1959).

18. E J. W. Verwey and J. Th. G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam, 1948.
19. Serge Tacvorian, Compt. rend. 234, 2363-2365 (1952).
20. M. E. Wadsworth et al., Re Surface Chemistry of Thoria - Progress Report Jan. 31, 1959, University of Utah.

APPENDIX

The Cake Resuspension Index

Determination of the cake resuspension index (CRI) affords a method for determining a cake's ease of resuspension or redispersion by agitation in water. The value obtained is a measure of cake resistance to disintegration and is probably related to the cake hardness. The CRI is determined by shaking small pieces of cake (3 to 4.5 g of 1/8- to 1/4-in. pieces which are 1/8 to 1/16 in. thick) in 35 ml of distilled water in a 50-ml sample bottle on a mechanical shaker. To obtain comparable results, the desirable shaking time must be determined experimentally for each shaker. After shaking, the contents of the bottle are poured on a sieve (stainless steel, 10 mesh) and washed with distilled water. The CRI, which increases with increasing resistance to disintegration, is equal to the weight on the sieve times 10/initial weight.

The CRI can be used to evaluate the ease of particle degradation in thoria batches. An aqueous suspension of the oxide is treated in a Waring Blendor, after which the settled slurry is allowed to dry under atmospheric conditions. The CRI of the resulting cake is then determined. Such CRI determinations exhibit great sensitivity to particle size, which reflects the extent of particle degradation during agitation. CRI tests on 800°C-calcined oxide were effective in predicting which batches would not cake and which might cake. Oxide with a CRI below 4 to 5 (for Waring Blendor treatment time of 70 min) did not cake, while those with higher CRI often did. High CRI means only that the oxide particles are easily degraded, which is one of the necessary conditions for cake formation.

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