Investigation into Yield Behavior of Fresh Cement Paste:Model and Experiment

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by Gang Lu and Kejin Wang

*In the present study, a yield stress model of cement paste is developed based on a theoretical approach. In this model, cement particles are assumed as rigid spheres uniformly distributed and suspended in water. The interparticle force is considered resulting from the electrostatic and dispersion forces of the cement particles. Two types of tests—a direct shear and a rheometer test—are performed on a group of cement pastes made with different water-cement ratios (*w/c*), and the results are used for verification of the validity of the newly developed model. The study demonstrates that the newly developed model can not only predict the yield behavior of cement pastes but also describe the correlations among the yield stresses obtained from different experimental methods.*

Keywords: cement paste; rheology; yield stress.

INTRODUCTION

The rheological behavior of a cementitious system, or a freshly made paste, is greatly related to the hydration process of its cementitious materials. The hydration process depends not only on the material characteristics (such as particle distribution, chemical composition, water-to-cementitious material ratio [*w*/*cm*], and admixtures) but also on the hydration time, construction process (such as mixing and placement procedures), and environmental conditions (such as temperature and relative humidity). The complexity of the hydration process made study of the rheology behavior of a fresh cementitious material very challenging. Currently, most studies on cement and concrete rheology are experimentally dependant. The experimental results vary largely because of the different materials investigated, equipment used, and test methods applied. Little work has been done studying cement paste rheological behavior based on a theoretical approach.

In the science of rheology, two important parameters are often used to describe rheological behavior of a material: yield stress and viscosity. Yield stress is the shear stress required by a viscoelastic material for initiating a plastic deformation. It is the maximum shear stress under which the material is at rest but beyond which the material will start to flow or deform. Yield stress is strongly influenced by the magnitude of the interparticle forces and spatial particle distribution of the material studied. Differently, viscosity is the resistance of a material to flow, and it describes the material behavior in a dynamic state. The present study investigates the yield behavior of a cement paste before the cement paste starts to flow.

A great deal of studies have been conducted to measure the yield stress of fresh cementitious materials, most of which measure Bingham yield stress rather than the "true" yield stress.[1,2] According to the science of rheology, the true yield stress is defined as the maximum shear stress at the strain rate of zero; however, in many commonly used test methods, the reliable true yield stress of a fresh cementitious material is hard to obtain. Therefore, the yield stress is often determined by the intercept of the linear portion of a flow curve, or the shear stress-strain rate curve, of the tested material on the shear stress axis (or at zero shear rate). This yield stress is commonly referred to as "apparent" yield stress. For a cement-based material, shear stress generally increases nonlinearly with increased shear rate because of the particle agglomeration, which even makes the determination of apparent yield stress of the material difficult. Hence, the down load portion (or down-curve) of a rheological hysteresis curve, which often shows that the shear stress of a material linearly decreases with reduced strain rate, is often used. The yield stress determined from the linear portion of the down-curve is called Bingham yield stress.[2] Bingham yield stresses of various fresh cementitious materials have been reported by many researchers in the absence of the true yield stresses.[1,2] In addition, although researchers have indicated that a normal stress, often resulting from a material self-weight and an external load, has significant influence on shear stress of a material,[3] in most rheological studies, the effect of the normal stress on the shear stress of a cementitious material is commonly neglected.

Qualitative and quantitative disagreements among the rheological parameters of cementitious materials measured from different experiments have been reported by many researchers.[4] The differences in the shear history of a test and the plug flow and slippage of the tested material at the surfaces of the test device all contribute to the large variations of the experimental results; however, the results obtained from each individual test device and method do describe rheological behavior of the tested materials. Thus, it is believed that some relationships may exist among the results from the commonly used test devices and methods. A theoretical approach to the material rheological behavior may be able to explain the variations and to express the relationships among these test results.

In the 1940s, Derjaguin and Landau[5] and Verwey and Overbeek[6] developed the DLVO theory, which describes the force between the charged surfaces of particles interacting through a liquid medium. In this theory, the combined effect of van der Waal's attraction and electrostatic repulsion on the particle interaction is explicated using the double layer of counter-ions (also called the double-layer theory). This theory has been widely used for modeling of the yield stress of particle suspensions. Many studies have shown that this

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yield stress is dependent on the interparticle forces, particle volume fraction, size, distribution, and surface characteristics.[7-11]

Recently, the DLVO theory is increasingly applied to the study of cement paste.[12-17] Flatt[12-14] considered the interparticle potential and sedimentation behavior of a cement suspension, and he developed a model for predicting the interaction between two adjacent cement particles in a different solution. Yang et al.[17] studied the interparticle action of cement particles in an alcohol solution; however, limited researchers have considered the combined effects of the interparticle forces, particle volume fraction, and size distribution of cement particles on the yield stress of cement pastes with difference water-cement ratios (*w*/*c*).

Lately, in the course of the development of self-consolidating concrete (SCC) technology, a concept of excess paste has been proposed and well received for studying fresh concrete rheology.[18,19] The thickness of excess paste in concrete is closely related to the aggregate particle volume and size distribution, and it actually represents the interparticle distance, which is a key component in the study of interparticle forces. Thus, the combination of the DLVO theory and the excess paste concept may lead to an improved model for predicting yield behavior of cementitious materials.

The objective of the present study is to develop an improved model for predicting yield behavior of cementitious materials by using the DLVO theory together with the excess paste concept. This study contains two parts: 1) the theoretical model development; and 2) experimental verification of the validity of the new model. In the model development, cement particles are simplified as rigid spheres with the same (average) diameter uniformly dispersed and suspended in water. The shear force between two adjacent cement particles is evaluated based on the work done by Flatt.[12-16] The average shear force of all cement particles in a unit volume of a cementitious material is then determined according to the concept of probability. A group of cement pastes made with a different *w*/*c* are tested using a direct shear box and a rheometer. The yield stresses calculated from the present model are compared with those measured from the direct shear and rheometer tests.

RESEARCH SIGNIFICANCE

Most existing studies on cement and concrete rheology are dependent on the experimental protocol. Qualitative and quantitative disagreements among the rheological parameters measured from different experiments have been reported; however, limited work has been done studying the rheological behavior of cement-based materials based on a theoretical approach. In the present study, a theoretical yield stress model of cement paste is developed. This new model can well predict the yield behavior of cement pastes, explain important factors that affect paste yield behavior, and describe the correlations among the yield stresses obtained from different experimental methods. These research results fill the previously mentioned gap in cement rheology study.

THEORETICAL APPROACH

Assumption and simplification

To assist in modeling, a cement paste system is simplified, and the following assumptions are made:

1. A fresh cement paste is considered as a suspension system with cement particles uniformly suspended in water;
2. The cement paste studied is freshly made and the cement hydration has little effect on the paste rheological behavior at this stage;
3. There is no entrapped or entrained air void in the cement paste;
4. All cement particles are rigid spheres and have an equal size in diameter (an average diameter); and
5. The distance between any two cement particles is always larger than zero, and the spaces among the cement particles are filled with water.

For a given specific gravity of cement (S_c) and *w*/*c*, the volume of mixing water ($V_{mixing\ water}$), volume of cement (V_{cement}), number of cement particles, and total surface area in a unit volume of paste ($A_{all\ particles}$) can be calculated as follows

$$V_{mixing\ water} = \frac{1}{1 + \frac{1}{S_c \frac{w}{c}}} \quad (1)$$

$$V_{cement} = \frac{1}{1 + S_c \frac{w}{c}} \quad (2)$$

$$N = \frac{V_{cement}}{\frac{4}{3}\pi\bar{r}^3} = \frac{3}{4\pi\bar{r}^3}\frac{1}{1 + S_c \frac{w}{c}} \quad (3)$$

$$A_{all\ particles} = NA_{single\ particles} = \frac{3}{\bar{r}}\frac{1}{1 + S_c \frac{w}{c}} \quad (4)$$

where $\bar{r}$ is the average radius of cement particles, N is the number of cement particles in a unit volume of cement paste, and $A_{single\ particles}$ is the surface area of an individual cement particle. In the present study, the cement specific gravity (S_c) of 3.15 and the average cement particle diameter ($2\bar{r}$) of 15 micrometers are used.[7,20]

Two states of a cement paste are considered in the modeling: a suspension state and a compacted state. In a suspension state, the distance between two adjacent cement particles in the paste is assumed larger than zero, and the spaces among the cement particles are filled with water. At the compacted state, the cement particles are assumed all in contact. The water that fills the spaces between compacted cement particles is defined as "water between particles." The volume of the water between particles ($V_{water\ between\ particles}$) in a unit volume of a paste is mainly depending on the particle packing of the cement. The rest of the mixing water that separates the cement particles is defined as excess water. In the present study, the volume of the excess water ($V_{excess\ water}$) and the average interparticle distance (h) in a unit volume of a paste are

$$V_{excess\ water} = V_{mixing\ water} - V_{water\ between\ particles} = \left(1 - \frac{p}{1-p}\frac{1}{S_c\frac{w}{c}}\right)\frac{1}{1 + \frac{1}{S_c\frac{w}{c}}} \quad (5)$$

$$h = 2 \times \frac{V_{excess\ water}}{A_{all\ particles}} = \frac{2}{3}\bar{r}\left[S_c\frac{w}{c} - \frac{p}{1-p}\right] \quad (6)$$

where p is the void ratio of the paste ($p = 1 - V_{cement}$); V_{cement} is the volume of the cement in the paste studied; and $V_{excess\ water}$ is the volume of the total mixing water used in the paste.

Shear force between two cement particles

In a bulk suspension solution, a repulsive potential U_R, which arises from the electrostatic force between two particles with the same electron charges, can be given as[15]

$$U_R = 2\pi\varepsilon_0\varepsilon_r\bar{r}\psi^2\ln\{1 + \exp[-\kappa h]\} \quad (7)$$

where $\bar{r}$ is the mean particle's radius; h is the distance between particle surfaces; ψ is the zeta potential, which can be determined experimentally; κ is given by $\kappa = e\sqrt{(I_C N_A)/(\varepsilon_0\varepsilon_r kT)}$; e is the charge of an electron; N_A is Avogadro's number; ε_r is the relative dielectric constant of the liquid medium; ε_0 is the dielectric permittivity of free space; and k is Boltzmann's constant. A value of $k = 1.7$ can be taken in calculation of cement suspension.[15] The variable T is the environmental temperature. The ionic strength of the bulk solution, I_C, is defined as $I_C = (1/2)\Sigma C_i z_i^2$, where C_i is the ionic concentration of ion i in moles per liter, z_i is the valency of ion i, and the summation is over all ion species.

In the same solution, an attractive potential, U_A, arising from the London-van der Waals force, can be expressed as[12]

$$U_A = -\frac{A_H}{12}\left[\frac{4\bar{r}^2}{h^2 + 4\bar{r}h} + \frac{4\bar{r}^2}{h^2 + 4\bar{r}h + 4\bar{r}^2} + 2\ln\left(1 - \frac{4\bar{r}^2}{h^2 + 4\bar{r}h + 4\bar{r}^2}\right)\right] \quad (8)$$

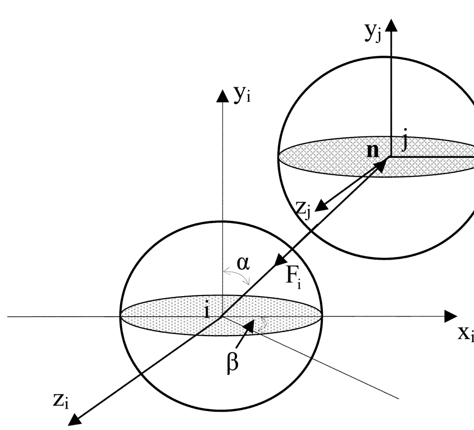

Fig. 1—Two-particle interaction model.

where A_H is the Hamaker constant, which is determined by properties of the suspending material and the suspension liquid medium.

Various Hamaker constant (A_H) values have been proposed by different researchers, and the values for cementitious materials vary from 4.55×10^{-20} J to 1.68×10^{-21} J.[13,14,21] As discussed hereafter, the Hamaker constant used in the present study is determined from a curve fitting of experimental data.

Based on Eq. (7) and (8), the interparticle electrostatic (F_E) and dispersion forces (F_U) of a buck suspension solution can be derived as[12]

$$F_E = -2\pi\varepsilon_0\varepsilon_r\bar{r}\psi^2\frac{\kappa e^{-\kappa h}}{1 + e^{-\kappa h}} \quad (9)$$

$$F_U = \frac{A_H\bar{r}}{12h^2} \quad (10)$$

Thus, the total interparticle attractive force (F_t) between adjacent two cement particles is

$$F_i = F_E + F_U = \frac{A_H\bar{r}}{12h^2} - 2\pi\varepsilon_0\varepsilon_r\bar{r}\psi^2\frac{\kappa e^{-\kappa h}}{1 + e^{-\kappa h}} \quad (11)$$

Assuming that cement particles are equal-sized rigid spheres, the interparticle attraction force of any two adjacent cement particles can be calculated according to the three-dimensional (3D) model, as shown in Fig. 1. In this figure, the vector $\boldsymbol{n}$ connects the centers of two particles, and it is determined by angles α and β as described in the following

$$\boldsymbol{n} = (\sin\alpha \cdot \cos\beta \cdot \boldsymbol{i} + \cos\alpha \cdot \boldsymbol{j} + \sin\alpha \cdot \sin\beta \cdot \boldsymbol{k}) \quad (12)$$

The interparticle force F_i, determined by Eq. (11), is on the vector $\boldsymbol{n}$. The probability that the interparticle force generates in a given direction ($P(\alpha, \beta)$) can be expressed by[22]

$$P(\alpha, \beta) = \frac{\sin\alpha \cdot d\beta \cdot d\alpha}{\pi} \quad (13)$$

where the range of α and β are $\alpha \in [0, \pi/2]$ and $\beta \in [-\pi/2, \pi/2]$, respectively.

Hence, the average value of the interparticle force along the x_i direction is given as

$$\bar{F}_x = \iint F_i \boldsymbol{n}_x P(\alpha, \beta) = \iint\left(\frac{A_H\bar{r}}{12h^2} - 2\pi\varepsilon_0\varepsilon_r\bar{r}\psi^2\frac{\kappa e^{-\kappa h}}{1 + e^{-\kappa h}}\right) \cdot \sin\alpha \cdot \cos\beta\frac{\sin\alpha}{\pi}d\alpha d\beta \quad (14)$$

where $\alpha \in [0, \pi/2]$ and $\beta \in [-\pi/2, \pi/2]$.

Equation (14) can be simplified as

$$\bar{F}_x - 0.5\left(\frac{A_H\bar{r}}{12h^2} - 2\pi\varepsilon_0\varepsilon_r\bar{r}\psi^2\frac{\kappa e^{-\kappa h}}{1 + e^{-\kappa h}}\right) \quad (15)$$

Shear stress of a cement paste

Equation (15) gives the shear force generated by two adjacent cement particles dispersed in water. Considering a horizontal plane of a unit volume of a cement paste cube, one can assume that there are N cement particles having the average diameter of $2\bar{r}$. Thus, the overall shear force applied on this plane due to all interparticle action is $N\bar{F}_x$, where N is the number of particles in a unit shear plane (Eq. (3)).

Combining Eq. (3), (6), and (15), the shear stress of cement paste (τ_p) can be obtained as

$$\tau_p = \frac{3}{8\pi\bar{r}^3}\frac{1}{S_c\frac{w}{c}+1}\left\{\frac{A_H\bar{r}}{12\left(\frac{2}{3}\bar{r}\left[S_c\frac{w}{c}-\frac{p}{1-p}\right]\right)^2} - 2\pi\varepsilon_0\varepsilon_r\bar{r}\psi^2\frac{\kappa e^{-\kappa\left\{\frac{2}{3}\bar{r}\left[S_c\frac{w}{c}-\frac{p}{1-p}\right]\right\}}}{1+e^{-\kappa\left\{\frac{2}{3}\bar{r}\left[S_c\frac{w}{c}-\frac{p}{1-p}\right]\right\}}}\right\} \quad (16)$$

Equation (16) gives the theoretical calculation of the overall shear stress of a freshly made cement paste. Because the spaces among the cement particles are assumed to be always filled with water, the friction force between the cement particles can be considered as zero, and the shear stress of the cement paste results only from the cohesion force between the cement particles. This cohesion force is correlated to the specify gravity S_c of cement particles, *w/c,* and mean cement particle radius $\bar{r}$.

Simplification of the shear stress model

For a practical application, Eq. (16) can be simplified by replacing some parameters with typical values. Table 1 lists these parameters and values used in the present study (assuming the water temperature of the cement paste is 25°C [77°F]). Using the values listed in Table 1, Eq. (16) is further simplified as Eq. (17)

$$\tau_p = 2.83\times10^{14}\cdot\frac{1}{3.15\frac{w}{c}+1}\left\{\frac{2.5\times10^4A_H}{\left[3.15\frac{w}{c}-0.9417\right]^2} - 2.7\times10^{-10}\frac{e^{-8500\left(3.15\frac{w}{c}-0.9417\right)}}{1+e^{-8500\left(3.15\frac{w}{c}-0.9417\right)}}\right\} \quad (17)$$

It is noted that the typical values listed in Table 1 are selected from literature, and they may be slightly different from those of the pastes presently studied. Some assumptions used for the present model may also cause some numerical errors. For example, cement particles were assumed as rigid spheres with a single-sized diameter, and the distance between any two cement particles was assumed always larger than zero. These assumptions are necessary for the study of cement interparticle action in a suspension system, but they are different from an actual cement paste. To correct these minor errors, a curve fitting of experimental data is used to determine the value of Hamaker constant A_H.

As shown in Eq. (17), the shear stress of a cement paste is now varying only with *w/c* because the Hamaker constant A_H is a constant, not a variable. When the *w/c* is multiplied with an experimental scaling parameter D, the form of Eq. (17) does not change. Using the experimental scaling parameter D, Eq. (17) becomes

$$\tau_p = 2.83\times10^{14}\cdot\frac{1}{3.15D\frac{w}{c}+1}\left\{\frac{2.5\times10^4A_H}{\left[3.15D\frac{w}{c}-0.9417\right]^2} - 2.67\times10^{-10}\frac{e^{-8500\left(3.15D\frac{w}{c}-0.9417\right)}}{1+e^{-8500\left(3.15D\frac{w}{c}-0.9417\right)}}\right\} \quad (18)$$

The factor D can also be determined from curve fitting of actual experimental data. There are two major reasons for introducing the experimental scaling parameter D.

First, besides the assumptions used, some properties of actual cement paste (such as chemical compositions of cement and the suspension solution) are also unable to be fully considered in the present model, which also have significant influence on the model results. Using the parameter D can bridge the gap between the model and experimental results caused by these assumptions and simplifications used in the model.

Second, as mentioned previously, experimental results are often depending upon the test equipment, method, and environmental conditions. Because of these variables, disagreements among the rheological parameters of cementitious materials measured from different experiments are often reported by many researchers; however, the results obtained from each individual test device and method does describe the rheological behavior of the tested materials. This indicates that there may be some correlations among these test results. Because the interparticle distance is the most important factor of interparticle action in a cement paste and it is principally determined by *w/c*, multiplying the *w/c* with a scaling factor D permits one to combine all the material and testing uncertainties into one parameter $D\cdot(w/c)$, thus making the comparison of the experimental results possible.

When different test methods are selected for a cement rheology study, different D values can be used in Eq. (18) and, thus, the effects of the test methods on the rheological test results may be described.

EXPERIMENTAL WORK

Materials, proportions, and mixing procedures

Type I portland cement was used in the experiments, and its chemical and physical properties are shown in Table 2. Cement pastes were made with different *w/c* and without any supplementary cementitious materials (SCMs) and chemical admixtures. The direct shear tests were performed for pastes with a *w/c* of 0.30, 0.35, 0.40, 0.42, 0.45, and 0.48. (It is difficult to test a wetter mixture with the direct shear device.)

Table 1—Values of parameters used in model simplification[5,7,8,12,20]

Parameter	ε_r	ε_0	ψ	S_c	p	$2\bar{r}$	κ
Typical value	80	8.8542×10^{-12} $C^2N^{-1}m^{-2}$ (2.5411×10^{-14} $C^2lb^{-1}in.^{-2}$)	2.17 mV	3.15	48.5%	15×10^{-6} m (0.0006 in.)	1.7 nm^{-1} (4.3×10^7 $in.^{-1}$)
Reference	12	12	5	7, 20	7	7, 20	8

Rheometer tests were performed for the pastes with a *w/c* of 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, and 0.60. All cement paste samples were mixed with a mixer according to ASTM C305.[23] The temperatures of mixing water and cement were all controlled at 25°C (77°F). The environmental temperature and relative humidity during the paste mixing and testing were 25 ± 1.5°C (77 ± 2.7°F) and 36 ± 3%, respectively.

Test methods

Direct shear test—A direct/residual shear apparatus was used in accordance with the ASTM D3080.[24] In the test, the freshly mixed cement paste was placed into the cylindrical shear box, which was made of two separate halves (upper and lower halves) and enclosed a shear area (A) of 3167 mm^2 (4.9 in.^{2}). The paste sample was consolidated with a tamper for 32 times in accordance with ASTM C109.[25] Then, a selected vertical or normal load (P_v) was applied to the sample. Under the applied normal load, a horizontal or shear force (P_h) was also applied and it made the two halves of the shear box move relatively one to the other, thus shearing the tested paste. The shear rate used in the present study was controlled as 1 mm/min (0.00394 in./min). The total shear deformation was 5 mm (0.2 in.). The entire shear test process (from the contact of the cement with water to the end of the test) took approximately 15 minutes.

On the shear plane, where the two halves separated, there are two stresses: 1) a normal stress σ_n due to an applied normal load ($\sigma_n = P_v/A$); and 2) a shearing stress τ resulting from the applied horizontal load ($\tau = P_h/A$).

Rheometer test—A rheometer was used to measure the rheology parameters of the cement pastes. The vane of the rheometer has four blades 7.5 mm (0.3 in.) in width and 30 mm (1.2 in.) in height extending outward from the shaft at 90-degree angles. The capacity of the torque of the rheometer ranges from 1.5 to 50 mN·m (0.01 to 0.4 lb·in.). After the freshly mixed cement paste was placed into the rheometer, the sample was presheared at a low vane rotation speed of 130 rpm for 60 seconds. Then, the vane was stopped for 60 seconds, within which time the mixing vane was lifted and the sample was gently stirred to mitigate the formation of preferential shear planes due to particle orientation. The sample was then subjected to a controlled rate hysteresis loop where the rotation speed was increased from 0 to 218 rpm over a 60 second period and then immediately decelerated back to 0 rpm. The transformation from torque-rotational speed to shear stress-rotational speed was made in accordance to the details provided in Reference 26.

RESULTS AND DISCUSSIONS

Direct shear test results

Typical results of the direct shear tests from two sets of cement paste samples (*w/c* = 0.3 and 0.4) are shown in Fig. 2. It is observed that at the low *w/c* (0.3), the shear stresses of cement paste samples clearly increased with the normal stress applied. At the high *w/c* (0.4), however, the shear stresses of the corresponding cement paste samples was much lower and did not change very much with increased normal stress.

Figure 3 gives the relationship between the maximum shear stresses obtained from the curves in Fig. 2 and their corresponding normal stresses. The relationship follows the format of the Mohr-Coulomb equation and, therefore, these curves are called the Mohr-Coulomb failure curves of cement pastes. The intercept of the linear line on the shear stress axis indicates the cohesion of the cement paste. The shear stress of the cement paste under zero normal stress in Fig. 3 represents the rheological true yield stress, under which the cement paste material is in a static state. The angle between the linear line and the shear stress axis signifies the friction angle, which indicates the effect of normal stress on shear stress.

Figure 3 depicts that the true yield stresses measured from direct shear test, that is, the shear stresses under zero normal stress of the cement pastes, decrease with increased *w/c*. This trend is consistent with the result from general rheological study of cement paste because increased *w/c* improves flow ability of a cement paste.[4] Figure 3 also illustrates that the friction angle of a cement paste decreases as its *w/c* increases. A significant change in shear stress is observed when the *w/c* increases from 0.3 to 0.4.

As illustrated in Fig. 3, for a cement paste with a low *w/c* (<0.4), shear stress increases significantly with the applied normal stress while, for a cement paste with a higher *w/c*, the shear stress of the paste does not change very much with its normal stress, and the friction angle of the paste is small. This is very important information for studying the rheological behavior of a cement paste with a low *w/c* (<0.4). It implies that conducting a rheometer test for a cement paste with a *w/c*

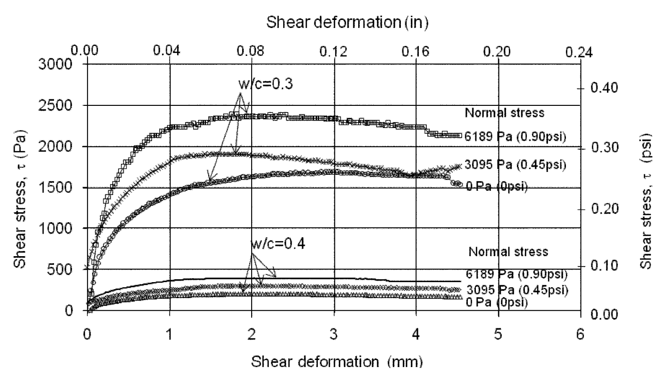

Fig. 2—Typical direct shear test results.

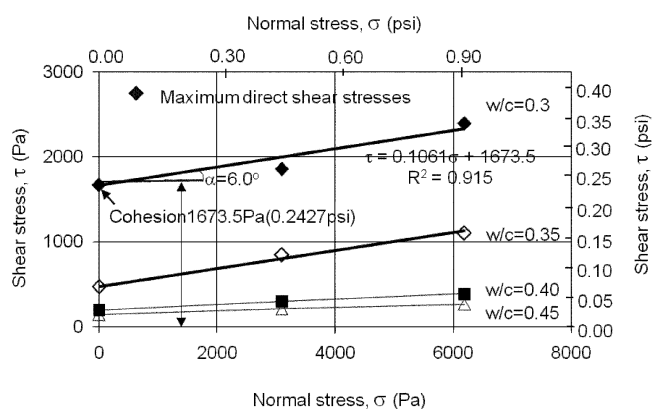

Fig. 3—Mohr-Coulomb failure curves of fresh cement pastes.

Table 2—Chemical and physical properties of cement

Major oxide composition, %	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
	64.20	20.80	5.55	2.25	1.91	2.96
Physical properties	Specific gravity: 3.15			Fineness: 373 m^2/kg		

lower than 0.4 without considering the effect of normal stress is not appropriate. Such a normal stress may result from the self-weight of the cement paste located above the shear zone or a confining stress from the boundary of the rheometer device.

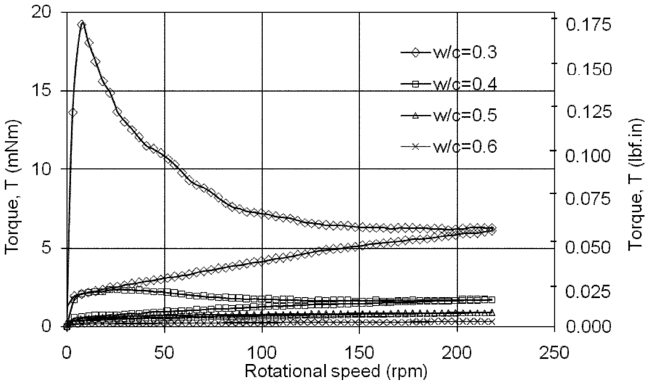

Fig. 4—Effect of w/c *on paste rheological behavior.*

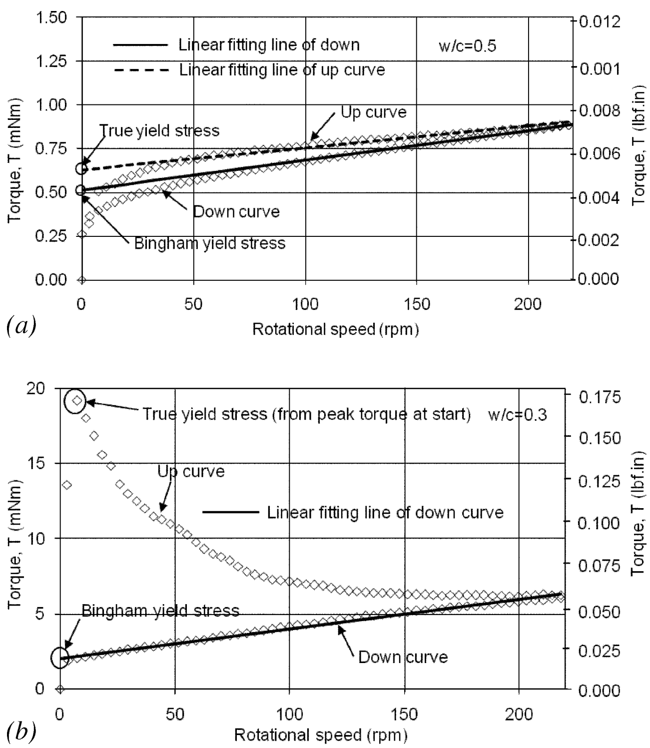

Fig. 5—True and Bingham yield stress defined from typical flow curves: (a) up-curve without peak value; and (b) up-curve with peak value.

Rheometer test results

Figure 4 shows the flow curves, the torque (mN·m) versus the vane rotation speed (rpm), of cement pastes with a different *w*/*c* from rheometer tests. Consistent with that observed from direct shear tests, a significant change in the shapes of the flow curves occurs when *w*/*c* decreases from 0.4 to 0.3. As seen in Fig. 4, the rheometer test generally produces a hysteresis loop, which contains two parts: the up- and down-curves. The area enclosed by the up- and down-curves reflects the thixotrophical behavior of a paste. Figure 4 demonstrates that the thixotrophical behavior of the paste with a low *w*/*c* is more significant than that of a paste with a high *w*/*c*. This indicates that higher energy is required for the low *w*/*c* paste to make the shear deformation happen.

In the present paste rheometer tests, the up-curve of a hysteresis loop reflects the behavior change of the original cement paste (without deagglomeration) from a solid state to a flow state. Thus, the yield stress calculated from the torque of this up-curve corresponding to the vane rotation speed or the paste deformation of zero is most likely the true yield stress. On the other hand, the down-curve of a rheometer test reflects the behavior of the tested paste under a shear after its particle agglomerations are broken down. During this testing period, the cement paste possesses Bingham behavior. Thus, the Bingham yield stress can be calculated from the torque of the down-curve corresponding to the vane rotation speed of zero.

Figure 5 illustrates that the up-curves have two different types of shapes: one with a clear peak torque (for the pastes with *w*/*c* = 0.3 and 0.4) and one without a visible peak torque (for the pastes with *w*/*c* = 0.5 and 0.6). For the up-curve without a clear peak, as shown in Fig. 5(a), because there is no distinguished maximum torque before the paste flows and the minimum stress value is zero, a linear curve fitting of the up flow curve appears the best way to obtain the yield stress of the up-curve. In the present study, a linear curve fitting of the up flow curve is performed for the up-curve without a clear peak value, and the shear stress calculated from the torque corresponding to the interception of the linear curve with the torque axis is defined as the true yield stress. For the up-curve with a clear peak, as shown in Fig. 5(b), the true stress of a cement paste is calculated from the peak value of the torque of the up-curve because the peak generally occurs at a very small rotation speed.[26] The Bingham yield stress is determined from the torque corresponding to the interception of the linear portion of the down-curve with the torque axis.[2] The true and Bingham yield stresses from both the rheometer and direct shear tests for all samples are listed in Table 3, and the discussions of these test results are given in the following section.

Comparison of test results

Table 3 illustrates that the true yield stresses measured from the direct shear tests and rheometer tests. These two

Table 3—Rheological yield stress of cement pastes

w/*c*	0.30	0.35	0.40	0.45	0.48	0.50	0.55	0.60
Bingham yield stress from rheology test, Pa (psi)	153.5 (0.0223)	51.3 (0.0074)	38.8 (0.0056)	30.5 (0.0044)	NA*	25.5 (0.0037)	10.8 (0.0016)	10.0 (0.0015)
True yield stress from rheology test, Pa (psi)	1547.2 (0.2244)	395.7 (0.0574)	189.2 (0.0274)	53.3 (0.0077)	NA	53.2 (0.0076)	16.5 (0.0024)	15.7 (0.0023)
True yield stress from direct shear test at 0 normal stress, Pa (psi)	1673.5 (0.2427)	473.6 (0.0687)	202.1 (0.0293)	148.4 (0.0215)	142.1 (0.0200)	NA	NA	NA

*Test was not performed and result is not available.

true yield stresses are very close, and both are much higher than the Bingham yield stresses obtained from the rheometer tests. All yield stresses in Table 3 decrease with increased *w/c* regardless of the testing and measuring methods. The good agreement between these two true yield stresses confirms that the true yield stress is the one that exists before any work is done on the pastes.[1] The agglomeration of cement particles would significantly affect the value of the true yield stress of the paste. The small differences between the true yield stresses obtained from the direct shear and rheometer tests may be associated with the two different test methods.

The Bingham yield stress is obtained from the down flow curve, where all cement particle agglomerations have been broken down. Because little or no structure is remaining, less stress is required for the cement paste to flow. Thus, the Bingham yield stress is lower than the true yield stress measured from the up flow curve. Because the Bingham yield stress measurement would be reliable only when the paste structure has been fully broken down by shearing, the measurement may be critically dependent on the details of the test procedure employed.

Comparison of model and test results

The previous discussions on Table 3 have proven that even though the values of the yield stress obtained from different tests are different, the trends of the effect of *w/c* on yield stress of cement pastes resulting from these tests are similar. Because of this, an experimental scaling parameter *D* can be introduced in Eq. (18). Using different *D* values, as described in the following, the relationships between the results from different rheological tests can be established.

First, Eq. (18) is used to fit the true yield stress obtained from the direct shear tests (Fig. 6). This good curve fitting results in an R^2 value of 0.9988. From the curve fitting, factors A_H and *D* are obtained as 2.80×10^{-17} and 1.25, respectively.

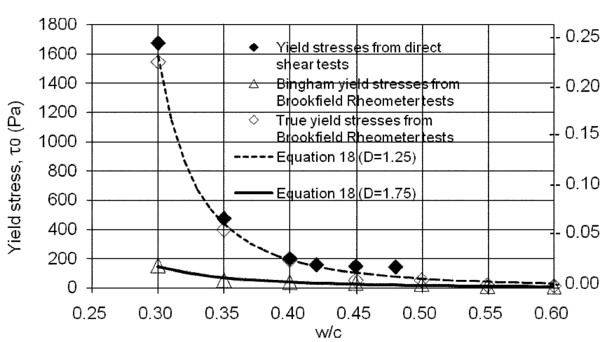

Fig. 6—Fitting of test data using Eq. (18).

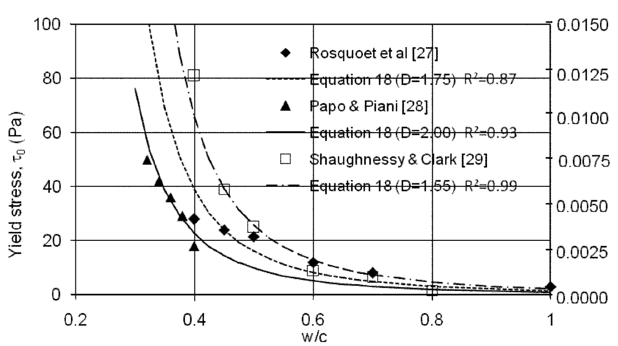

Fig. 7—Curve fitting of published data using Eq. (18).

Given that $A_H = 2.80 \times 10^{-17}$, Eq. (18) is then applied to fit the true yield stress data obtained from the rheometer tests. This curve fitting results in an R^2 value of 0.9990 and an unchanged *D* value of 1.25. The same *D* value obtained from the curve fittings of the true yield stresses from the direct shear and rheometer tests indicates that these two test methods are directly correlated.

Using $A_H = 2.80 \times 10^{-17}$, Eq. (18) is once again used to fit the Bingham yield stress data obtained from the rheometer tests (Fig. 6). Consequently, the curve fitting results in an R^2 value of 0.9669 and a different *D* value of 1.75. This suggests that there is a difference but also a correlation between the yield stress from the direct shear and the Bingham yield stress from the rheometer tests.

Application of present model to published rheometer test results

To verify the validity of the newly developed model, Equation 18 is also employed to fit some published experimental data. Figure 7 shows the results of the Eq. (18) curve fitting on three sets of yield stress data collected from different literatures, that is, the data resulted from different types of rheometer, test procedures, and different ranges of *w/c* in pastes. The Hamaker constant A_H of 2.80×10^{-17} is again used for the curve fittings.

Figure 7 illustrates that the newly developed yield stress model fits all selected, published experimental data very well (R^2 = 0.87 to 0.99). The experimental scaling parameter *D* is 1.75 for the test data provided by Rosquoet et al.[27] The data covered a large range of *w/c* (0.35 to 1.00), representing high-, normal-, and low-strength cement pastes. These test data were obtained from a rheometer with a coaxial cylinder spindle.[27] The experimental scaling parameter *D* is 2.0 for the test data provided by Papo and Piani.[28] The data covered quite a small range of low *w/c* (0.30 to 0.40), most of which were corresponding to high-strength pastes. They were obtained from a rate-controlled coaxial cylinder viscometer.[28] The experimental scaling parameter *D* is 1.55 for the test data provided by Shaughnessy and Clark.[29] The data covered *w/c* of 0.4 to 0.8, representing normal- and low-strength cement pastes. These data resulted from both concentric cylinder rotary viscometer and cone and plate viscometer.[29] Figure 7 also implies that some relationships exist among the different rheological test results obtained with different test methods, and these relationships can be connected by the experimental scaling parameter *D*.

CONCLUSIONS

In the present study, a yield stress model of cement paste is developed based on a theoretical approach. In this model, the cement paste is considered as a suspension system and cement particles are assumed as rigid spheres uniformly distributed in the system. The shear stress of cement paste is determined by the interparticle forces alone with probabilistic approach. To verify the validity of the newly developed model, two types of tests (direct shear and rheometer) are performed for a group of cement pastes with a different *w/c*, and the model has been applied to three sets of published experimental data. The results indicate the following:

1. The newly developed model can not only predict the yield stress of a cement paste but also correlate the yield stresses from different experimental methods using an experimental scaling parameter *D*.

2. A normal stress has significant effect on yield stress of a cement paste with a low *w/c* (≤0.4). Therefore, the normal stress, possibly resulting from the material self-weight and external loads, should be considered in paste rheology tests.

3. The true yield stresses measured from the direct shear test and rheometer tests as described in the present study are very close, especially at a low *w/c* (≤0.4). The agglomeration of cement particles would significantly affect the value of true yield stress of the paste.

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NOTATION

A_H	=	Hamaker constant
$A_{all\ particles}$	=	total surface area of all cement particles in unit volume of cement paste
$A_{single\ particle}$	=	surface area of single cement particle in unit volume of cement paste
F_E	=	interparticle electrostatic force
F_U	=	interparticle dispersion force
$\overline{F}_x$	=	average value of interparticle force along *x* direction
h	=	interparticle distance
I_C	=	ionic strength of bulk solution defined as $I_C = (1/2)\Sigma C_i z_i^2$, where C_i is ionic concentration of ion *i* in moles per liter and z_i is valency of ion *i*
k	=	Boltzmann's constant
N	=	number of cement particles in unit volume of cement paste
N_A	=	Avogadro's number
$P(\alpha, \beta)$	=	probability of collision occurring at certain location
p	=	void content of cement particles
$\overline{r}$	=	mean radius of cement paste
S_C	=	specific gravity of cement
T	=	temperature
U_A	=	attractive potential
U_R	=	repulsive potential
V_{cement}	=	volume of cement particles in unit volume of cement paste
$V_{excess\ water}$	=	volume of excess water in unit volume of cement paste
$V_{voids\ among\ cement\ particles}$	=	volume of voids in cement particles
V_{water}	=	volume of water in unit volume of cement paste
w/c	=	water-cement ratio
α	=	angle of direction; refer to Fig. 1
β	=	angle of direction; refer to Fig. 1
ε_0	=	dielectric permittivity of free space
ε_r	=	relative dielectric constant of liquid medium
κ	=	thickness of electrical double layer defined by $e\sqrt{(I_C N)/(\varepsilon_0\varepsilon_r kT)}$
τ	=	shear stress of cement paste
ψ	=	zeta potential

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