UNCLASSIFIED

OAK RIDGE NATIONAL LABORATORY

Operated By

UNION CARBIDE NUCLEAR COMPANY

 POST OFFICE BOX P
 OAK RIDGE, TENNESSEE

ORNL
CENTRAL FILES NUMBER

CF-57-4-77

EXTERNAL DISTRIBUTION AUTHORIZED

COPY NO. 158

DATE: April 22, 1957

 SUBJECT: The Choice in Thorium Oxide Slurries for the
 Prevention of Caking in Circulating Systems

TO: Distribution

FROM: R. N. Lyon

Distribution:

1. HRP Director's Office	29. F. L. Culler	58. S. I. Kaplan
Rm. 259, Bldg. 9204-1	30. J. S. Culver	59. P. R. Kasten
2. G. M. Adamson	31. R. J. Davis	60. M. T. Kelley
3. W. L. Albrecht	32. E. P. Epler	61. A. S. Kitzes
4. H. F. Bauman	33. J. R. Engel	62. J. O. Kolb
5. S. E. Beall	34. H. L. Falkenberry	63. R. B. Korsmeyer
6. A. M. Billings	35. D. E. Ferguson	64. U. Koskela
7. D. S. Billington	36. J. D. Flynn	65. K. A. Kraus
8. E. G. Bohlmann	37. D. F. Frech	66. J. A. Lane
9. J. C. Bolger	38. J. H. Frye	67. R. E. Leuze
10. C. J. Borkowski	39. C. H. Gabbard	68. S. C. Lind
11. G. E. Boyd	40. W. R. Gall	69. R. B. Lindauer
12. N. C. Bradley	41. E. H. Gift	70. M. I. Lundin
13. J. C. Bresee	42. T. H. Gladney	71-85. R. N. Lyon
14. N. A. Brown	43. H. E. Goeller	86. R. O. Maak
15. F. R. Bruce	44. A. T. Gresky	87. E. A. Mason
16. J. R. Buchanan	45. J. C. Griess	88. J. P. McBride
17. W. D. Burch	46. J. D. Grimes	89. H. F. McDuffie
18. C. A. Burchsted	47. R. H. Guymon	90. H. A. McLain
19. A. D. Callihan	48. P. A. Haas	91. H. M. McLeod
20. G. H. Cartledge	49. J. P. Hammond	92. R. A. McNees
21. C. E. Center	50. R. J. Harvey	93. J. R. McWherter
22. R. A. Charpie	51. P. N. Haubenreich	94. O. Menis
23. R. D. Cheverton	52. J. W. Hill	95. E. C. Miller
24. C. J. Claffey	53. J. P. Jarvis	96. R. L. Moore
25. H. C. Claiborne	54. S. Jaye	97. R. C. Moren
26. C. W. Collins	55. G. H. Jenks	98. C. W. Nestor
27. E. L. Compere	56. W. H. Jordan	99. E. O. Nurmi
28. S. J. Cromer	57. R. W. Jurgensen	100. L. F. Parsly

NOTICE

(con't on page 2)

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

2

Distribution (con't)

101. M. L. Picklesimer
102. R. G. Pitkin
103. L. R. Quarles
104. W. D. Reel
105. D. M. Richardson
106. G. W. Rivenbark
107. R. C. Robertson
108. J. N. Robinson
109. A. M. Rom
110. M. W. Rosenthal
111. H. C. Savage
112. H. W. Savage
113. W. F. Schaffer
114. R. E. Schappel
115. H. K. Search
116. C. H. Secoy
117. C. L. Segaser
118. E. M. Shank
119. E. D. Shipley
120. M. J. Skinner
121. A. H. Snell
122. I. Spiewak
123. R. W. Stoughton
124. C. D. Susano
125. J. A. Swartout
126. E. H. Taylor
127. D. G. Thomas

128. P. F. Thomason
129. M. Tobias
130. D. S. Toomb
131. W. E. Unger
132. R. Van Winkle
133. B. S. Weaver
134. B. H. Webster
135. H. O. Weeren
136. A. M. Weinberg
137. T. A. Welton
138. R. R. Wiethaup
139. J. C. Wilson
140. R. H. Winget
141. C. E. Winters
142. W. L. Wright
143. F. C. Zapp
144. ORNL Document Reference
Library, Y-12
145. Central Research Library
146-147. REED Library
148-150. Laboratory Records

External

151-157. Westinghouse PAR Project
158-172. TISE-AEC
173. F. C. Moesel, AEC

3

The Choice in Thorium Oxide Slurries for the Prevention
of Caking in Circulating Systems

R. N. Lyon

Summary

A qualitative theory for cake formation in ThO_2 slurries is presented. The sphere formation which occurs in "Standard" slurry can be explained on the same basis. The irregular and unpredictable yield strength is easily fitted into the theory. On the basis of this theory, the writer has been led to the conclusion that only colloidally stable slurries, or slurries with crystallites or comminution-resistant particles which are large enough to overcome colloidal effects (probably larger than 0.1μ) can be used with assurance in a ThO_2 reactor system. This conclusion holds for 300 gm/kg slurries as well as for more concentrated mixtures.

Premises

ThO_2 slurries are usually lyophobic suspensions, that is, the mechanical condition of least energy occurs when the particles are clustered as closely together as possible.

The force which tends to draw the particles together is the London force⁽¹⁾ (van der Waal attractive force) which varies as the minus seventh power of distance in the case of very small particles, e.g., ions or molecules, which are close enough to permit neglecting the relativistic effects*.

*The finite velocity of electromagnetic radiation causes mismatching in the molecular dipoles and weakens the London force to the point of extinction at distances greater than about $100 \text{ \AA}$.⁽²⁾ At still greater distances, dipole phase mismatching may even cause a very mild repulsion.

4

Flocculation

It can be shown analytically that the London force causes the attraction between a sphere and an infinite slab (a large particle) to vary inversely with the square of the distance between them, and directly with the first power of the diameter of the sphere, when the gap between them is small compared to the diameter of the sphere.

It follows directly that because of the rapid reduction of force with distance, two particles will be held together in approximately the attitudes with which they happen to approach each other. This leads to loose flocs which may collapse slowly under the force of gravity or their own centripetal attraction.

Because of the seventh power reduction of force with distance between individual atoms or molecules, the nearest molecules of each particle control the force between the particles. Since an attractive force also exists between molecules of the liquid and the solid surface, the net energy of attraction between two particles is the total energy of attraction minus the energy required to displace the intervening liquid from the solid surfaces.

The Effect of Particle Size

The force between one particle and another increases roughly as the first power of the diameter of the particle. In a flowing stream the hydrodynamic forces will vary roughly as the cube of the particle diameter, since the area on which the fluid acts is proportional to the square of the particle diameter, and the effective velocity acting on the particle in a shearing liquid will vary, on the average, as the first power of particle diameter. The increase in moment arm of the hydrodynamic force is offset by the increase in moment arm of the attractive force. Thus, in a flowing stream, the ability of a particle to cling to another, or to a pipe wall, will be roughly proportional to the inverse square of the particle diameter. Initially ThO_2 , as now made,

5

occurs as particles averaging about one or two microns in size. The particles are skeletons composed of crystallites, which, for the 800°C fired oxide, are about 200-250 Å in diameter. The particles probably have a porosity of about 60%, judging from the settled bed density.

Because of their large size, the original particles initially do not tend to flocculate, but behave instead like fine silt and settle to a density of about 1500 to 2000 gm/kg. If they are broken down however, so that smaller fragments are formed, the colloidal, lyophobic nature of the ThO₂ can take effect and the material becomes flocculated, with a settled bed density of 300-500 gm/kg at room temperature. At higher concentrations the slurry then consists in effect of one large floc.

There is no evidence to date that the crystals of ThO₂ are broken up by circulation, and there is evidence accumulated over several years that firing ThO₂ at higher temperatures and hence enlarging the crystals produces slurries which do not form as strong flocs. It was this fact which led to raising the firing temperature for ThO₂ manufacture from 650°C to 800°C, the practical limit of the available large scale firing facility. The London-van der Waal attraction and its limit, the electron sharing chemical bond, are undoubtedly affected by the adjustment which the surface atoms have made in the ThO₂ crystal. Threshold energy to make adjustments may be supplied by heating the particle to an elevated temperature. Thus, in addition to ThO₂ crystal growth in the vestigial oxalate skeletons, heating to higher temperatures may modify the specific surface activity of the crystal.

Effect of Silicate, Oxalate and other Ions

It is proposed that the effect of oxalic acid or sodium silicate on ThO₂ in a slurry is to form a surface coating of groups or ions which causes water to be attracted preferentially and converts the lyophobic suspension to a

6

lyophilic suspension. If this concept is correct, it parallels the action of a detergent on droplets of oil or on many solid surfaces. It may be, however, that in contrast to the detergent, the oxalate or silicate is bonded more energetically to the ThO_2 , which would increase the durability of the association.

It is proposed that sulfate and many other ions, while they may be attached more or less energetically to the ThO_2 , produce changes in suspension behavior by either altering the net attractive force between particles or by forming a charge barrier (double layer, zeta potential) between the particles, or both.

The double layer-zeta potential theory is the most widely held theory of the stability of lyophobic colloids⁽²⁾⁽³⁾⁽⁴⁾, but the behavior of silicated or oxalated ThO_2 appears to the writer to resemble much more closely a completely lyophilic suspension.

If one accepts the foregoing discussion, it would be expected that the slurry properties would vary with changes in temperature, particularly where the ions are not bonded strongly to the surface. Such variations are usually found both in high pressure settling tests and in high temperature viscosity measurements. That little consistency is found in data obtained with different slurries, merely emphasizes our ignorance of the effect of past history and current environment on the surface behavior of the particles.

The yield strength of a slurry may increase with increase in temperature, for example, due to a replacement of one type of ions by another of opposite sign. This would result in a reduction in zeta potential and a strengthening of the flocs. As the temperature continues to rise however, the zeta potential would begin to build up with the opposite sign and the suspension would become more stable and the yield strength would be reduced. An initial upward trend of yield strength with temperature followed by a reversal has been observed in several ThO_2 slurries.

7

A Proposed Mechanism for Floc Densification by Hydrodynamic Forces--Formation of Muds, Cakes and Spheres

Since a floc in a shearing liquid will be subjected to shearing forces, there is a tendency to break the attachments between particles. If, however, the floc is dense so that particles in a group reinforce each other's attachment, more shearing stress is required to break up the group. Occasionally, also, the shear stress on the floc will merely supply the energy required to cause the particles to roll over one another in the floc until the particles drop into positions which are strongly enough reinforced to resist further movement.

It is proposed that this mechanism of continuously breaking up the weaker attachments so that stronger ones can form is the basic cause of cake and mud formation on the component surfaces of a slurry loop, and that this mechanism also causes spheres which develop in some circulating systems.

In mixing barrels, and other stirred containers, a thick mud sometimes occurs around the sides. The mud is of higher density than the bulk of the slurry, and according to the proposed theory it occurs, not as is often suggested, by centrifugal action, but because of the continuous brushing of particles near the wall into positions which are firm enough to resist further action.

In loops, muds are frequently formed in the pressurizer slightly above the inlet. Here the liquid is agitated by the entering stream, but the agitation is not violent enough to break up the mud. Similar muds were also found with the platelet form of $\text{UO}_3 \cdot \text{H}_2\text{O}$ where the flat platelet surfaces permitted good attachment between particles.

In the loop proper the action is usually too violent to allow a mud to survive, but when the net attraction between the particle surfaces is

particularly high, the particles can accumulate in a very dense cake*. The first major example of this was run 200A-3**. Here, because the velocity was only 10 ft. per sec., the shear stress was not high enough to strip off a dense cake which accumulated along the pipe walls. The density and strength of a cake are a measure of the shear stress at the wall, the net attraction between particle surfaces, the degree which particles have been reduced in size and the shape of the particles. Cakes have also been found in pump impellers and in corrosion sample holders where, due to flow separation or reduction, a shear existed which was strong enough to produce cake but not strong enough to strip it off.

Sphere Formation

During the past year certain slurries have formed ThO_2 spheres, which are usually all of about the same size in a given run, but which vary from run to run between about 5μ and 100μ . Refractive index measurements indicate that the spheres are slightly less dense at the center than at the outside, but the average density has been measured by two independent groups as greater than 8.

The spheres under the microscope appear to be transparent, indicating that the particles of which they are composed are small compared with the wavelength of visible light. In spite of their high density, the spheres are easily broken, and they do not appear to increase the corrosion or abrasion of stainless steel in a pump loop or toroid.

*In this discussion, a "cake" is distinguished from a "mud" by being a material which breaks rather than flows when subjected to a stress which is sufficient to cause permanent deformation.

**A more complete discussion of this run in a 200-gpm high pressure loop is discussed in reference 5.

It is proposed that the spheres are formed by a process of compaction and accretion in the turbulent stream.

Initially, when the agglomeration has a small diameter, the compaction does not need to be as dense but as particle fragments are attached to the surface the required degree of mutual reenforcement becomes higher until a size is reached beyond which particles cannot be added permanently.

If the circulating conditions are changed, for example, by transferring the slurry to another loop, the stable size of the spheres may be changed and the spheres may grow or shrink to the new equilibrium diameter.

It is proposed that the hard shiny cake with a thickness of several hundredths of an inch, and often found on such surfaces as the upstream side of orifice plates, is formed by the caking of particles similar to those which form spheres.

It appears that the particles in spheres, as well as in the cakes and muds, are held largely by London forces. The ease with which the spheres can be broken in spite of the low void fraction is to be compared with the resistance to breakdown exhibited by the original less dense skeleton structure of the oxide. If bridging or chemical bonding, in the sense of electron sharing, occurs between particles in muds, cakes or spheres it must be limited to the relatively few atoms which approach within a few Angstrom units of each other. The very high melting point (over 3200°C) and low solubility of ThO_2 also imply very little bridging is possible between particles in a flocculated slurry.

Professor Milligan of Rice expressed the opinion, in an informal discussion⁽⁶⁾, that in a crystalline material such as ThO_2 , electron sharing is limited to atoms within each crystal and essentially no sharing occurs between crystals, even in the original calcined material. The strength of the original particles is due to the unusual degree of contiguity between crystals which

permits van der Waal forces to be more effective. In any case, it is difficult to visualize a rearrangement of atoms in adjacent crystals to justify themselves enough for fully developed electron sharing to any appreciable extent at 300°C.

Discussion

If the foregoing theory is valid, it follows that consistent physical properties and freedom from caking can only be assured in a colloiddally stable slurry or in a slurry, the particles of which remain large enough to be essentially unaffected by London-van der Waal forces. Sphere formation, mud formation or development of an appreciable yield strength at concentrations below 2000 gm Th/kg H₂O (or in many cases, higher concentration) will always imply the possibility of cake formation.

Stable slurries, on the other hand, will settle to a very dense bed which will be redispersed slowly, but without difficulty, since no strong forces other than gravity are holding the particles; while the bed itself will be more or less dilatant and not very susceptible to rapid gross deformation. The slowness with which colloiddally stable beds redisperse should not be confused with the difficulty of redispersing colloiddally unstable cakes.

ThO₂ crystals appear to be remarkably resistant to comminution under pumping conditions, although only limited experience has been obtained at where the crystals approach 0.1μ in size (~1600°C calcination temperature). Thus, it appears that high firing of oxalate or oxide made from oxalate may be one way of controlling the ultimate particle size and therefore, the colloidal behavior of ThO₂ Slurries.

Recently ThO₂ spheres formed in a 100-gpm loop from batch LO-14 have been fired at various temperatures up to 1600°C. In subsequent toroid tests

11

the attack rate on stainless steel was not increased by firing. These spheres averaged 15-20 μ and a very tentative conclusion can be drawn that either the spherical shape reduces attack on stainless steel by large ThO₂ particles in a slurry, or that the spheres retain enough softness to minimize the attack rate. (It is believed that original calcined oxalate particles above about 3 or 4 μ are responsible for the initial high attack on stainless steel by freshly prepared slurry).

If the apparent results with calcined spheres are confirmed it would appear that a spherical shape may be extremely beneficial and the efforts of Houdry to obtain small spherical particles should be increased or augmented.

In an investigation by D. G. Thomas⁽⁷⁾, two runs in 100A loops at 300°C for 107 hours and 600 hours with sodium silicate in ThO₂ have shown remarkable promise for a permanently stable oxide slurry. During the runs the concentration was more constant than in ordinary loop runs, and the attack rates were low. After a three-day shutdown, the full circulating concentration was regained shortly after restarting the loop. All samples taken were slowly settling Newtonian suspensions.

It appears unwise to put complete confidence in silicated slurry at the present time because it is not known how irreversibly the silicate is attached. The success achieved to date, however, indicates that silicate should be considered very seriously as the means for obtaining a lyophilic system, and hence, one which will not cake or flocculate.

Silicate might also be considered as a supplement to calcined sphere or large crystal slurries in order to stabilize the suspension of any small fragments which may be formed by partial breakdown of the particles.

Fragmentary settling rate data have been obtained, on the other hand, which seem to show that the beneficial effect of silicate may be lost at elevated temperature.⁽⁸⁾

Conclusions

Based on the foregoing discussion:

1. The only reliable slurries for reactor operation are colloiddally stable (i.e., lyophilic) slurries, or slurries where the particle size remains large enough to minimize the influence of surface forces.
2. Slurries with crystallite size above 0.1μ (oxalate fired above 1600°C) may meet the requirements of 1. Possible a larger crystallite size will be required.
3. High fired spherical particles up to 15 or 20μ may meet the requirements of 1 without producing excessive abrasion.
4. Silicate and other additives should be studied to determine whether conditions can be found to give a permanently stable (lyophilic) suspension.
5. Blanket components should be developed to resuspend colloiddally stable particles and to avoid plugging by sediments rather than developed to handle non-Newtonian suspensions of ambiguous properties.
6. Testing of stable or large particle or crystallite slurries should be pushed, even to the point of excluding non-Newtonian or sphere forming slurries.
7. Basic studies on the surface properties of ThO_2 are needed. Capillary size measurements, crystallite size, the size density and strength of aggregates and flocs, the adsorption energy of ions and groups as a function of temperature, the influence of ions on the zeta potential, and on the floc bond strength-- these data, because of their more basic nature, can provide insight into the varied behaviors of ThO_2 slurries in loops. They can show how a stable slurry can be made and how it can be kept stable, and they can show what direction to take in developing methods for redispersing a cake which may form because of failure to keep the slurry stable. In short, such studies can provide the only sure light by which we can find our way to a satisfactory blanket slurry and system.

13

REFERENCES

1. F. London, Z. Physik, 63, 245 (1930).
2. Verway and Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier Pub. Co., New York (1948).
3. Kruyt, "Colloid Science" Elsevier Pub. Co. (1949).
4. "A General Discussion on Coagulation and Flocculation", Part 1, pp. 9-228, Faraday Society, Aberdeen, Great Britain (1955).
5. ORNL CF 55-12-32
6. ORNL CF 57-4-54 (to be published)
7. ORNL CF 56-11-2; also memoranda from D. G. Thomas to R. B. Korsmeyer dated January 3, 8, 14 and 22, 1957.
8. HRP Quarterly Report for Period ending January 31, 1957, ORNL-2272, p.149.