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RELATIONSHIP BETWEEN CALCINING TEMPERATURE AND PARTICLE DENSITY OF THORIA SLURRIES

D. M. Eissenberg

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D. M. Eissenberg

ABSTRACT

The variation in rheological behavior and other physical properties of thoria slurries with the calcining temperature of the thoria powder is explained on the basis of the relation between the calcining temperature and the bulk density of the individual thoria particles.

Indirect experimental measurements of the bulk particle density by viscosimetry and by measurement of centrifuged-bed densities agreed with each other and fell within the predicted density limits of 3.7 g/cc and 9.7 g/cc (for oxalate-precipitated thoria). Nitrogen adsorption porosimetry of one sample was consistent with the bulk-density measurement.

INTRODUCTION

The utilization of a thoria slurry as the fertile material in a breeder nuclear reactor requires that the concentration of the thoria be sufficiently high to minimize neutron losses due to escape or nonproductive absorption (in the container material, water, or corrosion and fission products). A thorium weight concentration of 1000 g/liter has been proposed[1] to optimize the neutron utilization for a reactor in which the thoria suspension is placed in a blanket region concentric with the neutron-generating core.

In order to minimize the problems of pump wear, pipe erosion, and particle dropout, and to produce particles capable of withstanding circulation in a high-temperature radioactive loop, the major effort in the development of thoria slurries has been devoted to producing particles in the 0.5- to 5-μ mean-particle-size range. In this range, thoria slurry

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[1] J. F. Hogerton and R. C. Grass (eds.), Reactor Handbook – Engineering, p 669, McGraw-Hill, New York, 1955.

flocculates (agglomerates) in most reactor environments due to the essentially hydrophobic nature of the thoria surface. The resulting flocculated suspension is non-Newtonian, possessing a shear-dependent viscosity and a large sediment volume.

Variation in Properties Due to Calcining Temperatures

It has been recognized that such properties as the viscosity, dropout velocity, settling rate, and sediment volume varied with the maximum temperature at which the powder was calcined during manufacture. These effects were in addition to variations in properties due to particle size and shape and slurry concentration. No explanation had been given for this variation except to assign to the material fired at lower temperatures the designation "more flocculated," since the yield stress, coefficient of rigidity,[2] and the sediment volume were higher and the settling rate was lower[3] for the lower-temperature-fired material. It is proposed in this paper to assign the effect on the slurry properties of the final calcining temperature to the variation in the effective bulk density of the slurry particle with firing temperature.

Predicted Bulk Density of the Particles

The ORNL production of thoria suitable for reactor use has generally been restricted to a method involving the homogeneous precipitation of thorium oxalate crystals of controlled particle size. These crystals are then calcined in air at the desired temperature. It is possible to predict on this basis a bulk particle density of the thoria, assuming that the calcining process does not alter the size or shape of the particle.

The crystal density of thorium oxalate is 4.64 g/cc.[4] Assuming that all the oxalate is calcined to oxide, the final dry particle density will be the density of thorium oxalate multiplied by the ratio of the molecular weight of ThO_2 to that of $Th(C_2O_4)_2$, or 3.00 g/cc. (With the void spaces filled with water, the bulk particle density would be 3.71 g/cc.) This represents the particle density if no shrinkage occurs during calcining, and represents therefore the lower limit of particle density as a function of firing temperature. As an upper limit, the thoria particle density will approach the crystal density of thoria, which is 9.69 g/cc.[4]

METHODS USED FOR THE MEASUREMENT OF THE BULK DENSITY OF THE PARTICLES

Two indirect, independent methods were used in this study to measure the relative bulk density of the particles: viscosity measurement and sediment-

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[2] J. P. McBride et al., HRP Quart. Progr. Rept. July 31, 1958, ORNL-2561, p 287.

[3] Ibid., p 286.

[4] N. A. Lange (ed.), Lange's Handbook of Chemistry, 7th ed., p 287, Handbook Publishers, Sandusky, Ohio, 1949.

volume measurement. Both methods include an effect of the particle shape, which limits their precision as a means of determining the absolute porosity of the particles. Both methods are indirect in that they measure properties which are related to the volume fraction of solids in the water matrix at an assumed constant shape factor, rather than measuring density directly.

Viscometry

The specific viscosity of a nonflocculated suspension of rigid, spherical, uniform-sized particles has been found by many investigators theoretically and experimentally to be a function of the volume concentration of solids only, and independent of size or density of the particles. The explicit relationship between specific viscosity and volume concentration for nonspherical, nonuniformly sized, rigid particles must be determined experimentally. However, the specific viscosity will theoretically be independent of particle bulk density. Thus, for suspensions of particles of about the same size, shape, and size distribution, a comparison of the viscosity-concentration curves will yield the desired relative bulk density. Since the thoria suspensions of interest are normally flocculated, it was necessary to add small quantities of dispersing agent in order to obtain the nonflocculated (Newtonian) viscosities. In this work, sodium pyrophosphate was used. In one instance, however, nitric acid was used in order to verify that the results were in fact independent of the nature of the dispersant.

Viscosity Equipment

The viscosity measurements were carried out in an 18-mil-ID vertical capillary-tube viscometer, 18 in. long. Measurements were made with flow upward through the tube. A stirred autoclave acted as the lower reservoir, and a volume-calibrated glass cylinder acted as the upper reservoir and flow-measuring device. Compressed air provided the driving force, and pressure was read with a mercury manometer. The viscometer was calibrated with water, and the calibration was checked against other viscometer tubes with a 50% glycerol–50% water solution. The tube and lower reservoir were temperature regulated. For two of the slurry runs, the temperature controller may have been in error by as much as 2°C. For the other two runs, however, the temperature was regulated to ±0.1°C.

Volume Fraction of Solids in Settled Beds

The volume fraction of solids in a settled bed is defined as the gross volume fraction occupied by a unit volume of solids after they have been permitted to settle from a more dilute state. For equal-sized spheres,[5] the experimental volume fraction solids is 0.60. For granular material,[6]

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[5] G. Herdan, Small Particle Statistics, 2d ed., p 183, Academic Press, New York, 1960.

[6] G. G. Brown et al., Unit Operations, p 214, Wiley, New York, 1950.

it is a function of the shape of the particles (sphericity) and the size distribution. Thus, for particles of the same size distribution and shape, a comparison of the settled-bed concentrations (weight bases) will yield the desired relative bulk particle densities. Since the suspensions are normally flocculated, either a dispersant should be added or the sedimenting should take place under a gravitational (centrifugal) force sufficiently high so that the attractive forces which tend to form a loose structure are overcome. Previous investigation[7] indicates that both methods yield essentially the same values for settled-bed concentration. Because centrifuging is more rapid, it was used in this study.

Centrifuge Equipment

An International Clinical Centrifuge was used, with a calibrated tapered centrifuge cup of 15-ml volume. The weighed samples were centrifuged for 15 min. The initial concentration was sufficiently high so that the final bed height was above the conical portion of the centrifuge tube. It was found that with this procedure the final concentration of the settled bed was not dependent on the final bed height.

EXPERIMENTAL RESULTS

Thoria Preparations Tested

Two thoria slurries were investigated. One, DT-4, had been fired at 650°C; the second, DT-12,13, had been fired at 1600°C. Otherwise, the preparation methods were the same.[8] Some of the properties of these preparations were included in Table 1. Electron photomicrographs of the two preparations (Figs. 1 and 2) show similar structures; that is to say, essentially the particles are relic structures of the original thorium oxalate crystal. The DT-12,13 sample shown in Fig. 2 had been pumped for several thousand hours before being photographed, whereas the DT-4 sample shown in Fig. 1 was unpumped.

As noted in Table 1, a large reduction in the internal surface area occurs with high firing, accompanied by an increase in crystallite size. It is the volume associated with this surface area that would be responsible for lower bulk particle density in the 650°C-fired thoria.

Effect of Pumping on Thoria Properties

Both preparations were pumped in a high-temperature stainless steel loop. The pump in both instances was a 200-gpm canned-motor type. Since the total loop volume was about 20 gal, the slurry made a trip through the

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[7] D. M. Eissenberg, Concentration of Settled Beds of Thoria Slurry, ORNL-3107, p 11, (Apr. 18, 1961).

[8] K. O. Johnsson and R. H. Winget, Pilot Plant Preparation of Thorium and Thorium-Uranium Oxides, ORNL-2853 (Dec. 8, 1959).

Table 1. Properties of Thoria Particles

	Logarithmic Mean Particle Size μ	Logarthmic Standard Deviation[a]	Surface Area (BET Method) (m^2/g)	Crystallite Size (X-Ray Line-Broadening Method) (A)
DT-4, unpumped	1.3	1.7	31	108
DT-4, pumped	0.85	2.3	39	120
DT-12,13, unpumped	1.6	1.4	1.0	>2500
DT-12,13, pumped	1.4	1.5	1.0	>2500

[a]Defined (for a log-normal cumulative distribution curve) as the ratio of the diameter which is larger than 85 wt % of all particles to the logarithmic mean particle diameter. Thus it is a statistical measure of the size distribution.

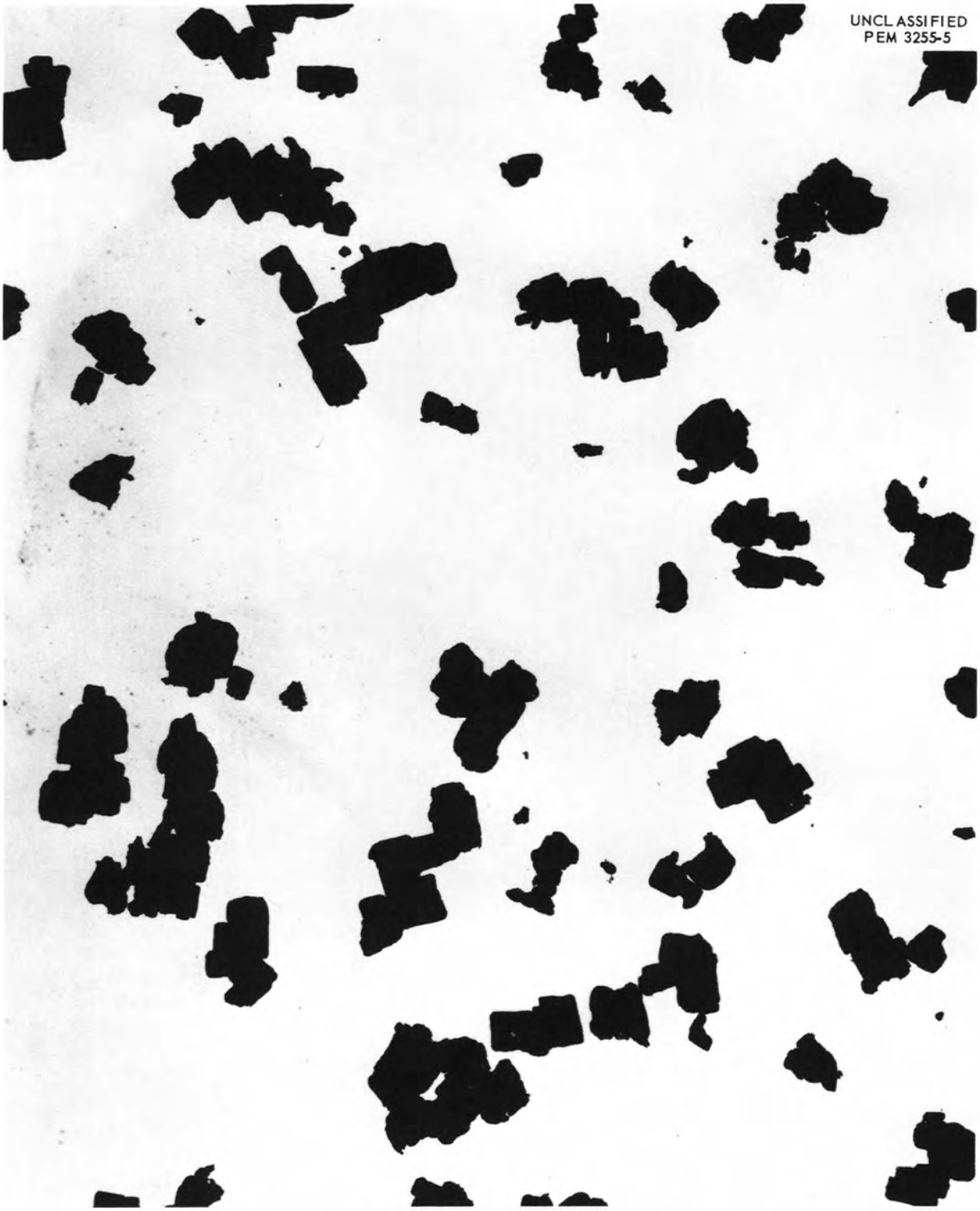

Fig. 1. DT-4 Thoria, Unpumped.

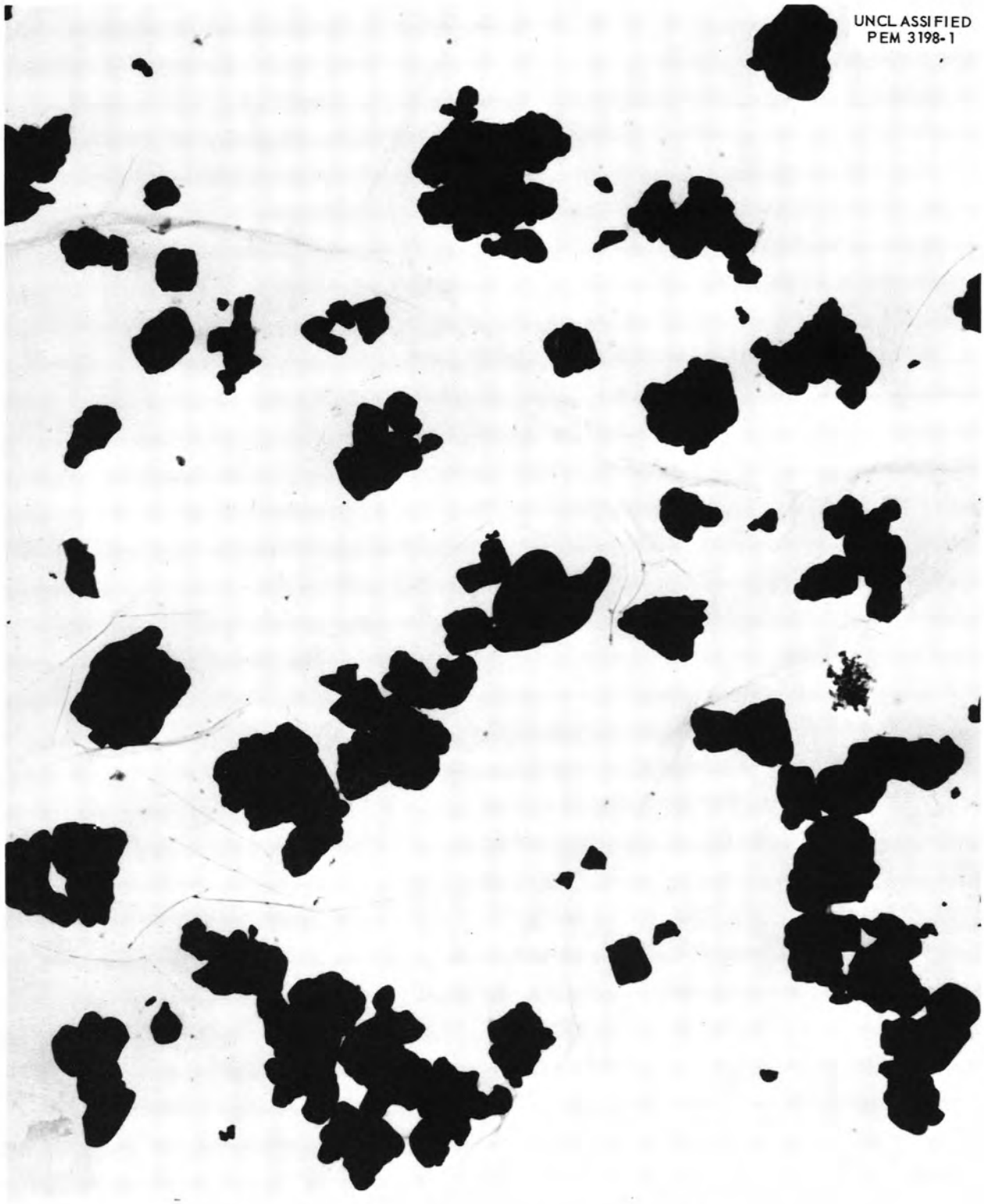

Fig. 2. DT-12, 13 Thoria, Pumped.

loop every 6 sec. The DT-4 slurry had been pumped for approximately 1000 hr, while the DT-12,13 had been pumped over 3000 hr.

The principal result of pumping the thoria slurries is to decrease the mean particle size. The surface area and crystallite size remain practically unchanged. An electron photomicrograph shows the size reduction (Fig. 3) for the low-fired preparation. Some rounding of the particles seems to have occurred also.

Viscometry Data

The relative-concentration curves for both sluries were obtained for samples before and after high-temperature pumping (Figs. 4 and 5). Four different curves were obtained. Under the assumption that the size distributions for the four samples are the same (see Table 1), the following relationship is valid:

$$\frac{C_1}{\rho_1} = \frac{C_2}{\rho_2} = \frac{C_3}{\rho_3} = \frac{C_4}{\rho_4} \qquad (1)$$

where ρ is the particle bulk density, and C, the weight concentration, is evaluated at the same relative viscosity for all four samples.

The further assumptions are made that the bulk density of DT-12,13 pumped particles is equal to the crystal density of 9.69 g/cc. This is probably a high value since there are surface irregularities which would tend to decrease the bulk density below the solids density. Since the surface irregularities of all the slurries are believed to be about the same, they will be compared solely on the basis of internal pore volume.

A comparison of the concentrations of each slurry obtained at a relative viscosity of 2 is shown in Table 2. The bulk densities calculated from Eq. (1) are also given.

Settled-Bed Data

Included in Table 2 are the settled-bed concentrations for three of the four slurries. The assumption is made again that the DT-12,13 pumped particles have the crystal density of thoria. This, coupled with the assumption that the volume fraction solids in all the centrifuged beds are equal, yields the bulk particle densities shown in Table 2.

DISCUSSION OF RESULTS

The bulk density of unpumped DT-4 is found to be around 4 g/cc. Since the theoretical minimum bulk density for thoria is 3.7 g/cc, this is a reasonable value, especially in view of the large internal surface area and low calcining temperature.

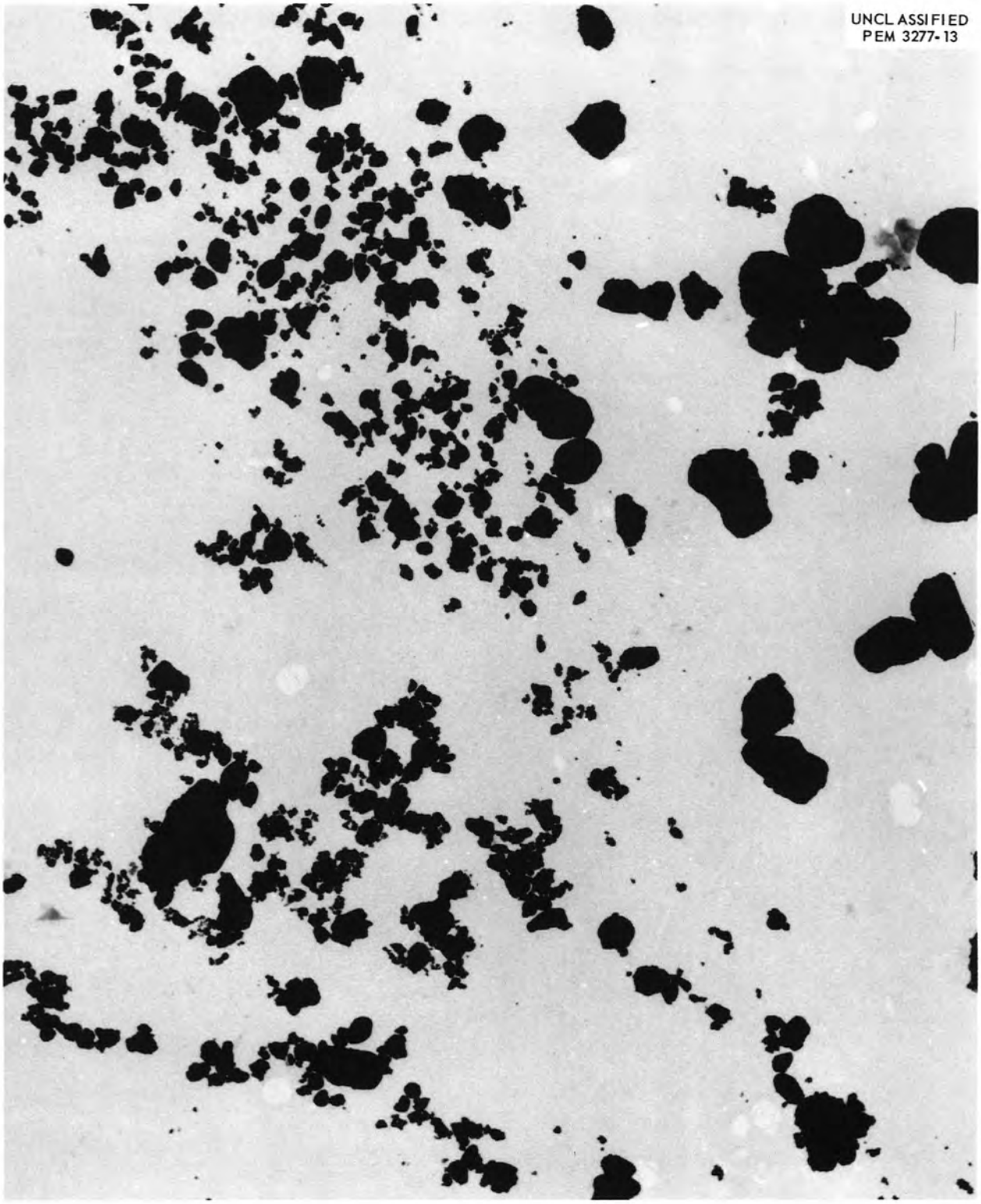

Fig. 3. DT-4 Thoria, Pumped.

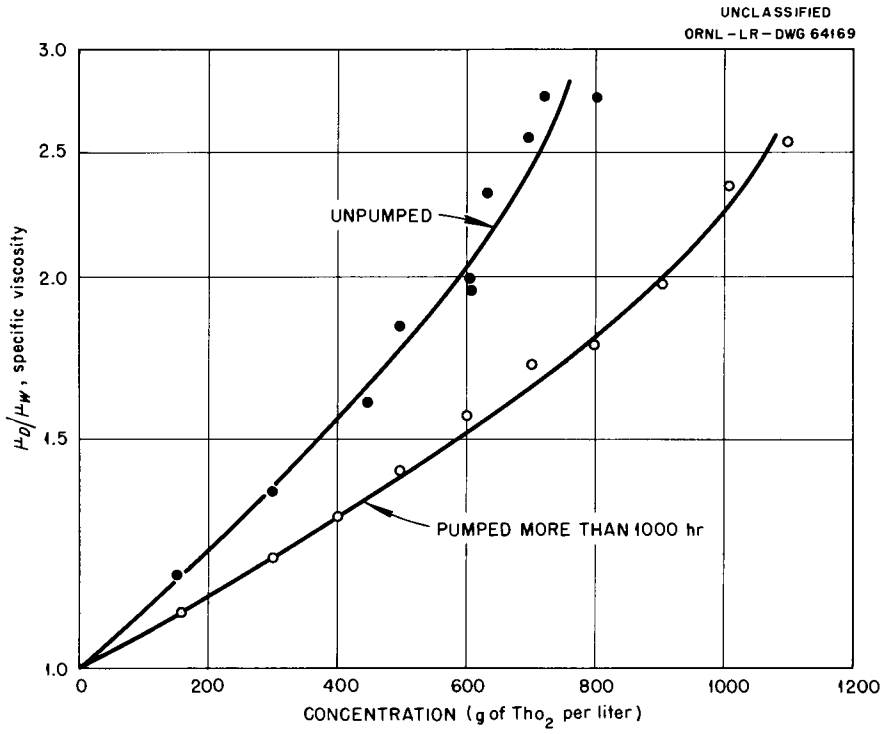

Fig. 4. Concentration Dependence of Specific Viscosity for 650°C-Calcined Thoria.

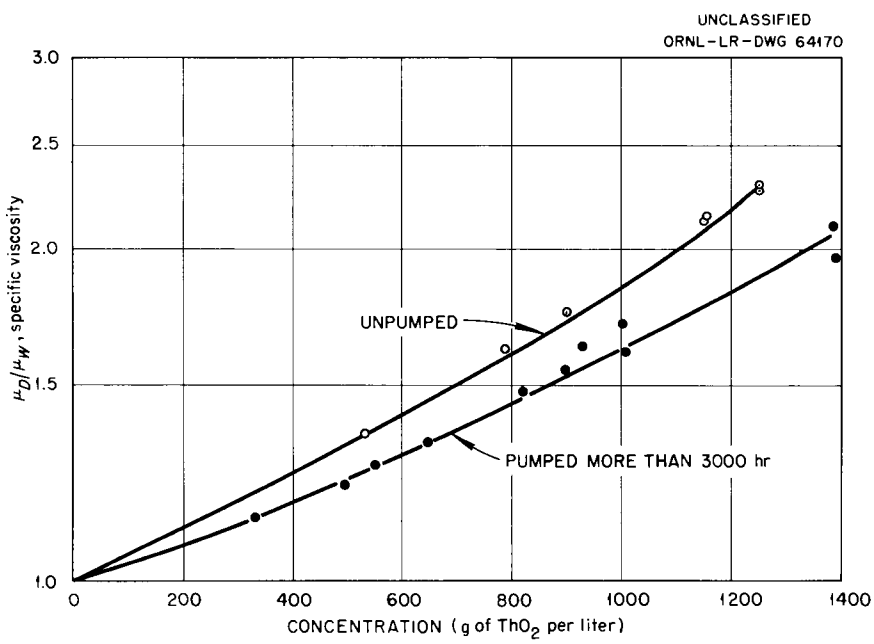

Fig. 5. Concentration Dependence of Specific Viscosity for 1600°C-Calcined Thoria.

Table 2. Comparison of Calculated Bulk Particle Densities

Preparation	Concentration at Viscosity Twice That of Water (g of solid/total cc)	Particle Density (g/cc of solid)	Concentration of Centrifuged Bed (g of solid/cc of solid)	Particle Density (g/cc of solid)
DT-4, unpumped	580	4.2	1772	4.0
DT-4, pumped	900	6.6	2772	6.3
DT-12,13, unpumped	1110	8.1		
DT-12,13, pumped	1330	9.7[a]	4270	9.7[a]

[a]Assumed to be the density of thoria crystals.

The effect of pumping, as noted previously, is to break up the particles (Fig. 3). If one of the causes of the breakup of these particles is the presence of large void spaces within the particle, then the resulting fragments will have a higher bulk particle density. In addition, there is probably some rounding of the corners of the particles during pumping, which also would tend to increase the apparent bulk density.

The smaller fractional increase in bulk density with pumping of the higher-fired slurry is probably due to the absence of internal void volume (as measured by the nitrogen-surface-area method and the more effective sintering of adjacent crystallites. The increase in apparent bulk density can be attributed to rounding of the particles.

The agreement between the viscometry results and the sedimentation results is considered very good since the influence of particle shape will be different for the two methods.

CONCLUSIONS

The effect of the calcining temperature of thoria on its slurry properties is inferred to be due to its influence on the bulk particle density. It seems likely that the differences noted in the rheological behavior of the flocculated thoria, drop-out behavior, settling rates, and flocculated sediment volume are all due to this factor.

Pumping was found to increase the effective bulk density as a result of particle fracture and rounding.

In order to correctly evaluate the physical properties of slurries and their variations with other factors (particle size, electrolyte environment, shape), measurements should be made by one or both of the two methods used here to estimate the bulk density of the particles.

ACKNOWLEDGMENTS

The electron photomicrographs were prepared under the direction of T. E. Willmarth.

The nitrogen-adsorption pore-volume analysis was conducted by P. G. Dake and E. A. Woy. The samples were prepared and the viscometer was operated by C. A. Gifford and H. G. Moore.

APPENDIX

Subsequent to the experimental work described in this report, a sample of DT-4 unpumped slurry was submitted for pore-volume measurement based on computations from nitrogen-adsorption isotherms.[9] The resulting value for summation of pore volume (pores up to 360-A radius) was 0.044 cc/g. This value can be compared with a calculated pore volume of 0.177 cc/g, based on a wet bulk density of 4.2 g/cc. The difference is likely due to large pores (greater than 360 A). This is partially confirmed by noting that the pumped DT-4 slurry has a calculated pore volume of 0.057 cc/g, based on a wet bulk density of 6.6 g/cc. As stated in the "Discussion of Results," one effect of pumping is to break the particle along existing (larger) pores. Thus the pore-volume value of the material should approach the nitrogen-adsorption pore volume as the larger pores disappear due to particle fracturing during pumping.

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[9] E. P. Barrett, L. G. Joyner, and P. P. Halenda, J. Am. Chem. Soc. 73, 373 (1951).

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