Yield Stress of Suspensions Loaded with Size Distributed Particles

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A new theoretical approach is proposed for the yield stress of concentrated, flocculated particulate suspensions. Explicit cognizance is taken for the three-dimensional, mechanically rigid particle network held together by interparticle forces wherein the mean coordination number in the assemblage increases and the separation between the particles decreases with an increase in the volume fraction of the solid phase. The Rump-Molerus model relating isotropic normal stress and isotropic normal interparticle force in a bed of single-sized spheres is modified to incorporate the size distribution of particles and extended to the suspension network. The model estimates the yield stress as a function of solids loading for various kinds of size distribution and is in reasonable agreement with experimental data when the surface properties of the particle are held constant.

Introduction

In particulate processing, the flow of the suspension is critically important to both the energetics and, indeed, to the ultimate success of the unit operation. There are a large number of primary and secondary operations in the minerals and manufacturing industries that fall into this category, and processes such as solids filtration, pumping, and thickening are but three relevant examples to this work. In nearly all particulate processing, the state of dispersion of the particles in the fluid and the volume concentration of particles are important, simply because these two parameters are the prime determinants of suspension viscosity. Concomitantly, the process is more often than not viscosity limited at high solids concentrations.

The solids concentration is an easily understood parameter, but the role of the surface chemistry of a particle in particulate processing is less explicitly resolved. For example, in filtration and dewatering operations, the suspension needs to be flocculated to effect the process in a timely manner, however, this in turn results in the suspension exhibiting non-Newtonian flow behavior with increasing solids concentration. The transition concentration is considered classically as the gel point, and flocculated particulate suspensions in excess of this concentration typically exhibit a yield stress. This yield stress is a mechanical rigidity exhibited by the three-dimensional, space filling particulate network, with each particle exhibiting an attractive interparticle force.

Yield stress plays an important role in a wide variety of industrial systems and products: the manufacture, storage, and application of paints, dyestuffs, pigments, paper coatings, printing inks, detergents, ceramic slips, carbon pastes, cosmetics, pharmaceutical formulations, and soon, and in the transportation of coal-water slurries, beneficiation of mineral ores and treatment, and disposal of fine particulate wet wastes. Indeed, in many situations pertaining to the processing of flocculated or semistabilized concentrated suspensions, yield stress turns out to be of greater relevance than viscosity. It is also of considerable theoretical interest as yield stress is dependent on the spatial disposition of particles, that is, their structural arrangement in the suspension and the nature and magnitude of the surface forces operating between them (Strenge, 1993). This is distinct from a classical suspension of noninteracting hard spheres, where model considerations negate the forces between particles and the spatial arrangement of particles is most usually geometric. Charged stabilized monodisperse particle suspensions also form crystalline yield stress fluids at a high volume fraction. Both of these examples show a mechanically rigidity as a result of a geometric particle constraints, the gel point of flocculated, ultrasmall particle suspensions may be as low as 5 vol. %.

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In order to predict the yield stress of a given suspension, as well as extract from the measured yield stress meaningful information on its microscopic structure, it is necessary to develop a theoretical framework for relating this property with the important suspension parameters. In the first instance, this requires a better understanding of the yield stress in its own right.

Yield stress, which is exhibited by a class of non-Newtonian particulate fluids, is defined as the minimum stress required for generating flow in the suspension. This apparently straight-forward description, however, includes a number of subtle and complex issues that are associated with this rheological phenomenon (Nguyen and Boger, 1992). These include, among others, distinction between the elastic and the true yield stress, relationship between the shear yield stress and the compressive yield stress, effect of the suspension's processing history, role of the measurement techniques and instruments, and, finally, the question of whether yield stress is a material property of the suspension which manifests abruptly at a threshold concentration of particles (gel point) or is an artifact due to limitations of the yield stress measuring instrument.

It is not our intention in this article to explore the nature of the yield stress measurement. Our objective is to take the results of a simple shear yield stress measurement for a flocculated particulate suspension using a vane technique (Nguyen and Boger, 1985), which has been shown to scale with the interparticle force (Leong et al., 1993) and present a plausible mathematical model of yield stress, which explicitly includes the size distribution of the particles and takes cognizance of conformation and structure of the particles and the particle interaction forces. The expected outcome was a systematic description of the determinants of the changes in the structure of flocculated suspensions across a wide volume fraction range.

Background

Although a large amount of experimental work including techniques and instrumental development has been carried out on yield stress, its analysis has remained mostly empirical and its quantitative description somewhat unsatisfactory. This is in spite of a number of attempts made, mainly in the 1960s and 1970s, which include the single particle and aggregate network models (Tempel, 1961, 1979), the floc model (Micheals and Bolger, 1962), the elastic floc model (Hunter and Nicol, 1968; Firth, 1976; Firth and Hunter, 1976a,b), and the cell model (Tanaka and White, 1980). As discussed elsewhere (Gupta, 1994; Leong et al., 1995), these models are based on assumptions and premises which are at best questionable. Moreover, the models do not explicitly account for the polydispersity of particles (which surely must play a significant role in determining yield stress) and have had only limited success in predicting the effects of particle size distribution, solid concentration, and the surface chemistry of the particles in aqueous suspensions.

Whereas yield stress at a fixed concentration was found to vary inversely with the square of the particle size or of some percentile size such as 10-percentile (Thomas, 1961; Buscall et al., 1987; Leong et al., 1995), the network models predict an inverse relationship with particle size and the cell model leads to an inverse cube dependence at the isoelectric point of a particle suspension and a more complex relationship elsewhere. The floc and elastic floc models, on the other hand, incorporate a secondary floc size effect. In contrast, the simulation studies of Doi and Chen (1989) suggest that the cluster mass and size are not the key parameters for determining the rheological properties of flocculated suspensions.

Yield stress increases rather steeply with an increase in the solid content of the suspension. The power law representation of yield stress shows a value of 3 (Thomas, 1961) or 4 (Leong et al., 1995) for the exponent on ϕ, the volume fraction of a particulate phase in the suspension. For compressive yield stress of filter cakes in ultrahigh pressure filtration cells, the exponent can become as high as 8 to 10 or even more. The cell model reflects the measured trends in yield stress at the i.e.p. insofar as it has a 2/3 power dependency on ϕ at very low solid concentrations, which tend to infinity as the loading approaches dense packing. In this context, the ability of some models to fit data and extract apparently fractal information may reflect simply an ability to linearize the power law dependency over a relatively small volume fraction range.

On the whole, the deficiencies in the existing models call for a fresh approach to the problem. We propose one such approach where the focus is not so much on the suspension per se as on the particle structure therein. Alternative approaches to the problem such as utilizing the concept of fractals is fundamentally different from ours and, although not mutually exclusive, is more akin to detailing the nature of the interparticle force than the yield stress.

Irrespective of whether the particles are suspended as singlets, doublets, chains, in more isometric clusters, or some combination of these entities, the presence of a yield stress, by definition, implies the existence of a 3-D, mechanically rigid particulate structure. The structure is not regular, but it spans the whole fluid space with localized gaps, if necessary. That such a structure is realizable even in relatively dilute suspensions may be inferred from the data compiled by Allen (1982) who tabulates 36 space filling so-called nonsimple regular packings of equal spheres in which three configurations have a coordination number of three with solid concentrations of 5.6, 4.5, and 4.2 vol. % only.

It is therefore possible to visualize the structure as a bed of loosely or, depending on the solid concentration, densely packed particles, with certain qualifications:

(1) Unlike in the conventional bed of particles, gravity plays a negligible role and the stability of the assemblage is primarily due to interparticle forces of attraction.

(2) As demonstrated by the 2-D aggregation model experiments (Horvolgyi et al., 1994) and the 2-D and 3-D computer simulation studies (Doi and Chen, 1989a,b; Sunada et al., 1993; Haw et al., 1994), all neighboring particles that lie directly in the line-of-sight need not be in contact with the reference particle. In other words, particles are distributed not only in their coordination number but also in the interparticle separation distance from the nearest neighbors.

(3) The coordination number increases and the proportion of neighbors not in direct contact decreases concurrently with an increase in the volume fraction of solid phase.

Buscall and coworkers (1984) describe this change in terms of the progressive engagement of the floc tentacles with rapid

elimination of weak, low coordination linkages. Eventually, when a high enough solid concentration is reached, all nearest neighbor particles lie in contact with any given central particle. Note that by contact, we mean the closest permissible surface separation between two particles in the presence of a tightly bound layer(s) of water molecules or strongly adsorbed film of surfactants and other hydrated products, as the case may be. In the former case, the closest distance of approach in coagulated clusters is customarily taken to be about 5.5 Å, which corresponds to two layers of adsorbed water molecules.

Yield Stress Model

The staring point of the proposed yield stress model is Rumpf's widely quoted derivation for the tensile strength of a bed of randomly packed monosize spheres (Rumpf, 1962). For the sake of continuity, we first state the principal equations of the model and then extend these to an expression for the yield stress of suspensions of size distributed particles. Consider a randomly oriented plane slicing through a bed of spherical particles of diameter X. As shown in Figure 1, the probability that the center of any arbitrarily chosen sphere cut by the plane lies at a distance z, $0 \le z \le X/2$, and below the plane is simply $2/X$. Therefore, the mean area of the disks generated from the spheres cut by the plane is

$$a = \int_0^{X/2} \pi \left(\frac{X^2}{4} - z^2 \right) \frac{2}{X} dz = \frac{\pi}{6} X^2 \tag{1}$$

The number of spheres sliced in a unit area of the cut plane is as follows:

$$n = \frac{1 - \epsilon_A}{a} \tag{2}$$

where the areal porosity ϵ_A is equal to the volume porosity ϵ_V, which, of course, is equal to 1-ϕ. Hence, combining Eqs. 1 and 2 yields

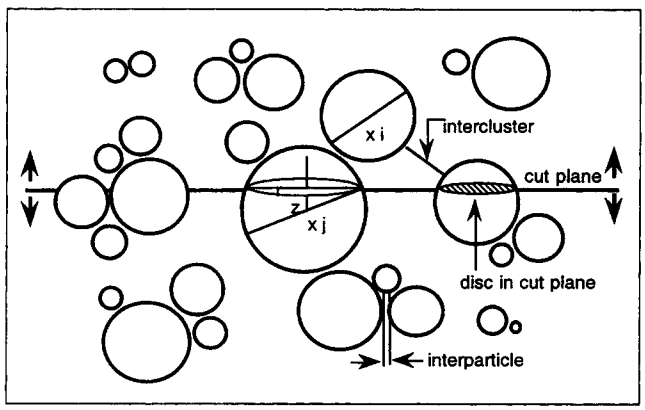

Figure 1. Randomly oriented plane slicing through a bed of spherical particles.

$$n = \frac{6}{\pi} \frac{\phi}{X^2} \tag{3}$$

If H is the bonding force between two monosized neighboring particles, the mean force F_m on a particle in the normal direction to the cut plane due to all neighbors coordinated around the exposed dome of the sphere is

$$F_m = \frac{HK(\phi)}{2} \int_0^{X/2} \frac{X^2 - 4z^2}{X^3} dz = \frac{HK(\phi)}{6} \tag{4}$$

where K is the coordination number of the particle. The tensile strength P of the bed is n times F_m which from Eqs. 3 and 4 is

$$P = \frac{\phi HK}{\pi X^2} \tag{5}$$

Molerus (1975) later extended this equation to any isotropic normal stress and isotropic normal interparticle bonding force. Tsubaki and Jimbo (1984) cite Nagao as well as Kanatani to the effect that the equation is a general expression for relating stress and force at the contact of particles, irrespective of tensile, compressive, or shear stress.

In order to extend the Rumpf-Molerus model to size-distributed particles that are usually encountered in suspensions, it is more convenient for numerical computations to break up the distribution into discrete sizes in which m_i is the mass fraction of particles of size X_i, $i = 1,2,3 \ldots$ It will be seen that the expression for yield stress now becomes

$$P = \frac{1}{6} \sum_j n_j \sum_i K_{ij} H_{ij} \tag{6}$$

where n_j is number of spheres of size X_j in the cut plane and K_{ij} is the mean number of spheres of size X_i coordinated around a sphere of size X_j in a bed of size distributed particles. So far, H or H_{ij} for a system of particles with a size distribution has been defined as the bonding force between two spherical particles in contact (see Eq. 4). Expressing the interparticle or colloidal force in terms of the DLVO theory (Hunter, 1991), we will in this article consider only that case where there is *no long-range electrostatic force* and only a van der Waals attractive force. We will also need to address the problem of zero separation as described by Leong et al. (1993). Thus, at a particular minimum surface separation h_o, there is a hard wall repulsion added to the van der Waals attraction to give an attractive well at $h_o/2$ out from each sphere. The force of attraction due to van der Waals interactions between two particles of size X_i and X_j is

$$H_{ij} = \frac{1}{12h^2} \left[\frac{X_i X_j}{X_i + X_j} \right] \tag{7}$$

where A is Hamakar constant and h is the surface separation distance between the two particles. The total area of all

disks formed in the cut plane from spheres of size X_j is given by

$$n_j a_j = (1-\epsilon_A)S_j = \phi S_j \tag{8}$$

where Sj is a fraction of the surface area of powder belonging to the particles of size X_j, that is

$$S_j = \frac{m_j}{X_j \sum_j \frac{m_j}{X_j}} \tag{9}$$

and a_j, the mean disk area belonging to the jth size particles, is given by replacing X in the righthand side of Eq. 1 by X_j. Substitution of the resulting expression in Eq. 8 yields

$$n_j = \frac{6\phi}{\pi X_j^2} S_j \tag{10}$$

In a series of articles Suzuki and coworkers (1981, 1983, 1985) have shown that the number of spheres of size X_i coordinated around a Xj size particle in a bed of size distributed spheres is given by

$$K_{ij} = S_i K_{ij}(b) \tag{11}$$

where $K_{ij}(b)$ is the number of X_i particles that are coordinated around a X_j particle in a binary mixture of these sizes only, and it is a function of the size ratio X_j/X_i and the coordination number $K(\phi)$ in a bed of monosize particles

$$K_{ij}(b) = 0.134K(\phi)\left[\frac{\frac{X_j}{X_i}+1}{1+\frac{X_j}{X_i}-\sqrt{\frac{X_j}{X_i}\left(\frac{X_j}{X_i}+2\right)}}\right] \tag{12}$$

Substitutions of Eqs. 7 and Eqs. 10–12 into Eq. 6 finally results in the desired expression for yield stress

$$P = \frac{0.011}{\pi}\frac{A\phi K(\phi)}{h^2(\phi)}\sum_j \frac{S_j}{X_j}\sum_i S_i \times\left[\frac{X_i}{(X_j+X_i)-\sqrt{X_j^2+2X_iX_j}}\right] \tag{13}$$

where both K and h are shown as dependent on the volume fraction solid in the suspension. The model can be implemented provided these functional relationships are known, as is discussed next.

At least a dozen or more equations have been proposed for relating coordination number K with volume fraction solid ϕ of monosize spheres (Suzuki et al., 1981). These are meant primarily for a gravity-stable bed of particles in close contact with relatively high values of ϕ. The relationship of Gotoh cited by Suzuki et al. (1981)

$$K(\phi) = \frac{36}{\pi}\phi; \qquad \phi \le 0.47 \tag{14}$$

is an exception in that it is more relevant to the region of interest for yield stress of suspensions, where ϕ is nominally in the range 0.05 to 0.45. Earlier, Iwata and Homma (1974) assumed a binomial distribution for the coordination number and a Gaussian distribution for the contribution by regular geometric packings for computing the distribution of nearest neighbors in a randomly packed bed in the range $0.1 \le \phi \le 0.7$. Figure 2 shows the mean coordination number plotted as a function of ϕ, which can be approximated by a straight line in the range $\phi \le 0.5$. The Gotoh equation is also shown in Figure 2. The two relationships are quite comparable and the difference in slopes is somewhat irrelevant at this juncture, as should become clear later on. Accordingly, we have chosen the Gotoh expression for inclusion in Eq. 13.

In light of the comments made in the background section on the nature of the suspension's structure in general and interparticle spacing in particular, it is convenient to introduce a crowding factor χ for relating the mean interparticle spacing h with ϕ in following manner

$$h = h_0 \chi(\phi) \tag{15}$$

where h_o is the closest distance of approach (as discussed earlier). Although we do not know the precise nature of the crowding factor, it must eventually tend to unity with increasing ϕ as flocculated clusters and chains linkup to form a dense continuous close packed network.

Model Verification

The characterization of powders and preparation of their suspensions were discussed by Leong et al. (1993), and the

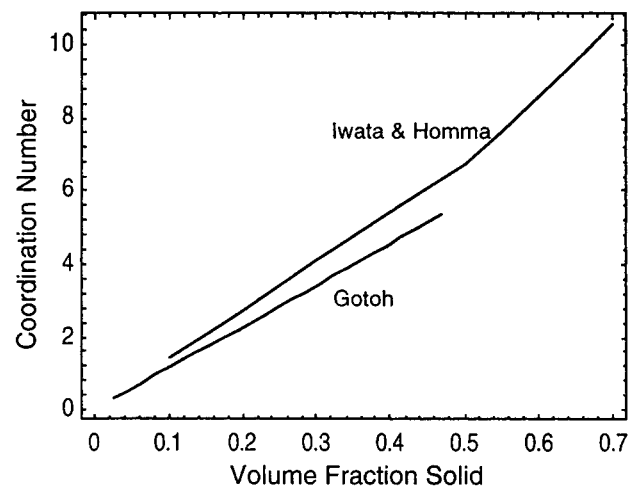

Figure 2. Relationship between coordination number and volume fraction solid in a bed of particles according to Gotoh equation and the binomial-Gaussian model of Iwata and Homma.

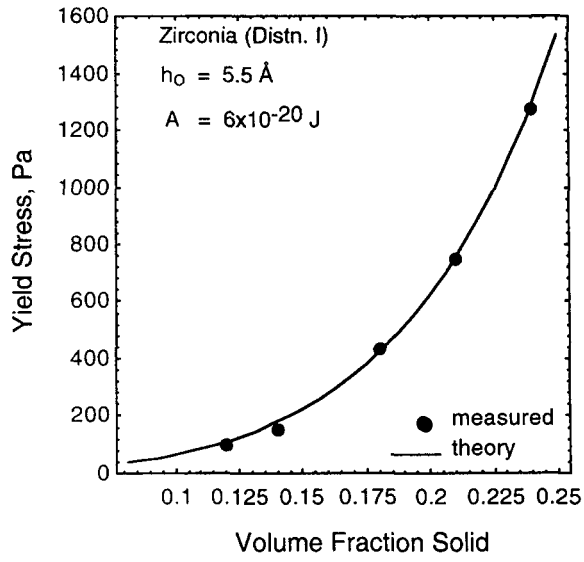

Figure 3. Measured and theoretical yield stress of suspensions made with zirconia Distribution I shown in Figure 4.

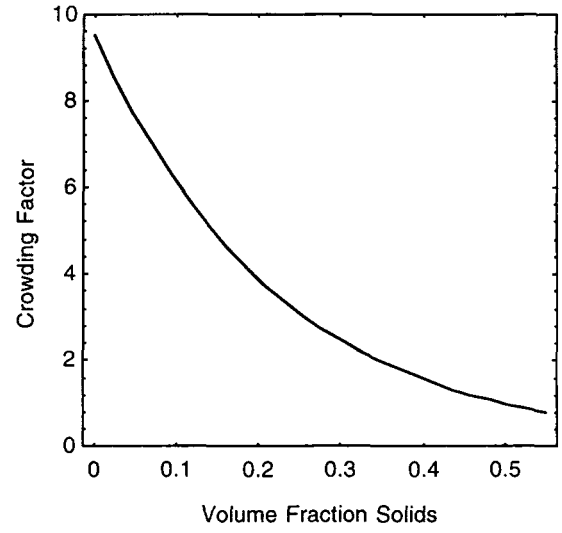

Figure 5. Computed crowding factor as a function of solid concentration.

measurement of yield stress by the vane-spindle technique has been described in detail by Nguyen and Boger (1992). All yield stress data discussed in this article pertain to coagulated suspensions at the isoelectric point. This ensures that there is no electrostatic repulsion contribution to the force of interaction. The Hamakar constant for zirconia and titania in water was calculated using Liftshitz theory and spectroscopy data and reconfirmed with atomic force microscope measurements (Larson et al., 1993). These values are 6.5×10^{-20} and 6×10^{-20} Joules for rutile and zirconia, respectively. The closest distance of approach h_o for zirconia was assumed to be 5.5 Å, corresponding to one water molecule of 2.75 Å diameter adsorbed irreversibly to each surface. Figure 3 compares the measured yield stress with the theoretical yield stress at different solid concentrations of a zirconia powder whose size distribution is labeled as "Dist. I" in Figure 4. Not surprisingly, the overall agreement is quite good since the crowding factor was adjusted to force fit the model in Eq. 13 with the experimental data. The resulting crowding factor could be described by the following expression

$$\chi = 9.5\exp[-4.5\phi] \tag{16}$$

Figure 5 shows the plot of the crowding factor which starting from about 9 decreases to unity as the volume fraction of solid in the suspension approaches 0.5. In other words, the mean separation distance in the vicinity of the gel point (the point at which the 3-D flocculated structure first exhibits a yield stress) is about nine times the closest distance of approach and all neighbors are in contact with the central particle at about 50 vol. % solid concentration. Incidentally, the

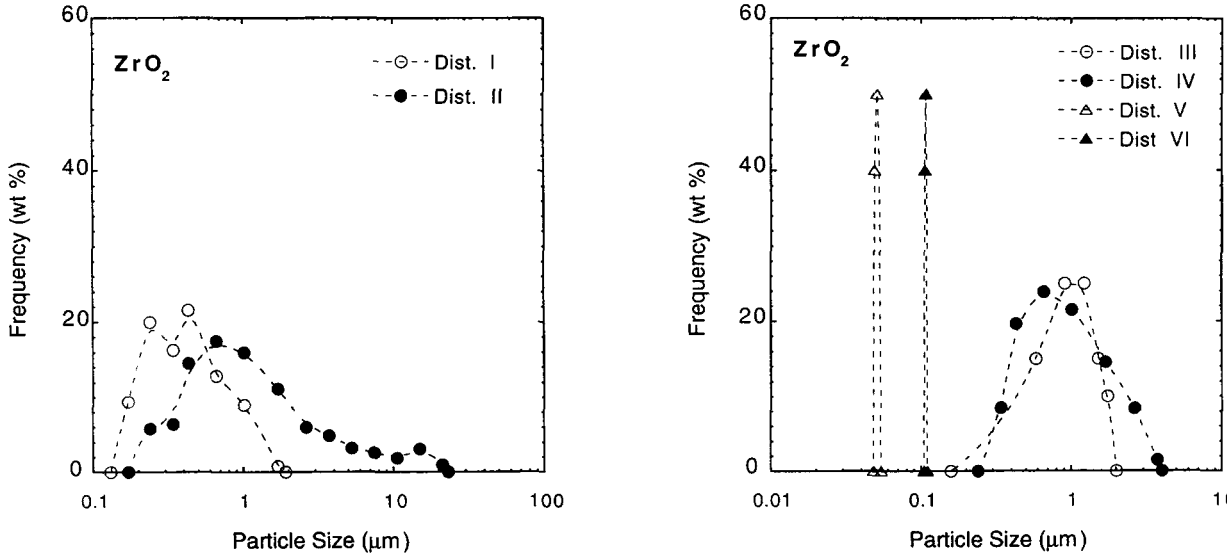

Figure 4. Particle-size distributions of six zirconia powder samples.

coordination number at this solid fraction in a bed of spheres is 6 to 7. Equation 16 was employed without any modification in the computation of yield stress for all other systems. Although the form of χ is by its nature empirical, it in combination with $K(\phi)$ reflects the coordination and interparticle spacing in a flocculated suspension. The true test of the validity of the form of χ is thus in its application in an unperturbed form to a variety of particle size and size distribution.

Figure 4 presents size distributions of six zirconia samples tested in the present study. Two distributions are close to single-sized, and because of the limited availability of the material, were used in low concentration studies up to 2.5 vol. %. Four further polydisperse samples were tested in the relatively narrow range of 16.9 to 18.1 vol. % solids. Distribution II had the broadest size range. Distribution III was right skewed, while the other three were left skewed. The theoretical and the measured yield stress for all of these distributions are compared in Figure 6.

Although Distributions I, II, and IV have similar shapes, the highest yield stress is exhibited by Distribution I. This is attributed due to the presence of a higher level of fines. Distributions II and IV have comparable amounts of fines, but the yield stress of the former is significantly higher because of its more pronounced polydispersity. On the other hand, Distributions II and III differ considerably in both shape and size dispersion, and yet their yield stress values are similar. These results suggest that the size distribution plays a highly complex role in determining yield stress, a factor which our model is able to account for with reasonable accuracy.

Effect of Additives

Under favorable conditions, the yield stress decreases in the presence of surfactants adsorbed on the surface of the particles. If t Å represents the diameter of an irreversibly

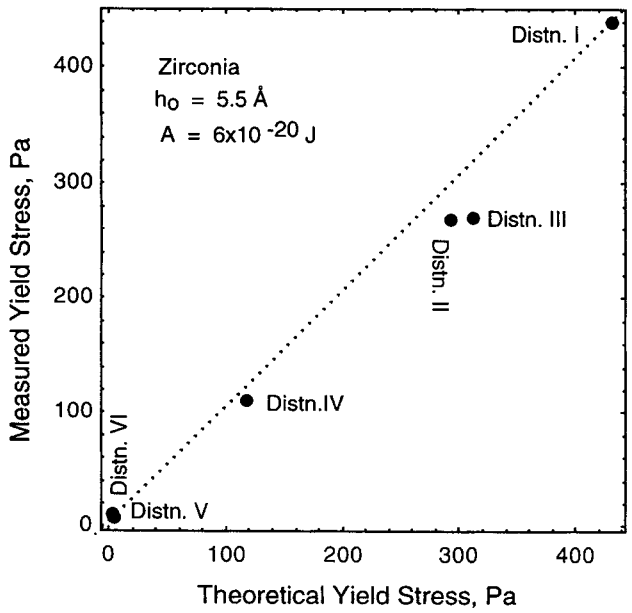

Figure 6. Measured and theoretical yield stress of suspensions made with zirconia of six size distributions.

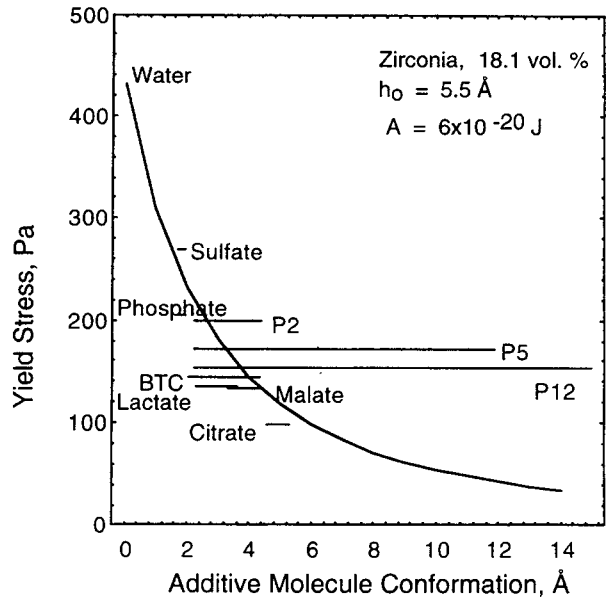

Figure 7. Yield stress of a zirconia suspension treated with different surfactants.

adsorbed molecule, the closest distance of approach between two particles may increase in the following manner

$$h_{o,ad} = h_0 + 2t \tag{17}$$

Substitution of the extended separation distance $h_{o,ad}$ in place of h_o in Eq. 13 permits us to estimate the yield stress of suspensions that have been treated with surfactants of different sizes. Again, we consider systems of zero electrostatic repulsion (that is, all adsorbed surfactant are at a pH and surfactant concentration that gives zero zeta potential). Figure 7 shows yield stress of 18 vol. % zirconia (Dist. I) as a function of diameter t. The measured value of the yield stress for a suspension is given by the horizontal line and the extent of the line takes into account all molecular configuration (Leong et al., 1993). The agreement on the whole is quite satisfactory, considering especially the uncertainty that exists in our knowledge of the conformation of the adsorbed molecules.

Suspensions of three pigment grade titania powders, designated as filter discharge, final product, and trimethylpropane (TMP) treated final product, were also tested against the yield stress model. The size distributions of the powders in Figure 8 show that the final product samples are much finer than the filter discharge titania, however, the untreated and the TMP treated final products are similar. Figure 9 shows that reasonable agreement with the model is possible in the case of the filter discharge powder provided h_o is increased to 8.75 Å, implying the presence of approximately three adsorbed layers of water molecules or some other form of adsorbed species between the particle surfaces. This conclusion is in conformity with the generally held belief that titania has a greater tendency to hydrate than zirconia.

The yield stress data reveals that for the same solid loadings, the yield stress of coarser filter discharge powder is higher than that of the micronized-milled (that is, finer) final product. With currently available knowledge, it is difficult to

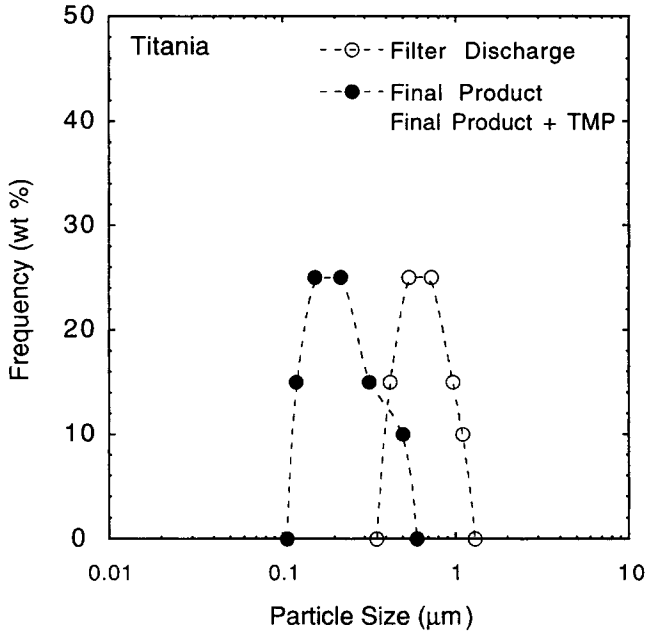

Figure 8. Particle-size distributions of titania powder samples.

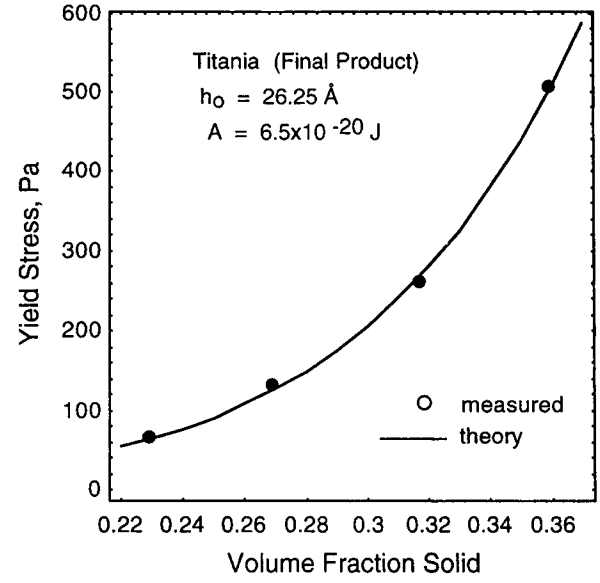

Figure 10. Measured and theoretical yield stress for final product titania.

deal with such seemingly anomalous behavior without making assumptions regarding the particulate structure. One possibility is to assume that the closest distance of approach h_o between two particles is greater in the case of the finer titania powders which, of course, has the same effect as increasing the preexponential term in the crowding factor in order to scale up h_o. The model curves for yield stress in Figures 9 and 10 were calculated with h_o equal to 26.25 and 30 Å, respectively. The agreement with the measured yield stress is then quite good over a fairly broad range of solid loading, and the increase in h_o in the presence of TMP is systematic with the expected change for a molecule of this size. The measured and theoretical yield stress for TMP treated final product titania is shown in Figure 11.

Despite the agreement, there is no fundamental basis for the increase in h_o and an equally likely explanation is that the particle-sizing data for the micronized material is not representative of the true particle size (that is, the particles were not as aggregated as sizing would suggest) or that the continuity of the alumina-silica coating on the particles changes on micronization. Either explanation is more pleasing than a change in h_o, despite the fits in Figures 9 and 10, because the form of the crowding factor stays constant. It also serves to highlight that the comparison of these samples may not be appropriate since the integrity of the surface coating is unlikely to be constnat throughout the process.

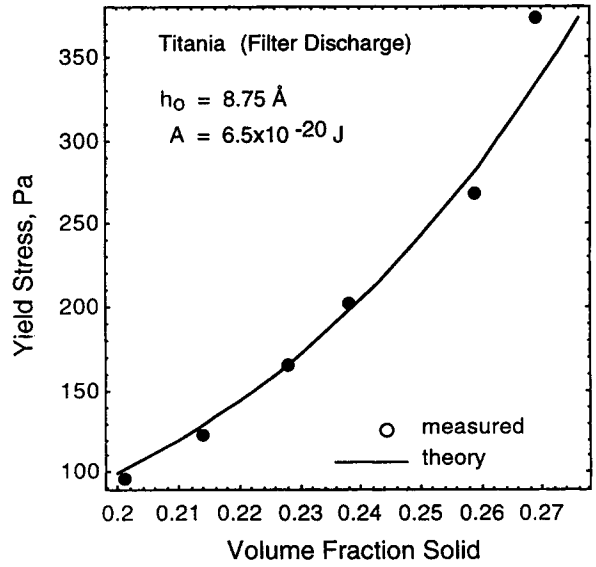

Figure 9. Measured and theoretical yield stress for filter discharge titania.

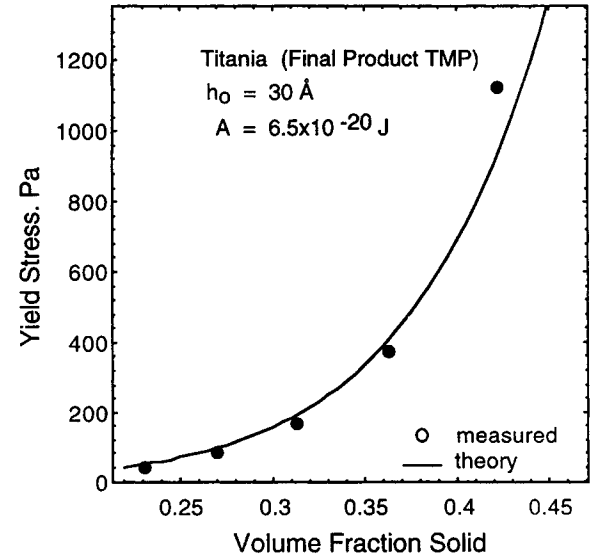

Figure 11. Measured and theoretical yield stress for TMP treated final product titania.

Discussion and Summary

A more realistic model of yield stress than what has been presented here would in all likelihood start with a trivariate distribution in particle size, coordination number, and interparticle distance. However, this more general approach immediately presents some formidable problems in derivation/identification of the distribution from first principles or experimental data. It, therefore, becomes necessary to resort to appropriate average values for these random variables. The difficulty is compounded by the fact that the coordination number and interparticle spacing are unlikely to be stochastically independent: intuitively, an increase in coordination should be accompanied by narrowing of distances between the neighbors. It turns out that because of the K/h^2 term in the yield stress model in Eq. 13, these two act as scalar for each other. As a consequence, it is not possible to conclude from the satisfactory agreement between the experimental data and the model predictions that the Gotoh function and the crowding factor do indeed faithfully mirror the microstructure of the suspension. What may be inferred is that the effect of the volume fraction solid in the suspension has been taken into account adequately through its functional relationships with K and h.

These deficiencies not withstanding, we have constructed a theoretical framework which utilizes reasonable and generally accepted values of the Hamakar constant, interparticle spacing, and coordination number along with the particle-size distribution of the powder to estimate an important rheological property of particulate fluids with an acceptable margin of error. The robustness of the model is reflected in the ability to describe both a zirconia and a titania particulate system and, more recently, this has been extended to alumina without adjustment of the form of $K(\phi)$ or $\chi(\phi)$ (Kapur et al., 1996). In all cases, particles sit at the potential energy minimum and although it would be convenient to have an independent measure of h_o, the values for the distance of the closest particle approach as predicted appear reasonable in the context of work using x-ray diffraction on well characterized clay suspensions (Tateyama et al., 1996).

The data interpretation involving a number of size distributions clearly demonstrates the role of particles in the lower size range in dominating the yield stress of a suspension. This confirms the efficacy of taking, for example a ten percentile value for the particle size rather than a mean size for widely distributed particle systems to scale the yield stress although the data also confirms the need to consider the whole distribution adequately. Comparisons of the zirconia data (presented here) to a phenomenological scaling model, assuming a percentile size, is not presented here, however, an adequate comparison can be made with a scaling model elsewhere in the literature (Leong et al., 1995).

In summary, the model presented here, while not generalizable without application to a number of other model systems, at least reflects observed trends in the yield stress of real particle suspension systems across a wide volume fraction range.

Acknowledgments

The work was supported by funding through the Advanced Mineral Products Research Centre, a Special Research Centre of the Australian Research Council. Discussions with Professor DYC Chan are gratefully acknowledged.

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Manuscript received May 30, 1996, and revision received Nov. 18, 1996.