

Yield stress for particle suspensions within a clay dispersion

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Synopsis

This article focuses on suspensions of coarse particles within a clay dispersion. The behavior of such suspensions is generally dictated by the colloidal fine fraction, notably its yield stress. The dependence of this yield stress on the solid concentration (in coarse particles) is examined. It has been experimentally shown that adding coarse particles usually induced an increasingly marked enhancement of yield stress. However, in some cases, adding a small amount of coarse particles led to a decrease in bulk yield stress. We propose two mechanisms responsible for variations in bulk yield stress. First, at low concentrations, depletion of clay particles may be sufficient to induce an increase in the bulk yield stress. Two values for the depletion layer thickness have been found depending on the coarse particle type. At large concentrations, the substantial increase in bulk yield stress has been ascribed to the development of a coarse particle network within the dispersion. In this case, yielding results from the breakdown of indirect (lubricated) contacts between particles. © 2001 The Society of Rheology. [DOI: 10.1122/1.1343879]

I. INTRODUCTION

Suspensions of solid particles are frequently encountered in manufacturing processes and in natural flows. Typical examples include debris flows on mountain slopes, which cause death and property damage each year, and fresh concrete, extensively used in building. For such materials, engineers are greatly interested in inferring the bulk flow properties (to predict workability for mortar, spreading for mud, etc.) directly from the particle size distribution without resorting to laboratory investigations, which are most often impractical and expensive. The article presented here is intended as a further step in this direction.

Particle size distribution and shear rate both influence the behavior of these suspensions. When the particle-size distribution is great, typically ranging from 0.1 μm to 1 cm, the interactions between particles and the surrounding fluid are varied. For relatively small shear rates, the finest particles are generally very sensitive to Brownian motion effects or colloidal forces while coarse particles experience frictional or collisional contacts or hydrodynamic forces. As a result, bulk behavior is very complex and depends on many parameters: solid concentration, size and shape of the particles, size distribution, the nature of the ambient fluid, and so on. To date, from both experimental and theoretical points of view, little is known about the rheological behavior of these suspensions.

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Within the context of coal slurries, Sengun and Probstein (1989a, 1989b, 1994) have performed a series of experimental investigations as well as a theoretical analysis on the high shear-rate limit (hydrodynamic behavior). They considered polymodal suspensions (i.e., with high size distribution) as bimodal suspensions, an important new concept; indeed, these suspensions can be seen as a suspension of force-free particles in a water–colloid dispersion. The colloidal fine fraction is assumed to act independently of the coarse fraction. Because it is the interstitial fluid, it imparts most of its rheological features to the entire suspension, like suspensions of noncolloidal particles within a Newtonian fluid. The coarse fraction is expected to contribute mainly to the rise in viscosity (through hydrodynamic dissipation).

A similar point of view was adopted by Coussot and Piau (1995) in their study of water–debris mixtures. These authors showed experimentally that (i) the type of bulk behavior is dictated by the presence of clay particles and (ii) both the solid concentration and the range of size distribution of coarse particles affect the rheological parameters. The yield stress varied with the coarse fraction concentration. This result contrasts with the approximation made by Sengun and Probstein (1989a, 1989b) on the noninteraction between coarse and fine fractions. Since the yield stress in such suspensions mainly originates from colloidal interactions, the observed increase (resulting from coarse particle addition) indicates that such interactions may indeed exist.

Independently, several experiments have been devoted to the rheology of fresh concrete, cement, and mortar (a mixture of sand, cement, and water). Over the last decade Banfill (1990, 1991, 1998, 1999) has performed extensive investigations on the parameters influencing mortar rheology. He has shown that mortar exhibits the viscoplastic behavior of fresh mortar after a process that he called *structural breakdown* (during shear, a significant part of links between cement particles is broken and adhesive contacts are replaced by lubricated contacts) [Banfill (1991)]. He also revealed that, at a given solid concentration, the rheological parameters were very sensitive to the sand fineness. For instance, he found that the yield stress was substantially enhanced when increasing the fine sand fraction [Banfill (1998, 1994)]. In their reviews on the concrete and cement rheology, Hu (1995) and Mansoutre (2000) reported several results published in the technical literature which showed a significant variation in the yield stress when the cement composition was changed. Furthermore, in her rheological study of tricalcic silicate (a major component of Portland cement, ranging in size from 3 to 100 μm), Mansoutre and co-workers (1999, 2000) used a controlled-stress parallel affixed to a parallel plate geometry in order to measure the variations in the bulk yield stress and the normal stress for different solid concentrations and cement compositions. She found that at low and intermediate concentrations yield stress resulted from colloidal interactions since it was linearly dependent on the ionic strength and that yield stress grew as a power function of the solid concentration. When the solid concentration exceeded a critical value, the yield stress increased much more rapidly and a nonzero normal stress arose. She interpreted this as a result of “*dilatant behavior*.” Moreover, she showed that the increment in yield stress produced by this phenomenon was to a large extent a linear function of the normal stress. She concluded that, at high concentrations, bulk yield stress resulted from both colloidal and frictional interactions.

The first objective of this study was to find the key parameters of the coarse fraction (solid concentration, grain shape, diameter) that affect the yield stress, with an attempt to explain the physical phenomena behind this variation by examining the reliability of the approximation on the noninteraction between solid fractions. To that end, we have investigated the effect of unimodal and bimodal distributions of the coarse fraction on the yield stress value. This series of experiments can serve as a discriminating test of the role

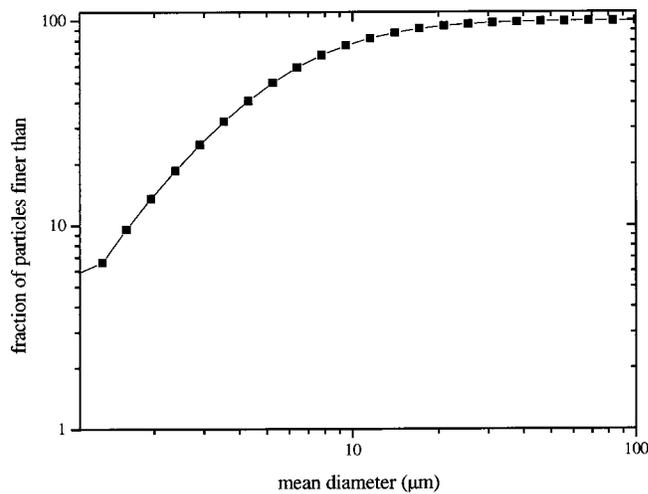


FIG. 1. Volume size distribution of the kaolin sample.

played by the type and size distribution of coarse particles. In addition, different theoretical models available for colloidal systems are examined and tested for further insight into the yield stress increase induced by the coarse fraction.

II. EXPERIMENTAL PROCEDURE

A. Materials

For the fine fraction, we used natural kaolin clay provided by Silice et Kaolin and by Prolabo (France). The particle density was approximately 2650 kg/m^3 . The chemical composition was kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) 99.84%, calcium 0.025%, chloride 0.025%, sulfate 0.0025%, and organic impurities 0.1%. The grain size distribution was measured by a Malvern laser granulometer (see Sec. II B for particulars). The volume median diameter of the particles was estimated to be $5.5 \mu\text{m}$ (see Fig. 1) while computation of the volume average diameter (d_v) gave $8 \mu\text{m}$ (defined as $\sum x_i d_i$ where x_i is the volume fraction of particles that have a diameter d_i). The number and surface average diameters were estimated to be 0.7 and $3.6 \mu\text{m}$, respectively. The relatively large mean particle size was approximately 1–20 times greater than the expected size of an individual particle (a plate-like rigid alumino-silicate particle, whose typical size ranges from 0.3 to $2 \mu\text{m}$), indicating that the dispersion was weakly flocculated. Indeed, kaolin particles in water form a colloidal dispersion. The colloidal interactions result mainly from van der Waals attraction between negative faces and positive edges (and to a lesser extent from electrostatic repulsion forces between faces). For our tests, the dispersion $p\text{H}$ ranged from 7.3 to 7.9 in water and was around the value ($p\text{H} \approx 7.5$) corresponding to the particle isoelectric point (neutrality of the double layer surrounding particles) [Huifang *et al.* (1991); Lagaly (1989); Melton and Rand (1977)]. Close to the isoelectric point, ionic strength has little influence on the yield stress and van der Waals attractive forces are predominant. To hinder flocculation completely, we should have substantially increased the $p\text{H}$ (up to 10) in order to have negative charges on both the edges and faces and thus repulsion between plates [Brown *et al.* (2000)]. This was not achieved here because we needed to estimate the mean size of the aggregates (see Sec. III).

TABLE I. Main features of solid particles (coarse fraction).

Material	Composition	d_v (mm)	Grain size distribution
1	Glass	0.36	Poorly sorted
2	Glass	0.97	Poorly sorted
3	Glass	2	Well calibrated
4	Glass	3	Well calibrated
5	Sand	0.33	Poorly sorted
6	Sand	1.2	Poorly sorted
7	Polystyrene	1.05	Well sorted

For each test, we prepared a clay dispersion by adding a given volume of kaolin to clear water. The dispersion was then vigorously mixed by hand for more than 20 min. The solid concentration in kaolin ϕ_k (kaolin volume to total volume) was usually 25%. The corresponding density of the dispersion was 1417 kg/m^3 , with uncertainty of less than 1%. For sensitivity tests, we used more concentrated kaolin dispersions (30% and 35%) and a 6% bentonite dispersion. The rheological characteristics of the dispersions were investigated using a Haake controlled-rate rheometer with a parallel plate geometry (gap: 3 mm, radius: 25 mm). The plate surfaces were roughened with fine sandpaper (equivalent diameter of sand granules 0.2 mm). As is usual for this kind of material [Coussot (1995); Coussot and Piau (1994)], we used a Herschel–Bulkley model to fit experimental data and estimate the yield stress, which was found to be 39 Pa, with uncertainty of less than 10%. Compared to other clays (especially smectites), kaolinite exhibits few thixotropic effects, but as with other clays, its flow curve may be characterized by a yield stress and minimum to low shear rates. At high shear rates, changes in particle interactions [Coussot (1995)] may affect the rheological behavior. Floc growth and particle ordering may also induce effects on the rheological behavior [Brown *et al.* (2000); Jogun and Zukoski (1999); Jogun and Zukoski (1996); Seidel *et al.* (1999)]. Thus, the Herschel–Bulkley model can be used only as a first approximation to fit experimental data.

For the coarse fraction, we used sand grains, polystyrene beads, and glass beads. The main characteristics of these materials are reported in Table I. Apart from 1.05 mm polystyrene beads as well as 2- and 3-mm-diam glass beads, the material was poorly sorted and graduated in size. The chemical composition of the glass beads was silica 73%, sodium oxide 13%, calcium oxide 8%, magnesium oxide 4%, and alumina 2%. For sand, we used sand extracted from the Hostun quarry, commercialized by Silice et Kaolin. We tested two samples by fine sand (volume average diameter of 0.33 mm) and medium sand (1.2 mm). Hostun sand is a natural sand widely used as a test material in French and European soil mechanics laboratories [Flavigny *et al.* (1990); Lancelot *et al.* (1996)]. Contrary to most river sand, quarry sand is not rounded and is very abrasive. The chemical composition of the sand was silica 99.17%, alumina 0.25%, iron oxide 0.17%, lime 0.14%, magnesia 0.14%, soda 0.05%, and potassium hydroxide 0.02%. Figure 2 gives the size distribution of the poorly sorted coarse materials determined using either a Malvern granulometer (for the fine glass beads) or sieves (for the sand and medium glass beads).

B. Experimental setup and procedure

To measure the size distribution of fine particles, we used a Malvern laser granulometer which records particle populations within the range of 0.1–2000 μm . This apparatus measures diffraction and diffusion of a laser beam across a dilute suspension of particles

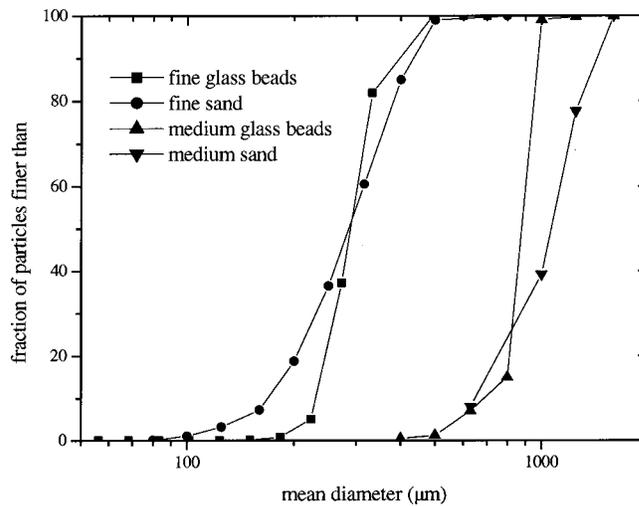


FIG. 2. Volume or mass size distribution of the poorly sorted materials.

in clear water (at constant temperature). It then infers the size distribution of the particles using specific methods (e.g., Fraunhofer's theory, assimilating particles to plate-shaped particles, for clayey materials). Different procedures were used to test the measurement sensitivity. For instance, to limit flocculation, ultrasonic waves and an antiflocculation agent (a 5% sodium-hexametaphosphate solution) were used. Adding phosphate ions limits flocculation caused by the edge-to-face attraction since these ions preferentially bind to plate edges [Nicol and Hunter (1970)]. Ultrasonic waves are used to break large flocs. For the materials tested, these two methods did not significantly change the particle size distribution (we observed a deviation of less than 20%). Moreover, for kaolin, we compared the results obtained with the laser granulometer with those given by the usual sedimentation test (as described in the French standard AFNOR NF P 94-068). Deviation in the mean size estimation between the two was less than 5%.

Determining the yield stress using laboratory rheometers is somewhat difficult due to the presence of the coarse fraction. Given the sole objective of determining the yield stress, we preferred to use a semiempirical method referred to as a "slump test." It involves filling a cylinder with the material to be tested, lifting the cylinder off, and allowing the material to flow under its own weight. The profile of the final mound of material as well as the difference between the initial and final heights can provide an estimation of the yield stress. So far this type of test has been used extensively to evaluate the workability of fresh concrete. More recently, attention has been drawn to the use of the slump test method as a means of measuring the yield stress of slurries. As such a test is still very new and almost confidential as to its rheometry, details of the experimental procedure and its limitations shall be presented.

Pashias and Boger (1996) developed an approximate theoretical model, inspired from an earlier model proposed by Murata, for inferring the yield stress τ_c from the difference (s) between the initial and final values. The authors have found

$$\frac{S}{h} = 1 - 2 \frac{\tau_c}{\rho gh} \left[1 - \ln \left(2 \frac{\tau_c}{\rho gh} \right) \right], \quad (1)$$

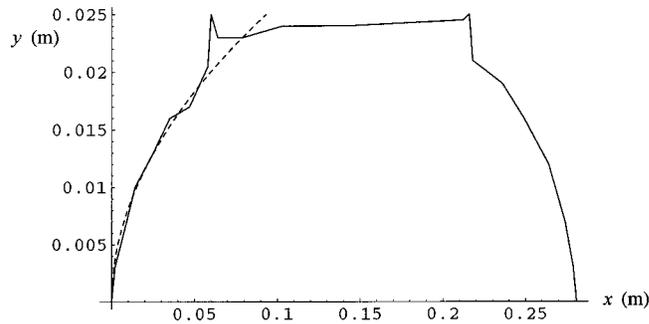


FIG. 3. Profile of a deposit obtained using a kaolin dispersion and cylinder 3. The dashed line represents the curve fitted from experimental data using Eq. (2).

where h is the cylinder height and ρ the material density. They tested several mineral suspensions and compared the yield stress value deduced from slump measurements to the ones obtained using a vane rheometer. Good agreement was found. Schowalter and Christensen (1999) used a similar approach with fresh concrete and a conical slump test. Close examination of experimental data published by Pashias and Boger (1996) shows deviation from the theoretical curve for yield stress values in excess of approximately $0.15\rho gh$. For yield stress values lower than $0.15\rho gh$ (or for $s/h > 0.4$), the uncertainty was less than 10% for their tests. An explanation of the deviation for higher yield stress values lies perhaps in the weakness of the assumption of elastoplastic behavior for very cohesive materials.

Coussot *et al.* (1996) developed an alternative approach based on an interpretation of the deposit shape. They showed that the free surface profile (the relationship between the material height y and the distance from the edge x) depends on the yield stress only. On a flat horizontal surface, the free surface profile has the following expression:

$$\frac{\rho gy}{\tau_c} = \sqrt{2 \frac{\rho gx}{\tau_c}}. \quad (2)$$

Comparisons between rheological data deduced from a (parallel plate) rheometer and free surface profile measurements showed acceptable agreement for fine mud suspensions and debris flow materials. The uncertainty was less than 20%, within the boundaries of acceptable uncertainty for rheometrical measurement. The calculation procedure was then critically reviewed and extended by Wilson and Burgess (1998). The main restriction in the use of Eq. (2) stems from the long-wave approximation, which implies that the mound height must far outweigh the extension of the deposit: $h - s \gg \tau_c / (\rho g)$.

Although the two procedures for estimating the yield stress can be applied to the slump test, they are restricted in their use due to the basic assumptions. In practice, we filled a cylinder with the material to be tested. We lifted the cylinder off. The slumping phase typically lasted a few seconds (for the materials tested) before the material stopped abruptly. No creep motion was then observed. This was probably due to a minimum in the flow curve, which inhibited creeping. We measured the slump height s and the free surface profile at different abscises from the edge $y_i(x_i)$. By using built-in routines in the Mathematica 4.0 software system, it is straightforward to solve nonlinear equation (1) or to fit a curve given by Eq. (2) from experimental data $y_i(x_i)$. An example is given in Fig. 3. Preliminary tests were performed to test both methods. We also used different types of cylinders. Table II presents the geometrical characteristics of each cylinder and the re-

TABLE II. Comparison of methods.

Cylinder	h (mm)	$2R$ (mm)	S (mm)	τ_c (Pa)	$\frac{s}{h}$	τ_c (Pa)	$\frac{\rho g(h-s)}{\tau_c}$
1 (steel)	108	94	81	51	0.7	46	7.4
2 (PVC)	111	43	87	43	0.78	78	3.2
3 (steel)	119	36	96	37	0.81	149	2.03

sults of the two tests. Table II also includes criteria which can serve to verify whether the computations are consistent with the assumptions upon which each rheometric treatment is based. It follows that, for the method presented by Pashias, and Boger (1996) the s/h ratio lies within the range of 0.75–0.81 and thus the model can be fully applied. The deviation between the yield stress value computed in this way and the one found using a parallel plate rheometer ranges from 5% (cylinder 3) to 30% (cylinder 1). For the method developed by Coussot *et al.* (1996), the $\rho g(h-s)/\tau_c$ ratio is slightly larger than 1; therefore it cannot be expected that such a method would provide accurate measurements of the yield stress. As a result, the deviation (compared with the actual yield stress value) ranged from 18% to 280%; this method was not suitable for these experimental conditions (material and cylinder). Consequently, only the results obtained using Pashias and Boger's method will follow. For practical reasons (notably for testing materials with high yield stress values), we mainly used the second cylinder (111 mm in height and 43 mm in diameter). Additional tests were carried out to test the reproducibility of the measurements.

The first source of uncertainty concerns the flatness of the mound top. As exemplified in Fig. 3, the top surface is not entirely flat: it is relatively bulged and surrounded by small levees. As values of slump height, we took average values of the entire surface. Uncertainty on s is about 1 mm and errors induced on the yield stress measurement can be as high as 10%. Forty tests were run to examine the distribution of measurements around their mean value (43 Pa) in the case of kaolin dispersion. For each test, the same sample was used and mixed at the beginning of the test. We slowly stirred the sample to avoid, as much as possible, incorporating air. The standard deviation of this test series was evaluated at 1.83. The probability distribution of experimental data was closer to a uniform distribution than to a Gaussian distribution. Tests were also carried out for glass bead suspensions within a clay dispersion (see Fig. 4). In that case, a dramatic decrease in the yield stress measurement was observed, followed by a rapid increase. The reproducible character of this phenomenon may indicate that after a given time a chemical reaction between the glass bead surface and the interstitial phase modified the fluid composition and consequently the yield stress. This point was not clear since, on the one hand, no variation in the pH was detected between the beginning and the end of the tests and, on the other hand, little influence of ion concentration was expected since the dispersion was close to the particle isoelectric point. Moreover, no such phenomenon was observed with suspensions of sand grains or polystyrene beads. The characteristic time associated with this reaction was long (several hours) if the suspension was at rest, but only a few minutes were required if the suspension was frequently set into motion. To avoid this problem, a suspension sample was prepared for each test and used immediately after preparation.

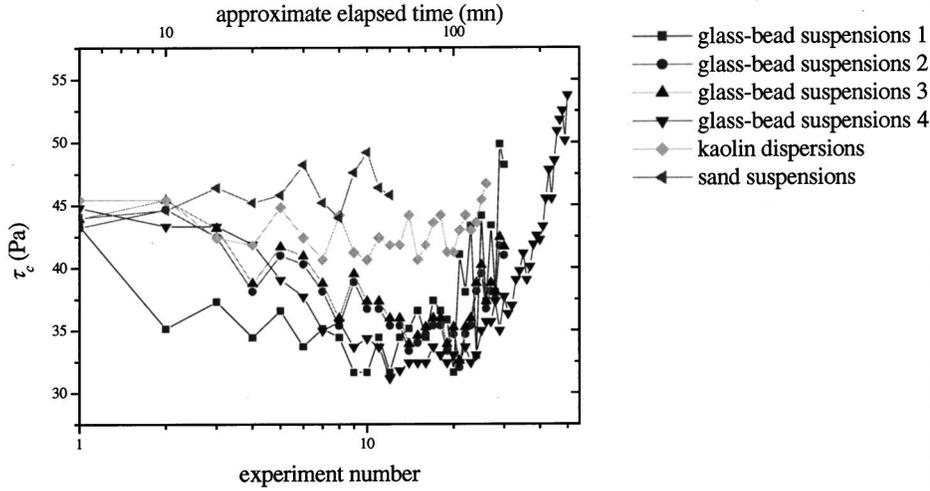


FIG. 4. Reproducibility tests. The solid lines represent the variation of the measured yield stress of glass bead suspensions (within a water–kaolin dispersion) at the same concentration ($\phi = 25\%$). The dashed line corresponds to the case of water–kaolin dispersion (at the same concentration, $\phi_\kappa = 25\%$). In the abscissa is the experiment number.

III. EXPERIMENTAL RESULTS

The experiments sought to determine the relationship between the yield stress of the tested suspensions and the solid concentration of the coarse fraction ϕ , defined as the ratio of the volume occupied by the coarse fraction to the total volume. To compare the results, it is convenient to scale the solid fraction by its maximum (random) value ϕ_m in order to compare the different suspensions. Moreover, the reduced fraction ϕ/ϕ_m is a key parameter in most theoretical models, since geometrical parameters characterizing particle arrangement (coordination number, mean distance between particles) are a function of the reduced fraction. Section III A will be devoted to estimating the maximum solid concentration for unimodal and bimodal suspensions. We will then present the experimental results for unimodal and bimodal suspensions in Secs. III B and III C, respectively.

A. Computation of the maximum solid concentration

For unimodal suspensions, experiments combined with numerical simulation lead to an accurate estimate of the maximum (random) solid concentration $\phi_m = 0.635 \pm 0.05$ [Meakin (1993)]. For bimodal suspensions, different models have been presented for predicting the maximum solid concentration ϕ_m^* . Here we used the analytical model developed by Gondret and Petit (1997) from a former model proposed by Ouchiyama and Tanaka (1981). The maximum solid concentration is expressed as a function of the size ratio λ (the diameter ratio of small to large particles) and the composition parameter ξ defined as the volume occupied by the small particles to the total volume of the coarse fraction. It is defined as the minimum value of two maximum solid concentrations ϕ_1^* and ϕ_2^* .

$$\phi_m^* = \min(\phi_1^*, \phi_2^*). \quad (3)$$

The first maximum solid concentration gives the limiting curve of a bimodal concentration:

$$\phi_1^* = \frac{\phi_m}{1-\xi} (\xi \rightarrow 0), \quad (4)$$

$$\phi_1^* = \frac{\phi_m}{1-(1-\xi)(1-\phi_m)} (\xi \rightarrow 1). \quad (5)$$

For middle values of ξ , this model overestimates the maximum solid concentration, which must be replaced by the value determined using the cell approach proposed by Ouchiyama and Tanaka (1981). Following the work of Gondret and Petit (1997) (and correcting a typographical error), it can be found that the second maximum solid concentration is

$$\phi_2^* = \frac{N_S \tilde{d}_S^3 + N_L \tilde{d}_L^3}{\frac{N_S}{\Gamma} (\tilde{d}_S + 1) + N_L \left\{ (\tilde{d}_L - 1)^3 + \frac{(\tilde{d}_L + 1) - (\tilde{d}_L - 1)^3}{\Gamma} \right\}}, \quad (6)$$

where N_S and N_L represent the fractions of small and large spheres, \tilde{d}_S and \tilde{d}_L , the diameters of the small and large particles normalized by the mean diameter \tilde{d} , and Γ a parameter. Each of these parameters are functions of ξ and λ :

$$N_S = \frac{\xi \lambda^3}{\xi \lambda^3 + (1 - \xi)}$$

and

$$N_L = \frac{1 - \xi}{\xi \lambda^3} N_S, \quad (7)$$

$$\tilde{d}_S = \frac{d_S}{\tilde{d}} = \frac{\xi \lambda^3 + 1 - \xi}{\xi \lambda^3 + (1 - \xi) \lambda}$$

and

$$\tilde{d}_L = \frac{d_L}{\tilde{d}} = \lambda \tilde{d}_S, \quad (8)$$

$$\Gamma = 1 + \frac{4}{13} (8\phi_m - 1)$$

$$\times \frac{N_S (1 + \tilde{d}_S)^2 [1 - (3/8)/(1 + \tilde{d}_S)] + N_L (1 + \tilde{d}_L)^2 [1 - (3/8)/(1 + \tilde{d}_L)]}{N_S \tilde{d}_S^3 + N_L [\tilde{d}_L^3 - (\tilde{d}_L - 1)^3]}. \quad (9)$$

Good agreement is obtained with experimental data and numerical simulation results, apart from small size ratios (λ less than 3) for which the model underestimates the maximum solid concentration [Gondret and Petit (1997)]. We have reported typical variations of the maximum solid concentration with respect to both parameters ξ and λ in Fig. 5.

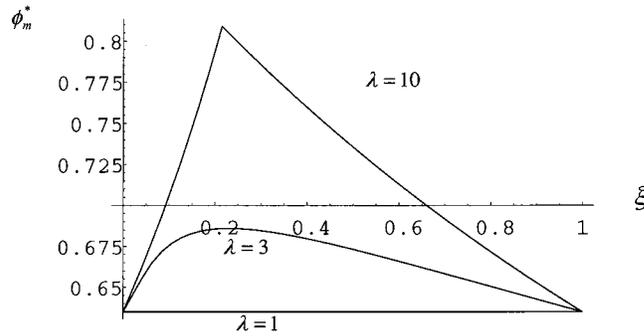


FIG. 5. Maximum solid concentration of a bimodal suspension as a function of the proportion of small spheres ξ for different size ratios λ .

B. Unimodal suspensions

Figures 6 (well-sorted materials) and 7 (poorly sorted materials) show the logarithmic variation of the yield stress as a function of solid concentration in the case of unimodal suspensions. For both Figs. 6 and 7, we have scaled the solid concentration by the maximal value $\phi_m \approx 0.635$. It is worth noting that this value is suitable for suspensions of perfectly monosized spherical particles. For irregular grains or particles that are graduated in size, such a value is approximate. A monotonic increase of the yield stress for increasing solid concentrations can be seen in both Figs. 6 and 7. This behavior is very similar to that observed for the viscosity of force-free particle suspensions within a Newtonian fluid. Apart from this common important feature, well-sorted and poorly sorted materials behave differently. We will first review the main characteristics for each material class, then examine the differences between them.

With regard to well-graded materials, we consider that, on the whole for the range of materials tested, the yield stress variation did not depend on the bead characteristics (diameter, material). At low reduced solid fractions ϕ/ϕ_m , typically less than 30%,

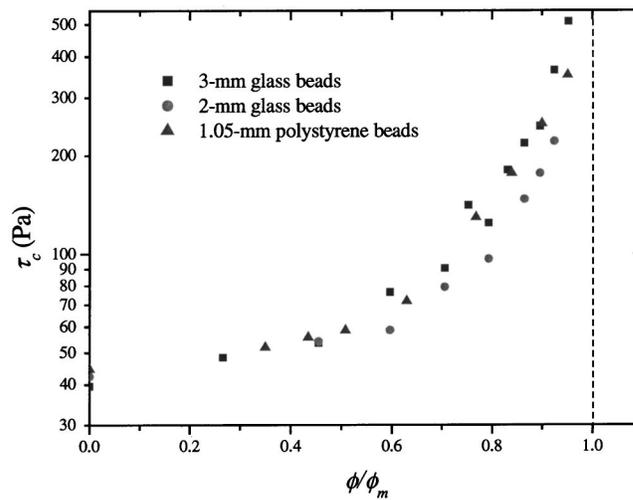


FIG. 6. Variation of the yield stress as a function of the solid concentration (of the coarse fraction) for unimodal suspensions of well-sorted beads.

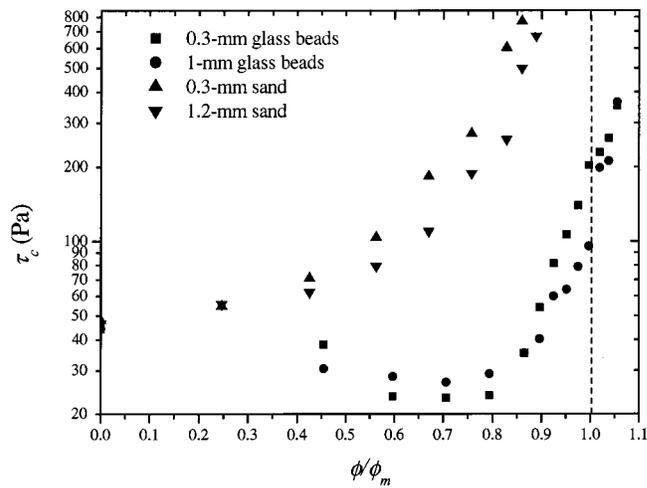


FIG. 7. Variation of the yield stress as a function of the solid concentration for poorly sorted materials for unimodal suspensions of poorly sorted particles.

adding particles produces effects whose magnitude matches the uncertainty of the measurements. Reproducibility tests performed for various samples of the same mixture at a solid concentration of 30% have shown that the deviation from one to another is less than 10%. For intermediate reduced concentrations (between 30% and 70%), a significant increase can be observed in Fig. 6. Moreover, the experimental points do not belong to a single curve. The data scattering (roughly 30%) is much larger than the uncertainty of the measurements (10%). For concentrated suspensions (reduced solid fraction in excess of 70%), reproducibility tests showed a wider deviation from one test to another for the same material: the range of variations of the yield stress was found to be as high as 30% of the mean value. When the solid concentration was close to the maximum solid concentration ($\phi/\phi_m \rightarrow 1$), the yield stress increased sharply and continuously. With our experimental conditions, the largest reduced solid fraction ϕ/ϕ_m was approximately 0.95. It was not possible to achieve larger values because, after lifting the cylinder up, we could not detect any slumping.

In contrast with well-graded materials, Fig. 7 shows that, for poorly sorted materials, the yield stress variation was mainly sensitive to the particle type. Indeed, data for sand and glass beads define two distinct curves independent of the particle size. For sand, the yield stress increase was very regular and more pronounced compared to that for glass beads. Glass beads were characterized by peculiar behavior. First, for reduced fractions up to approximately 0.7, the bulk yield stress dropped to a minimum value, equal to approximately half the kaolin yield stress. After reaching this minimum it increased significantly when the reduced solid fraction came closer to 1; since we scaled the solid concentration ϕ by the maximum value suitable for monosized particles, it is not surprising that the reduced fraction ϕ/ϕ_m exceeded 1 for slightly polydisperse materials. The position of the minimum was reproducibly located at $\phi/\phi_m \approx 0.7$. Further tests were carried out with more concentrated kaolin dispersions (30% and 35%) and 6% bentonite dispersion. They led to results similar to those obtained with a 25% kaolin dispersion.

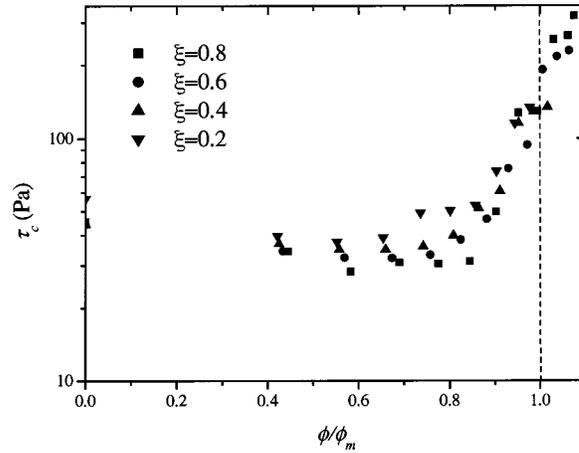


FIG. 8. Variation of the yield stress as a function of the solid concentration (of the coarse fraction) for a bimodal suspension of glass beads. The diameters used were 1 and 3 mm ($\lambda = 3$).

C. Bimodal suspensions

First, Figs. 8 and 9 specify the measurements obtained with glass beads for two different size ratios ($\lambda = 3$ and 10). As was the case previously for monosized particles, the yield stress increased as a function of the solid fraction apart from poorly sorted glass beads, for which a yield stress decrease was observed at low concentrations. The behavior in the vicinity of the maximum solid concentration was also similar, except that it was possible to obtain solid concentrations in excess of the theoretical maximum value given by Eq. (1). This is not surprising since Ouchiyama and Tanaka's (1981) model used for computing the maximum random solid concentration is known to underestimate ϕ_m [Gondret and Petit (1997)]. The experimental curves corresponding to each value of ξ were very close but did not coincide perfectly. Due to the uncertainty of the theoretical

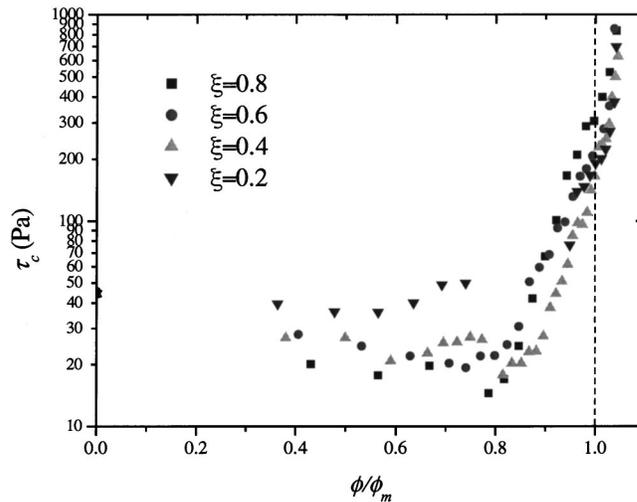


FIG. 9. Variation of the yield stress as a function of the solid concentration (of the coarse fraction) for a bimodal suspension of glass beads. The diameters used were 0.3 and 3 mm ($\lambda = 10$).

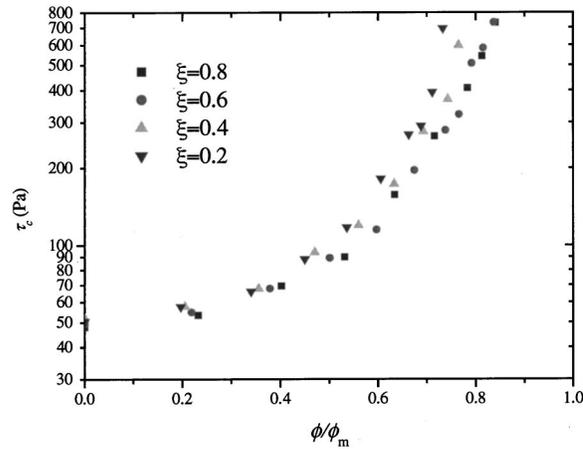


FIG. 10. Variation of the yield stress as a function of the solid concentration (of the coarse fraction) for a bimodal suspension of sand grains. The diameters used were 0.35 and 1.2 mm.

value ϕ_m , it is not possible to say whether this slight deviation reflects an effect of the bimodal distribution or can simply be ascribed to computational error. A decrease in the bulk yield stress was observed just like that for poorly sorted glass beads. The minimum was located approximately at $\phi/\phi_m \approx 0.6$ and the mean reduction in the bulk yield stress was 25% for $\lambda = 3$ and 50% for $\lambda = 10$. Thus we found that the larger the bead ratio was the more pronounced this decrease was. Interestingly enough, and common to both series of experiments ($\lambda = 3$ and 10), we also found that, for a given value of ϕ/ϕ_m ranging from 0 to 0.8, the bulk yield stress increased with an increasing proportion of large particles, namely, when the ratio ξ decreased. Such a variation was particularly obvious in the vicinity of the minimum ($\phi/\phi_m \approx 0.5-0.7$): in this case, it ranged from approximately 30% ($\lambda = 3$) to 100% ($\lambda = 10$). For ϕ/ϕ_m in excess of 0.95, this trend was reversed: a larger bulk yield stress resulted as the fine particle content in the suspension rose. But the maximum deviation in the bulk yield stress between the finest and coarsest suspensions was less than 25%. For both size ratios, the trend reverse at $\phi/\phi_m \approx 0.95$ was very abrupt and occurred after the beginning of the rapid increase in the bulk yield stress ($\phi/\phi_m > 0.85$).

Figure 10 gives data obtained with sand grains. On the whole, the trend was similar to that observed previously for unimodal suspensions. The largest concentrations produced a substantial increase in the bulk yield stress and this enhancement was more pronounced for mixtures with a low small particle content (low values of ξ) than for suspensions with a high small particle content. Unlike the glass beads, the ξ curves (sets of data with a given ξ) did not collapse into a single curve but deviated from each other when the reduced fraction ϕ/ϕ_m increased. For low and intermediate concentrations, the sand behavior contrasted significantly with that observed for bimodal suspensions of glass beads. First, no decrease in the bulk yield stress was observed. Second, the yield stress increase was more regular and more rapid for sand than for glass beads. Third, no significant variation in the yield stress was observed when the mixture composition was changed: the yield stress was not sensitive to the fineness of sand for $\phi/\phi_m < 0.5$.

D. Summary

The various series of coarse particle experiments have shown significant changes in the bulk yield stress with the solid concentration (in the coarse fraction). As soon as the solid concentration was as high as half the maximum solid concentration, coarse particles had a pronounced and increasing influence on the yield stress. The yield stress tended toward infinity for solid concentrations close to the maximum value ϕ_m . Data scattering increased with increasing solid concentration. This pattern was in agreement with previous results reported by Wildemuth and Williams (1985) with weakly colloidal systems (coal–glycerin slurries), Banfill (1994) with mortars, Coussot and Piau (1995) and Coussot (1997) with sand–clay suspensions, Coussot and co-workers (1998) with natural slurries, and Mansoutre (1999, 2000) with cement. The present experimental study gives further indications about the role of particle features on bulk yield stress.

The size distribution had complex effects on the yield stress. For intermediate solid concentrations (between 40% and 70% of the maximum solid concentration), the bulk yield was fairly independent of the mean particle size for unimodal suspensions. But, for bimodal suspensions, the lower the fine particle content, the larger the bulk yield. For larger concentrations (except for sand), the opposite trend was generally observed: the yield stress was more sensitive to concentration changes with finely graded materials than with coarsely graded materials. Banfill (1994) also found that sand grading produced no variation in the bulk yield stress for $\phi_t = 66\%$ whereas for $\phi_t = 70\%$, the yield stress increased significantly when the relative proportion of fine particles was increased, in agreement with our results.

The grain shape (spherical or rounded) was also a key parameter in determining the bulk yield stress: the more irregular the particles, the larger the yield stress was. In contrast, the particle material (glass or polystyrene) had no effect, on the whole, within the range of our tests due to measurement uncertainty.

Anomalous behavior was observed for poorly sorted glass beads: the bulk yield stress first decreased, reaching a minimum value at $\phi/\phi_m \approx 0.6\text{--}0.7$, then increased rapidly for $\phi/\phi_m \rightarrow 1$. Very similar behavior was also observed by Tattersall and Banfill (1983) with fresh concrete and by Mansoutre (2000) with cement.

IV. DISCUSSION

Here we will consider the different points summarized in Sec. III. First of all, we will review the physical mechanisms responsible for yielding in suspensions whether they are made up of colloidal particles or coarse particles. In Sec. IV B we will compare the results provided by different models with our experimental data.

A. Origin of yielding in suspensions: Previous results

For weakly colloidal dispersions, such as kaolin dispersions, the behavior is fairly well described on the macroscopic scale by a viscoplastic constitutive equation such as the Herschel–Bulkley model [Coussot and Piau (1994)] (with the reservations raised in Sec. II A). To our knowledge, a complete physical explanation of this behavior is still lacking. As for strongly colloidal particles (smectite), the yield stress originates mainly from colloidal interactions between particles. To date only the order of magnitude of the yield stress can be computed. This is generally achieved by considering constant surface chemistry conditions (pH close to the pH corresponding to the particle isoelectric point). Under these conditions, with the double layer being electrically neutral, electrostatic

repulsive forces are negligible and the dispersion behavior is governed by the van der Waals attractive forces. The dispersion thus exhibits the maximum yield stress [Scales *et al.* (1998)].

Potanic *et al.* (1995, 1966) developed a phenomenological fractal model to determine bulk behavior of weakly aggregated dispersions. They assumed that particles form aggregates which in turn are connected to a network. Thus they interpreted bulk yield stress as a consequence of chain breakup due to thermal fluctuations and rupture under compressive force. Another conceptual model inspired from glassy dynamics was proposed by Sollich *et al.* (1997), by Sollich (1998) and by Fielding *et al.* (2000) and co-workers. They showed that the bulk mechanical properties can be related to the internal structure (described in terms of the particle energy distribution). To date such models are able to mimic bulk behavior over a wide range of flow conditions but cannot specify the effects of particle size, size distribution, or solid concentration on the yield stress of a particulate fluid.

Kapur *et al.* (1997), then Scales *et al.* (1998) proposed a mean-field theory for particles governed by the van der Waals attractive forces. The input values of the model were the Hamaker constant A , the coordination number C_N , the mean particle diameter d , and an interparticle separation parameter h_0 , which must be fitted from experimental data. The yield stress is computed as the summation of all pairwise interparticle forces (per unit area). More recently, Zhou *et al.* (1999) improved this model by taking into account a broader size distribution of particles, but limited their attention to systems at the isoelectric point. They found that the maximum yield stress can be written as

$$\tau_k(\phi_k) = K \left(\frac{\phi_k}{1-\phi_k} \right)^c \frac{1}{d^2}, \quad (10)$$

where $K = 3.1Ab/(24\pi h_0)$, and b and c are two parameters to be fitted from experimental data. They proposed the following explanation for the variation in yield stress with increasing solid concentration. A weakly flocculated dispersion may be seen as a series of weakly interconnected aggregates (flocs) made up of strongly interacting particles. At low solid concentrations, yielding results from the breakdown of the weak links between flocs. At high solid concentrations, yielding is a consequence of the rupture of interparticle bonds and resistance to the deformation of networks. This means that a critical solid concentration ϕ_c separating the two domains should exist. When $\phi_k < \phi_c$, structural effects due to weak links between flocs prevail over those due to geometric resistance and the yield stress varies with a solid concentration as $\tau_k \approx K\phi_k^c/d^2$. This effect is included in Eq. (10) since it can be derived from Eq. (10) by taking a series expansion to chief order at $\phi_k = 0$. When $\phi_k > \phi_c$, the geometric resistance becomes more pronounced, resulting in a much higher dependence on the solid concentration $\tau_k \approx K\phi_k^{c'}/d^2$, with $c' > c$. Zhou *et al.* (1999) considered that, from a microstructural point of view, the geometric resistance enhancement is reflected by the increase in particle contacts. Assuming that the coordination number is given by Rumpf's expression [$C_N = 3.1/(1-\phi_k)$], they arrived at the conclusion that the yield stress may be scaled as a power function of $\phi_k/(1-\phi_k)$. The series expansion at $\phi_k = 0$ implies that the exponent must be c . Moreover, their experiments with alumina suspensions showed that the critical solid concentration ranged from 0.26 to 0.44 and depended on the particle diameter.

In noncolloidal systems, evidence of yielding behavior has been clearly reported by Husband *et al.* (1993) (with polyisobutylene/calcium carbonate suspensions). They ob-

served that for solid concentrations in excess of a critical value ($\phi \approx 0.47$) suspensions exhibited a yield stress. Moreover, this yield stress increased dramatically when the solid concentration came closer to the maximum concentration. In this case, the authors attributed yielding behavior either to particle jams or weak polymer–particle interactions, but they did not provide quantitative justification in their explanations. Such behavior was also observed by Wildemuth and Williams (1985) with coal–glycerin slurries, by Kytömaa and Prasad (1993) with 2 mm glass beads in a water–glycerol solution, by Coussot (1997) with 100 μm polystyrene beads in water–glycerol solutions, and by Jomha *et al.* (1990) with 2 μm polystyrene beads in water. In the latter case, the authors related the yield appearance to structural changes in particle arrangement (glass transition) at a critical solid concentration ($\phi = 0.58$). In contrast yielding was not observed for concentrated Brownian particles [de Kruif *et al.* (1985)] (at a low Péclet number).

Wildemuth and Williams (1985) have suggested that the existence of a yield stress in noninteracting particle suspensions is a consequence of dependence of the maximum solid concentration on the shear stress. Using heuristic arguments, they have shown that a yield stress should arise over a given range of solid concentrations (ϕ_0, ϕ_∞):

$$\tau_c(\phi) = \sqrt[m]{A \left(\frac{\phi/\phi_0 - 1}{1 - \phi/\phi_\infty} \right)}, \quad (11)$$

where A , ϕ_0 , and ϕ_∞ are three parameters. ϕ_∞ is the high-shear limit of the solid concentration and ϕ_0 corresponds to a kind of percolation threshold. The model has been successfully tested by Wildemuth and Williams on coal slurries.

B. Application to bead suspensions within a clay dispersion

We have examined the different models presented above within our context. Figure 11 shows the yield stress variation as a function of the total solid concentration (volume of solid to total volume), which can be computed as follows: $\phi_t = \phi_k(1 - \phi) + \phi$. Figure 11 also shows cases of both water–kaolin dispersion and glass–bead suspensions within a 25% kaolin dispersion (data of Fig. 6). For clarity, only results of calibrated glass beads are reported (see Figs. 12 and 13 for other materials). For kaolin, we have applied the model proposed by Zhou *et al.* We used the least-square method to fit our data with Eq. (10). We found $c = 5.15$ and $K/d^2 = 11585$. The mean diameter used by Zhou *et al.* is an average surface diameter computed as follows: $d = 1/\sum x_{vi}/d_i$, where $x_{vi} = v_i/\sum v_i$ is the volume fraction ratio of particles of diameter d_i and volume v_i . Here, using data from Fig. 1, we found $d = 3.52 \mu\text{m}$, thus $K = 1.43 \times 10^{-7}$. A closer examination of the yield stress curve shows that, in agreement with Zhou *et al.*'s scheme, the yield increase is more pronounced for solid concentrations in excess of a critical value: $\phi_c \approx 0.25$ – 0.26 . Using two different power expressions to fit yield stress data for $\phi_k < \phi_c$ and $\phi_k > \phi_c$, we found $c = 4.6$ and $c' = 7.6$. These two exponents are similar to those found by Zhou *et al.* (1999): $c = 4.2$ and $c' = 8.5$. It is worth noting that fitting data with a power expression over a limited range of solid fractions ($\phi_k < \phi_c$) and over the entire range of concentrations tested does not provide the same exponent c since we have $c = 4.6$ for the former case and $c = 5.15$ for the latter. In the following, since we used concentrated dispersions ($\phi_k \geq \phi_c$), we take $c = 5.15$. The power-law dependence of the yield stress on the solid concentration may be connected with the fractal model of Potanin *et al.* (1995) through the relationship between exponent c and fractal dimension d_f : $c = 3/(3 - d_f)$. Here the coefficient $c = 5.15$ gives a fractal dimension of 2.42. According to Potanin *et al.* (1995), the typical floc size in a quasi-

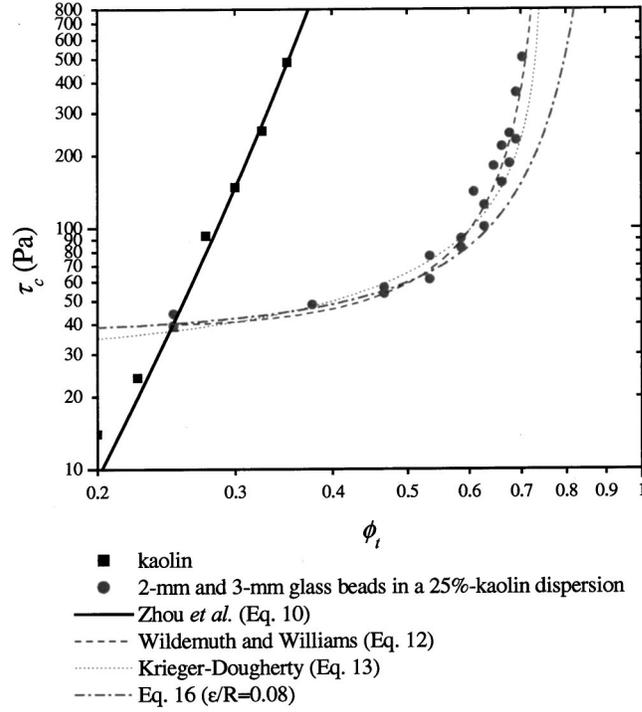


FIG. 11. Variation of the yield stress as a function of the solid concentration in kaolin. The thick line represents Eq. (10) whose parameters were fitted from experimental data. The thin lines correspond to various empirical expressions tested for well-sorted bead suspensions. We have reported the data in Fig. 6 after transforming the solid concentration ϕ into a total solid concentration ϕ_t .

equilibrium structure, a , is then $a \sim r\phi_k^{-1/(3-d_f)} \sim r\phi_k^{-0.58}$, with r the kaolin particle radius. In a 25% kaolin dispersion (with $r \sim 1 \mu\text{m}$), this gives $a \sim 7 \mu\text{m}$, which is consistent with the volume average determined in Sec. II A.

First we extended the empirical model proposed by Wildemuth and Williams to the present context, where the interstitial fluid was a viscoplastic fluid. In this case, the yield stress provided by Eq. (11) must be understood as a contribution of coarse particles to the bulk yield stress. We have thus considered that the bulk yield stress can be expressed as

$$\tau_c(\phi) = \tau_k(\phi_k) \left[1 + \alpha \left(\frac{\phi/\phi_0 - 1}{1 - \phi/\phi_\infty} \right)^{1/m} \right], \quad (12)$$

where $\tau_k(\phi_k)$ is the yield stress of the kaolin dispersion, and α and m are two parameters to be fitted. Here we can consider that $\phi_0 = \phi_k$ and $\phi_\infty = 1 - \phi_k$. The least-square method gave $\alpha = 0.11$ and $m = 0.77$. As shown in Fig. 11, this model provides results which fit our data well over the whole range of concentrations. Other expressions tested for fitting experimental data can also give interesting results, although they are less complete. For low solid concentrations (here, $\phi_t < 50\%$), the yield stress variation can be described by the following fitted function:

$$\tau_c = 27.34 \left(1 - \frac{\phi_t}{\phi_{t,m}} \right)^{-0.79}, \quad (13)$$

where $\phi_{t,m}$ is the maximum solid concentration possible due to the existence of a fine fraction ϕ_k , here, $\phi_{t,m} = \phi_\infty = 0.75$. Equation (13) is structurally very similar to the expression given by Krieger and Dougherty for the viscosity of spherical-particle suspensions in Newtonian fluids [Krieger and Dougherty (1959)]. As pointed out by Coussot and Ancey (1999), this is not very surprising since the same reasoning as that used by Krieger and Dougherty can be applied to the computation of yield stress. For larger solid concentrations, Eq. (13) no longer captures the experimental data. The curve described by an expression similar to Eq. (10) comes closer to the data:

$$\tau_c = 5.35 \left(\frac{\phi_t}{1 - \phi_t} \right)^{5.15}. \quad (14)$$

The most intriguing result is that the curves given by Eqs. (10) and (14) are parallel since the exponent in both equations is identical.

Although the phenomenological models and empirical expressions can provide interesting relationships for the bulk yield stress increase, they require fitting certain parameters and they give no physical reason why the bulk yield stress should increase when adding coarse particles to a colloidal dispersion. Thus, it is of great interest to take a good look at this issue. The particulate contribution to bulk stress in a suspension may be computed as the volume or ensemble average of interaction forces \mathbf{f} between particles, whatever the type of interaction [Ancey *et al.* (1999); Jongshaap and Mellena (1995)]: $\boldsymbol{\sigma} = \Sigma_V \mathbf{f} \otimes \mathbf{r} / V = n_d \langle \mathbf{f} \otimes \mathbf{r} \rangle$, where V refers to a control volume, \mathbf{r} the distance between the mass centers of two interacting particles, and n_d the number density. Here, since we have two populations of grains (colloidal and coarse particles), we can express the particulate contribution to bulk stress as follows: $\boldsymbol{\sigma} = \phi_k(1 - \phi) \boldsymbol{\sigma}_{\text{col}} + \phi \boldsymbol{\sigma}_{\text{coarse}}$, where $\boldsymbol{\sigma}_{\text{col}} = \langle \mathbf{f} \otimes \mathbf{r} \rangle / V_p$ and $\boldsymbol{\sigma}_{\text{coarse}} = \langle \mathbf{f} \otimes \mathbf{r} \rangle / V_p$ are the elementary contributions of colloidal and coarse particles, respectively, both calculated on a test particle (of volume V_p). In so doing, we have implicitly assumed that there is no interaction between the two populations of particles. In fact, even without interaction forces between colloidal and coarse particles, interplay between the populations may arise as a result of depletion in a way similar to colloidal dispersion in polymeric liquids [Russel *et al.* (1992)]. Indeed, in the vicinity of a solid wall or a large particle surface, the solid concentration in clay particles (or flocs) decreases, inducing a slight increase in the (effective) solid concentration in clay. To evaluate this effect, we assume that over a thickness ϵ around the solid surface, the clay particles are expelled. The new clay concentration is

$$\tilde{\phi}_k \approx \phi_k + n \frac{\phi_k 4\pi R^2 \epsilon}{\text{free volume}} \approx \phi_k \left(1 + 3 \frac{\phi}{1 - \phi} \frac{\epsilon}{R} + \mathcal{O}(\epsilon/R) \right), \quad (15)$$

where n denotes the number of coarse particles (per unit volume) and R the radius of a coarse particle. The free volume is the volume that is not occupied by coarse particles: $(1 - \phi)V$. The thickness of the depletion layer depends on the curvature of the solid surface $1/R$, its roughness size, the floc size a , and the chemistry surface conditions. For $a/R \rightarrow 1$, we have $\epsilon \rightarrow 0$ and for $a/R \ll 1$, we can expect that $\epsilon = \mathcal{O}(a)$. When depletion results mainly from geometrical constraints, an estimation of ϵ can be obtained using Ben-Aïm's (1970) research on wall effects of sphere arrangements. Ben-Aïm found that for spheres of diameter d there is a decrease in solid concentration over a distance $d/2$. The reduction ratio in a solid concentration was evaluated at $k = 11/16$. Assuming here that flocs can be assimilated into spheres of diameter d much smaller than R , we find that $\epsilon = 5a\phi_k/32$.

When the concentration in coarse particles is low, it is reasonable (and usual) to neglect the corresponding contribution to bulk stress. In this case, bulk stress can be

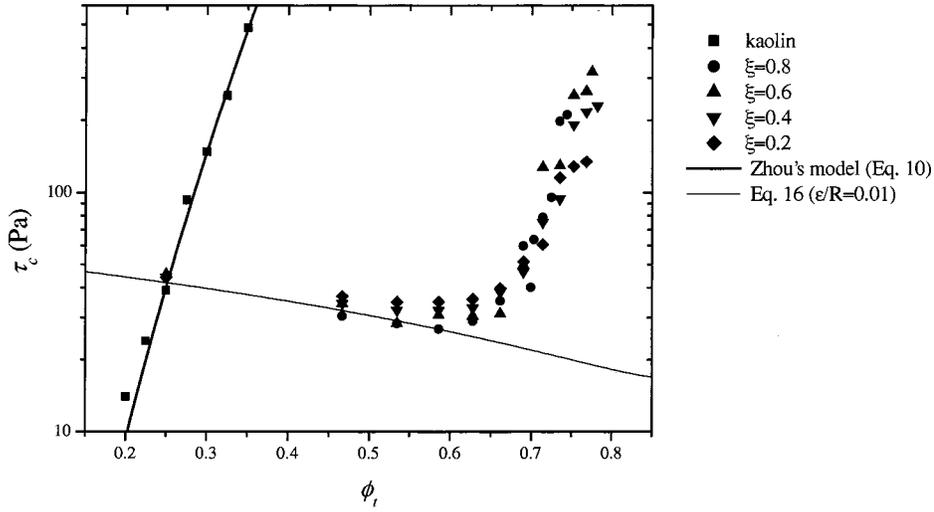


FIG. 12. Variation of the yield stress as a function of the solid concentration in kaolin. The solid thick line represents Eq. (10) whose parameters were fitted from experimental data. The solid line correspond to Eq. (16). We have reported the data in Fig. 8 after transforming the solid concentration ϕ into a total solid concentration ϕ_t .

approximated as follows: $\boldsymbol{\sigma} \approx n_k \langle \mathbf{f} \otimes \mathbf{r} \rangle (1 - \phi)$, where $n_k = \phi_k / V_p$ is the number density of colloidal particles. Using Eq. (10), we deduce that the bulk yield can be expressed as

$$\tau_c(\phi_k, \phi, \epsilon) = K \left(\frac{\tilde{\phi}_k}{1 - \tilde{\phi}_k} \right)^c \frac{1 - \phi}{d^2}. \quad (16)$$

Numerical simulations of Eq. (16) show that a critical ratio $\eta_c = \epsilon / R = 0.043$ separating two behaviors exists. For $\epsilon > \eta_c R$ bulk yield stress increases when adding coarse particles and decreases otherwise ($\epsilon < \eta_c R$). Since we have observed either a decrease or an increase in the bulk yield stress when adding particles, we have adjusted the switch parameter $\eta = \epsilon / R$ for Eq. (16) to fit our experiment's data. For well-graded materials and sand, we have found that the range $\eta = 0.08 - 0.09$ gives good results in the yield stress fitting at low and intermediate solid concentrations ϕ_t , as shown in Figs. 11 and 12. Agreement is even better because the suspension is concentrated in kaolin, as shown in Fig. 12 with sand suspensions in 25% kaolin and 30% kaolin dispersions. For poorly sorted glass beads, we found the range $\eta = 0 - 0.02$ (see Fig. 13). It is worth noting that our experiments, which involve different materials, shapes, and sizes, lead to two distinct narrow ranges for η . Furthermore, the fitted values of η may be as much as 70 times higher than the value determined by considering purely geometrical constraints [$5a\phi_k / (32R)$]. This shows that, if depletion is the correct explanation for the increase/decrease of the bulk yield stress, it cannot originate from geometrical constraints but is likely to result from surface repulsion forces between kaolin and coarse particles or significant changes in floc structures.

For the suspensions tested, Eq. (16) underestimates the bulk yield stress at high solid concentrations. Figure 14 expresses the variation of the difference $\Delta\tau_c$ between the measured yield stress and the value provided by Eq. (16) as a function of the total solid concentration ϕ for well-sorted materials. The resulting points lie on a curve parallel to the kaolin yield stress curve. The deviation $\Delta\tau_c$ becomes significant for total solid con-

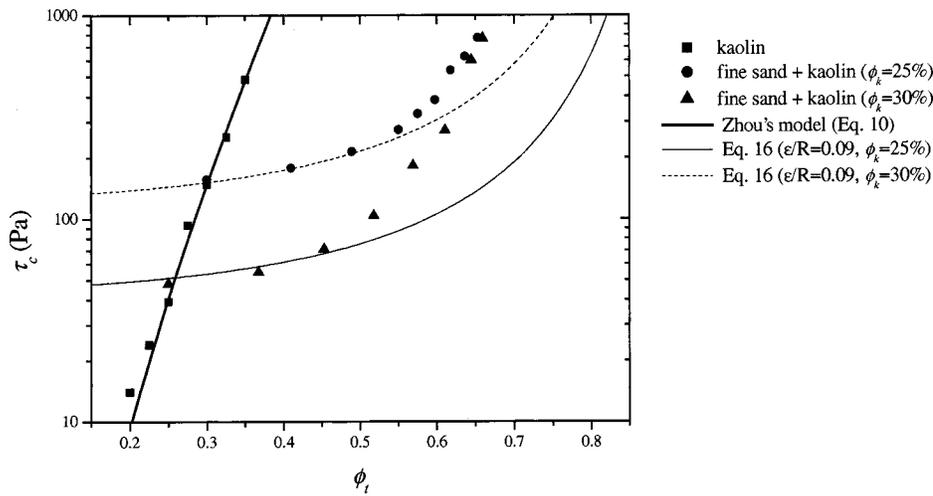


FIG. 13. Variation of the bulk yield stress of a fine sand suspension within a kaolin dispersion as a function of the total solid concentration. For the kaolin dispersion, two concentrations were tested: $\phi = 25\%$ and 30% .

centrations in excess of 0.6 (or $\phi > 0.45$). A possible way of explaining this sharp deviation at high solid concentrations is by an increasing role of interactions between coarse particles, like in Newtonian suspensions. The similarities between $\Delta\tau_c$ and τ_k could mean that coarse particles surrounded by kaolin particles interact with each other as colloidal particles do. But, contrary to fine particles, such interactions do not depend on the particle surface area. Different points in Fig. 14 support this assertion. First, experimental data lie on a single curve, whatever the coarse particle diameter. Then, if we include a surface average diameter of the kaolin/bead suspensions into Zhou *et al.*'s model, we find a curve which is not parallel to the kaolin yield curve at all. For Zhou

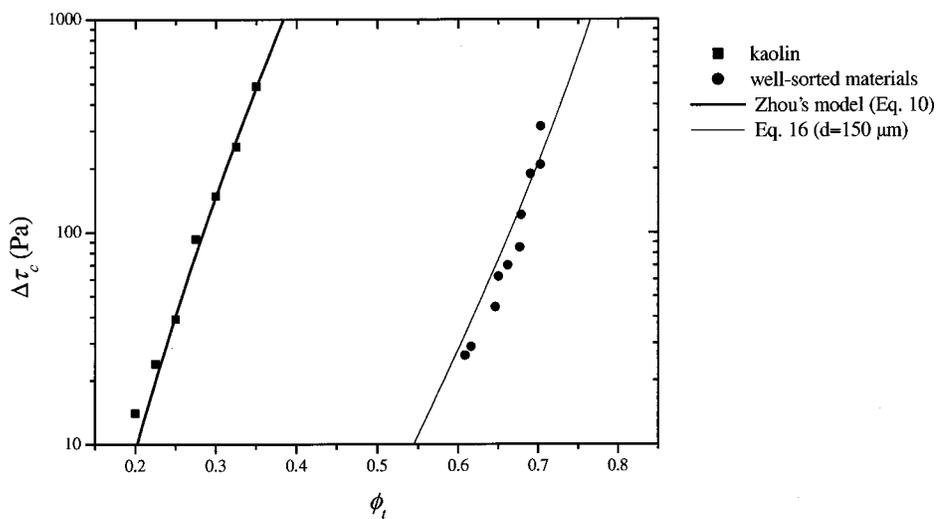


FIG. 14. Variation of the difference $\Delta\tau$ between the bulk yield stress and Eq. (16) for well-sorted bead suspensions within a 25% kaolin dispersion as a function of the total solid concentration. The solid thick line represents Eq. (10) whose parameters were fitted from experimental data. The solid line corresponds to Eq. (10), with $d = 150 \mu\text{m}$.

et al.'s model to fit the experimental data in Fig. 14, we must take a diameter $d = 150 \mu\text{m}$ independent of the coarse particle diameter.

Like in concentrated Newtonian suspensions, we can expect that coarse particles interact via contact forces. The particle contribution to bulk stress can be expressed as $\boldsymbol{\sigma}_{\text{coarse}} = n_{dp} \langle \mathbf{f} \otimes \mathbf{r} \rangle$, with n_{dp} the number density of coarse particles, \mathbf{f} the contact force, and \mathbf{r} the distance between the mass centers of two neighboring particles. To our knowledge, in the case of viscoplastic interstitial fluid, no analytical expression of the contact force is known despite numerical investigations [Tichy (1991)]. However, it can be expected that when yielding occurs the contact force depends mainly on the mean distance between two neighboring particles h and the yield stress of the interstitial phase τ_k : $\mathbf{f} = \mathbf{f}(h, \tau_k)$. Since the relative distance between two grains h/R can be expressed as $2\xi/(1-\xi)$ where $\xi = 1 - \sqrt[3]{\phi/\phi_m}$, using a mean-field approximation we infer that the particle contribution must scale as $\boldsymbol{\sigma}_{\text{coarse}} \propto \phi C_N |\mathbf{f}(\phi/\phi_m, \tau_k)|/R^2$, where C_N is the coordination number (number of contacts) and R the particle radius. In bimodal suspensions, C_N is a function of the solid concentration ϕ along with the parameters λ and ξ . C_N increases when the solid concentration (or the radius ratio λ) is increased. For a given solid concentration, C_N is higher for suspensions in which a few large particles are surrounded by many small particles (ξ close to 1) than for suspensions in which large particles occupy most of the solid volume (ξ close to 0). This explains why in Figs. 8 and 9 bulk yield stress increased substantially upon an increase of the relative proportion of fine particles. For unimodal suspensions, we can use Rumpf's relationship ($C_N = 3.1/(1-\phi)$). A comparison of the expression $\boldsymbol{\sigma}_{\text{coarse}}$ with Eqs. (13) and (14) yields $\mathbf{f}(h, \tau_k) \propto \tau_k h^{-2/3}$.

V. CONCLUDING REMARKS

In this work we have shown that the yield stress of a coarse particle suspension within a colloidal dispersion depends a great deal on the solid concentration in coarse particles. Other parameters such as particle shape or size distribution can also significantly affect the yield stress. At first, this is surprising since we expect yielding behavior to originate only from colloidal interactions within the fine fraction. Several mechanisms are probably involved and their occurrence depends on the material features. For low and intermediate concentrations ($\phi < 0.4$), depletion is sufficient to explain both the decrease and the slight increase in the yield stress when adding coarse particles. For larger concentrations ($\phi > 0.4$), the increase is sharp and the yield stress seemingly tends toward infinity when the solid concentration approaches its maximum value. In this case, everything happens as if the coarse particles surrounded by fine clay particles interacted with each other as colloidal particles. In fact, since the corresponding contribution does not depend on the particle surface area but rather on the coordination number, it is thought that coarse particles interact via elastoplastic forces at points of (indirect) contact. Here indirect contact refers to contact lubricated by the kaolin dispersion. In this case, yielding is a consequence of the breakdown of indirect contacts between coarse particles.

The proposed explanations remain speculative. We have found a fairly large depletion layer thickness and consequently further investigations on this point are required. Although we attempted to avoid any disturbing effect in our experiments, further tests with polymeric gels should be carried out to check that some properties exhibited by our experiments do not result from poorly controlled chemistry surface conditions. Another point also deserves further investigation: the sharp increase in bulk yield stress at high solid concentrations has been ascribed to the increasing number of indirect contacts between coarse particles. The resulting elastoplastic lubrication force has been estimated

at $\tau_k/h^{2/3}$, where τ_k is the kaolin yield stress and h the distance between the surfaces of two neighboring particles.

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References

- Ancey, C., P. Coussot, and P. Evesque, "A theoretical framework for very concentrated granular suspensions in a steady simple shear flow," *J. Rheol.* **43**, 1673–1699 (1999).
- Banfill, P. F. G., "Use of the ViscoCorder to study the rheology of fresh mortar," *Mag. Concr. Res.* **42**, 213–221 (1990).
- Banfill, P. F. G., "The rheology of fresh mortar," *Mag. Concrete Res.* **43**, 13–21 (1991).
- Banfill, P. F. G., "Rheological methods for assessing the flow properties of mortar and related materials," *Constr. Build. Mat.* **8**, 43–50 (1994).
- Banfill, P. F. G., *Proceedings of the British Masonry Society No. 8* (British Masonry Society, London, 1998).
- Banfill, P. F. G., "The influence of fine materials in sand on the rheology of fresh mortar," in *Proceedings of the International Conference on Utilizing Ready Mix Concrete and Mortar*, held at the University of Dundee, Sept. 1999, edited by R. K. Dhir and M. C. Limbachiya (Thomas Thelford, London), pp. 411–420.
- Ben-Aïm, R., "Etude de la texture des empilements de grains. Application à la détermination de la perméabilité des mélanges binaires en régime moléculaire, intermédiaire, laminaire," thesis, University of Nancy, Nancy, France 1970.
- Brown, A. B. D., S. M. Clarke, P. Convert, and A. R. Rennie, "Orientational order in concentrated dispersions of plate-like kaolinite particles under shear," *J. Rheol.* **44**, 221–233 (2000).
- Coussot, P., "Structural similarity and transition from Newtonian to non-Newtonian behavior for clay–water suspensions," *Phys. Rev. Lett.* **20**, 3971–3974 (1995).
- Coussot, P., *Mudflow Rheology and Dynamics* (Balkema, Rotterdam, 1997).
- Coussot, P. and C. Ancey, *Rhéophysique des Pâtes et des Suspensions* (EDP Sciences, Les Ulis, France, 1999) (in French).
- Coussot, P. and J.-M. Piau, "On the behavior of fine mud suspensions," *Rheol. Acta* **33**, 175–184 (1994).
- Coussot, P. and J.-M. Piau, "The effects of an addition of force-free particles on the rheological properties of fine suspensions," *Can. Geotech. J.* **32**, 263–270 (1995).
- Coussot, P., S. Proust, and C. Ancey, "Rheological interpretation of deposits of yield stress fluids," *J. Non-Newtonian Fluid Mech.* **66**, 55–70 (1996).
- Coussot, P., D. Laigle, M. Arratano, A. Deganutti, and L. Marchi, "Direct determination of rheological characteristics of debris flow," *J. Hydraul. Eng.* **124**, 865–868 (1998).
- de Kruif, C. G. d., E. M. F. van Iersel, and A. Vrij, "Hard sphere colloidal dispersions: Viscosity as a function of shear rate and volume fraction," *J. Chem. Phys.* **83**, 4747–4725 (1985).
- Fielding, S. M., P. Sollich, and M. E. Cates, "Aging and rheology in soft materials," *J. Rheol.* **44**, 323–369 (2000).
- Flavigny, E., J. Desrues, and B. Palayer, "Le sable d'Hostun," *Rev. Française Géotechnique* **53**, 67–70 (1990).
- Gondret, P. and L. Petit, "Dynamic viscosity of macroscopic suspensions of bimodal sized solid spheres," *J. Rheol.* **41**, 1261–1274 (1997).
- Hu, C., "Rhéologie des bétons fluides," thesis, École Nationale des Ponts et Chaussées, Paris, 1995.
- Huifang, Z., P. F. Low, and J. M. Bradford, "Effects of pH and electrolyte concentrations on particle interaction in three homoionic sodium clay suspensions," *Soil Sci.* **151**, 196–207 (1991).
- Husband, D. M., N. Aksel, and W. Geissle, "The existence of static yield stresses in suspensions containing noncolloidal particles," *J. Rheol.* **37**, 215–235 (1993).

- Jogun, S. M. and C. F. Zukoski, "Rheology of dense suspensions of platelike particles," *J. Rheol.* **40**, 1211–1232 (1996).
- Jogun, S. M. and C. F. Zukoski, "Rheology and microstructure of dense suspensions of plate-shaped colloidal particles," *J. Rheol.* **43**, 847–871 (1999).
- Jomha, A. I., A. Merrington, L. V. Woodcock, H. A. Barnes, and A. Lips, "Recent developments in dense suspension rheology," *Powder Technol.* **65**, 343–370 (1990).
- Jongshaap, R. J. J. and J. Mellema, "Stress tensor expressions for dispersions," *J. Rheol.* **39**, 953–959 (1995).
- Kapur, P. C., P. J. Scales, B. V. Boger, and T. W. Healy, "A theoretical framework for the yield stress of suspensions loaded with size distributed particles," *AIChE J.* **43**, 1171–1179 (1997).
- Krieger, I. M. and T. J. Dougherty, "A mechanism for non-Newtonian flow in suspensions of rigid spheres," *Trans. Soc. Rheol.* **3**, 137–152 (1959).
- Kytömaa, H. K. and D. Prasad, "Transition from quasistatic to rate dependent shearing of concentrated suspensions," in *Proceedings of Powders and Grains*, University of Birmingham, 1993, edited by C. Thornton (Balkema, Rotterdam, 1993).
- Lagaly, G., "Principles of flow of kaolin and bentonite dispersion," *Appl. Clay Sci.* **4**, 105–123 (1989).
- Lancelot, L., I. Shahrour, and M. Al Mahmoud, "Comportement du sable d'Hostun sous faibles contraintes," *Rev. Française Géotechnique* **74**, 63–74 (1996).
- Mansoutre, S., "Des suspensions concentrées aux milieux granulaires lubrifiés: Étude des pâtes de silicate tricalcique," thesis, Université d'Orléans, Orléans, France, 2000.
- Mansoutre, S., P. Colombet, and H. Van Damme, "Water retention and granular rheological behavior of fresh C₃S paste as a function of concentration," *Cem. Concr. Res.* **29**, 1441–1453 (1999).
- Meakin, P., "Application of experimental and numerical models to the physics of multiparticle systems," *Adv. Phys.* **42**, 1–127 (1993).
- Melton, I. E. and B. Rand, "Particle interactions in aqueous kaolinite suspensions," *J. Colloid Interface Sci.* **60**, 308–336 (1977).
- Nicol, S. K. and R. J. Hunter, "Some rheological and electrokinetic properties of kaolinite suspensions," *Aust. J. Chem.* **23**, 2177–2186 (1970).
- Ouchiyaama, N. and T. Tanaka, "Porosity of a mass of solid particles having a range of sizes," *Ind. Eng. Chem. Fundam.* **20**, 66–71 (1981).
- Pashias, N. and D. V. Boger, "A fifty cent rheometer for yield stress measurement," *J. Rheol.* **40**, 1179–1189 (1996).
- Potantin, A. A. and W. B. Russel, "Fractal model of consolidation of weakly aggregated colloidal dispersions," *Phys. Rev. E* **53**, 3702–3709 (1996).
- Potantin, A. A., R. De Rooi, D. Van den Ende, and J. Mellema, "Microrheological modeling of weakly aggregated dispersions," *J. Chem. Phys.* **102**, 5845–5853 (1995).
- Probstein, R. F., M. Z. Sengun, and T.-C. Tseng, "Bimodal model of concentrated suspension viscosity for distributed particle sizes," *J. Rheol.* **38**, 811–829 (1994).
- Russel, W. R., D. A. Saville, and W. R. Showalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1992).
- Scales, P. J., P. C. Kapur, S. B. Johnson, and T. W. Healy, "The shear yield stress of partially flocculated colloidal suspensions," *AIChE J.* **44**, 538–544 (1998).
- Schowalter, W. R. and G. Christensen, "Toward a rationalization of the slump test for fresh concrete: Comparisons of calculations and experiments," *J. Rheol.* **42**, 865–870 (1999).
- Seidel, O., F. Bagusat, and H.-J. Mögel, "Time periodic viscosity suspension of concentrated suspensions at constant shear rates," *Rheol. Acta* **38**, 305–310 (1999).
- Sengun, M. Z. and R. F. Probstein, "Bimodal model of slurry viscosity with applications to coal slurries. Part 1. Theory and experiment," *Rheol. Acta* **28**, 382–393 (1989a).
- Sengun, M. Z. and R. F. Probstein, "Bimodal model of slurry viscosity with applications to coal slurries. Part 2. High shear limit behaviour," *Rheol. Acta* **28**, 394–401 (1989b).
- Sollich, P., "Rheological constitutive equation for a model of soft glassy materials," *Phys. Rev. E* **58**, 738–759 (1998).
- Sollich, P., F. Lequeux, P. Hébraud, and M. E. Cates, "Rheology of soft glassy materials," *Phys. Rev. Lett.* **78**, 2020–2023 (1997).
- Tattersall, G. H. and P. F. G. Banfill, *Rheology of Fresh Concrete* (Pitman, London, 1983).
- Tichy, J. A., "Hydrodynamic lubrication theory for the Bingham plastic flow model," *J. Rheol.* **35**, 477–495 (1991).
- Wildemuth, C. R. and M. C. Williams, "A new interpretation of viscosity and yield stress in dense slurries: Coal and other irregular particles," *Rheol. Acta* **24**, 75–91 (1985).
- Wilson, S. D. R. and S. L. Burgess, "The steady, spreading flow of a rivulet of mud," *J. Non-Newtonian Fluid Mech.* **79**, 77–85 (1998).
- Zhou, Z., M. J. Solomon, P. J. Scales, and D. V. Boger, "The yield stress of concentrated flocculated suspensions of size distributed particles," *J. Rheol.* **43**, 651–671 (1999).