

# Influences of Mixing Methods on the Microstructure and Rheological Behavior of Cement Paste

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Relationships between mixing methods and both rheological properties and microstructure of cement pastes are described. In particular, a newly observed peak stress, determined at low constant shear rate, is correlated with various mixing methods and the size of inhomogeneities or agglomerates within cement pastes. The results of this research impact on the importance of laboratory mixing techniques when applying results to field concrete. Advanced Cement Based Materials 1995, 2, 70–78

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he microstructure of fresh cement paste and its relationship to various methods of mixing on the one hand and to flow behavior on the other are poorly understood. In particular, identification of microstructural defects associated with various mixing processes is important in order to establish control of the mechanical properties of cement.

Broadly speaking, rheology is the study of relationships between stress, deformation, and rate of deformation of suspensions or fluids [1]. The rheological behavior of cement paste is frequently described as Bingham plastic flow [2,3], for which the relationship between stress and rate of deformation can be expressed with two parameters, the Bingham yield stress  $\tau_B$ , and plastic viscosity  $\eta_{PL}$ , as

$$\tau = \tau_{\rm B} + \eta_{\rm PL} D \tag{1}$$

where  $\tau$  is shear stress and D is the shear rate.

The influences of different mixing energies on the rheological behavior of cement paste generally have been studied qualitatively. Early research demonstrated that the flow of cement paste is sensitive to shear history and intensity of mixing [2,4]. Cement

Address correspondence to: Hamlin M. Jennings, Department of Civil Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208. Received February 5, 1994; Accepted July 22, 1994 paste mixed using a high speed blender exhibits a lower Bingham yield stress, plastic viscosity, and less structure breakdown than does a paste mixed following American Society for Testing and Materials (ASTM) standards [4].

Relationships between mixing and the microstructures of cement paste are poorly understood [2,5]. It is obvious that the purpose of mixing fine powder such as cement is to reduce the scale and extent of clusters or clumps, and thereby to wet all surfaces. Because the homogeneity of cement paste has not been evaluated quantitatively, the importance of small clusters remaining in the paste due to insufficient mixing has not been recognized.

This article addresses the effects of mixing from both the microstructural and rheological points of view. Our interests are in what microstructural defects result from insufficient mixing, and how they change the flow behavior of cement paste. The objectives of the present research are: (1) to understand the effects of mixing methods on certain rheological properties of cement paste; (2) to identify and investigate microstructural defects associated with various mixing methods; (3) to correlate these microstructural defects with rheological properties; and (4) to identify and formulate a measurable parameter to quantify the extent of mixing, which also characterizes the microstructural defects of the paste. In this article, a low energy mixer refers to a 1/6-hp paddle mixer capable of 150 to 300 rpm as required by ASTM standards, and a high energy mixer refers to a 1/2-hp mixer capable of speeds above 3000 rpm (e.g., a heavy-duty food blender).

# **Background on Mixing**

Mixing is an operation of reducing or eliminating the inhomogeneities in a mixture by mechanical action, which can also achieve thermal or material uniformly and/or enhance a rate process. Two basic physical processes are active in a mixing operation: intensive and extensive mixing [6].

Intensive mixing, or dispersion, efficiently reduces the scale of the agglomerates of particles or droplets bonded by surface tension. For instance, the dispersion of a fine powder into a viscous fluid requires intensive mixing. The agglomerates of the fine particles can be ruptured when subjected to hydrodynamic stresses exceeding the strength of the interparticle bonds in the agglomerates. An intensive mixer provides high local stress even though the shear rate of the global fluid may not be high. For example, roll mills or extruder types of mixers are more apt to break agglomerates than ordinary simple shear mixers because of the high local shear stresses that can be achieved.

Extensive mixing or blending incorporates miscible phases simply by deforming the fluid. Such a process is governed by the shear strain history of the paste. For instance, in laminar shear flow the relative motion between streamlines across the flow brings about deformation of fluid elements. This results in an increased area of interface between the components, so that the extent of inhomogeneities is reduced.

There are many types of mixers, some of which enhance the intensive mixing process and some of which enhance the extensive process. The choice of mixer depends on the nature of the components to be mixed. An intensive mixer will help disperse cohesive powders, such as cement powder. In an ideal mixture of cement paste, cement paste should be free of clumps, every particle would be surrounded by water, and the mixture would exhibit low viscosity. A homogeneous cement mix can be obtained by a mixing process that provides enough stress to break these agglomerates.

Currently, no established method exists that quantifies how well a paste is mixed. A quantitative measure of the extent of mixing should be capable of giving the extent of homogeneity of the spatial distribution of mass (or temperature) [6]. The measure of how well the cement paste is mixed should at least characterize the size of inhomogeneity or agglomerates.

The mixing procedure classified in ASTM C305 is commonly used to prepare laboratory samples of paste or mortar all around the world. According to this standard [7], a paddle mixer should have at least 1/6-hp power. The procedure for mixing cement paste includes rotation at 140 rpm for 0.5 minutes and rotation at 285 rpm for 1 minute. Thus, the maximum rotation speed is about 300 rpm. A heavy-duty food Hobart mixer is typically used to simulate a paddle mixer in the laboratory. It is an extensive type of mixer. One of the motivations of this research is to evaluate the extent of mixing following the ASTM standard and to understand the applicability of results obtained in a laboratory when they are applied to field concrete.

An understanding of both the mechanisms of intensive mixing and the nature of the cohesive powder is important for achieving an understanding of efficient mixing of cement. The term "cohesive powder" commonly refers to a powder having structures that inhibit flow. Microstructural features, such as agglomerates, grits, or clusters normally develop in such powders. In this article these features will be collectively referred to as agglomerates. Fine powder, or powder with high surface area, typically exhibits high cohesive forces. The agglomerates in a cohesive powder are attributable either to attractive forces (e.g., electrostatic charging and/or van der Waals forces) between particles, or to bonding between the particles due to moisture [8]. The force required to break these structures depends on the strength of the interparticle bonds.

Cement powder has high surface area. The Blaine surface area of cement powder is usually between 300 and 400 m²/kg [9]. Because cement powder stored in a bag is generally highly compacted, due to its own weight and that of other bags above it during transportation and storage, van der Waals forces probably contribute significantly to the adhesive force. In addition, cement powder is chemically reactive with water. Even before mixing cement with water, slight amounts of moisture on the surface can result in the formation of early reaction products that bridge neighboring particles. If an envelope of these bridging particles occurs, a cluster is formed. In our experience, agglomerates with diameters of about 1 mm or less are typically present even in some fresh bags of cement.

The forces required to break the structure of agglomerates are transmitted through the fluid during mixing. In the case of two particles that form a dumbbell, the maximum dispersive force from a steady shear flow of a Newtonian fluid, known as the dispersive force,  $F_{\text{max}}$ , is [6]:

$$F_{\text{max}} = 3 \, \pi \eta R_1 R_2 D \tag{2}$$

where  $\eta$  is the viscosity of the fluid,  $R_1$  and  $R_2$  are the radii of the particles, and D is the shear rate. Equation 2 shows that the depressive force is proportional to the viscosity,  $\eta$ , of the fluid. More power is needed to break two attached particles in a lower viscosity fluid than in a high viscosity fluid.

Equation 2 is modified here in order to apply to the cement system. In a Newtonian fluid the shear stress is  $\eta D$ , while for a Bingham fluid or suspension, such as cement paste, the shear stress is  $\tau_B + \eta_{PL} D$  (from eq 1). Thus, the dispersive force resulting from mixing cement paste should be:

$$F_{\text{max}} = 3 \pi R_1 R_2 (\tau_B + \eta_{PL} D).$$
 (3)

# **Experimental Method**

#### Rheometer

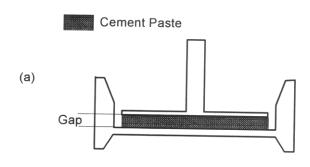
The flow behavior of cement paste was studied using a shear rate controlled rheometer, the Haake CV20N. It is equipped with two sets of sensor systems, plate-plate and cone-plate, as shown in Figure 1a and b. As the sample holder rotates at a given speed, a resistive torque from the sample is detected by the top sensor, which is converted to shear stress. The relation between rotation speed, n, and shear rate, D, is

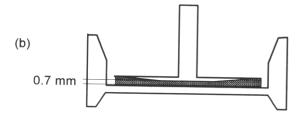
$$D = Mn (4)$$

where n is the given rotational speed in revolutions per minute and M is a geometric constant of the specific sensor system.

The advantage of the cone sensor system is that the shear rate is constant over the radius. Both cone sensors PK45 and PK30 have a cone angle of 4°. The diameter of PK45 is 41.74 mm, and that of PK30 is 27.83 mm. Both cone sensors were truncated by the manufacturer to provide a clearance of 0.35 mm. A nontruncated tip would just touch the bottom plate and, in the case of cement, cause binding. The relative position of a cone sensor and the bottom plate is fixed, and thus *M* for a cone sensor is a single value, 1.5 for both PK45 and PK30. The cone sensor PK45 used in this work was truncated further in order to increase the clearance to 0.7 mm [10]. This truncation resulted in a negligible change in *M* [10].

On the other hand, in a plate sensor system the





**FIGURE 1.** Illustration of rheometer. (a) Plate-plate sensor; (b) truncated cone-plate sensor.

shear rate is not constant over the radius. However, the advantage is that the relative position of the sensor and the bottom plate (i.e., the gap as shown in Figure 1a) is adjustable. This minimizes binding in suspensions. For a given gap, the shear rate at the center is zero, while that at the edge is maximum. This edge value is defined as the shear rate. The *M* factor is inversely proportional to gap. The diameter of the PQ30 is also 27.83 mm, and its *M* factor is

$$M = \frac{1.457}{\text{Gap (mm)}}.$$
 (5)

Table 1 shows the rotational speeds for three shear rates of our three sensors at various gaps (plate-plate only), using eqs 4 and 5.

Shear stress of a Newtonian fluid in a cone-plate sensor system is a linear function of shear rate. Ideally, the flow curve (shear stress versus shear rate) of a Newtonian fluid measured in a plate-plate rheometer using various gaps (as defined in Figure 1a) should be identical to that measured in a cone-plate rheometer, when complications such as those caused by an uneven distribution of shear rate over the radius or slippage at the interface are negligible. Extensive study [10] has shown that slippage does not occur with these sensor systems under normal testing conditions.

To check effects of gap, the flow curves of a Newtonian fluid, calibration oil of viscosity 4.85 Pa-s, were obtained at shear rates up to  $100\ s^{-1}$ , using the PK30 and PQ30 at gaps of 1.0, 0.8, 0.6, 0.4, and 0.2 mm. The results in Figure 2 show that the agreement between measurements obtained with the PK30 and PQ30 at gaps larger than 0.6 mm is satisfactory. When the gap is small, however, the viscosity of calibration oil measured with the PQ30 is lower than 4.85 Pa-s. In contrast, the viscosity of cement suspensions measured at very small gap (<0.3 mm) is typically larger than that measured at large gaps [11]. It is likely that as the gap approaches the size of cement agglomerates, direct friction between cement agglomerates and both the sensor and the bottom plate results in a larger shear stress. For cement paste, the effect of agglomerates is

TABLE 1. Rotation speed of Haake CV20N with plate and cone sensors

Shear Rate D (s <sup>-1</sup> )	Plate Sensor PQ30 n (rpm)		Cone Sensor PK45 or PK30
	Gap = 1 mm,	0.1 mm	n (rpm)
100	68.9	6.9	66.7
10	6.9	0.7	6.7
2	1.4	0.1	1.3

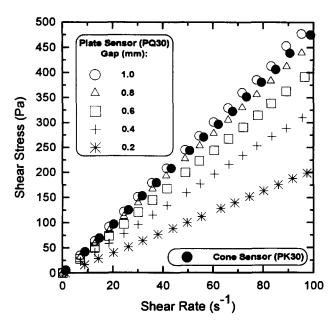


FIGURE 2. Flow curves of calibration oil measured using cone and plate sensors.

very important at small gap sizes. Based on this effect, an empirical parameter called limiting gap is studied here to detect the extent of inhomogeneity within cement paste.

#### Limiting Gap

Gap, as defined in Figure 1a, is a parameter to investigate the connection of the rheological behavior of cement paste to that of fresh concrete [11]. Minimum usable gap [11] is the smallest gap at which viscosity reaches the highest measurable value of the instrument used to detect it. It is a function of the water:cement ratio (w:c) and the degree of flocculation. At a w:c of 0.55 and with the lowest degree of flocculation (with addition of 2% sodium polyacrylate), the minimum usable gap was about 70 µm, which is two to three times the average size of cement particles and roughly equal to the size of the largest particles. The main criticism [12,13] of this work is that gap may not be a scientifically fundamental parameter because of the complications that can be introduced using a platetype sensor (i.e., slippage and varying shear rate over the radius).

Limiting gap is proposed in this work as an empirical parameter that characterizes the extent of mixing in cement. A typical relationship of shear stress ratio versus gap size for cement paste at a fixed shear rate is illustrated in Figure 3, where the shear stress ratio is  $\tau_{\rm h}/\tau_{\rm H}$  (details are described below).  $\tau_{\rm H}$  is the shear stress that is independent of the size of the gap (larger than 0.3 mm) and is taken as the bulk value, while  $\tau_h$ is a function of gap. Typically, when the gap is small,

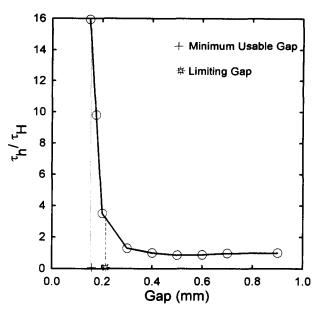


FIGURE 3. Shear stress versus size of gap measured by a plate-plate sensor for cement paste.

the shear stress ratio increases slowly with decreasing gap until it reaches three. At smaller gaps (gap <0.2 mm in Figure 3), the shear stress ratio increases dramatically. Thus, limiting gap denotes the gap at which the measured shear stress is about three times that of bulk value. This parameter is useful as an empirical parameter to quantify the degree of mixing.

# **Experimental Procedure**

Two sets of experiments were conducted with the following objectives: one set (set A) to study the effects of mixing methods on the rheology behavior, and the other set (set B) to define the combined influences of w:c and mixing on the structure of agglomerates and to address the problem of quantifying the extent of mixing.

#### Mixing

Type I Portland (continental) cement was used in all the experiments. Within the range of type I cements, all of the results reported here are generally applicable, so that the detailed composition is not considered important.

SET A. The w:c ratio was fixed at 0.37. Simple shear mixing at both high and low energy mixing methods was studied. The first paste was mixed by hand for 5 minutes; the second paste by a paddle mixer (a 1/6-hp paddle mixer at 300 rpm) for 5 minutes (this method slightly exceeds the ASTM mixing requirement); and the third by a 1/2-hp Osterizer blender at 3000 rpm for 1 minute. In addition to these mixing methods, a fourth paste was prepared by passing dry cement powder through a 150- $\mu$ m sieve prior to hand-mixing for 5 minutes. The purpose of sieving was to break apart the dry clusters before mixing, and it was used only for this last mixing procedure.

**SET B.** W:c ratios of 0.50, 0.45, 0.40, and 0.35 were used. In addition to extensive mixing, as described above, ball milling with large aggregates (aggregates used in concrete) was used to prepare pastes. The purpose of ball milling was to simulate intensive mixing by means of increasing the local stress at the contact between two aggregates in order to efficiently break the agglomerates or clusters (possibly this procedure simulates mixing in a truck). In this method, cement paste was mixed initially by hand for 1 minute, and then large aggregates of about 1 to 2 cm (the volume ratio of paste to aggregate was 1:1) were added, and the paste was milled together for 20 minutes. The aggregate was then removed.

#### Time of Test

Set A samples of the cement pastes were tested immediately after mixing, and then new samples were each tested after 1, 1.5, and 2 hours. To avoid sedimentation, the pastes were rotated at a speed of 60 rpm in small, cylindrical, plastic containers until testing. In set B, the cement pastes were tested shortly after mixing.

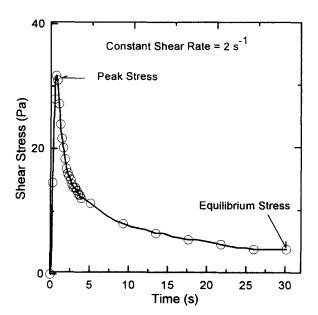
#### Rheological Measurements

SET A. The cement paste was tested under constant steady shear test with a 45PK cone sensor. The shear rate was 2 seconds<sup>-1</sup> for 30 seconds. Typical results are shown in Figure 4. During this test, the shear stress of cement paste reached a peak value, which we define as the peak stress, and then decayed to a constant value, which we call the equilibrium stress. Only the peak stress was considered for discussion in this article.

SET B. To determine the limiting gap, the relationships of shear stress ratio  $(\tau_h/\tau_H)$  versus gaps ranging from 0.1 to 1.0 mm using the PQ30 sensor were determined. A constant shear rate of 100 seconds  $^{-1}$  was chosen to avoid low rotational speed (<1 rpm) at small gaps (see Table 1). The peak stress at a gap of 1.0 mm was  $\tau_H$ , which was considered as independent of gap. Peak stress at a given gap (<1.0 mm) was  $\tau_h$ . A series of tests was carried out for each paste to obtain  $\tau_h$ , using a range of gaps starting at 0.9 mm and decreasing by 0.1 mm. Finally, the stress ratio,  $\tau_h$ : $\tau_H$ , was calculated as a function of the size of gap for each w:c.

#### Microstructure

The microstructures of cement pastes at 20 minutes and 1, 2, and 5 hours were observed in an environ-



**FIGURE 4.** Shear stress versus time of cement paste under a constant shear rate of 2 seconds<sup>-1</sup>.

mental scanning electron microscope at 70% relative humidity and 10°C. To study the microstructure of the bulk paste, a small amount of cement paste was simply placed on the flat surface of a sample holder. After mixing, the state of hydration, or extent of penetration of water into the agglomerates, was observed by removing an agglomerate from the paste and placing it on the surface of a sample holder. The agglomerate was then cut with a razor so that the cross-section could be examined. This procedure was repeated numerous times and was highly reproducible.

#### **Results and Discussion**

# Relationship Between Flow Behavior and Mixing Methods (Set A)

The peak stresses of the cement pastes at different times are plotted in Figure 5. The peak stresses of cement paste mixed by hand and by paddle increased faster and had higher values than did that of paste mixed by a high energy blender. Paste made by hand mixing a sieved cement had nearly the same peak stress as that made by the high energy blender. The similarity of the peak stress of cement paste made using sieved dry powder to paste produced by high energy mixing suggests that the clusters remaining in the former two pastes could be responsible for the higher values and faster increase in the peak stresses. Since sieving physically separates and breaks agglomerates, one must conclude that aggregates contribute significantly to the flow behavior of cement paste.

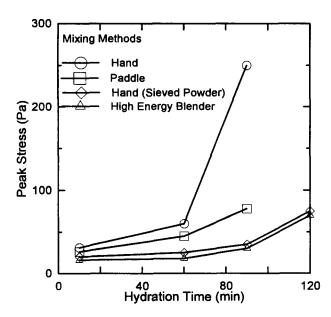


FIGURE 5. Influences of mixing methods on the peak stress of cement paste.

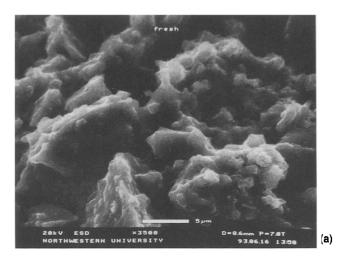
### Effect of Mixing Methods on the Microstructure of Cement Paste (Set A)

The appearance of cement pastes prepared by the various mixing methods differed. The texture of paste made from paddle or hand mixing was rough and gritty. The size of the agglomerates was about 0.3 mm on average (the scattering was 30%), as determined by spreading the paste on a glass slide and observing under an optical microscope.

On the other hand, pastes prepared with a high energy blender or by hand mixing sieved powder had a fine and creamy appearance. This suggests that a wellmixed paste was obtained by these two methods, in which the size and quantity of clusters were reduced significantly.

The micrograph in Figure 6a was taken in the bulk region of a 20-minutes-old paste that was originally paddle mixed. The particles are wet and covered with hydration product. The micrograph in Figure 6b shows a cross-section of an agglomerate taken from the same paste. In contrast to the particles in the bulk region, the surfaces of the particles within the agglomerate are clean and dry. Five hours later this microstructural difference persisted. The particles of paste from the bulk region, as shown in Figure 7a, were thickly covered with hydration products, while the particles inside an agglomerate, as shown in Figure 7b, were still dry and unhydrated. This observation was repeated dozens of times and demonstrates that agglomerates that are not ruptured during mixing may remain unhydrated for a long time.

The properties of a hydrated cement paste (e.g., modulus, strength, and thermal expansion) and those



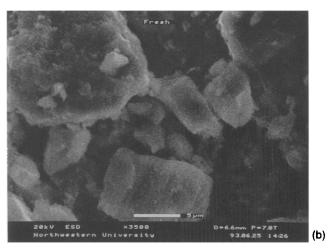


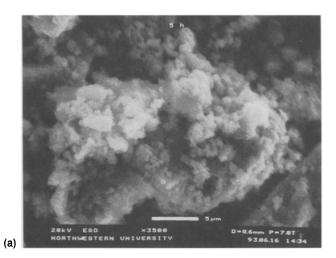
FIGURE 6. Micrographs of paddle-mixed cement paste (20 minutes old). (a) Bulk region; (b) cross-section of an agglomerate.

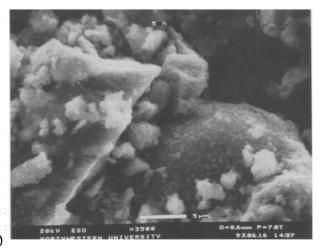
of agglomerates of dry cement powder must be quite different. Thus, microcracks and residual stresses have more chance to form in a poorly mixed paste than in a well-mixed paste. Agglomerates remaining in a paste after mixing are potential sources for microstructural defects.

## Dependence of Flow Behavior on Gap Size (Set B)

The peak stress ratios,  $\tau_h/\tau_H$ , of pastes (w:c = 0.45) mixed by various methods are plotted in Figure 8 as functions of gap size. Limiting gap can be determined in such a figure as the gap at which the peak stress ratio equals 3. As shown in Figure 8, this limiting gap of cement paste is sensitive to the extent of mixing. The lower the limiting gap, the more intense the mixing

Table 2 lists the limiting gaps of cement pastes mixed



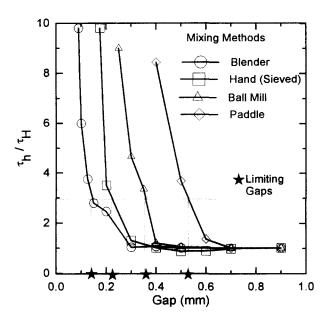


**FIGURE 7.** Micrographs of paddle-mixed cement paste (5 hours old). (a) Bulk region; (b) cross-section of an agglomerate.

by various methods at a w:c of 0.50, and the estimated size of inhomogeneity of the paste. Considering a paste made by mixing with a blender to be agglomerate free, its size of inhomogeneity should be on the order of the largest particle (i.e., 40 to 100  $\mu m$ ). The size of agglomerates of paste made by hand mixing sieved powder should be about the size of the sieve, 150  $\mu m$ . Those in a paste mixed by paddle mixer were observed with the optical microscope to be 300  $\mu m$ . From a comparison of the above estimates with the measured limiting gaps listed in Table 2, one can conclude that the limiting gap of a dilute cement suspension equals one to two times the size of inhomogeneity of a paste.

# **Dependence** of Limiting Gap on the w:c Ratio (Set B)

The limiting gaps of cement pastes mixed by all the methods studied here increased with decreasing w:c as



**FIGURE 8.** Shear stress ratios of cement pastes as a function of gaps.

shown in Figure 9. The limiting gap of pastes made by high energy blending increased linearly with w:c from 0.35 to 0.50. The limiting gaps of pastes prepared by hand mixing sieved powder and paddle mixing increased linearly with w:c from 0.40 to 0.50, but radically faster when the w:c was less than 0.40. Figure 9 also shows that the limiting gap of the paste made from ball milling at a w:c of 0.5 is lower than that of the paste made from paddle mixing. The local shear stress created between aggregates during milling was indeed higher than that generated in a paddle mixer. However, the milling efficiency decreased greatly with decreasing w:c values.

Limiting gaps for all mixing methods studied depend not only on the scale of particles of agglomerates, but also on w.c. These observations suggest that when mixing ceases, particles dispersed during mixing tend to form flocs (particles associated together when the interparticle potential reaches a minimum). The number of flocs increases with solid concentration.

The reason for the effect of mixing method on the peak stress shown in Figure 5 is easily understood by

**TABLE 2.** Comparison of limiting gap with estimated size of inhomogeneity of cement paste

Mixing Method	Limiting Gap (µm)	Size of Inhomogeneity (µm)
Blender	100	40-100
Hand (sieved)	150	150
Ball mill	200	100-200
Paddle	370	300

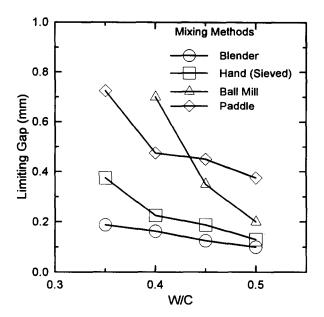


FIGURE 9. Limiting gaps of cement pastes at various w:c.

examination of Figure 9. In set A tests, the PK45 cone sensor was used. The gap between the truncated flat part of the sensor and the bottom plate was fixed at 0.7 mm. It can be seen from Figure 9 that at a w:c of 0.37, the limiting gaps of pastes mixed by the blender and by hand mixing sieved powder were far below 0.7 mm, while that made by paddle mixing was near 0.7 mm. Thus, wall effects due to the clusters in a poorly mixed paste were probably responsible for its higher peak stress in our measurements.

#### Calculation of Dispersive Force

To calculate the maximum dispersive forces exerted on a cement agglomerate during mixing using eq 3, the maximum shear rates of the paddle and the blender mixer under experimental conditions were first determined. The shear rate distributions in these mixers are complicated. However, only the maximum shear rate is of interest here. The first approximation made is that the most intensive shear motion occurs between two imaginary coaxial cylinders, in which the radius of the inner cylinder,  $R_b$ , is that of the paddle or blade, and  $R_c$ , the radius of the outer cylinder, is that of the mixing bowl. If a laminar shear flow is assumed, the maximum shear rate is located at the inner cylinder and can be calculated using the equation for a coaxial rheometer [2] as:

$$D_{\text{max}} = \frac{2R_{\text{c}}^2}{R_{\text{c}}^2 - R_{\text{b}}^2} \, \omega \tag{6}$$

where angular velocity  $\omega$  (in rads/second) is obtained

from rotational speed and N (revolutions per minute), since  $\omega = N\pi/30$ .

A second approximation made during this calculation is that a dumbbell is formed by a cement particle of radius  $R_1$  attached to an agglomerate of radius  $R_2$ . The radius of the cement particle is 5 μm (the average size of cement particles is about 10 µm). Averaging the data summarized by Tattersall and Banfill [2], the Bingham yield stress and plastic viscosity of w:c = 0.5 cement paste are 12 Pa and 0.16 Pa-s, respectively. Calculation results of maximum dispersive forces from the paddle and the blender mixer are listed in Table 3.

As expected, in an extensive mixer dispersive force can be increased only by increasing the shear rate. The results in Table 3 show that the dispersive forces produced by the blender mixer at high shear rate are 10 times those produced by the paddle mixer. The maximum rotation speed of a paddle mixer is about 300 rpm following ASTM [7]. The calculation in Table 3 shows that such a mixing procedure can generate a maximum shear rate of about 130 seconds<sup>-1</sup> and a dispersive force of about  $9 \times 10^{-7} N$  on agglomerates of 0.3 mm. Such a dispersive force is not enough to break the cement agglomerates or those smaller than 0.3 mm (experimental results show that these agglomerates remain after paddle mixing).

Ball milling in a manner similar to an intensive mixer has the advantage of breaking agglomerates at low rotational speed. Milling cement paste with aggregate at a rotational speed of 100 rpm for 20 minutes broke apart agglomerates nearly as well as blender mixing at a rotational speed of 3000 rpm for 1 minute when the paste has a w:c <0.5, as shown in Figure 9. In practice, during the transportation of fresh concrete in the truck, cement paste is subjected to ball milling by aggregates. Thus, the flow properties and microstructure of a field cement paste are quite different from a paddle-mixed paste. Because the most common mixing procedure to prepare cement paste in research laboratories follows ASTM C305 [7], caution must be exercised when applying laboratory results to the field.

**TABLE 3.** Calculation of dispersive forces during mixing of cement paste

Input Parameters $R_1 = 5 \mu \text{m},  \eta_{\text{PL}} = 0.16  \text{Pa-s},  \tau_{\text{B}} = 12  \text{Pa}$				
	Agglomerate R <sub>2</sub> (μm)	Calculation $D_{\text{max}}(s^{-1}),$ $F_{\text{max}}(N)$		
Paddle: $N = 300 \text{ rpm}$ $R_c = 100 \text{ mm}$	100	$123, 3 \times 10^{-7}$		
$R_{\rm b} = 70 \text{ mm}$	300	$123, 9 \times 10^{-7}$		
Blender: $N = 3000 \text{ rpm}$ $R_c = 55 \text{ mm}$	100	$1055, 2 \times 10^{-6}$		
$R_{\rm b} = 35 \text{ mm}$	300	$1055, 6 \times 10^{-6}$		

#### **Conclusions**

- 1. The rheological behaviors of cement pastes during the first 2 hours are strongly influenced by mixing methods. Cement pastes mixed by hand or by paddle mixer have higher and, with time, more rapidly increasing peak stresses than those prepared by high energy blender mixing. Agglomerates initially existing in cement powder, and later remaining in the paste due to insufficient mixing, are responsible for the higher value and faster increase in peak stress.
- 2. The agglomerates remaining in a poorly mixed cement paste are on average 0.3 mm. An empirical parameter, limiting gap, is used to quantify the extent of mixing. It is about one to two times the size of inhomogeneity of the paste. Due to the cohesive nature of cement powder, an intensive mixer would have an advantage in mixing cement.
- 3. Cement particles inside an agglomerate remain essentially unhydrated for at least 5 hours, and possibly much longer. These clusters are probable sources of microstructural defects in a poorly mixed hardened cement paste.
- 4. Although the results presented above are intuitive, they contain strong implications about the applicability of results obtained from paddle-mixed paste to field concrete; in short, paddle mixing does not mimic the paste portion of concrete under many conditions.

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