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Interparticle Potential and Sedimentation Behavior of Cement Suspensions

Review and Results from Paste

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A fundamental theory in colloid science is the DLVO theory (named after the four contributors: Derjaguin, Landau, Verwey, and Overbeek). This theory and relevant basic concepts are reviewed and applied to cement systems to determine the state of flocculation for cement pastes. Both theoretical and experimental evidence suggest that normal, neat cement suspensions are either flocculated or coagulated. Because of the high ionic strength in the aqueous phase, the degree of flocculation or coagulation is not sensitive to the variation of the zeta potential, for zeta potentials between −20 mV and 20 mV. © 1997 Elsevier Science Ltd. ADVANCED CEMENT BASED MATERIALS 1997, 5, 1–7

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The microstructure of a cement suspension influences its flow and sedimentation behaviors at early ages. Some microstructural aspects, such as the state of flocculation and particle packing (spatial distribution of particles), are not well known, although it is commonly stated that cement paste is a flocculated system. According to the DLVO theory, the state of flocculation of a colloid suspension is a function of interparticle potential, consisting of repulsive and attractive parts. Varying the interparticle potential allows one to control the degree of flocculation. One reason why DLVO theory has not been extensively applied to cement might be the complications due to hydration products on the particle surface of the cement grains, which has the effect of confusing the analysis of surface charge. Powers pioneered research into this area, studying the interparticle forces and their effects on the flocculation of cement systems [1]. He observed that the specific volume of the cement sediment varies when the interparticle forces change. The quantitative correlation was not reported.

In this paper, basic DLVO theory is applied to cement systems to determine the state of flocculation of cement suspensions. Data on sedimentation, zeta potential, and ionic concentration are reported to support the theoretical predictions of DLVO theory.

Background

A colloid suspension is typically defined as a suspension of particles smaller than 10 μm [2,3]. Three basic types of forces determine the rheological behavior and resulting microstructure of colloid suspensions: Brownian forces; colloid forces, such as electrical static forces and van der Waals forces; and hydrodynamic forces occurring during settling or mixing [4].

DLVO Theory

Most colloid suspensions consist of particles with charged surfaces (see refs. 3, 5, and 6, for example). The electric double-layer model [3,5] describes the structure of the electrostatic field surrounding a charged particle in an electrolyte, as shown in Figure 1. Due to the net charge at the surface of a particle, a compact layer of counterions is attracted to the interface. This thin layer of fluid adjacent to the surface is called the *inner layer* or *Stern layer*. The exact structure of this layer is not understood, although it is known to be immobile.

Outside the Stern layer, in the bulk solution, a region called the *diffuse layer* exists. The boundary between the inner and diffuse layers is known as the *shear plane*. The diffuse layer carries a significant charge due to high concentrations of ions repelled from the inner layer. These repelled ions have the same sign charge as the

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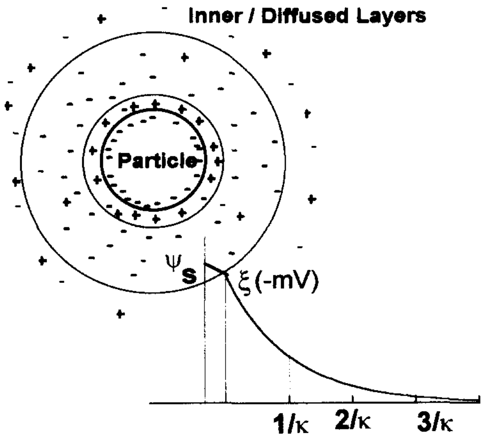

FIGURE 1. Electric double-layer model.

surface of the particle, producing an electrical potential, ψ_d, beginning at the shear plane and decaying with distance. In the bulk solution, positive and negative ions are balanced, the electrical potential vanishes, and ions move freely. Therefore, it is the structure of this diffuse layer that is most important in determining the interaction between two charged particles. The diffuse layer can be described using two parameters: the electrical potential, ψ_d, and the thickness, $1/\kappa$, where κ is the Debye-Huckel parameter.

The electrical potential at the shear plane is also called the zeta potential, ζ, and is the only value of potential that can be determined experimentally [5]. This is done by applying an electrical field to a suspension such that charged particles with their attached Stern layers move toward the electrode of opposing sign. Using this observation, the zeta potential can be calculated from the measured particle mobility. The electrical potential, ψ, decays with distance from the shear plane as:

$$\psi = \psi_d \exp[-\kappa(r - a)] \tag{1}$$

where r is the radial distance outward from the center of the particle and a is the particle radius.

The thickness of the electrical double layer is a function only of bulk electrolyte concentration and temperature and can be determined by:

$$\kappa = e\sqrt{\frac{I_c N}{\epsilon_0 \epsilon_r kT}} \tag{2}$$

where e is the charge of an electron, N is Avogadro's number, ε_r is the relative dielectric constant of the liquid medium, ε_0 is the dielectric permitivity of free space, and k is Boltzmann's constant. The ionic strength of the bulk solution, I_c, is defined as:

$$I_c = \frac{1}{2}\sum C_i z_i^2 \tag{3}$$

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 water at 25°C, $\varepsilon_r = 80$ [7,], thus:

$$\kappa(nm^{-1}) = 3.288\sqrt{I_c}. \tag{4}$$

The diffuse double-layer thickness in colloidal dispersions is typically about 1–100 nm. In highly ionic electrolytes, the diffuse double-layer is greatly compressed. For example, the ionic strength of cement paste is high, typically 0.1 M (moles per liter), so the diffuse double-layer is approximately 1-nm thick [8].

REPULSIVE POTENTIAL. A repulsive potential, U_R, arises from the electrostatic force between two charged particles of the same sign. As the two particles approach each other, their double layers interact and create a repulsive potential. If $\kappa a \gg 1$, the repulsive potential of the double-layer model, U_R, can be expressed as:

$$U_R = 2\pi\varepsilon_0\varepsilon_r a\zeta^2 \ln\{1 + \exp[-\kappa(r - 2a)]\} \tag{5}$$

where $(r - 2a)$ is the separation of surfaces between particles.

ATTRACTIVE POTENTIAL. An attractive potential, U_A, arising from the London-van der Waals force, can be written as follows [5]:

$$U_A = -\frac{A_H}{12}\left[\frac{4a^2}{r^2 - 4a^2} + \frac{4a^2}{r^2} + 2\ln\left(1 - \frac{4a^2}{r^2}\right)\right] \tag{6}$$

where A_H is the Hamaker constant, which is sensitive to the type of material and liquid medium. Table 1 lists the Hamaker constants of materials that are similar in composition to the cement system.

DLVO theory takes into account the total interparticle potential by summing attractive and repulsive potential as shown in eq 7:

$$U_{tot} = U_R + U_A. \tag{7}$$

TABLE 1. Hamaker constants of some materials in water [2]

Material	$A^H \times 10^{20}$ (J)
Crystalline quartz	1.7
Fused silica	0.85
Calcite	2.23

The attractive potential is taken to be negative and, as shown in equation 6, it falls off as $1/r^2$. This attractive potential is exerted over a much greater distance than the repulsive potential. The repulsive potential falls according to $\exp[-\kappa(r - 2a)]$ over short separations between particle surfaces (see eq 5). Thus, the thickness of the diffuse layer, $1/\kappa$, represents the distance between surfaces within which the repulsive potential is significant.

State of Flocculation

As shown previously, the attractive potential is simply a function of r (center-to-center separation of particles), while the repulsive potential varies with distance from particle surface because it depends on the ionic strength and the zeta potential. Holding the zeta potential and particle size constant, while varying the ionic strength, produces the three basic types of total potential curves depicted in Figure 2. Three parameters can be defined from these curves: the primary minimum, ψ_{min}, the secondary minimum, ψ_{sec}, and the primary maximum, ψ_{max}. These three parameters are important for determining the stability of the suspension. The probability of particles existing outside the primary minimum is a measure of the stability of the dispersion. The primary maximum, ψ_{max}, prevents particles from falling into the primary minimum, thus improving the stability of the dispersion.

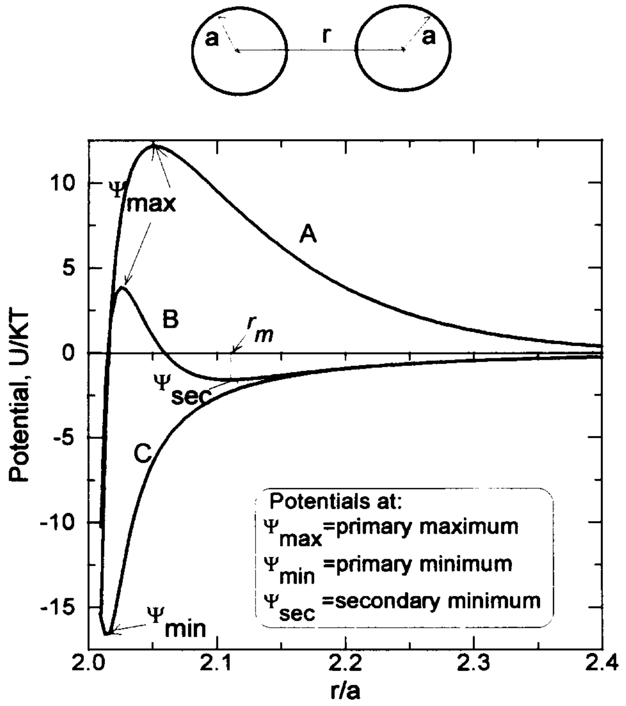

FIGURE 2. Illustration of interparticle potentials: curve A, stable dispersion; curve B, flocculated suspension; and curve C, coagulated suspension.

CURVE A: STABLE DISPERSION. At low ionic strength and high surface potential, the repulsive potential exceeds the attractive potential at all interparticle separations. In this case, particles repel each other and the suspension exists in a stable state. The larger the primary maximum, the more stable the dispersion.

CURVE B: FLOCCULATED SUSPENSION. At moderate ionic concentrations, both the primary maximum, ψ_{max}, and the secondary minimum, ψ_{sec}, are non-zero. The secondary minimum is located at a center-to-center particle separation r_m, which is the equilibrium separation. When two particles are located at a secondary minimum, they are in an equilibrium position relative to each other and are then flocculated. Many particles flocculated together constitute a floc. If $-\psi_{sec}/kT > 20$, then the system is strongly flocculated. If $-\psi_{sec}/kT << 20$, then the system is weakly flocculated. When $-\psi_{sec}/kT \approx 1$, the energy well is broad, and the state of flocculation is easily reversible.

CURVE C: COAGULATED SUSPENSION. As the ionic concentration increases to a critical value, called the *critical concentration* [5], ψ_{max} vanishes, and particles are rapidly and irreversibly flocculated at the primary minimum. As long as the concentration of the electrolyte is greater than the critical concentration, the interparticle potential, and thus the state of flocculation, does not depend on ionic concentration.

This critical concentration can be estimated by taking the total potential previously shown in eq 7, and its first derivative with respect to r, equal to zero. Using the double-layer model, the critical concentration, n_c, of a single ionic species in water at room temperature for the condition of $ez\psi_s/4kT < 1$ is [5]:

$$n_c = 3.648 \times 10^{-35} \frac{\zeta^4}{z^2 A_H^2} \tag{8}$$

where z is the valence of the ionic species and A_H, ζ, n_c are expressed in joules, volts, and M, respectively.

Application of the DLVO Theory to Cement Systems

The following two sections describe the application of the DLVO theory to cement systems and an experimental confirmation of its applicability. In the first section, the theoretical critical concentration for cement suspensions is calculated, and the real ionic strength is determined to predict the state of flocculation of normal cement suspensions. In the second section, an experimental method is described that uses sedimentation behavior to confirm the theoretical prediction.

Critical Concentration

The critical concentration for coagulation is proportional to the fourth power of the surface potential and is inversely proportional to the square of the ion valency, as shown in eq 8. Assuming $z = 1$ and using the Hamaker constant of calcite ($A_H = 2.23 \times 10^{-20}$ J [3]), the critical concentrations in equivalent cement suspensions were calculated for several selected zeta potentials; and these concentrations are shown in Table 2. Table 2 clearly illustrates that the critical concentration is less than 0.012 M when the zeta potential is less than 20 mV.

The ionic concentrations of ordinary portland cement (OPC) at water:cement (w:c) ratios of 10, 2, 0.45, and 0.35 are listed in Table 3. The ionic strengths of these cement suspensions were calculated using the definition in eq 3 as:

$$I_c = \frac{1}{2}\left(C_{Na^+} + C_{K^+} + 4C_{Ca^{+2}} + C_{OH^-} + 4C_{SO_4^{-2}}\right) \tag{9}$$

where the concentration of OH$^-$ was computed using the charge balance relation:

$$C_{Na^+} + C_{K^+} + 2C_{Ca^{2+}} = C_{OH^-} + 2C_{SO_4^{-2}}. \tag{10}$$

The relative dielectric constant, ε_r, is 80 for aqueous cement solutions [9]. The calculation in Table 3 shows that the ionic strength calculated from inductively coupled spectroscopy (ICP) data is at least 95 mM. Thus, the ionic strength of a normal cement paste is about one order of magnitude larger than the theoretical critical concentrations (<0.012 M), as determined under the condition of a zeta potential less than 20 mV. The absolute value of the zeta potential of a normal OPC is typically less than 20 mV, although it changes with hydration time [10]. This observation is also confirmed by our own measurements, as shown in Table 4, for the relevant range of samples explored in this study. Thus, normal cement paste has an ionic strength that is above the critical concentration for coagulation and, according to the DLVO theory, should be coagulated with an interparticle potential as depicted by curve C in Figure 2.

TABLE 2. Theoretical critical concentration, n_c (mM) with $A_H = 2.23 \times 10^{-20}$ J and $z = 1$ for ordinary portland cement

ζ(mV)	Calculated n_c (mM)
30	59.4
20	11.7
15	3.71
10	0.0734
5	0.0046
2	0.0012

Sedimentation

To study the bleeding process of cement systems, Radocea [11] developed a new method of analysis based on measuring changes in water pressure during sedimentation. This method can be used to quantitatively analyze sedimentation rate. Using the centrifuge sediment height technique, Miller et al. [12] measured the compressive yield stresses of cement pastes to determine the extent of consolidation in cement systems.

This paper focuses on the correlation between interparticle potential and sediment structure. Sedimentation tests were used qualitatively to observe the structure of cement suspensions, because flocculated suspensions and stable dispersions show quite different settling behavior, as described below. Sedimentation is defined as the height ratio of the total liquid to the total suspension, $(H - h)/H$, as shown in Figure 3.

Stable dispersions exhibit free sedimentation behavior. Following Stoke's law, particles settle freely (individually) at an equilibrium speed proportional to the square of the radii of the particles. As a result, certain characteristics dominate the sediment. Larger particles settle faster, while smaller particles remain suspended longer, and three distinct layers result, as illustrated in Figure 3a. On top is a cloudy liquid, in the middle is a free settling region, and on the bottom is large particle sediment. The volume packing density of the sediment, ϕ_{ms}, is the ratio of the volume of solids to the volume of sediment; for sediment in a stable dispersion, ϕ_{ms}, is close to the random close-packed value.

Particles in flocculated or coagulated suspensions consist of settling flocs rather than individual particles. If the flocs are large, the suspension settles rapidly. The sediment of a flocculated suspension has a smaller ϕ_{ms} than that of a stable dispersion, due to water trapped inside the flocs, that is, the sediment volume of a flocculated suspension is larger than it is in a dispersed suspension. Figure 3b shows this sediment; the liquid is clear and free of particles. When the volume fraction of solids exceeds a critical percolation threshold, ϕ_g, a continuous gel structure network is formed before the suspension settles.

A sedimentation test can effectively determine if a suspension is dispersed or flocculated. The sediment from a stable dispersion has a size gradient along the vertical direction, that is, larger particles are on the bottom, whereas the sediment of a flocculated or coagulated suspension does not have a size gradient along the vertical direction.

It is difficult to tell whether a suspension is flocculated or coagulated from its sedimentation behavior. A quantitative analysis of both the volume-packing density of the sediment, ϕ_{ms}, and sedimentation, $(H - h)/H$, as functions of time may differentiate a coagulated sus-

TABLE 3. Ionic concentrations determined using ICP, and calculations of ionic strengths for type I OPC in de-ionized (DI) water

	Ion	C_i (mM) w:c = 10	C_i (mM) w:c = 2	C_i (mM) w:c = 0.45	C_i (mM) w:c = 0.35
ICP data	K^+	7.13	15.3	119.60	123.94
	Na^+	1.44	3.2	27.12	28.14
	Ca^{+2}	22.00	26.0	22.28	18.31
	SO_4^{-2}	17.17	19.5	50.34	58.72
	SI^{+4}	0.29	0.09	0.40	0.05
	Mg^{+2}	0.01	0.00	0.02	0.04
	Al^{+3}	0.09	0.10	0.09	0.07
	OH–	19.50	32.35	93.30	70.79
	pH	12.29	12.51	12.97	12.85
Calculations	I_c(mM)	95.12	117.60	268.90	266.30
	$1/\kappa$(nm)	1.014	0.887	0.587	0.589

pension (curve C in Figure 2) from a flocculated suspension (curve B in Figure 2) because, for a flocculated suspension, the interparticle potential and degrees of flocculation vary with ionic concentration and zeta potential, whereas for a coagulated suspension they do not. If changing the zeta potential or varying the ionic strength of a non-dispersed suspension does not alter both ϕ_{ms} and sedimentation as a function of time, then it is a coagulated suspension. The volume packing density of sediment, ϕ_{ms}, can be calculated as:

$$\phi_{ms} = \phi_{original}\frac{H}{h_{final}} \qquad (11)$$

where $\phi_{original}$ is the solid volume fraction of the suspension at the beginning of the test and both H and h are defined in Figure 3.

Experimental Procedure

Two sets of sedimentation tests were carried out. Set A was used to determine whether or not cement suspensions are dispersed, while set B was used to investigate sedimentation behavior when the zeta potential is varied.

Type I portland cement was used in all of the experiments. Cement suspensions (52 ml each) were mixed in a blender for 1 minute and poured into plastic graduated cylinders (27-mm diameter). The sedimentation, $(H - h)/H$, was recorded over time until no change was observed for over 30 minutes.

For set A, two samples (A1 and A2) were made at the same solid volume fraction of 0.241. Sample A1 was

TABLE 4. Zeta potentials for cement pastes with varying alcohol-water content

Volume Percent Alcohol	w:c	Zeta Potential (mV)
0	166.7	-5.0
10	150.0	-3.0
20	133.4	-1.9
65.8	57.0	-1.7
80	33.3	-0.2
90.4	16.0	8.6
95	8.3	11.4
98.5	2.5	18.5
99.99	0.1	20.5

Note: w:c = water to cement ratio.

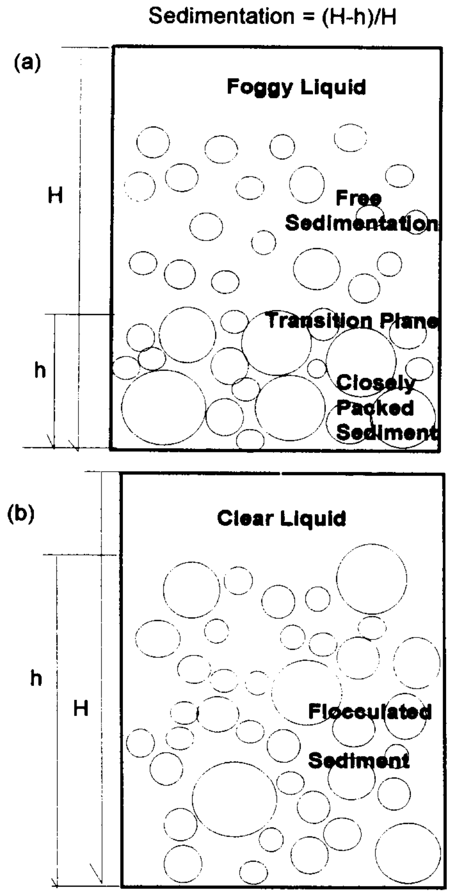

FIGURE 3. Illustrations of sedimentation behaviors of (a) stable dispersion and (b) flocculated suspension.

cement in isopropyl alcohol (99.99%) and sample A2 was cement in de-ionized (DI) water at w:c = 1. The particle-size distributions were analyzed using samples from the top and bottom of each sediment.

For set B, one cement in DI water with w:c = 1 was mixed and then divided into three portions for tests at 15 minutes, 1.5 hours, and 3 hours. These three samples were stored in plastic containers and rotated at 60 rpm until testing. Before each test, samples were mixed in a blender for 10 seconds. Sedimentation, zeta potential, and ICP were measured for each sample.

Zeta potential measurements were conducted using a Coulter Delsa 440. This instrument operates on the principle of electrophoretic light scattering. A reconstruction method was used to prepare cement samples for measurement, in which a small amount of unfiltered cement was dispersed into aqueous solution. This aqueous solution of cement paste was extracted using a 0.1-μm filter. The ionic concentration of aqueous solutions was determined with ICP in a Perkin-Elmer Plasma 40 Emission Spectrometer.

Results and Discussion

Set A

Completely different sedimentation behaviors and particle-size distributions (PSD) were observed for cement-alcohol and cement-DI water suspensions, as illustrated in Figures 4 and 5.

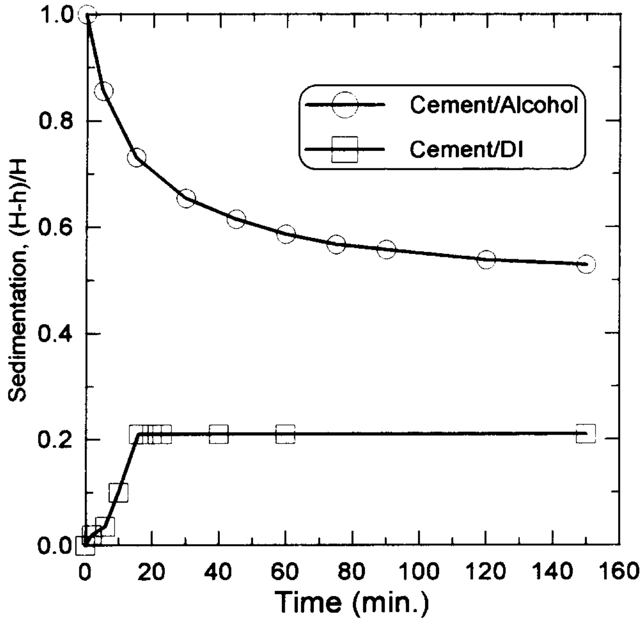

FIGURE 4. Sedimentation behaviors of cement in DI water and alcohol suspensions.

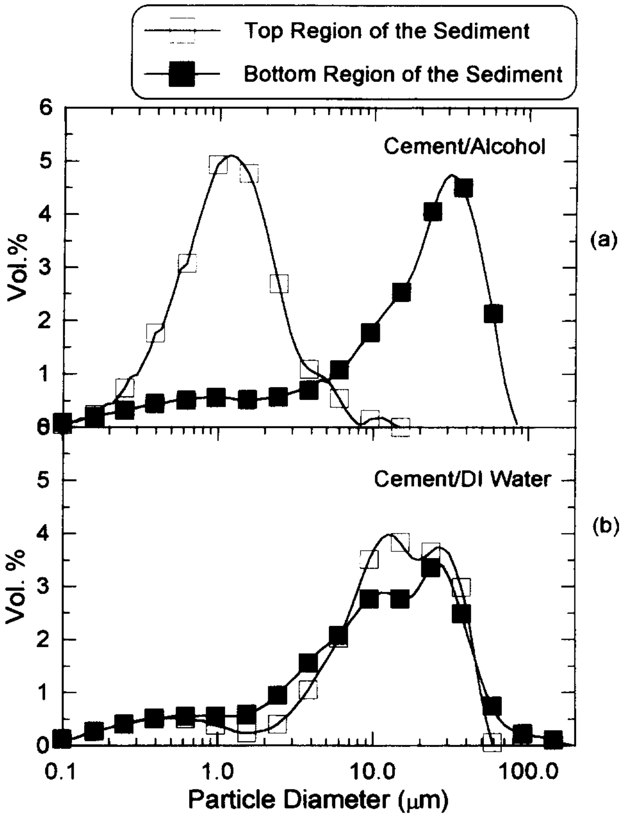

FIGURE 5. Particle-size distribution of cement sediments of (a) cement-alcohol dispersion and (b) cement-DI water suspension.

SAMPLE A1 (CEMENT-ALCOHOL, Φ = 0.241). After a sample of cement in alcohol was carefully poured into the cylinder, a dark gray region developed starting from the bottom of the cylinder. A transition plane separating dark and light gray regions was easily recognized and was recorded as the sedimentation height. The top fluid was slightly foggy even after 8 hours as a result of Brownian motion. The differential colors may result from variation of sediment particle size.

The gradient in particle size along the vertical axis was evident in the PSD results (Figure 5a). The sediment was dense and hard and was difficult to remove from the cylinder without force. This indicated a more closely-packed structure resulting from the sedimentation of a stable dispersion. The packing density of this sediment was calculated to be 0.51 using eq 11.

SAMPLE A2 (CEMENT-DI-WATER, W:C = 1, Φ = 0.241). With the specimens of cement in water, no color differential was observed. These suspensions generally separated slowly from the top liquid until a plateau was reached. The liquid at the top was clear and free of small particles. A comparison of the PSD in the top and bottom regions of sediment is shown in Figure 5b; only a small variation can be seen. The mean particle size was 17.75 μm in the bottom region of the sediment, and 16.6 μm in the top region. The sediment was voluminous and soft and could be easily poured from a test tube. The final volume-packing density of sediment for these three samples was 0.32. Comparison of these disparate sedimentation behaviors clearly demonstrates that the suspension of cement in water is not dispersed but rather flocculated or coagulated.

Set B

Ionic strength and zeta potential changed significantly with hydration time, as compiled in Table 5. Although the zeta potential varied in the range from −5 to −16 mV, the sedimentation of cement pastes at 15 minutes, 1.5 hours, and 3 hours showed almost identical sedimentation behavior as a function of time, represented by the lower curve in Figure 4. These observations suggest that cement suspensions are always coagulated and that the degree of flocculation does not vary with zeta potential and ionic strength. In other words, the ionic strength is always above a critical value for flocculation.

Conclusion

DLVO theory has been applied to determine the state of flocculation in cement suspensions. Both the theoretical prediction and sedimentation experimental evidence suggest that neat normal cement suspensions are coagulated. Because the ionic strength of a normal neat cement suspension is higher than the critical concentration, the degree of flocculation is not sensitive to variations in the zeta potential, at least for zeta potentials less than 20 mV.

TABLE 5. Ionic strength and zeta potential for ordinary portland cement paste at various hydration times for w:c = 1

Hydration Time (min)	Ionic strength (mM)	Zeta Potential (mV)
15	188	−5
75	147	−16
180	147	−9

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