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Viscosity of Portland Cement Paste as a Function of Concentration

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The flow behavior of Portland cement paste was studied as a function of its concentration. The relationship between viscosity and concentration was found to be well described by the Krieger-Dougherty equation. For pastes dispersed using a superplasticizer, the maximum volume fraction was found to be approximately 0.7, and the intrinsic viscosity was found to be approximately 5. Pastes that were not dispersed were considerably higher in viscosity; such flocculated pastes fit the Krieger-Dougherty equation, but gave a much lower maximum volume fraction, indicating fairly open flocs even at the high strain rate used for viscosity measurements (500 seconds^{-1}). ADVANCED CEMENT BASED MATERIALS 1995, 2, 62–69

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The flow behavior of a suspension depends primarily on the concentration of particles and the extent to which the particles are flocculated. Viscosity increases with increasing solids concentration and flocculation. Of the many attempts to model the relationship between viscosity and concentration, probably the most successful has been the equation developed by Krieger and Dougherty [1]. This equation has been widely used because it has strong theoretical underpinnings and the physical significance of its parameters are known. The validity of this equation has been established using rheological measurements on dispersed suspensions of spherical, monosized latex particles. A few publications have applied this equation to complex particulate systems, but none were found that applied it to Portland cement. The objective of this work was to determine whether the Krieger-Dougherty equation can be used to describe the relationship between viscosity and concentration of dispersed cement paste.

Cement paste is the suspension of Portland cement particles and water that comprises the continuous phase in concrete. When cement and water are first mixed, the paste is a fluid, though hydration reactions during the first few hours cause it to become progressively more solidlike in its behavior, until after some hours it can be seen to have developed measurable strength. The flow behavior of paste is important because it controls the flow behavior, and hence the processability, of concrete. The viscosity of cement paste is known to increase with increasing concentration of solid particles, and several empirical relationships between viscosity and cement concentration and fineness have been proposed [2–4] (as reviewed by Tattersall and Banfill [5] and by Struble [6]). These relationships have not found widespread use, undoubtedly because of their empirical basis. If a theoretically derived equation were shown to be valid, it could be used to model cement paste viscosity based only on independently measurable parameters.

Krieger-Dougherty Equation

The Krieger-Dougherty equation for viscosity of a dispersed suspension is

$$\frac{\eta}{\eta_c} = \left(1 - \frac{\phi}{\phi_M}\right)^{-[\eta]\phi_M} \qquad (1)$$

where η is the apparent viscosity of the suspension, η_c is the apparent viscosity of the continuous phase (or liquid phase), ϕ is the concentration of solids (by volume), $[\eta]$ is the intrinsic viscosity of the suspension, and ϕ_M is the maximum solids concentration (by volume). The maximum volume fraction ϕ_M depends on particle-size distribution and shape. It should be noted that ϕ_M is affected not by particle size, but rather by the particle-size distribution. The maximum volume fraction typically falls between 0.6 and 0.7 for monosized spherical particles. The intrinsic viscosity $[\eta]$ is a measure of the effect of individual particles on viscosity. It is defined as follows:

$$[\eta] = \lim_{\phi \to 0} \frac{\frac{\eta}{\eta_c} - 1}{\phi}. \qquad (2)$$

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The intrinsic viscosity value also depends on particle shape. Spherical particles have an intrinsic viscosity of 2.5. Thus all independent variables in the Krieger-Dougherty equation, concentration, particle-size distribution, and particle shape, relate to the density at which particles are packed in the suspension.

This equation was first described in 1959 without derivation by Krieger and Dougherty [1]; in a subsequent review, Krieger [7] presented the following derivation, the theoretical validity of which was later confirmed by Ball and Richmond [8]. A suspension of spherical particles behaves at low concentrations (below approximately 10%) according to the well-known Einstein equation:

$$\frac{\eta}{\eta_c} = (1 + 2.5\phi). \qquad (3)$$

This equation predicts that $[\eta]$ is 2.5 for spherical particles and measured values confirm this prediction. At higher concentrations, $d\eta/d\phi$ is greater than 2.5 due to crowding, and it increases with increasing ϕ until a limiting concentration is reached at which viscosity becomes infinite. Thus there is some limiting concentration at which particles become packed so tightly that they cannot flow. This behavior is demonstrated by the Mooney equation:

$$\frac{\eta}{\eta_c} = \exp\left[\frac{[\eta]\phi}{\left(1 - \frac{\phi}{\phi_M}\right)}\right]. \qquad (4)$$

This equation was derived by considering the suspension to be divided into two portions and computing the effect on viscosity of adding the second portion to the first, correcting the volume fraction of each portion for the effects of crowding by the other portion. The Mooney equation fits measured data at low concentrations but not at high concentrations. Krieger and Dougherty applied the crowding factor only to the second portion, thereby deriving eq 1, which provided a good fit across the full range of concentrations.

Since its original description, the Krieger-Dougherty equation has been shown to provide an excellent fit to data obtained for model systems (monosized spherical particles, typically neutrally buoyant in the suspending fluid) [9–12]. The equation is viewed with such confidence that it has been used to estimate the thickness of polymer grafted on the surface of latex particles [13]. It has also been applied to more complex systems, though with greater difficulty. Studies on a range of particulate systems (submicron spheres, ground particles, and glass rods and fibers) were reviewed by Barnes et al. [14]; other studies have included casein micelles in milk [15], ground glass in organic polymer (dental composite) [16], and ground coal slurries [17,18]. Barnes et al. [14] summarized values of the Krieger-Dougherty packing parameters: ϕ_M is near 0.6 to 0.7 for monosized spherical particles, lower (as low as 0.23) with increasing asymmetry, and higher with increasing polydispersity; $[\eta]$ is near 2.5 for spheres, higher (3 to 5) for angular but presumably equant particles, and still higher (4 to 10) for rods or fibers. As they noted, there is no theoretical basis for calculating ϕ_M for polydisperse particles; it can only be determined empirically from viscosity values measured at various volume fractions.

While dilute dispersed suspensions show Newtonian flow behavior, concentrated suspensions are often plastic or pseudoplastic in their behavior (for discussion of rheological behavior, see ref 19), so viscosity depends not only on volume fraction but also on shear stress or strain rate. To describe this relationship, Krieger and Dougherty [1] used the Williamson equation:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + \frac{|\tau|}{\tau_r}\right)^{-1} \qquad (5)$$

where η is apparent viscosity, η_0 is the limiting viscosity at low strain rate, η_∞ is the limiting viscosity at high strain rate, τ is the shear stress, and τ_r is reduced stress (defined by $\tau_r = \alpha kT/a^3$, where α is a fitted constant, k is Boltzmann's constant, T is temperature, and a is particle radius). Equation 1 produces a curve of the sort shown in Figure 1. In their various articles cited here, Krieger and colleagues measured viscosity versus stress across a sufficiently wide range of strain rates so as to fit the data to eq 5, thereby estimating η_0 or η_∞ to use in eq 1. For many suspensions, however, such a

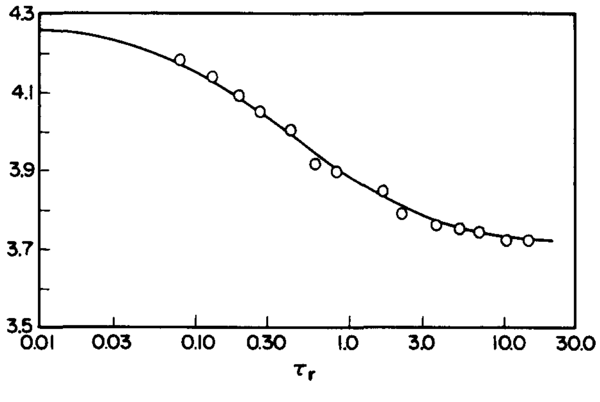

FIGURE 1. Relative viscosity versus reduced shear stress (defined in text) for a suspension of spherical particles (Figure 9 in Papir and Krieger [9], with permission). Circles are experimental data points and solid line is the curve predicted using the Williamson equation (η_0 = 4.258 and η_∞ = 3.716).

wide range of strain rate cannot be achieved and η_0 or η_∞ cannot be estimated. In that case, one must use viscosity at some arbitrary shear. It is not clear whether viscosity should be measured at a single strain rate or a single stress. Krieger [7] asserted that eq 1 could be applied using viscosity measured either at fixed strain rate or fixed stress. Based on studies of coal slurries, Wildemuth and Williams [18] presented a strong argument for using viscosity measured at a single shear stress, but more recently Cheng et al. [16] used viscosities measured at a single strain rate in their studies of crushed glass in polymer.

Both parameters in the Krieger-Dougherty equation, ϕ_M and $[\eta]$, depend on shear (whether strain rate or stress). It was noted by Krieger and Dougherty [1] and discussed more explicitly by Krieger [7] that the maximum volume fraction ϕ_M increases with shear. Barnes et al. [14] summarized data from monodispersed spherical index particles (Figure 2) in which ϕ_M was shown to be 0.63 at $\tau \to 0$ and 0.71 at $\tau \to \infty$. They noted that the maximum volume fraction of monodispersed spheres depends on the particular geometric arrangement, ranging from 0.52 for simple cubic to 0.74 for face-centered cubic. Thus it is reasonable that randomly packed spheres would pack more densely when subjected to a higher shear stress. Intrinsic viscosity often also increases with shear. Calculations of Hinch and Leal [20] showing how $[\eta]$ varies with aspect ratio for high and low shear are summarized in Figure 3. For an aspect ratio of unity (spheres), $[\eta]$ does not vary with shear level. However, for low aspect ratios (disc-shaped particles) and high aspect ratios (rod-shaped particles), $[\eta]$ decreases with increasing shear, reflecting the tendency of anisotropic particles to be aligned by the shear and thereby offer an average volume lower than that provided by the same particles when randomly oriented.

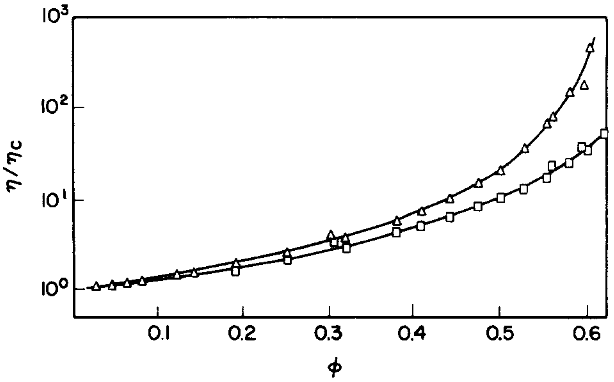

FIGURE 2. Relative viscosity versus volume fraction for suspensions of monodisperse spherical particles. Symbols are: △, low strain rate (η_0, ϕ_M = 0.632 and $[\eta]$ = 3.133); □, high strain rate (η_∞, ϕ_M = 0.708 and $[\eta]$ = 2.710) (Figure 7.8 in Barnes et al. [14], with permission).

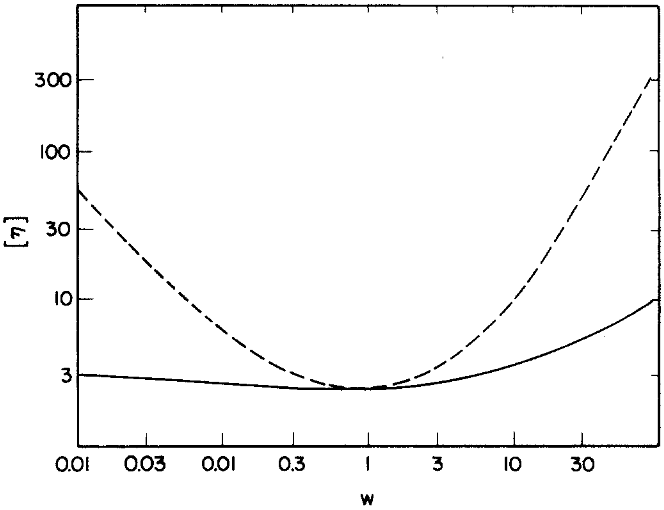

FIGURE 3. Intrinsic viscosity ($[\eta]$) at high shear (solid line) and low shear (dashed line) as a function of aspect ratio (w) (adapted with permission from Hunter [26]).

The Krieger-Dougherty equation was derived for dispersed particles, in which particle interactions are limited to random effects produced by Brownian motion. However, the equation has been applied to flocculated suspensions (most notably by Hunter and colleagues, as reviewed in ref 19). The equation is valid for flocculated suspensions, but the constants do not have the same physical significance [8].

Experimental Procedure

To determine whether the Krieger-Dougherty equation can be used to relate viscosity of cement paste to its concentration, rheological measurements were made on suspensions of Portland cement and water covering a moderate range of concentrations. Three commercial Portland cements were used:

1. type I Portland cement (Essroc Cement Co., Logansport, IN), the general-purpose cement in our concrete laboratory, consisting of C_3S, C_2S, C_3A, C_4AF, and $C\bar{S}H_2$
2. white Portland cement (Courtesy of Lehigh Portland Cement Co., manufactured by Aalborg A/S, Denmark), consisting of C_3S, low in C_2S, very low in C_3A, and no C_4AF, used in rheology studies by Struble and Sun [21] and in DSP studies by Sun et al. [22])
3. type V Portland cement (Courtesy of California Portland Cement Co., manufactured by Grupo Cementos Mexicanos, Hermosillo, Mexico), consisting of C_3S, low in C_2S, and C_4AF, very low in C_3A (In the cited studies this cement was incor-

rectly labeled as a Blue Circle Cement.), used in previous rheology studies [23].

Pastes were prepared by mixing about 100 g cement with the desired amount of deionized water. The concentration of cement (ϕ, expressed as cubic meters of cement per cubic meter of paste) ranged from approximately 0.35 to 0.6, equivalent to water:cement ratios (w:c, expressed as grams water per gram cement) from approximately 0.2 to 0.5. In most experiments the cements were dispersed chemically using a sulfonated naphthalene formaldehyde superplasticizer. The dosage of superplasticizer, 0.050 g solid superplasticizer per gram of cement, was selected to provide full dispersion. These chemically dispersed suspensions were limited to higher concentrations (ϕ of 0.5 to 0.6) to avoid errors in concentration due to settling of the larger cement particles. A few samples of the type I cement were also prepared without superplasticizer. These flocculated pastes were made at lower concentrations (ϕ of 0.35 to 0.5) because pastes of higher concentrations were too stiff to mix. Settling was not observed in these flocculated pastes.

The mixing procedure was designed to provide a uniform and reproducible starting condition for rheological measurements. Cement was added to water (in which superplasticizer, if used, was predissolved). Pastes were mixed using a paddle mixer (Kitchen Aid, model K45ss) at medium speed for about 5 minutes, then transferred to the rheometer. As soon as each paste was placed in the cup and the bob was lowered into the correct position, the cup was covered with a solvent trap to prevent evaporation of water during testing. Pastes were then sheared in the rheometer at a high strain rate (920 seconds^{-1}) for 45 seconds before rheological measurements were begun. As described elsewhere [23], we used this high shear mixing to take the paste through the irreversible structural breakdown described by Tattersall and Banfill [5] and thereby provide a reproducible starting condition.

Rheological measurements utilized a computer-operated strain rate controlled viscometer (Bohlin VOR rheometer). The measurements were carried out in the static shear mode, in which stress measurements are made at various strain rates. The strain rate was ramped from 14.6 to 921 seconds^{-1}, a process that required about 8 minutes. The rheometer was equipped with Couette (cup and bob) geometry; the radius of the inner cylinder was 7.0 mm and the gap was 0.7 mm. Because of the narrow gap, the strain rate was assumed to be constant across the gap. No special effort was made to roughen the cup or bob surfaces because there was no experimental evidence that slip was occurring [23].

Throughout the entire procedure (high shear mixing, equilibration, and testing) the temperature was maintained at 25°C by means of a circulating water bath. The entire testing procedure was completed within 15 minutes after cement and water were first mixed; little hydration of cement is expected during this early period, and no changes in flow behavior were observed that could be attributed to hydration effects.

Rheology Data and Analysis

The flow behavior of dispersed cement paste depends on concentration. Some typical flow curves are shown in Figures 4 and 5. Pastes at lower concentrations (or high w-c) showed Newtonian behavior, while pastes at higher concentrations (or low w:c) were more nearly pseudo-plastic or plastic. Only one of the dispersed cement pastes, the type V, showed a well-defined low strain rate plateau viscosity (and this only at the higher concentrations); other dispersed pastes generally fit a power-law relationship:

$$\tau = a\gamma^b \tag{6}$$

where τ is shear stress, γ is the rate of strain, and a and b are constants.

The type I cement was also studied in a flocculated condition (without superplasticizer). Flocculation altered the flow behavior considerably, as shown in Figure 4 for two pastes at the same concentration. Flocculated pastes were plastic at all concentrations.

Apparent viscosity values were measured at two strain rates, 25 and 500 seconds^{-1}, for pastes of various concentrations. Values at $\phi = 0$ were not measured, but were assumed to equal the viscosity of water.

Results and Discussion

Because the Krieger-Dougherty equation does not transform to a linear function, viscosity and concentration values were fitted to eq 1 using nonlinear regression. These calculations were carried out using Mathematica (Wolfram Research, Inc., Champaign, IL), and results are listed in Table 1. Figures 6, 7, and 8 show measured values (symbols), and Krieger-Dougherty curves (lines) computed using the values in Table 1. Some of the results reported here were also discussed in an earlier publication by Struble and Sun [21], in which the method for fitting data to the Krieger-Dougherty equation was described.

The experimental data fit the Krieger-Dougherty equation (eq 1) quite well. The calculated correlation

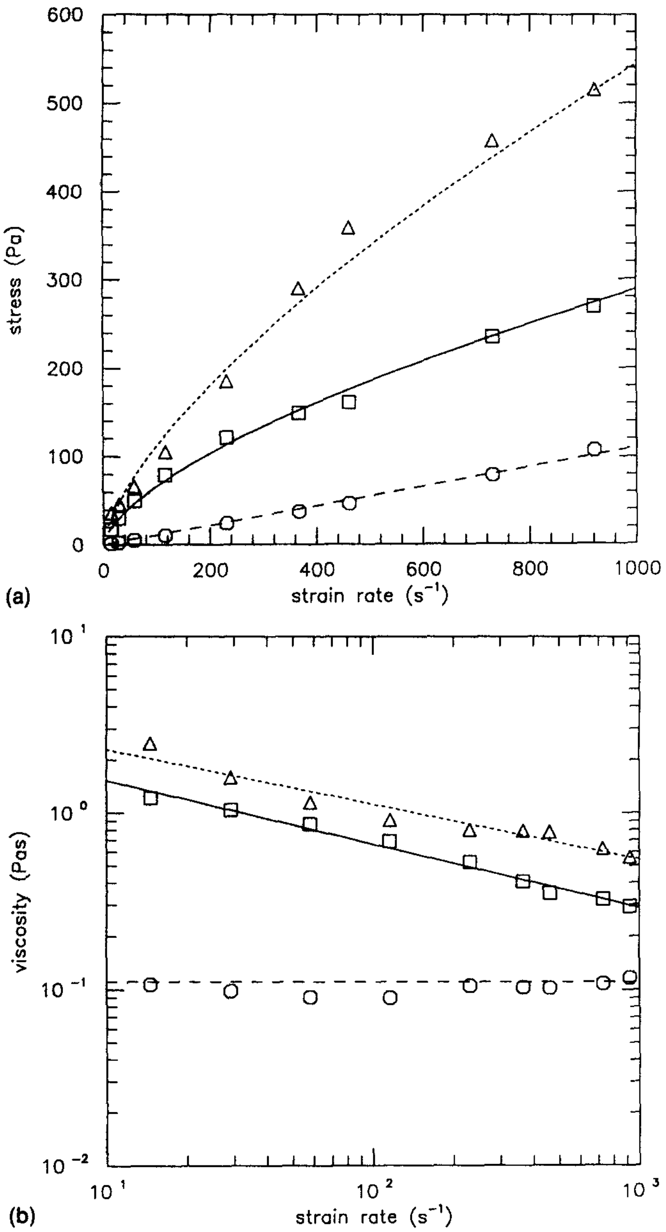

FIGURE 4. Flow curves for type I Portland cement: (a) stress versus strain rate and (b) viscosity versus strain rate. Symbols are: ○, w:c = 0.32 and 5% superplasticizer; □, w:c = 0.32 and 0% superplasticizer; and △, w:c = 0.23 and 5% superplasticizer. Lines were computed using eq 6.

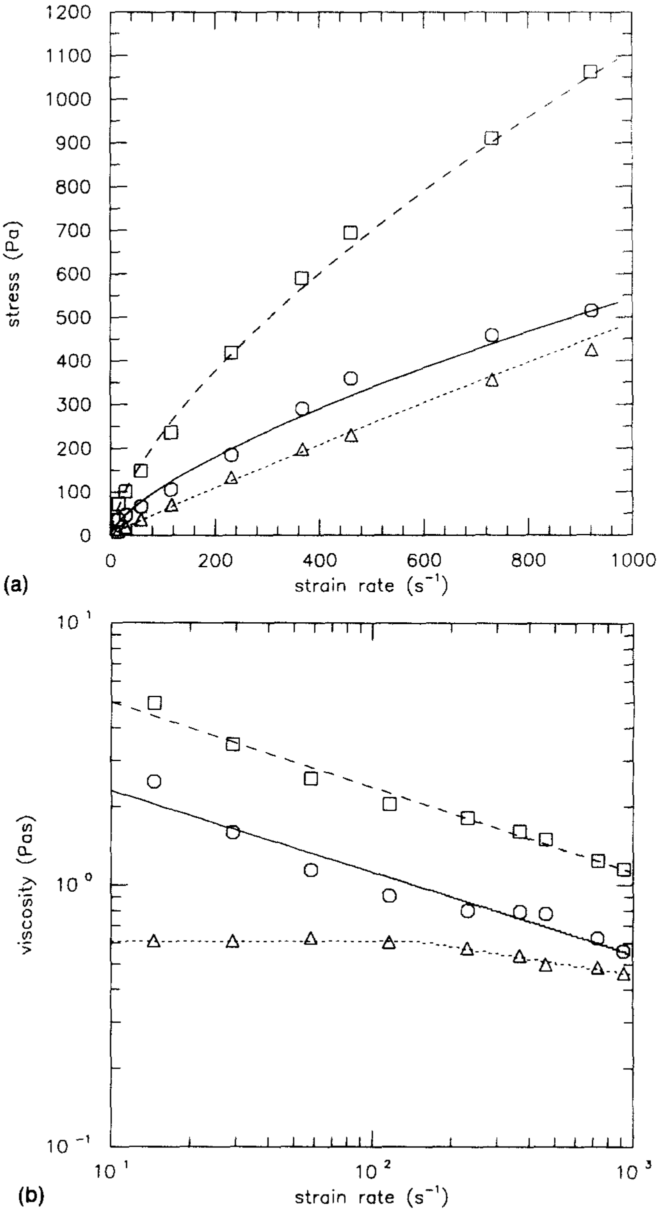

FIGURE 5. Flow curves for dispersed cements: (a) stress versus strain rate and (b) viscosity versus strain rate. Symbols are: ○, type I cement; □, white cement; △, type V cement. Lines were computed using eq 6.

coefficients (R^2) were generally greater than 0.99, and in every case greater than 0.90.

We presented details about the nonlinear regression analysis in the previous article [21]. These details included the error function (the sum of the squared difference between measured values and calculated values) and how it varies with the two Krieger-Dougherty parameters. The error function appears to have only one minimum, but this minimum is quite shallow, so it appears that the Krieger-Dougherty parameters are not well defined for cement. In the analyses described here the error functions gave similar solutions—unique but not well defined.

The cement pastes typically gave values of 0.7 for the maximum volume fraction (ϕ_M) and 6 for intrinsic viscosity ([η]). For dispersed pastes, values for ϕ_M ranged from 0.64 to 0.80, and values for [η] ranged from 4.5 to 6.0; ϕ_M averaged 0.7 and [η] averaged 5. The particle-size distribution of cement is quite broad, and particles are known to be angular and often elongate [24]. The broad particle-size distribution may (though does not necessarily) increase the ϕ_M value from that obtained

TABLE 1. Krieger–Dougherty parameters for cement–water suspensions

Cement	Strain Rate (s^{-1})	ϕ_M	$[\eta]$
Type I, dispersed	25	0.64	5.1
	500	0.76	6.2
Type I, flocculated	500	0.64	6.3
White cement, dispersed	25	0.67	5.7
	500	0.80	6.8
Type V cement, dispersed	Low strain rate limit	0.70	4.7
	25	0.68	4.5
	500	0.75	5.2

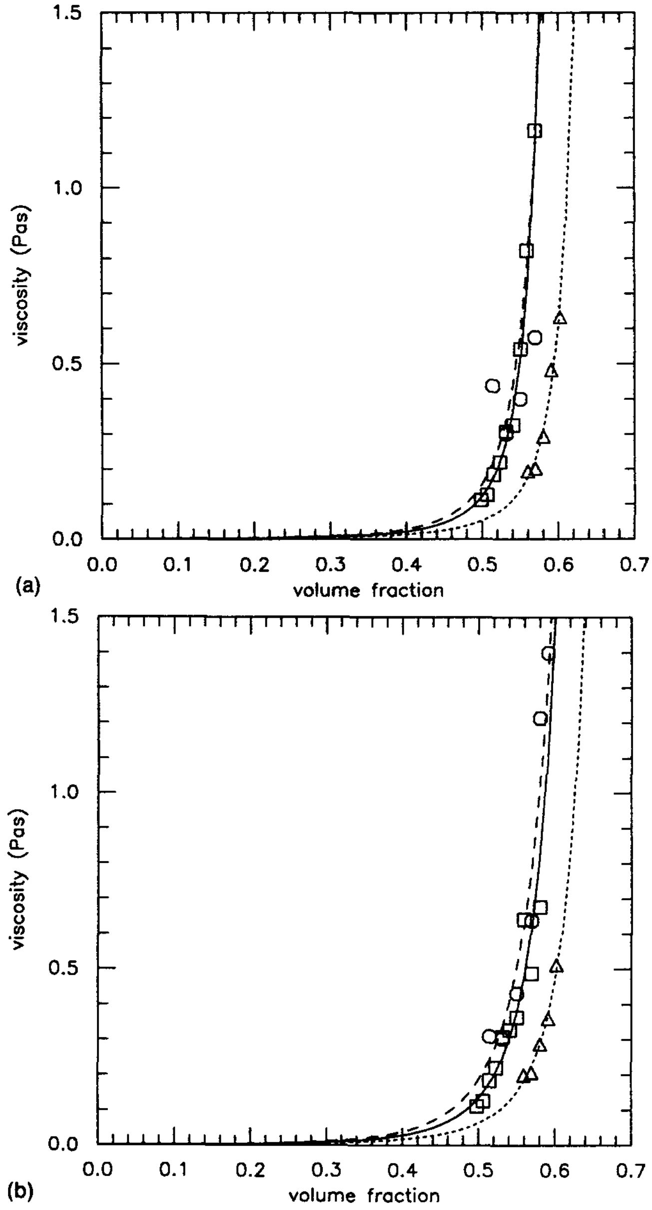

FIGURE 6. Krieger-Dougherty curves for dispersed cements: (a) at 25 seconds^{-1} and (b) at 500 seconds^{-1}. Symbols are: ○, type I cement; □, white cement; △, type V cement. Lines were computed using eq 1 with values listed in Table 1.

for monosized spheres (0.63 at low shear and 0.71 at high shear), and angular and nonequant particles decrease the ϕ_M value. Likewise, nonequant particles increase the value of $[\eta]$ compared with the value of 2.5 expected for spheres. We plan to continue these studies by determining whether these parameters can be estimated from the particle-size distribution and particle shape. At the moment, however, there are no direct quantitative relationships, so we did not measure particle-size distribution or particle shape of the cements used in these studies.

The Krieger-Dougherty parameters were not precisely the same for the three cements (Table 1). Values of ϕ_M did not vary appreciably among the three cements. Values of $[\eta]$ varied somewhat more, such that the Krieger-Dougherty curve for the type V cement is somewhat to the right of the other two in Figure 6.

Values of the Krieger-Dougherty parameters were found to vary with the strain rate. As shown in Table 1, both ϕ_M and $[\eta]$ were lower at 25 seconds^{-1} and higher at 500 seconds^{-1}. As discussed previously, ϕ_M is expected to increase with increasing strain rate, as we observed, but $[\eta]$ is expected to decrease with increasing strain rate for nonequant particles, the opposite of what we observed. We can offer no explanation for this unexpected behavior, which was shown by all the cements we tested.

As noted previously, the flow curves for the type V cement showed a plateau in viscosity at low strain rate, allowing us to estimate η_0 following the procedure used by Krieger and Dougherty [1]. Results using η_0 were very similar to the results using η at 25 seconds^{-1} (Table 1 and Figure 7).

Flocculation had a considerable effect on the Krieger-Dougherty results. The viscosity-concentration values of the flocculated type I paste measured at 25 seconds^{-1} could not be fitted to eq 1, though the values measured at 500 seconds^{-1} fit the equation well. It may be that wall slip contributed to the difficulty with values measured at the lower strain rate. At the higher strain rate, the value of ϕ_M obtained for the flocculated paste was considerably lower than the value obtained for the dispersed paste, while the value of $[\eta]$ obtained for the flocculated paste was only slightly lower than the value for the dispersed paste (Table 1). The curve for the flocculated paste lies considerably to the left of the curve for the dispersed paste in Figure 8. This difference reflects the fact that the flocculated paste has a much higher viscosity than the dispersed paste at the same volume fraction; in fact, it was only possible to measure flow curves for the two pastes for a single volume fraction; and these two flow curves were very different (Figure 6). These results are somewhat different from those of Asaga and Roy [25], who reported similar plastic viscosity values with and without super-

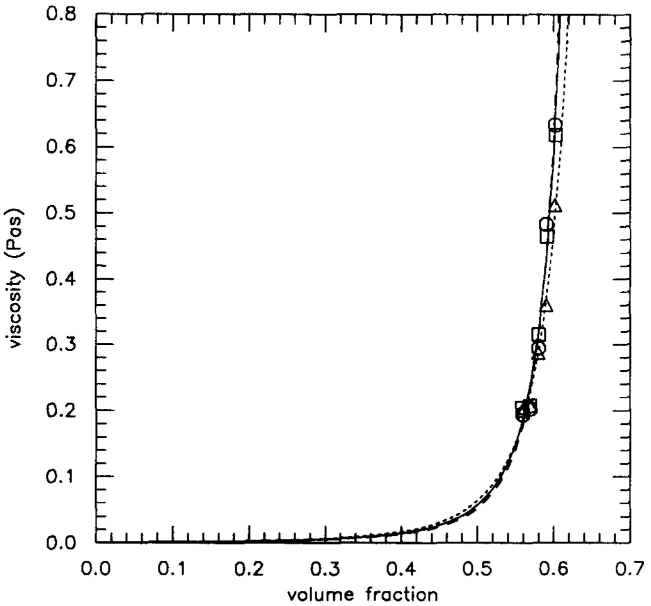

FIGURE 7. Krieger-Dougherty curves for dispersed type V cement at various strain rates. Symbols are: ○, low strain rate limit; □, 25 seconds^{-1}; △, 500 seconds^{-1}. Lines were computed using eq 1 with values listed in Table 1.

plasticizer. Admittedly, their results were at $\phi = 0.44$ (w:c = 0.4), a lower volume fraction than we were able to measure because of settling. However, their maximum dosage was only 0.8% superplasticizer, whereas we used 5% solid superplasticizer by weight of cement, so it is therefore likely that their suspensions were not fully dispersed. Hunter [19] has proposed that the lower maximum volume fraction of a flocculated suspension is an indication of the openness of the floc structure, even for viscosity measured at high strain rate, and that shear thinning behavior of flocculated suspensions at lower strain rates is due to breaking of bonds between individual flocs.

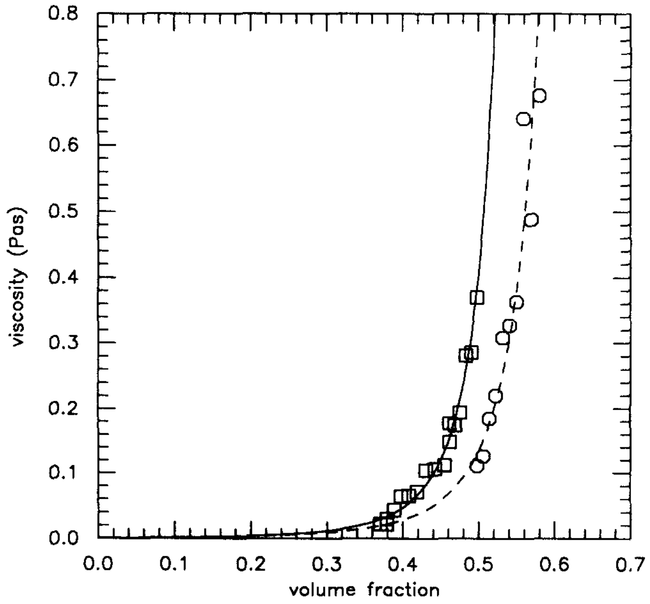

FIGURE 8. Krieger-Dougherty curves for type I Portland cement at high strain rate (500 seconds^{-1}). Symbols are: □, 0% superplasticizer; ○, 5% superplasticizer. Lines were computed using eq 1 with values listed in Table 1.

Conclusions

Viscosity values for dispersed cement pastes were found to vary with concentration according to the equation proposed by Krieger and Dougherty [1]. For dispersed paste, the Krieger-Dougherty parameters were approximately 0.7 for maximum volume fraction and 5 for intrinsic viscosity. Both parameters increased when the viscosity was measured at a higher shear rate. Pastes that were not dispersed were found to be considerably higher in viscosity. One flocculated paste, tested at a strain rate of 500 seconds^{-1}, fit the Krieger-Dougherty equation but gave a lower maximum volume fraction than the corresponding dispersed paste, indicating fairly open flocs even at the high strain rate used for viscosity measurements.

Acknowledgments

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