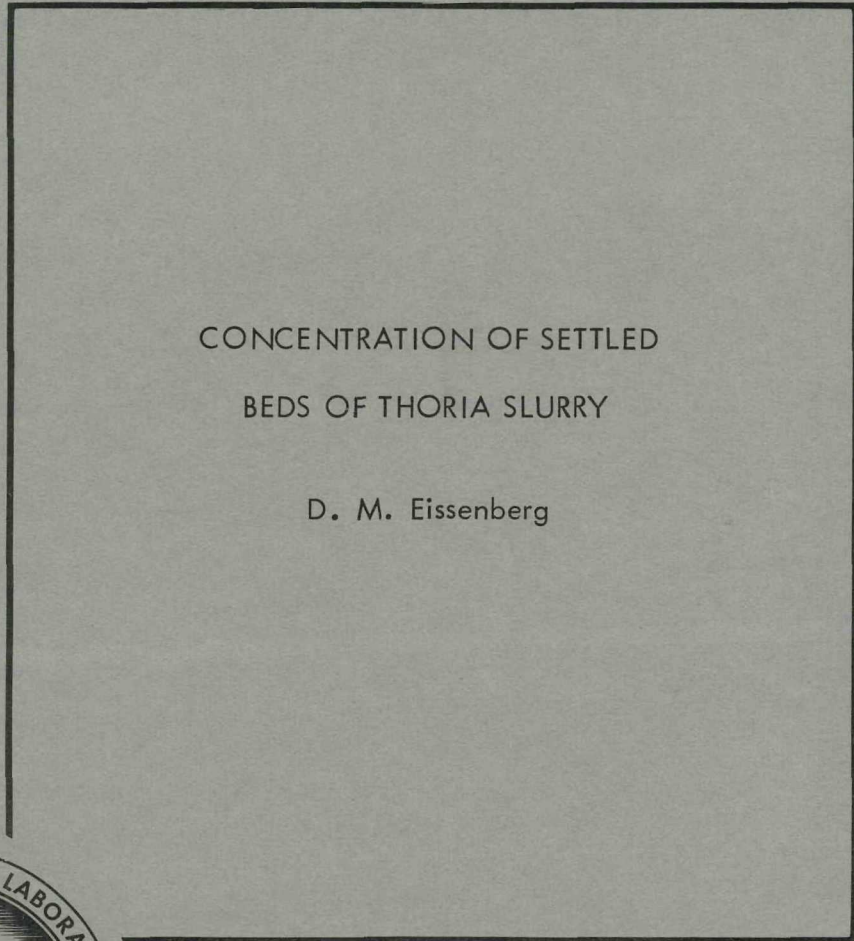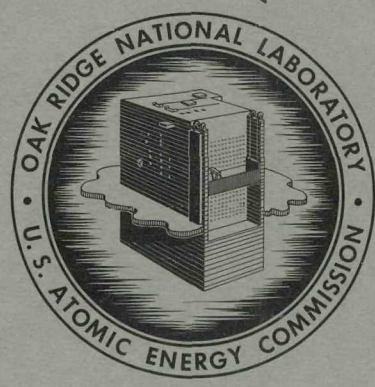P 325

CONCENTRATION OF SETTLED

BEDS OF THORIA SLURRY

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operated by
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for the
U.S. ATOMIC ENERGY COMMISSION

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D. M. Eissenberg

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CONTENTS

CONCENTRATION OF SETTLED BEDS OF THORIA SLURRY

D. M. Eissenberg

ABSTRACT

The variation in concentration of settled beds of flocculated aqucous suspensions of thoria was studied experimentally as a function of the calcination temperature and particle size of the thoria, the temperature and initial concentration of the suspension, and the concentration of added chromic acid. Values of the ultimate settled-bed concentration were obtained by several methods. Dilatant-plastic behavior of one suspension was considered responsible for the formation, in long vertical tubes, of intractable plugs.

INTRODUCTION

The use of an aqueous thoria suspension as the fertile material in a breeder reactor requires detailed knowledge of the behavior of the suspension in all possible operating conditions. At the present time, it is most likely that a suspension blanket will be made up of granular thoria particles approximately 1 μ in diameter, irregular in shape, and with electrically charged surfaces. Under reactor conditions, it is most probable[1] that the suspension will be flocculated (aggregated); that is, the particles will tend to cling together in loose flocs. The extent of this tendency toward flocculation at operating conditions will determine the design characteristics of the circulating system. For example, the resistance to flow, the ability to plug pipes, the ease of resuspension, and the dropout behavior are all functions of the extent to which the suspension is flocculated.

At the same time, there are a number of additional physical phenomena which are determined by the flocculation behavior and which could be used as a measure of the degree of flocculation. This report deals with one such physical phenomenon--settled-bed concentration (volume fraction solids) and its relationship to flocculation behavior.

The settled-bed concentration is defined as the equilibrium concentration of a suspension which has been permitted to settle under gravity isothermally and in the absence of any external disturbances. It has been used as a measure of the degree of flocculation of flocculated suspensions[2,3] because it represents an equilibrium between the force of gravity tending to compress the sediment and the interparticle forces tending to maintain the loose floc structure.

This report presents a mechanism of settled-bed structure and then treats experiments (primarily speculative and preliminary) which were performed in an attempt to find broad generalizations regarding variations in settled-bed concentration. Variations in the settled-bed concentration with firing temperature and particle size of the thoria and with temperature of settling and initial concentration of the suspension were studied for various thoria suspensions of interest to the

1

Thorium Breeder Program. It was intended that the generalizations derived from the study should serve as a guide to more thorough work if any specific result warranted it. Since these were screening experiments, the ground covered in this report is nowhere complete.

THEORY

Relation Between Settled-Bed Concentration of Flocculated and Nonflocculated Suspensions

A knowledge of the settled-bed concentration provides one of the easiest ways of deciding qualitatively whether a suspension is or is not flocculated, since the concentration (expressed as a volume fraction solids) can be compared with the volume fraction solids expected for randomly packed nonflocculated particles of similar shape. For example, for normal granular or crystalline particles randomly packed, the volume fraction of nonflocculated solids will be between 0.55 and 0.68(ref 4); and for spheres randomly packed, the volume fraction solids will be 0.60(ref 5). Typical flocculated thoria suspensions have settled-bed concentrations of 1000 to 2000 g of ThO_2 per liter. If the particle bulk density is assumed to be 6,000 to 10,000 g of ThO_2 per liter, then the volume fraction solids is of the order of 0.1 to 0.3.

The factor of 2 to 6 reduction in the settled-bed concentration observed for flocculated thoria suspensions, as compared with expected values for packed beds, is explained on the basis of interparticle forces. The forces arise from van der Waals - London interatomic attractive force[6] as modified by the influence of the surface electrical double layer. The attractive force serves to bind the particles into a structure or network. When this structure can support itself by transmitting force down through the bed to the vessel bottom or to the vessel walls, a settled bed will form which has a lower volume fraction solids than expected for randomly packed particles.

Attraction and Repulsion Forces Acting Between Particles

The attractive force acting between particles is due to the summation of all the separate interatomic van der Waals' forces of the atoms in each particle. Thus it is dependent principally on two variables, the distance of separation and the particle shape. The shape (actually, the radius of curvature at the point of closest approach) determines the rate of decay of the attractive force with distance: for parallel plates (infinite radius) the force follows a d^{-1} decay; for single atoms it follows a d^{-7} decay. The magnitude of the van der Waals' force can be calculated from thermodynamic data.

The influence of the electrical surface charge is to provide an electrostatic-force barrier which may prevent two particles from coming into contact due to the van der Waals' force. The surface charge is dependent on the ions on the surface, whether physically adsorbed or associated by chemical bond.

The distance from the particle surface up to which the surface charge provides an effective barrier depends on how the induced electrostatic force decays with distance. This is determined by a layer of ions of charge opposite the surface charge (counter-ions), which acts to discharge the particles. Such factors as temperature, dielectric constant, counter-ion valence, and counter-ion concentration affect the ion layer (double layer) thickness (distance in which the surface-induced potential will decay by a factor of e). If the surface-charge-induced repulsive force between a pair of particles is sufficiently greater than the van der Waals attractive force at large separation distances, then the particles

will normally remain apart, and no flocculation can occur (Fig. 1). If the repulsive force is greater than the attractive force at a small separation distance, then a secondary flocculation can occur (Fig. 2) in which the particles will be maintained at an equilibrium distance apart. If the repulsive force is nowhere greater than the attractive force, a primary flocculation will occur (Fig. 3).
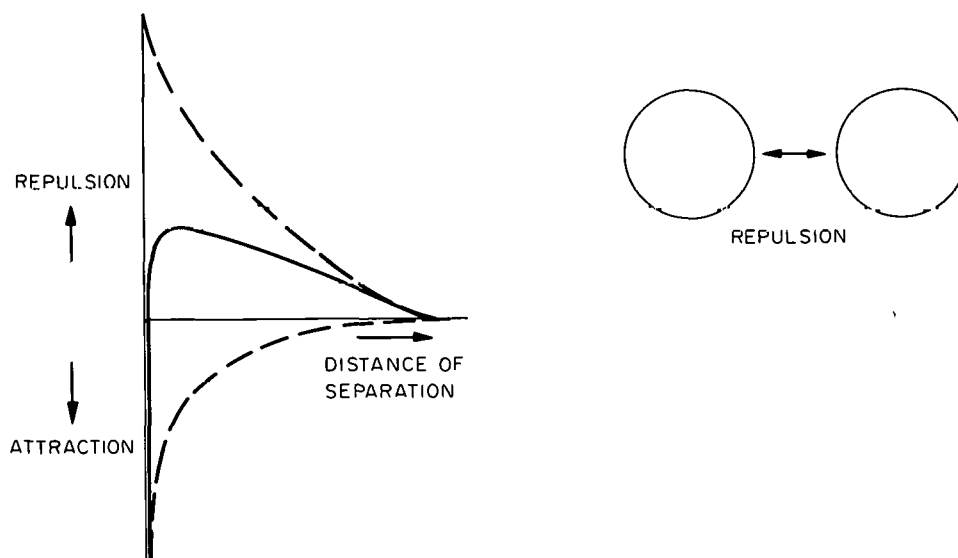
Fig. 1. Deflocculated Suspension. Electrostatic force greater than van der Waals' force at large separation distances. Particles cannot "cross over" electrostatic barrier.
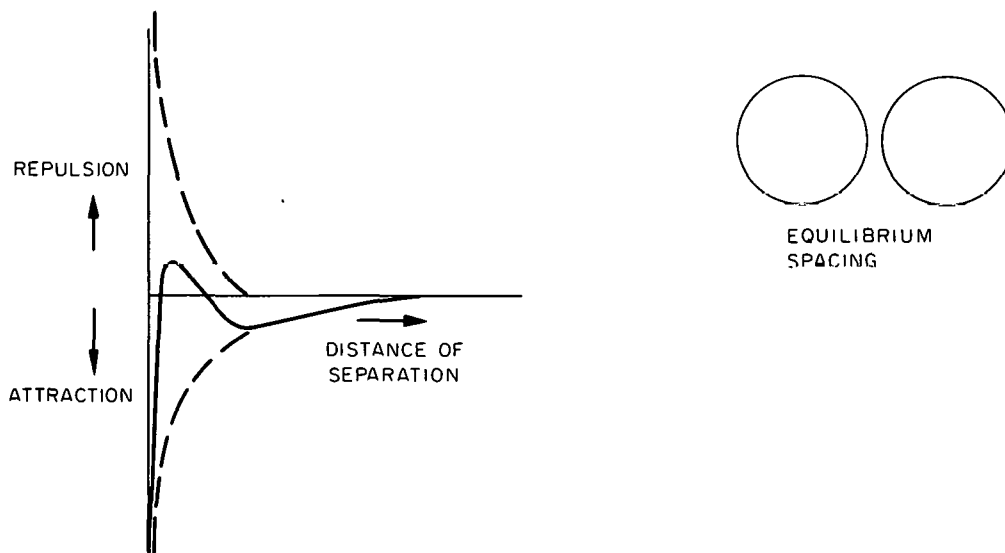
Fig. 2. Secondary Flocculation. Electrostatic force effective at small separation distances. Particles cannot "cross over" potential barrier. Bond strength (depth of secondary minimum) is a function of location at minimum.
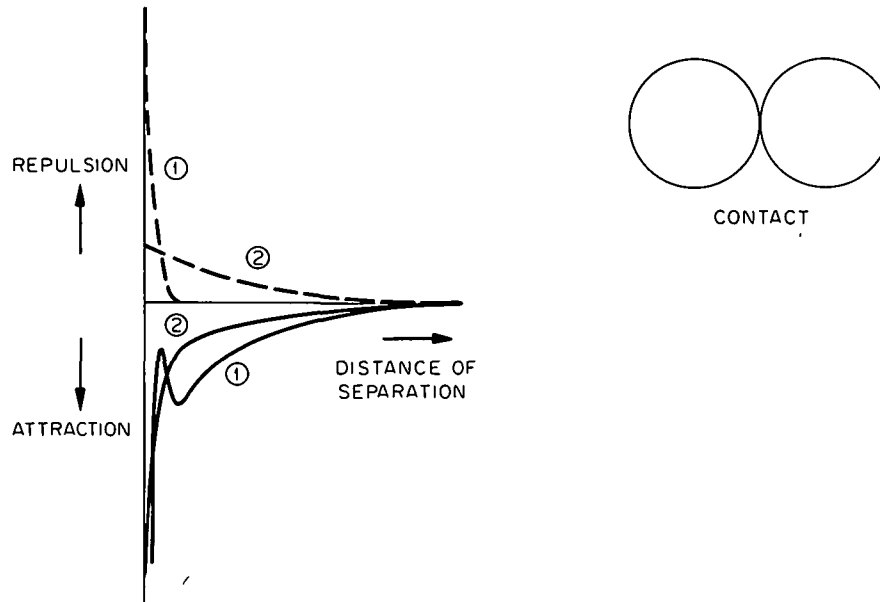
Fig. 3. Primary Flocculation (Two Forms). Electrostatic force insufficient to prevent interparticle contact, either because of high counter-ion concentration or valence (1) or because of low surface charge (2).

Gravity Force

In addition to the attractive and repulsive forces, the force of gravity will act upon a settled bed of each of the above types of suspensions. The gravity force acting between any two particles will depend on the height of settled bed above them and also on whether any of the gravity force from above has been transmitted to the walls of the container. There are conditions under which gravity may be the predominant force--for example, if the suspensions were settled in a centrifuge. There are other conditions under which gravity may be unimportant--as, for example, when a suspension is settling and there are sufficient body forces transmitted-to-the-container-walls,-or if-the-particle size-is-very-small.

EFFECT OF FIRING TEMPERATURE ON EVALUATION OF VOLUME FRACTION SOLIDS

The first factor to be considered is the effect of firing temperature of the thoria on the evaluation of settled-bed volume fraction solids. It has been observed[7] that at firing temperatures below 1600°C, the specific surface area, as measured by nitrogen adsorption, increases rapidly with decreasing firing temperature. This is clearly indicative of internal pores. The pore volume would reduce the particle bulk density to less than the thoria crystallite density. A knowledge of the correct bulk density is necessary to determine the volume fraction of particles in a settled bed for comparison between different preparations. A crude estimate of the maximum density of a bulk particle can be obtained by assuming that the internal pores are the spaces between faces of adjacent cubical crystallites. Crystallite sizes for typical slurries have been measured by x-ray diffraction, and measured values of specific surface area check closely with the predicted area based on cubical crystallites.[8] Further, from a study of pore size distribution[9] of typical 800°C-fired thoria slurries, the most probable pore width was found to

be 10 Å. Thus the volume fraction pores, assuming the 10 Å spacing between adjacent parallel faces, for a 15-m^2/g specific surface area preparation, would be 0.015 cm^3/g. Assuming a crystallite density of 10 g/cm^3, this gives a particle theoretical maximum density of 8.7 g/cm^3 for such a preparation.

An experimental method of estimating the relative particle density as a function of firing temperature is to compare the ultimate settled-bed concentrations measured in grams of ThO_2 per liter for slurries of oxides fired at different temperatures. Such information is included as part of Table 2. The mean ultimate concentrations for the one 650°C-fired, the five 800°C-fired, and the seven 1600°C-fired pure thoria suspensions were averaged and are shown in Table 1. Included are estimated values of the mean specific surface area.

Table 1. Ultimate Concentration and Estimated Surface Area
of Pure Thoria vs Firing Temperature

Firing Temp.(°C)	Average Value of Mean Ultimate Conc. (g of ThO_2 per liter)	Estimated Surface Area[7] (m^2/g)
650	2230	25
800	2720	15
1600	4110	1

If it is assumed that the particle shape of all three types was the same and that the particle density of the 1600°C-fired oxides was 10 g/cm^3 (corresponding to crystallite density), then the particle densities of the 650°C- and 800°C-fired preparations are 5.42 and 6.6 g/cm^3, respectively. Assuming that the pores are the spaces between adjacent cubical crystallites and using the estimated surface areas, the mean pore width is 33 Å.

It is noted that theoretically the ultimate concentration of the 1600°C-fired material should be 6000 g of ThO_2 per liter of settled bed. The lower experimental value is probably due to the particle sphericity not approaching that of granular or spherical material. As shape is not a function of firing temperature, it is not included in the relationship, but should be considered when comparing materials of different shape.

Because of the uncertainties involved in the calculation of the particle density, settled-bed concentrations are generally reported in grams of ThO_2 per liter, instead of volume fraction solids, unless a comparison between slurry preparations is desired.

EFFECT OF PARTICLE SIZE

If all other factors are kept constant, the effect of reducing the particle size of a flocculated suspension is to increase the relative importance of interparticle forces as compared to gravity, since per unit volume of material there would be more interparticle links. There should therefore be a decrease in the settled-bed volume fraction solids with decreasing particle size. It is desirable to estimate this relationship based on some theoretical model. Two models of sediment structure are possible, the first based on adjacent particles forming rigid bonds, and the second based on each particle being surrounded by a rigid lyosphere.

Theoretical Settled-Bed Concentration: Vold's Hypothesis

In a recent paper Vold[10] has calculated the volume concentration of spheres to be expected when they are dropped randomly, one by one, into a container, assuming that the spheres adhere rigidly at contact. She found, as principal results:

1. The mean number of contacts per particle was two. This is the theoretical minimum and may be a result of her method, rather than a general result.

2. The volume fraction of solids in the bed was very close to 0.128 for equal-sized spheres and also for two distributions of sphere sizes.

3. The volume fraction decreased if the assumption was made that one particle was pulled to another when they reached separation distances greater than 0.25 times the diameter.

The conditions of the calculation are somewhat different from simple floccu-lation, since most interparticle bonds actually form during settling for floccu-lated material. The main difference is that, in flocculation, bonds are formed isotropically; that is, if there are no other particles interfering, two particles will flocculate with equal probability at any angle θ from the vertical, since Brownian motion is the driving force rather than gravity. On the other hand, in Vold's hypothetical case (Fig. 4), if there is no other particle interfering, the probability for any angle of contact θ will not be a constant, since it is the horizontal position (two dimensions) which in her model involves equal probability. The probability frequency function for contact angle in her case is $\sin 2\theta$ (Appendix A), assuming no interference from other particles. Thus the most probable contact angle, as well as the mean contact angle, is $\pi/4$. But this is also the mean value of the angle assuming isotropic two-contact flocculation, since in that case there will be one contact in the upper and one in the lower hemisphere. The probability frequency function is then $2/\pi$, a constant for any angle between 0 and $\pi/2$. The mean angle of flocculation, then, for two contacts per particle (one in the upper and one in the lower hemisphere) is $\pi/4$.

If there is third-particle interference (that is, if a third particle prevents, under Vold's hypothesis, large angles of contact), then the mean angle of contact would be decreased. However, since large angles are also improbable ones (the fre-quency function being $\sin 2\theta$), the shift should be slight. Thus the mean angle of contact obtained by Vold should be very nearly the mean contact angle for isotropic two-contact flocculation.

The mean contact angle between particles will determine the settled-bed concen-tration; the smaller the angle, the lower the concentration. Thus the settled-bed volume concentration obtained by Vold should be comparable to that occurring by flocculation due to Brownian motion and van der Waals forces, since the mean contact angles are the same. Thus the minimum settled-bed volume fraction solids under the rigid bond hypothesis, should be 0.128 for flocculated suspensions.

It is interesting to note that Vold's third result (that the concentration decreases with increased distance of attraction) can be easily explained also on the basis of contact angle, since by her method of calculation the increased distance of attraction will, if there are interferences between particles, tend to decrease the mean contact angle, which would, in turn, lower the concentration.
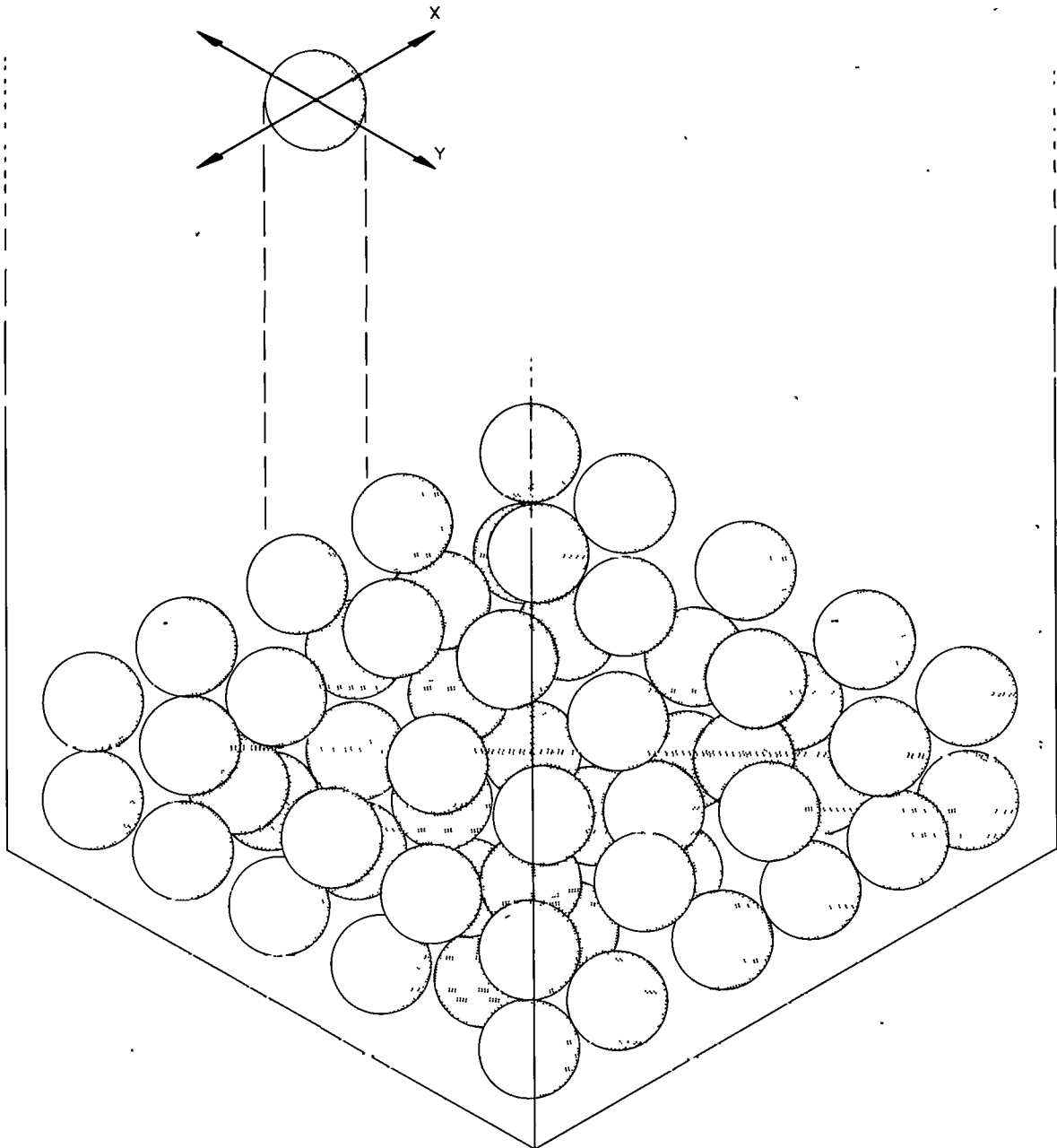
Fig. 4. Vold's Hypothetical Model. The values of x and y were chosen at random, and the position of first contact of each successive particle was calculated.

Vold cited experimental verification of the observed value of 0.128 settled-bed volume concentration for moist glass spheres in polar solvents. In that instance, the attractive force between particles is due to surface tension.

Tho accumption of rigid bonds will not be valid for large particle sizes where the interparticle bonds can no longer support the structure weight. Thus the rigid

bond hypothesis would predict a minimum volume fraction (0.128) and a maximum volume fraction (0.60 for spheres), with a transition region at a particle-size range where the force due to gravity per particle is the same order of magnitude as the force of interparticle attraction. This transition region should occur, for van der Waals type forces, at the upper particle-size limit of colloidal effects, which is around 1 to 10 microns.

Spherical-Lyosphere Hypothesis

An alternative hypothesis, that of a spherical lyosphere, can be used to derive an expression for variations in settled-bed concentration with particle size.

The assumptions of this model are:

1. spherical, uniformly sized particles,

2. constant lyosphere thickness due to electric double layer,

3. random packing of lyospheres,

4. lyospheres of sufficient rigidity to support the bed, or to transfer gravity force to the wall.

The relationship can be derived:

$$\phi = 0.60 \left(\frac{D}{D+2d} \right)^3 ,$$

where D = particle diameter,

       d = lyosphere thickness,

       ϕ = volume fraction of solids.

The volume fraction of solids will approach the value determined for random packing of spheres at large particle size. However, as particle size is reduced, this model predicts a sharp decrease in volume fraction solids of the settled bed, since the lyosphere thickness is a function only of the surface properties of the particle and not its size.

Experimental Data

A plot is shown (Fig. 5) of the variation of settled-bed concentration with particle size for four regular-shaped thoria suspensions. Two of the data points are for thoria "spheres."[11] These particles were spherical or were fragments of spheres, and had no measurable internal surface area. The other two points are for thoria "cubes." These particles were special experimental preparations[12] and closely resembled flattened cubes, also with no internal surface area. For these preparations, it was assumed that the bulk particle density was 10 g/cm3 and that the shape was spherical or granular.

Also in Fig. 5 are similar data[13] taken for glass spheres in glucose solution. The data do not include sufficiently small particle sizes to distinguish between the two models presented. However, under the lyosphere hypothesis, a curve can be fitted to the available data which corresponds to a lyosphere thickness of 0.5 micron (mean separation distance of 1 micron). For this value, the settled-bed volume fraction solids would be 0.075 for 1-micron particles and 0.022 for
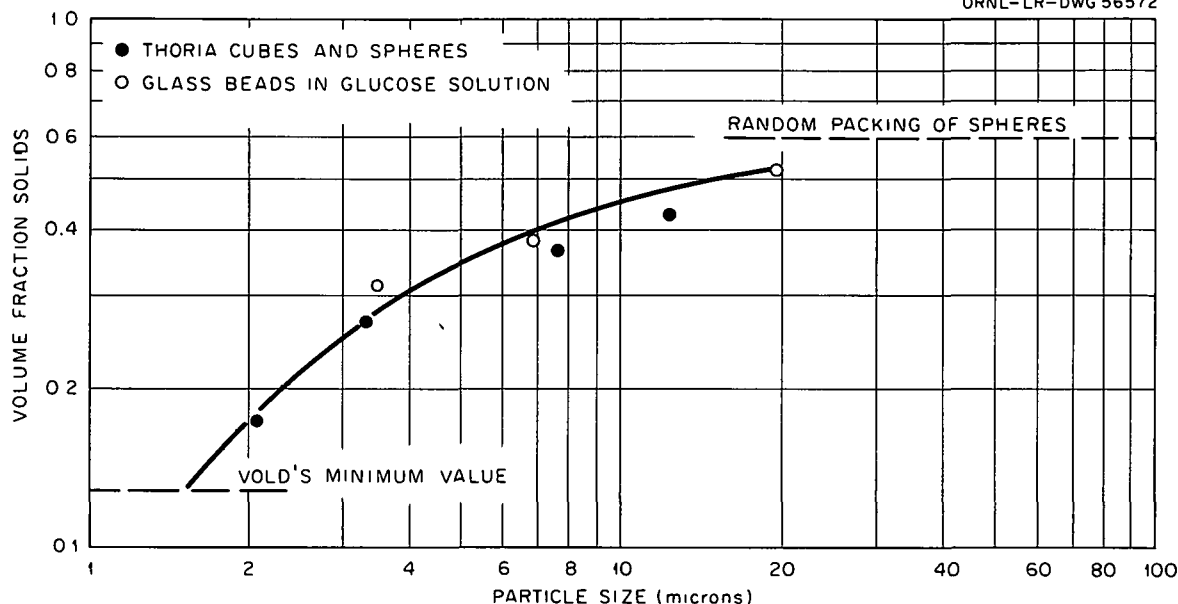
Fig. 5. Experimental Values of Solids Fraction of Settled Beds. The data lie in the region where the magnitude of the interparticle bond force is the same order as the weight of particle. Solid line calculated from lyosphere model assuming a 0.5-μ lyosphere thickness.

0.5-micron particles. The latter values are very low compared to those for typical thoria preparations of such sizes, even if irregularities in size distribution and shape are included. Thus it would be hazardous to attempt to extrapolate based on this concept.

Conclusions

With suspensions of thoria particles of sufficiently large size (perhaps > 15 micron) the influence of interparticle bonds can be neglected, and the settled-bed concentration will approach that of random-packed unflocculated particles. For very-small-particle flocculated suspensions, an extension of Vold's results predicts an asymptotic value of the settled-bed volume fraction solids probably not very different from 0.128 in the case of granular-shaped material, whereas the lyosphere model predicts a rapidly decreasing concentration with decreasing particle size. This latter prediction does not appear reasonable. However, the use of the lyosphere model within the range of 0.12 to 0.6 appears to give useful interpolations.

MEASUREMENT OF ULTIMATE SETTLED-BED CONCENTRATION

Introduction

As a result of the formation of an intractable settled bed in a vertical section of 200B loop piping following a high-temperature loop run,[14] a study was undertaken to define the problem of high-concentration settled bed more clearly.

Examination of the settled-bed plug revealed its dilatant nature. A sample of the slurry was sliced from the mass of material plugging the 3-in. pipe and was examined in a watch glass. The surface of the specimen was shiny, and the whole specimen had a rubbery consistency. Upon pressing lightly on a part of the specimen

with a small spatula, the area immediately adjacent lost its shiny appearance. The dull and then shiny appearance could be made to occur by alternately compressing and releasing a part of the specimen.

The concentration of the solids filling the pipe was obtained by means of a small slurry pycnometer. The pycnometer was a small clear plastic block with a cylindrical hole, which had been previously volume calibrated. The concentration was found to be 3200 g of solids per liter. A sample of this material was resuspended in distilled water in a 50-ml graduate and permitted to settle. The final concentration of that settled bed was 1800 g of solids per liter. It appeared that the slurry, although flocculated, had been able to concentrate more than expected. In order to determine whether the slurry bed reached a maximum concentration at 3200 g of solids per liter, samples of the resuspended material were subjected to three types of treatment each of which should concentrate the solids to a dense bed.

1. A sample was resuspended in distilled water in a 10-ml graduate cylinder and was permitted to settle, and the flocculated settled-bed concentration was obtained for comparison purposes. Then a saturated solution of sodium pyrophos-plate was added drop by drop, and the suspension was reshaken until it appeared to be totally dispersed and no agglomerates were visible. The dispersed suspension was then permitted to settle, and the final concentration was obtained.

2. A sample was resuspended in distilled water and was deposited drop by drop on a piece (at least 4 x 4 in.) of damp blotter paper. After each drop was added, the excess water was permitted to drain from the accumulated sediment, until a sufficient mound was built up to enable a sample to be removed by a spatula without having to scrape the blotter paper. The sample removed from the mound was placed in the slurry pycnometer, and its concentration was obtained.

3. A sample was resuspended in distilled water and added to a standard 15-ml conical-bottom centrifuge tube and centrifuged for 15 min at approximately 2000 g acceleration. If there was not enough solids to form a bed extending above the conical region, more suspension was added and the tube recentrifuged for 15 min. The final concentration was calculated when the final bed height was above the conical region.

The slurry used in the loop was a mixture of three preparations--MO-41, -43, and -44. These are initially-650°C-fired thoria preparations, with particles 2 microns in nominal diameter, onto which ammonium diuranate was adsorbed, and then the whole was refired at 1050°C. Thus the surfaces of the particles are expected to be chemically unlike that of pure thoria.

The results of the three tests with MO-41, -43, and -44 are included in Table 2, and the concentrations agree closely with the sample from the 200B loop plug. It appears then that some maximum concentration of the suspension had been reached. This is referred to as the ultimate concentration, and was probably re-sponsible for the dilatant behavior and the intractable plug.

Dilatancy

The property of a system to increase in volume (dilate) when subjected to shear is referred to as dilatancy. Dilatant systems are suspensions rather than true solutions. Since the actual property of dilation is neither important nor easily observable for small particle sizes, other properties in general have been taken to characterize a dilatant system. Dilatancy has been characterized by:

1. increasing viscosity with increasing shear stress,

Table 2. Comparison of Settled-Bed Concentration and Ultimate Concentration

All concentrations given in grams of solids per liter

Slurry Type	Treatment	Firing Temp. (°C)	Particle Size (μ)	Flocculated Settled-Bed Concentration Initial Conc.	Final Conc.	Dispersed	Centrifuged	Drained	Mean	Notes
LO-7	None	800	3.5	1063	1965	2520	2280	2700	2500	
LO-7	Micropulverized	800	1.0	1180	1815	3100	2860	3580	3180	
LO-7	Micropulverized	1600	2.2	2170	3150	4550	3470	5100	4373	
DT-25	None	800	1.8	1170	1570	2510	2290	2345	2382	
DT-25	Pumped	800	1.8	1250	1950	2340	2320	3390	3016	
DT-37	None	800	2.7	----	1200	2000	1960	2000	1987	
LO-39	Pumped	1600	1.5	----	1720	3680	5050	4320	4350	
DT-2,3	None	1600	5	928	1935	2810	2900	3340	3016	
DT-1	Pumped	1600	1.2	1445	1950	4775	4890	5200	4955	
DT-1	Pumped	1600	1.2	1810	2490	4390	4500	4600	4497	
DT-9	Pumped	1600	1.8	1034	1570	4120	3600	3980	3900	
LO-38	Pumped	1600	0.9	1260	2010	3900	3600	4300 3200	3750	
MO-41	Pumped	1050	2.2	907	2000	3200	3000	3220	3140	890 U/Th
MO-54	None	1050	2.3	1130	1940	2980	2760	3120	2953	1590 U/Th
MO-67	Pumped	1080	2.5	1280	2175	3388	4320	4560	4088	390 U/Th
LCC 1108	None	650	0.8	582	1075	2150	2220	2330	2233	
Flame Fired	None	---	---	----	----	5480	4870	5450	5267	

2. net flow of the suspending medium into a region of high shear
    stress (observed as a dulling of a surface being sheared).

Dilatancy has been studied by several authors.[15,16] Roeder[16] developed a
method of quantitatively comparing dilatant and nondilatant systems, based on the
force-speed relation for motion of a sphere through a dense suspension. He noted,
as a requirement for dilatancy for granular quartz or rice starch, that the volume
concentration must be in the narrow range 0.40 to 0.45. Another observation of
Roeder was that the most dilatant quartz-water systems were in the quartz size
range of 1.5 to 5 microns ($<$ 1.5-μ and $>$ 15-μ quartz particles formed weakly dila-
tant systems by his measurements).

Freudlich[15] stated that pronounced dilatancy and pronounced plasticity were
mutually exclusive. However, the results of Roeder illustrated that between the
two extremes of plasticity and dilatancy a region exists where both dilatancy and a
yield value may exist. The requirement for dilatancy is the (high) concentration
range and particle size. However, the plasticity of a system of this particle size
usually acts to prevent the system from concentrating (under gravity) to the dilat-
ant regions, and also masks (by virtue of high effective viscosity) the dilatant
characteristics.

A system which exhibits both dilatant and plastic behavior can be designated as
dilatant plastic.

Analysis of the 200B4 Plug

The 200B4 plug was noticed after a two-week shutdown of the loop following a
continuous 1400-hr run at temperatures above 200°C. The plug was first noticed
when the loop pump could not restore flow on startup. The plug was located at the
bottom of a 16-ft section of vertical 3-in.-ID pipe.

The plug did not flow with less than 1600 psi differential pressure across it.
Even that pressure was not able to completely resuspend the plug, however; the loop
was disassembled at a flange adjacent to the plug, and the plug was removed.

A model has been devised to account for the observed pressure drop. It
assumes two independent forces acting to prevent flow--a dilatant force and a yield
stress (plastic force). The dilatant force is a frictional resistance due to the
pressure exerted on the wall by the particles adjacent to it and is therefore pro-
portional to the local pressure at the wall. The yield stress is a constant fric-
tional resistance everywhere along the wall and is proportional to the volume
fraction solids and to particulate surface properties.

From Fig. 6 a force balance for element dx long yields

$$-\pi r^2 \frac{dp}{dx} dx = 2\pi r \, cp \, dx + 2\pi r \, \tau_y \, dx,$$

where r = tube radius,

p = local pressure,

x = axial distance,

c = coefficient of friction,

τ_y = yield stress.
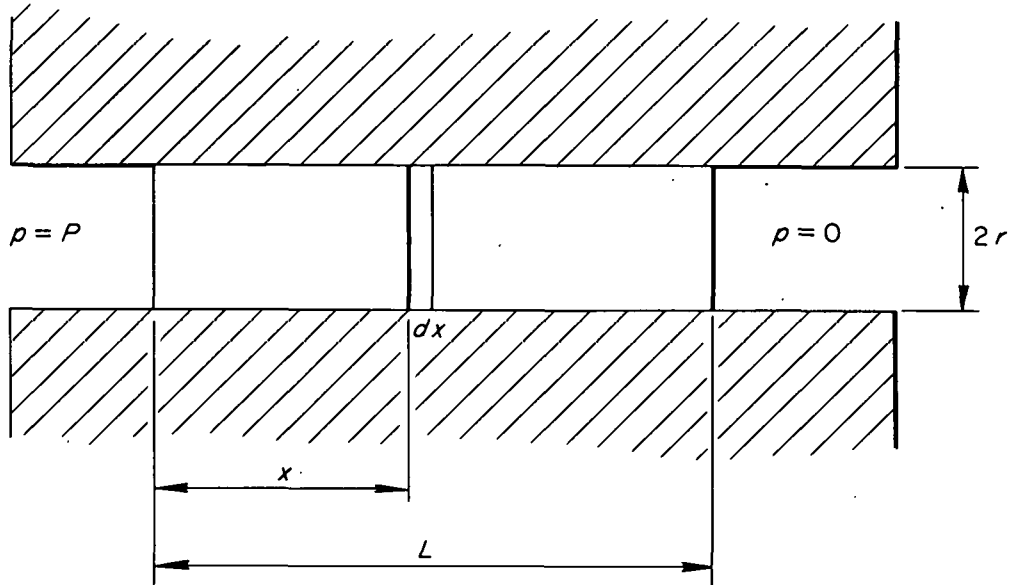
Fig. 6. Proposed Model of Intractable Dilatant Plastic Plug.

$$\frac{dp}{dx} + \frac{2cp}{r} = -\frac{2\tau_y}{r} ,$$

$$p = -\frac{\tau_y}{c} + B\, e^{-2cx/r} ,$$

where $x = 0,$

$p = P,$

$B =$ integration constant.

$$P = -\frac{\tau_y}{c} + B ,$$

$$B = P + \frac{\tau_y}{c} ,$$

$$p + \frac{\tau_y}{c} = \left(P + \frac{\tau_y}{c} \right) e^{-2cx/r} .$$

The criteria for a plug to just move is that $p = 0$ at $x = L$:

$$\frac{\tau_y/c}{p + \tau_y/c} = e^{-2cL/r} ,$$

$$P = \frac{\tau_y}{c} (e^{2cL/r} - 1) \, ,$$

$$P = \frac{\tau_y}{c} (e^{4c \, L/D} - 1) \, ,$$

where, in general, $e^{4c \, L/D} > > 1.$

Thus it can be seen that the pressure required to move a dilatant plastic plug is an exponential function of L/D. It was determined from gamma scanning that the 200B plug length was 36 in., equivalent to an L/D of 12. The coefficient of friction can be estimated to be between 0.10 and 0.20. On this basis, the effect of reducing the plug length to 24 in., for example, would be to lower the required pressure by a factor of 5 to 25. This illustrates a potential major problem of dilatant plastics: the combining of the two types of resistance forces to create an intractable plug.

An effort was made to duplicate the plug L/D in a 1/4-in. copper tube with the same slurry. The slurry was added drop by drop into a vertically mounted 1/4-in. copper-tube section which had a cotton wad near the lower end. This end was mounted in a vacuum flask, which was attached to a vacuum pump. After a plug was formed in this manner, the cotton was removed and nitrogen pressure was applied to the upper end. This process of plug buildup was difficult for several reasons. First, it was necessary to build up to the concentration of dilatancy without exceeding it. If the bed became overly dry, it would not transmit the local pressure to the wall. Secondly, the bed was frequently built up with internal cracks containing air. The cracks allowed part of the bed to be bypassed, decreasing the effective bed length. A plug was considered unsuccessful if it flowed at less than 1 psi, or if air leaked through it. Three plugs were successful, and results for them are plotted along with the point representing the 200B loop plug in Fig. 7. The value of the friction coefficient from this plot is 0.17; the yield stress is 13 lb/ft^2. Because of the difficulties in obtaining the data, the results are not as reliable as Fig. 7 would indicate.

DILATANCY TESTING

In order to determine whether other preparations exhibited dilatant behavior, a total of 17 slurry preparations were subjected to the three sedimentation methods listed previously: centrifugation, dispersion, and drainage. The resulting ultimate concentrations obtained are shown in Table 2 along with the particle sizes, firing temperatures, and the flocculated settled-bed concentrations obtained in 10-ml graduates. The value of the flocculated settled-bed concentration is subject to the variation with initial concentration, which is discussed in another section. It is noted here as a relative value to compare with the ultimate concentrations.

An attempt was made to compare the beds produced as to dilatant behavior by examination with a spatula. Qualitative dilatancy--the dulling of the surface adjacent to a sheared area--was observed with all but three preparations (pumped, 1600°C-fired thorias). Other tests to try to evaluate dilatancy differences between slurries were generally unsuccessful; a summary of these tests appears in ref 17. It should be assumed, therefore, that many flocculated preparations, if within the particle size range 1 to 5 μ and if concentrated to sufficiently high values, will show similar dilatant plastic behavior. It may become necessary therefore to avoid high-concentration settled beds by maintaining a suitable degree of flocculation, or if this is not possible, to prevent such beds from forming in long vertical pipes.
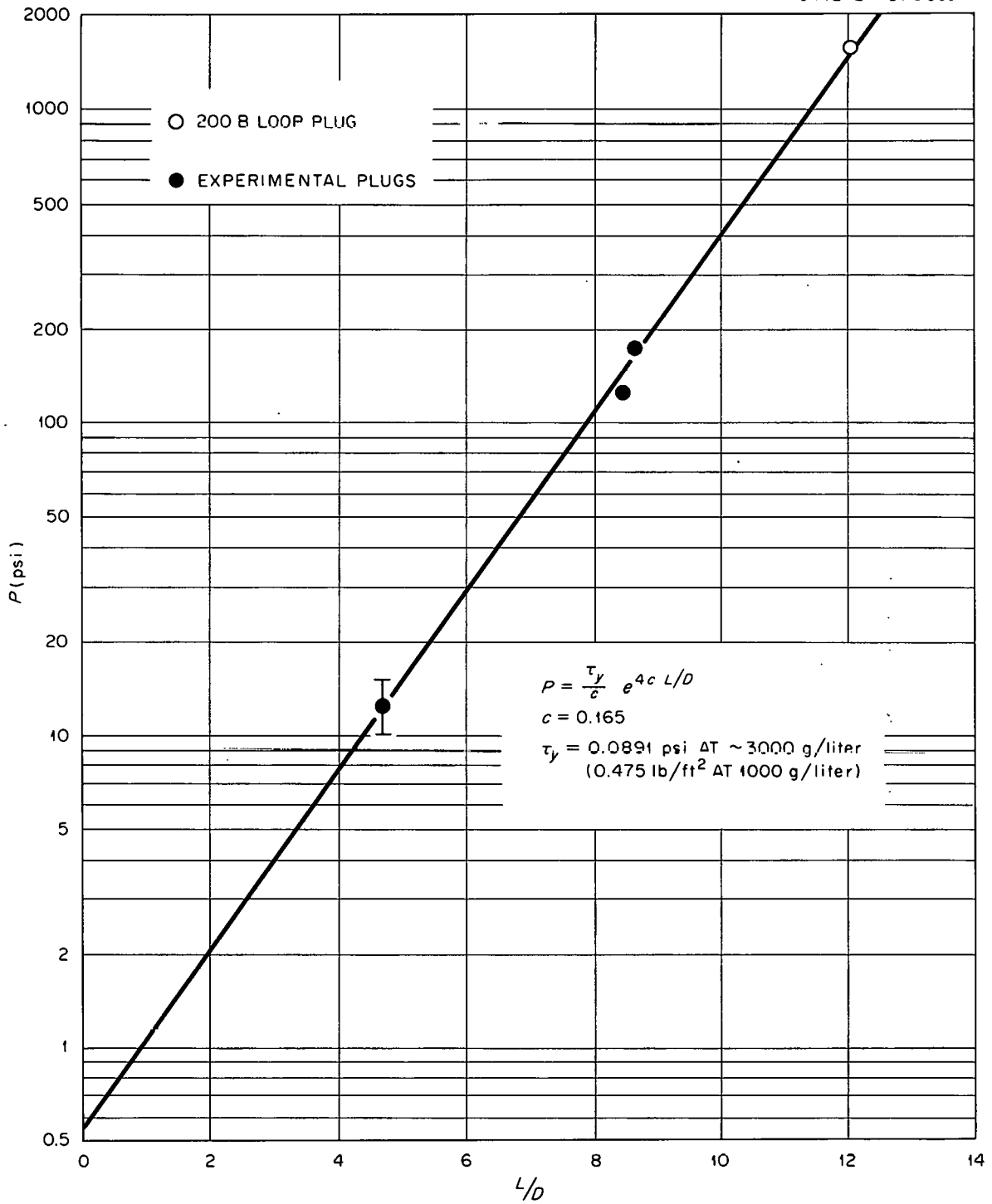
Fig. 7. Pressure Required To Move Dilatant Plastic Plugs.

EFFECT OF TEMPERATURE AND INITIAL CONCENTRATION

In the experiments described in this section, the effect of the temperature and the initial concentration on the settled-bed concentration was measured. This was done by comparing sediment heights at various temperatures for sealed slurry samples, thus holding constant all the particle and container effects. By maintaining a constant slurry inventory, the gravity force was held constant so that the effect of temperature on sediment volume could be directly related to its effect on degree of flocculation. Also, by holding the system volume constant but altering the initial concentration, it was possible to observe the effects of initial concentration on the settled-bed concentration.

Apparatus

The apparatus used was essentially the same as used by Reed and Crowley[18] for settling-rate experiments, and is shown in Fig. 8. It consisted of a vertical tube furnace fabricated from a solid aluminum block wound with resistance heating ribbon. Two 3/8- by 10-in. slits on opposite sides of the furnace permitted observation of the sample tube when in place in the center of the furnace. The furnace was mounted on a motor-driven rocking device so that it could be oscillated alternately 180° in a forward and 180° in a backward direction, the axis of rotation being at the center of the furnace (and the sample).

The sample tubes consisted of sealed Vycor (quartz) tubing 6 mm in inside diameter and about 27 cm long. The volume of each tube up to a scratch mark on the

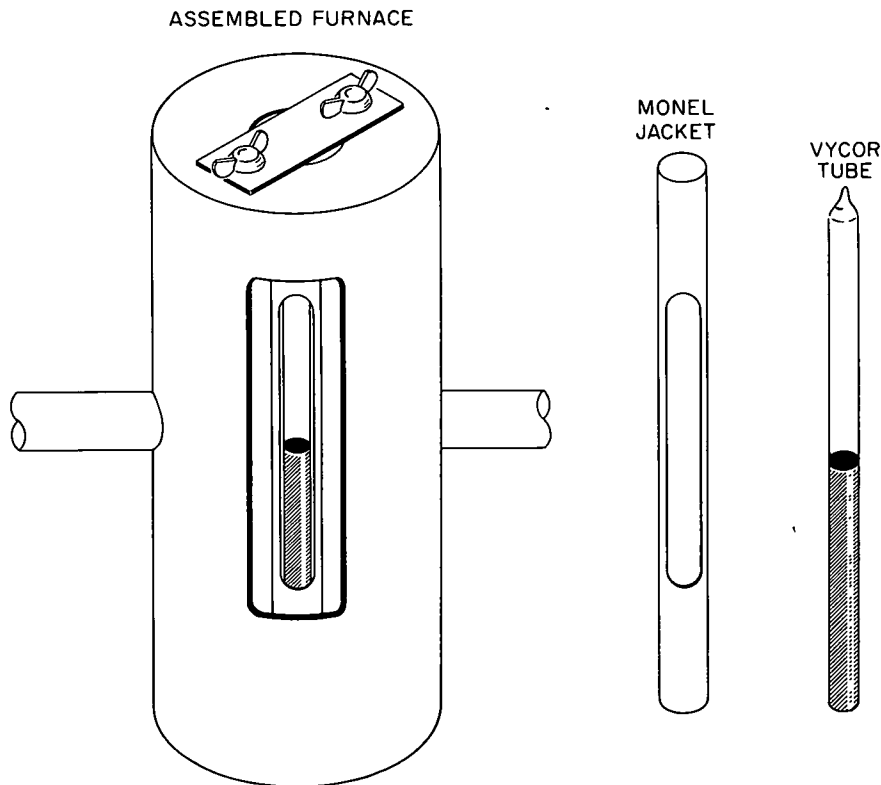ASSEMBLED FURNACE

MONEL JACKET

VYCOR TUBE

Fig. 8. Furnace Assembly.

tube wall approximately 15 cm from the bottom was calibrated with mercury, and the sample initial concentration was obtained by density measurement of the sample in each tube. After filling and weighing, the tube end was fused closed, leaving an air space above the slurry. The tube was then placed in a Monel tubular jacket, which had two 1/4- by 8-in. slits. The long edges of the slits were calibrated so that sediment height could be read. The Monel jacket was placed into the furnace, the excess space on top plugged with glass wool, and a holding clamp screwed on.

A thermocouple, inserted in the furnace so that the junction was adjacent to the sample-tube jacket, was connected to a Simplytrol controller which regulated the heater input by means of an on-off relay in the heater circuit. The temperature was controlled to within $\pm 2^{\circ}C$ of the selected temperature. A Plexiglas safety shield was installed on each side of the furnace to minimize the hazard due to occasional rupture of the Vycor tubes.

Procedure

The sealed Vycor tube containing slurry was inserted into the furnace, and the motor of the rocking device was turned on. The furnace was brought up to temperature while the rocking continued. After the desired temperature had been reached, rocking was stopped, with the Vycor tube in a vertical position as determined visually. Settling was permitted to proceed, at constant temperature, until an equilibrium settled bed was reached. For temperatures above $100^{\circ}C$, this equilibrium settled bed was achieved within about 20 min.

The final settled-bed height was read from the calibration on the Monel tube, and final concentration was calculated from this. The experiment was always repeated at least one time to ensure reproducibility.

In examining the settled beds after settling, it was observed that some of the beds at elevated temperatures would form visible crevices or would be separated into two or more beds by water or trapped air. In the cases where visible crevicing or separation occurred, the bed height was not recorded, and a rerun was made.

After the settled-bed height was recorded, the slurry was resuspended. At elevated temperatures, the bed was very difficult to resuspend by simple rocking. However, a small, pneumatic hand rivet gun was held against the furnace top to vibrate the bed while in an inverted position. This always succeeded in breaking up the sediment. The sediment did not appear rigid in these circumstances. Rather, it appeared sticky, similar to clay. This clay-like property was much less pronounced at room temperature.

Spontaneous Dispersion

In several instances after a suspension had been subjected to several cycles of being heated to elevated temperature and then cooled rapidly by removing the Vycor tube from the furnace while hot, it was observed that the material did not settle at room temperature with a clear supernatant, as was the normal case. Also, it was observed that the settled-bed concentration was considerably higher at all temperatures. It was concluded that an irreversible spontaneous dispersion had occurred, probably due to the formation of a silica coating on the suspension particles, the silica having been dissolved from the Vycor tube. The slurries that underwent spontaneous dispersion were not used in subsequent testing.

Results

The first series of experiments were to define whether there was an effect of temperature on settled-bed concentration. For this purpose, ten comparisons were

made of the settled-bed concentration at 200°C and at room temperature. The thoria and thoria-urania slurry preparations used were samples obtained from various circulating loops and were representative of oxalate-precipitated 1- to 3-micron-mean-diameter slurries with and without added uranium and before and after pumping, including high-temperature and low-temperature pumping. The data are presented in Table 3. It is noted that although the initial concentration was varied by a factor

Table 3. Settled Bed Concentration Ratios

All concentrations in grams of solids per liter

Slurry	Firing Temp. (°C)	Particle Size (μ)	Room-Temp. Initial Conc.	Settled-Bed Concentration		Ratio
				Room Temp.	200°C	
DT-6 unpumped	1600	2 μ	391	1249	752	0.602
DT-6 slightly pumped	1600	2 μ	418	1440	918	0.637
DT-6 pumped 1500 hr	1600	2 μ	547	1863	1049	0.563
DT-11 pumped*	1600	1.0 μ	292	1890	1195	0.632
DT-11 pumped	1600	1.5 μ	303	1501	955	0.636
DT-11 pumped	1600	1.5 μ	252	1348	719	0.533
MO-1 unpumped	1050	1.6 μ	225	1035	700	0.676
MO-1 pumped	1050	1.6 μ	321	1525	909	0.635
DT-15 pumped	1600	2.9 μ	644	2610	1768	0.677
LO-22 pumped	1600	1.8 μ	657	2560	1590	0.621

*This sample was pumped in a different loop than the following two samples.

of 3 and the settled-bed concentration at room temperature among the different slurries varied by a factor of 3, the ratio of settled-bed concentrations $C_{sb}(200°C)/C_{sb}(25°C)$ was within 11% of the mean value of 0.631 (at the 95% confidence level) for every slurry.

A second series of experiments was carried out to observe the variation with temperature within the range 25 to 200°C for the four slurry preparations. The results appear in Figs. 9 and 10.

Analysis of Results

Two general observations can be made from Table 3 and Figs. 9 and 10.

1. Increasing the temperature at which sedimentation occurs in sealed small tubes caused a gradual decrease in the settled-bed concentration.

2. Decreasing the initial concentration while holding the total system volume constant decreased the settled-bed concentration at all temperatures.

The two results interact, in that increasing the temperature from 25°C to 200°C decreases the initial concentration by 13%. However, the data indicate that such a 13% decrease in initial concentration due to thermal expansion of the water
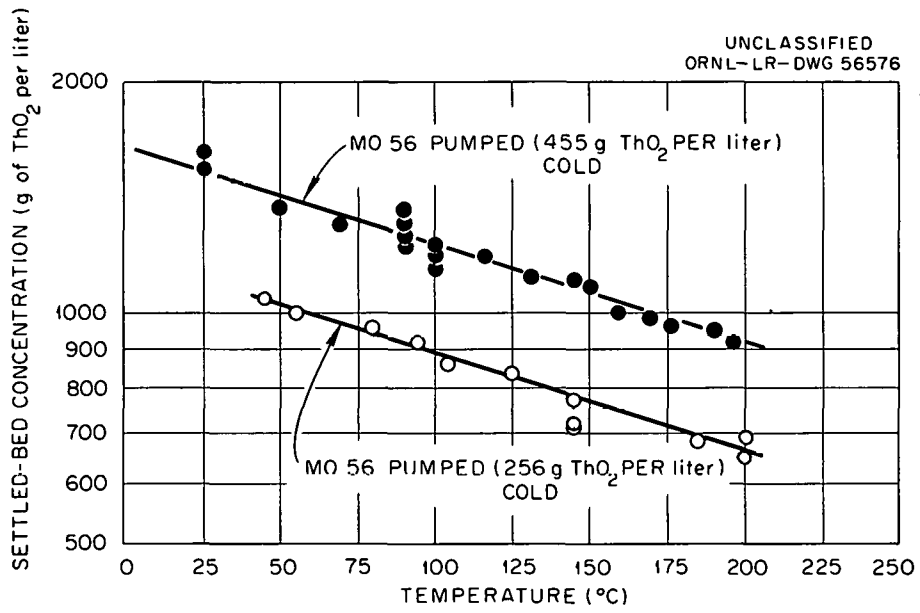
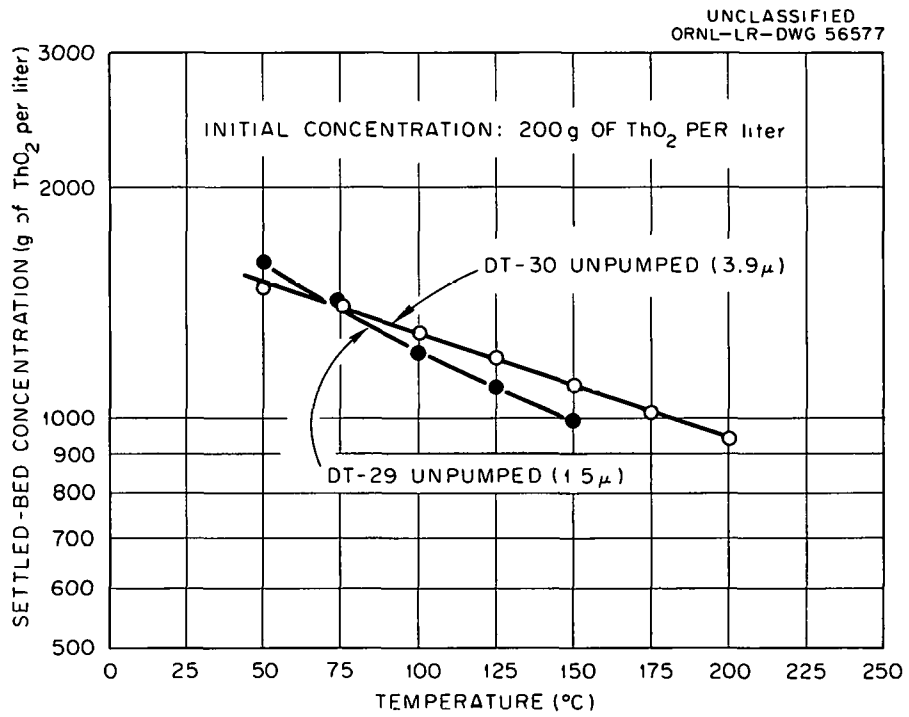Fig. 9. Effect of Temperature and Initial Concentration on Settled-Bed Concentration.

Fig. 10. Effect of Temperature and Particle Size on Settled-Bed Concentration.

is insufficient to explain the observed 37% decrease in settled-bed concentration. Therefore it is assumed that observations 1 and 2 are independently valid.

Proposed Mechanisms

The experiments were carried out by first homogeneizing the contents of the tubes by rocking followed by vibration. This process can be described as mechanical deflocculation. This was followed by permitting the suspension to settle quiescently.

It was observed that upon cessation of the mechanical deflocculation, visible flocs were rapidly formed, and these flocs then settled rapidly until a homogeneous mass was formed. After this (the onset of compaction concentration), settling occurred but at a much reduced rate until a settled bed was formed.

Consider the microscopic processes that occurred during this time.

Mechanical deflocculation broke up all (or nearly all) of the flocs so that the discrete particles were randomly distributed in the water. Upon cessation of the mechanical deflocculation, those adjacent particles which were within each other's attractive (van der Waal) force fields were drawn together--the magnitude of the attractive force being a strong inverse function of the minimum distance of separation.[19]

The bonds were initially very weak, but since the bond strength increased with decreasing distance apart, there was a tendency for the adjacent particles to pull together and increase bond strength. To do this, two forces had to be overcome: the force necessary to extrude the water from between particles and the mutual electrostatic repulsive force due to the electrically similar charged surfaces of the particles.

In the initial (hindered-settling) phase, as the flocs fell, they continued to draw together. The hydrodynamic resistance to closer approach would not have been controlling in a floc since the path of escape of the water is only to the outside of the floc. The limitation on the strength of a falling floc, if any, then would be the effect of the electrostatic repulsion due to surface change. (If there were no surface charge, the maximum strength in a floc would be determined by the effect of surface irregularities.) The combined effect, then, of van der Waals' attraction and electrostatic repulsion is to create a "potential well" at some small distance of separation of adjacent particles in the falling flocs--the distance at which the two opposing forces are equal. It is noted that while the suspension is in the hindered-settling phase, the effect of gravity can be neglected.

When the suspension enters the second (compaction) settling phase, it can be considered to be a single large floc. Three additional forces come into play: gravity, wall interaction, and hydrodynamic resistance.

The interaction of these three forces, plus electrostatic and van der Waals forces which fix the interparticle bond strength, is responsible for the final settled-bed concentration. Thus compaction settling (or more properly, floc crushing) will occur until an equilibrium is reached between gravity and the other four opposing forces. The process of floc-crushing actually serves to increase the mean number of interparticle bonds per unit volume. When this reaches a high enough value, the product of the interparticle bond strength and the number of bonds per unit volume is such that the bed can support itself against the force of gravity

by either transmitting the gravity forces to the adjacent wall, or to the container bottom, or both, and settling can cease; the time required for this to occur is a function of the hydrodynamic friction force of the escaping water. In the case where the bed is supported by a wall, any jarring of the container can reduce the friction at the wall and cause further settling.

In the case where the initial concentration is at or near the concentration of a floc, the entire settling process is of the floc-crushing type. If the particles are small enough (see the section, "Effect of Particle Size"), floc-crushing may not take place.

Relationship of Mechanism to Phenomena

1. With as many as five possible interacting forces involved in consideration of the mechanism of settled-bed formation, practically any result can be explained by the proper combinations.

2. Consider the previous statement that a settled bed represents an equililibrium between gravity forces and interparticle forces. In this connection we can include the wall interaction as being a result of interparticle forces. Essentially, then, those factors which increase the interparticle bond strength will tend to reduce the settled-bed concentration, provided that the bonds are strengthened while the suspension is not already fully settled.

3. To explain the temperature effect on settled-bed concentration then, it can be postulated that increasing the temperature will decrease the electrostatic repulsion force between particles. This will permit the particles, while settling, to approach each other (in flocs) more closely, resulting in increased bond strength within the flocs. Then, when the flocs form a settled bed, less compaction settling (floc crushing) will occur since fewer interparticle bonds are required to permit volume to support the suspension. The minimum volume fraction solids in a settled bed should correspond to the value calculated on the basis of rigid inter-particle bonds (0.128).

4. The effect of higher initial concentration on final settled-bed concentration is more elusive. It can be explained, however, by noting that during compaction settling the weight of the solids is transmitted down through the solids beneath. In this series of experiments, a constant total volume was used, so that the settled bed formed from a concentrated slurry contained more solids than that from a dilute slurry. The crevicing which occasionally occurred indicated that when the final settled bed was formed, the bed supported itself by wall interaction, and therefore final bed height was not a factor. It is also true, however, that at any time during compaction settling prior to formation of the final settled bed, the weight of the additional slurry was necessarily bearing down on the slurry beneath, tending to crush flocs to a greater extent than would otherwise have occurred without the additional bed weight. This would account for the variation with initial concentration in a constant-volume system.

5. It should be noted that the magnitude of the variation with temperature was more or less independent of the slurry preparation. Thus, assuming that the mechanism of surface-charge variation with temperature is the correct one, then this variation must be independent of the miscellaneous factors which distinguished the various slurries tested. This would be the case if the ion which charged the thoria surface (potential-determining ion) came from the water, that is, if the adsorbed ion were H^+ or OH^-. This, in fact, is consistent with findings regarding the surface chemistry of thoria suspensions.[20]

MISCELLANEOUS EXPERIMENTS

Effect of Chromic Acid

One of the alterations to a slurry resulting from pumping at high temperatures in a stainless steel loop under an oxygen overpressure is the gradual buildup of chromic acid due to corrosion. A series of samples of slurry LO-44, which is an 800°C-digested, unpumped slurry were prepared in 10-ml graduate cylinders, and varying amounts of chromic acid were added. The results are summarized in Table 4.

Table 4. Effect of Chromic Acid on Thoria Settled-Bed Concentration

| Graduate No. | Chromate Concentration | | Conc. (g of ThO_2 per liter) | | | |
	Total (mg of Cr per g of Th)	In Supernatant (µg of Cr per ml of Supernatant)	Initial	Final	pH	Millivolts
2a	0.130	2	1220	1620	8.3	-43
2-3	0.145	< 1	1125	1575	8.2	-47
7	0.296	< 1	1210	1540	7.7	-43
5a	0.584	2	1260	1620	7.0	-39
22	0.875	7	1180	1710	6.6	-39
6	1.73	36	1180	1725	4.4	+14
21	3.95	1,270	1165	1820	1.7	-47
1	10.85	8,260	1110	1930	0.9	--
24	17.1	19,700	1105	1875	0.6	--

The pH was obtained by using a glass electrode immersed in the slurry. The zeta potential was measured by microelectrophoresis.[21]

Results

There is a consistent increase in the settled-bed concentration with added chromic acid. At the same time, it is noted that the zeta potential remains relatively constant and at a high negative value. This result is consistent with the model proposed in the Introduction in which the influence of ions is to create a potential well at a equilibrium distance from the particle. It is recalled that the distance between the well "bottom" and the particle surface will determine the interparticle bond strength. Adding chromic acid apparently shifts the equilibrium distance away from the particle surface, preventing strong bonds from forming. This requires more bonds per unit volume to support the settled bed and thus a higher settled-bed concentration. This effect, however, is much less pronounced than the effect of temperature.

Chromic acid did not act to deflocculate the suspension. This is in contrast to hydrochloric acid, sulfuric acid, and nitric acid, which act within certain concentration ranges to deflocculate (disperse) thoria suspensions.

Effect of Applied Electrical Potential

Small quantities of representative pumped-thoria-slurry settled beds were placed in a watch glass, and a dc potential of up to 100 v was applied through the slurries between two stainless steel electrodes approximately 1 cm apart. Water was observed to flow toward the negative electrode and away from the positive electrode. By using the positive electrode as a spatula, it was possible to dry out portions of the slurry, and conversely, by using the negative electrode as a spatula, it was possible to lower the slurry concentration in a small area until it flowed readily.

There was no tendency for the slurry to form films on either electrode.

Appendix A

CALCULATION OF PROBABILITY FREQUENCY FUNCTION FOR ANGLE OF CONTACT
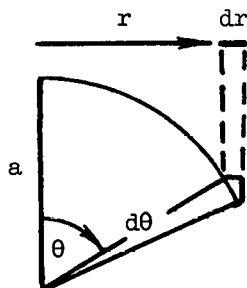ASSUMING PROBABILITY OF HORIZONTAL POSITION IS CONSTANT

Top View

Side View
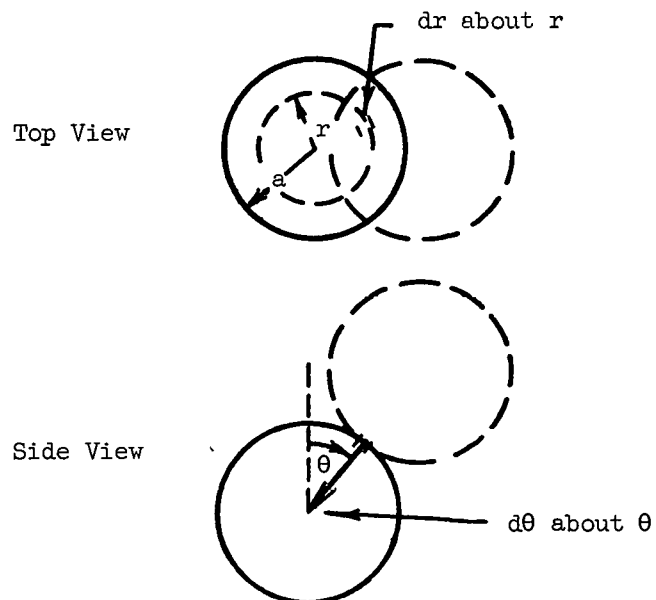
The frequency function for any horizontal position $\vec{r}$ from the center of a particle is:

$$f(\vec{r}) = \frac{1}{\pi a^2} , \qquad 0 \leq \vec{r} \leq a .$$

If every position $\vec{r}$ is equally probable, the probability of any $\vec{r}$ is given by

$$p(\vec{r}) = \frac{2\pi r \, dr}{\pi a^2} .$$

This can be expressed as a function of θ.

$$p(r) \ = \ \frac{2\pi r \ dr}{\pi a^2} \ ,$$

$$r \ = \ a \ \sin \theta,$$

$$dr \ = \ a d\theta \ \cos \theta.$$

$$p(r) \ = \ p(\theta) \ = \ \frac{2\pi \cdot a \ \sin \theta \cdot a \ \cos \theta \ d\theta}{\pi a^2} \ ,$$

$$p(\theta) \ = \ 2 \ \sin \theta \ \cos \theta \ d\theta,$$

$$p(\theta) \ = \ \sin 2\theta \ d\theta,$$

$$f(\theta) \ = \ \sin 2\theta, \quad 0 < \theta < \frac{\pi}{2} \ .$$

The mean value of θ, the angle of contact, is:

$$\bar{\theta} \ = \ \int_0^{\pi/2} \theta \ f(\theta) \ d\theta \ ,$$

$$= \ \int_0^{\pi/2} \theta \ \sin 2\theta \ d\theta \ ,$$

$$\bar{\theta} \ = \ \pi/4 \ .$$

Appendix B

CALCULATION OF SETTLED-BED CONCENTRATION BASED ON LYOSPHERE MODEL

Assumptions:

1. spherical uniform-sized particles,

2. constant lyosphere thickness,

3. random packing of lyospheres,

4. rigid lyospheres.

From assumption 3, the volume fraction of lyospheres in the settled bed is:

$$\phi_{bulk} = 0.60 \, .$$

But the volume fraction of particles in a lyosphere is:

$$\phi_{lyosphere} = \frac{\pi D^3/6}{\pi(D+d)^3/6} \, ,$$

$$\phi_{lyosphere} = \frac{D^3}{(D+d)^3} \, .$$

Then the volume fraction solids is the product:

$$\phi = 0.60 \frac{D^3}{(D+d)^3} \, .$$

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