

Cement Composition Effects on the Rheological Property Evolution in Concentrated Cement–Polyelectrolyte Suspensions

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We have studied the rheological property evolution and hydration behavior of white and ordinary portland cement (type I) pastes and concentrated cement–polyelectrolyte suspensions. Cement composition had a marked effect on the elastic property evolution ($G'(t)$) and hydration behavior of these suspensions in the presence of poly(acrylic acid)/poly(ethylene oxide) copolymer (PAA/PEO), even though their affinity to adsorb such species was nearly identical. Both white and ordinary portland cement pastes exhibited G'_0 values of $\sim 10^4$ Pa and fully reversible $G'(t)$ behavior until the onset of the acceleratory period ($t = 2$ h), where the pastes stiffened irreversibly. In contrast, cement–PAA/PEO suspensions exhibited G'_0 values of ~ 1 Pa and $G'(t)$ behavior comprised of both reversible and irreversible features. Interestingly, ordinary portland cement–PAA/PEO suspensions experienced a gel-to-fluid transition on high shear mixing at short hydration times (< 1 h), and the particle network did not rebuild until ~ 24 h of hydration. In sharp contrast, white portland cement–PAA/PEO suspensions remained weakly gelled throughout the initial stage of hydration even after high shear mixing. At longer hydration times (> 1 h), both cement–PAA/PEO suspensions exhibited $G'_i(t) \sim \exp(t/\tau_c)$ with τ_c values of 5.6 and 1.3 h for ordinary and white portland cement, respectively. Our observations suggest that hydration phenomena impact interparticle forces during early stage hydration and, ultimately, lead to initial setting through the formation of solid bridges at the contact points between particles within the gelled network.

I. Introduction

THE rheological property evolution of concentrated cement suspensions is poorly understood, despite its importance to concrete mixing and placement. Portland cement pastes consist of multiphase particles with a broad size distribution (~ 1 – 100 μm) suspended in an aqueous medium.¹ Such particles experience hydration reactions in aqueous media that are composition dependent, which lead to dramatic changes in both their surface and solution chemistry.¹ On contact with water, a thin hydration layer forms on the cement particle surfaces that ultimately grows as calcium silicate hydrate (C-S-H) deposition occurs near the onset of the acceleratory period. Concurrently, the solution ionic strength changes as particle dissolution occurs and new solid phases form, such as ettringite

$((\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O})_2 \cdot (\text{SO}_4)_3 \cdot 2\text{H}_2\text{O})$, calcium aluminate sulfate monohydrate $((\text{Ca}_2\text{Al}(\text{OH})_6)_2\text{SO}_4 \cdot \text{H}_2\text{O})$, and calcium sulfate dihydrate $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$ during early hydration and calcium silicate hydrate (C-S-H) at longer hydration times.

Lewis *et al.*² have recently studied the effects of sulfonate and carboxylate-based polyelectrolytes on the initial stability and flow behavior of concentrated cement suspensions. In such systems, long-range van der Waals interactions between particles must be overcome by electrostatic, steric, or other repulsive forces to induce the desired degree of stability.³ In the absence of polyelectrolyte species, cement pastes exhibit strong shear-thinning flow behavior. However, on the addition of a critical polyelectrolyte concentration, cement suspensions exhibit nearly Newtonian flow behavior indicative of their improved stability. Such observations are in good agreement with interparticle force calculations,^{2,4} which predict that cement particles (mean diameter ~ 10 μm) would flocculate into a strong, primary minimum in the absence of polyelectrolyte additions, whereas they would flocculate into a shallow, secondary minimum in their presence.

The influence of hydration phenomena on the rheological property evolution of concentrated portland cement pastes and cement–polyelectrolyte suspensions is a subject of great interest.^{2,4–6} Kirby and Lewis⁴ developed a new oscillatory shear technique to probe the elastic modulus evolution ($G'(t)$) of concentrated cement suspensions. In their approach, the “reversibility” of a cement particle network after a given hydration time is assessed by disrupting the structure under high shear, then measuring the rise of $G'(t)$ under quiescent conditions. For white portland cement–polyelectrolyte suspensions, they found that the initial value of G' , measured immediately on disrupting the suspension structure, increased exponentially with time, where $G'_i(t) = G'_{i,0} \exp(t/\tau_c)$ and τ_c was a characteristic hydration time assessed from calorimetry and conductivity measurements. Based on these observations, the $G'(t)$ behavior could be separated into reversible and irreversible components whose relative magnitude varied with increasing hydration time.

Here, we explore the generality of our observations for cement–polyelectrolyte suspensions of varying cement composition. Specifically, we have investigated pure ordinary portland cement pastes and cement–polyelectrolyte suspensions, with white portland cement systems serving as a benchmark. We show that cement composition has a marked effect on their rheological property evolution and hydration behavior, as characterized by elastic modulus, calorimetry, and solution conductivity measurements. The $G'(t)$ evolution of pure ordinary and white portland cement pastes was nearly identical; however, significant differences were observed in the presence of the polyelectrolyte-based species, i.e., a copolymer possessing a comblike architecture with poly(acrylic acid) (PAA) backbone and poly(ethylene oxide) (PEO) based teeth. For example, the ordinary portland cement–PAA/PEO suspension exhibited a remarkable gel-to-fluid transition during the deceleratory period of hydration, and a fluidlike response that persisted throughout the induction period. In sharp contrast, the white portland cement–PAA/PEO suspensions remained in a gel-like state throughout early stage hydration. At

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longer hydration times (>1 h), both cement–PAA/PEO suspensions exhibited an exponential dependence, $G'_i(t) \sim \exp(t/\tau_c)$, where τ_c depended on cement composition.

II. Experimental Procedure

(1) Materials System

An ASTM type I ordinary portland cement (W. R. Grace & Co., Cambridge, MA) and white portland cement (Lehigh Portland Cement Co., Yorktown, PA) were used in this study. The cement compositions, provided in Table I, were determined by X-ray fluorescence and Bogue analysis.¹ The ordinary and white portland cement powders had specific surface areas of 1.0 and 2.0 m²/g, respectively, as determined by BET (Model ASAP 2400, Micrometric, Norcross, GA). They also had respective mean diameters of 10.7 and 10.1 μm and similar particle size distributions ranging from 0.3 to 30 μm , as determined by particle size analysis (Model CAPA-700, Horiba, Ltd., Tokyo, Japan).

A polyelectrolyte-based copolymer^{7,8} served as the superplasticizer in this study. This species possesses a comb polymer architecture consisting of a poly(acrylic acid) (PAA) backbone, with one ionizable carboxylic acid group (COOH) per monomer unit, and charge neutral poly(ethylene oxide) (PEO) based “teeth” grafted at random intervals through imide linkages. The PAA/PEO comb polymer used here had a 5000 g/mol PAA backbone, 2000 g/mol PEO teeth, and a ratio of carboxylic acid to imide linkage groups of 7:1. The weight average molecular weight (M_w) and number average molecular weight (M_n) determined by gel permeation chromatography (GPC) analysis were 25 800 and 8380 g/mol, respectively.

(2) Adsorption Behavior

The adsorption of PAA/PEO comb polymers on ordinary and white portland cement was determined by total organic carbon (TOC) analysis (Model DC80, Dohrmann), which provided a quantitative measure of the nonadsorbed fraction of such species in solution. Cement suspensions with a water to cement ratio (w/c) of 0.35 (47 vol% cement) were prepared by adding an appropriate amount of cement powder to an aqueous stock solution of varying PAA/PEO concentration. On mixing for varying times (5 to 90 min), the suspensions were centrifuged at 2000 rpm for 10 min. The supernatant was immediately decanted and diluted with deionized water for the TOC measurement. Several aliquots of each sample were measured, and an average value was reported based on standard calibration curves (correlation

coefficient, R , was 0.998) obtained for PAA/PEO solutions of known composition.

(3) Hydration Behavior

Calorimetry and solution conductivity measurements were conducted to characterize the hydration behavior of ordinary and white portland cement pastes and suspensions. Concentrated suspensions were prepared ($w/c = 0.35$, $\phi_{\text{cement}} = 0.474$) by adding the appropriate amount of cement to an aqueous stock solution of varying PAA/PEO concentration. They were hand mixed for 30 s, capped, and placed in the calorimeter (Thermometric TAM AIR). The heat profile was recorded over a span of 48 h. The solution composition of pure cement pastes was determined by inductively coupled plasma (ICP). The solution conductivity could not be measured directly because of their solid-like nature. Such measurements, however, were conducted as a function of hydration time for cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi_{\text{cement}} = 0.474$) prepared at their critical PAA/PEO concentration (w^*) of 4 mg of PAA/PEO per gram of cement powder.

(4) Rheological Property Evolution

Oscillatory shear measurements were conducted on cement pastes and cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi_{\text{cement}} = 0.474$) using a controlled stress rheometer (Model CS-50, Bohlin Rheologi AB, Lund, Sweden) equipped with a vane tool geometry (cup diameter 27.5 mm, vane diameter 25 mm, vane height 20 mm).^{9–17} The suspensions were prepared by adding an appropriate amount of cement powder to aqueous stock solutions of varying PAA/PEO concentration. The samples were mixed under low shear conditions for 60 s followed by high shear mixing for 60 s to ensure homogeneity. After mixing, the suspensions were immediately transferred into the sample cup. The samples were presheared at a constant shear rate of 200 s⁻¹ applied for ~ 60 s, which was initiated 5 min after cement contact with water. Afterward, a thin layer of 1000 cP silicone oil was placed on top of the suspension to prevent water evaporation. Modulus data were acquired as a function of hydration time at a constant strain of $\sim 0.02\%$. This value was selected to ensure that the samples remained in the linear viscoelastic region throughout the measurement. These data were acquired after ten 1-Hz oscillatory stress cycles (for a total time of 10 s between measurements). These measurements were repeated on cement suspensions that were first allowed to hydrate for varying times before subjecting them to an additional preshear at a shear rate of 200 s⁻¹ for 60 s. Their modulus data were then collected following the same procedure outlined above for the fresh pastes. By studying the elastic property evolution in this manner, we could separate the observed G' evolution into both reversible and irreversible components, as first demonstrated by Kirby and Lewis.⁴

Table I. Chemical and Phase Composition of Type I White and Ordinary Portland Cement

Component	Chemical composition (%)	
	White	Ordinary
SiO ₂	21.74	21.09
Al ₂ O ₃	4.9	4.75
Fe ₂ O ₃	0.32	3.4
CaO	65.5	65.1
MgO	1.8	1.2
K ₂ O	0.22	0.69
Na ₂ O	0.23	0.18
SO ₃	3.36	2.94
LOI	1.39	0.83
Component	Phase composition (%)	
	White	Ordinary
C ₃ S	58.5	59.6
C ₂ S	18.2	15.5
C ₃ A	12.4	6.8
C ₄ AF	1.0	10.4
CSH ₂	7.2	6.3

III. Results

(1) PAA/PEO Adsorption on Ordinary and White Portland Cement

The adsorption of PAA/PEO comb polymers on ordinary and white portland cement is shown in Fig. 1 for concentrated cement suspensions of varying PAA/PEO concentration. The initial amount of PAA/PEO adsorbed (Γ) increased with increasing PAA/PEO concentration in suspension. At the critical PAA/PEO concentration (w^*) of 4 mg of PAA/PEO/(g of cement) required to promote suspension stability, the adsorbed amounts (Γ^*) were 1.6 and 1.35 mg/m² for ordinary and portland cement, respectively. At Γ^* , there was a significant fraction of nonadsorbed species in solution. This was quantified for both cement suspensions as a function of mixing time as shown in Fig. 2. For ordinary portland cement suspensions, PAA/PEO adsorption increased from 40% adsorbed initially to 50% adsorbed after 90 min of mixing. For white portland cement suspensions, PAA/PEO adsorption increased from 35% adsorbed initially to 65% adsorbed after 90 min of mixing.

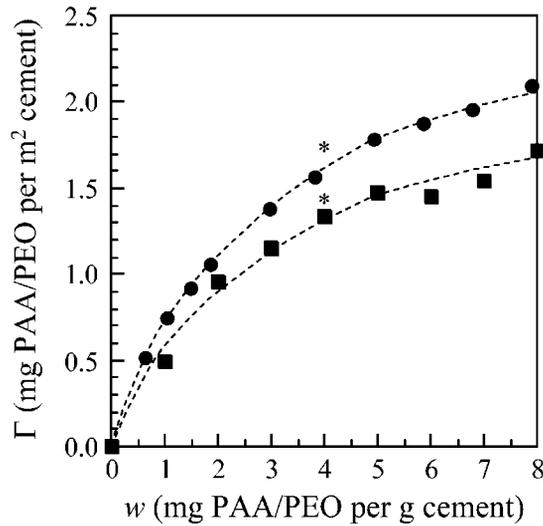


Fig. 1. Initial PAA/PEO adsorption ($t = 5$ min) on ordinary (●) and white (■) portland cement particles in suspension ($w/c = 0.35$, $\phi = 0.47$) as a function of the PAA/PEO weight fraction, w . The asterisks indicate the critical PAA/PEO weight fraction, w^* , for near-Newtonian flow. (Note, the dashed lines serve only to guide the eye.)

(2) Hydration Behavior of Cement Pastes and Cement–PAA/PEO Suspensions

The rate of heat evolution (dq/dt) as a function of hydration time is shown in Fig. 3 for concentrated cement suspensions of varying PAA/PEO concentration. These curves are divided into three regions of hydration behavior: (1) deceleratory period, (2) induction period, and (3) acceleratory period.^{18–20} For the pure cement pastes, the acceleratory period begins after ~ 2 h of hydration. The time required to achieve a minimum in dq/dt as well as the onset of the acceleratory period increased with increasing PAA/PEO concentration for both ordinary and white portland cements, as shown in Fig. 3. Such trends are a hallmark of their retarding nature. At the critical PAA/PEO concentration (w^*), the onset of the acceleratory period occurred at ~ 11 and 5.6 h for the ordinary and white portland cement suspensions, respectively. This nearly twofold difference in the onset of the acceleratory period does not arise because of differences in cement composition, but because of

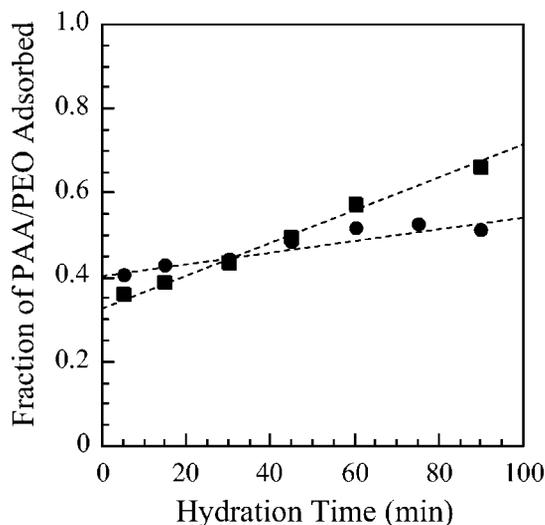


Fig. 2. Fraction of PAA/PEO adsorbed (at w^*) on ordinary (●) and white (■) portland cement particles in suspension ($w/c = 0.35$, $\phi = 0.47$) as a function of hydration time. (Note, the dashed lines serve only to guide the eye.)

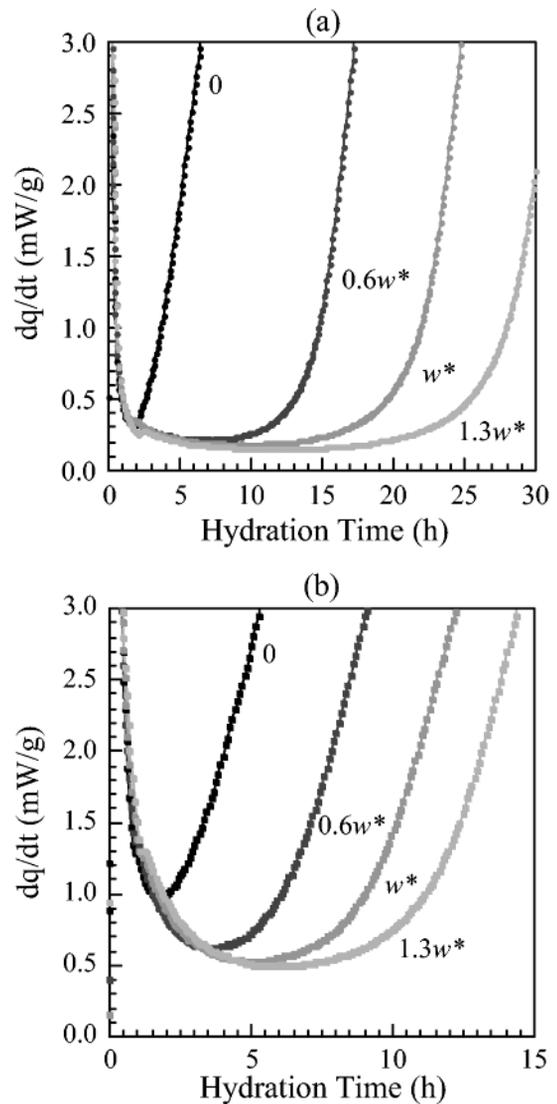


Fig. 3. Plots of the rate of heat transfer (dq/dt) versus hydration time for concentrated (a) ordinary and (b) white portland cement suspensions ($w/c = 0.35$, $\phi = 0.47$) of varying relative PAA/PEO weight fraction.

differences in the nonadsorbed PAA/PEO concentration, as will be addressed in a companion paper. Beyond the onset of the acceleratory period, the area under the $dq(t)/dt$ curves increased at similar rates for ordinary and white portland cement suspensions of varying PAA/PEO addition (i.e., the slopes of the $dq(t)/dt$ curves were ~ 1.2 mW/(g·h)).

Solution conductivity measurements could not be conducted on pure cement pastes because of their solid-like nature. Thus, their solution chemistry was characterized by ICP analysis, as shown in Table II. Based on these data, the ionic strength was calculated to be 0.52M and 0.19M for ordinary and white portland cement pastes, respectively.²¹ These values primarily reflect differences in their respective alkali contents.

The conductivity of concentrated cement–PAA/PEO (w^*) suspensions is shown as a function of hydration time in Fig. 4. These results were corrected by subtracting out the background conductivity associated with the nonadsorbed PAA/PEO species in solution. The measured conductivity is directly related to the amount of dissolved ions in solution. Thus, an increase or decrease in the solution conductivity with time reflects the dominance of either particle dissolution or hydration product formation. The conductivity was observed to increase rapidly at short hydration times, followed by a gradual rise until a maximum value was obtained. The value measured for ordinary portland cement–PAA/

Table II. Pore Solution Composition and Calculated Ionic Strength of Type I White and Ordinary Portland Cement

	Dissolved ion content			
	In OPC (M)	Contribution to $[I]_{\text{OPC}}$ (%)	In WPC (M)	Contribution to $[I]_{\text{WPC}}$ (%)
SO_4^{2-}	0.147	56.5	0.040	41.5
K^+	0.258	24.7	0.085	22.0
Ca^{2+}	0.022	8.4	0.029	29.5
Na^+	0.076	7.3	0.018	4.5
OH^-	0.032	3.1	0.009	2.3
$\text{Al}(\text{OH})_4^-$	2.3×10^{-4}	0.022	5.4×10^{-4}	0.140
$\text{Fe}(\text{OH})_4^-$	5.8×10^{-5}	0.006	3.6×10^{-5}	0.009

PEO suspensions at 5.6 h was 17.4 mS/cm, which was nearly twofold higher than that measured for white portland cement–PAA/PEO suspensions at 1.3 h. Such differences likely reflect the higher alkali sulfate content of the ordinary portland cement.^{22–24} Beyond these characteristic hydration times, τ_c , the measured solution conductivity decreased.

(3) Rheological Behavior of Cement Pastes and Cement–PAA/PEO Suspensions

The G' evolution of pure cement pastes as a function of hydration time is shown in Fig. 5. The four curves plotted correspond to cement pastes that were hydrated for ~5 min, 0.5 h, 1 h, and 1.75 h, respectively, before disrupting the evolving particle network under high shear. G'_i values of $\sim 10^4$ Pa were observed for ordinary and white portland cement pastes at 5 min hydration. Interestingly, ordinary portland cement pastes experienced a twofold decrease in their G'_i value with increasing hydration time before the onset of the acceleratory period (~2 h), whereas nearly constant values were observed for the white portland cement pastes. The high initial G'_i values and their reversible $G'(t)$ behavior (<2 h of hydration) are indicative of particle flocculation in a deep primary attractive minima, which is in good agreement with prior interparticle potential calculations.^{2,4} At the onset of the acceleratory period (~2 h), neither paste could be disrupted under high shear. Instrument limitations hindered our ability to make accurate measurements beyond these hydration times.⁶

The $G'(t)$ evolution of cement–PAA/PEO suspensions of varying cement and PAA/PEO composition are shown in Fig. 6. Several curves are presented in each plot, corresponding to

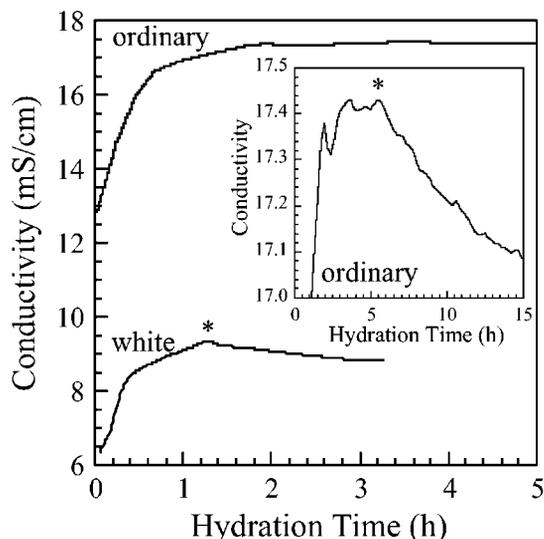


Fig. 4. Plot of conductivity as a function of time for concentrated ordinary (●) and white (■) portland cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$, $w = w^*$). The asterisks denote τ_c for each curve.

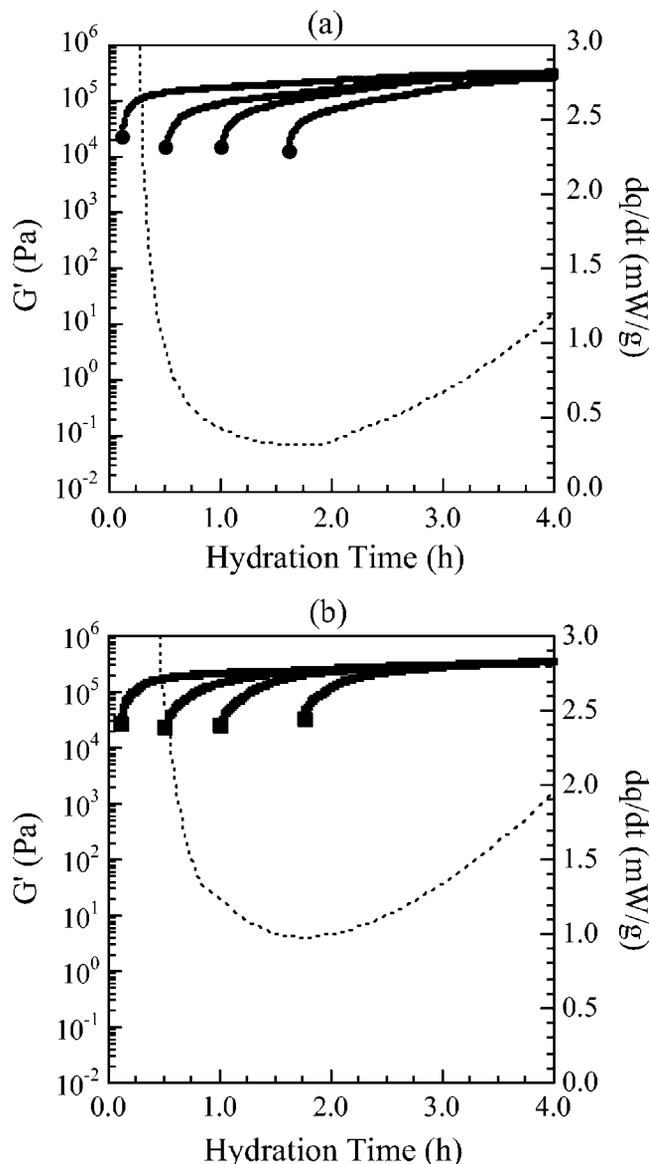


Fig. 5. Elastic shear modulus as a function of hydration time for (a) ordinary and (b) white portland cement pastes ($w/c = 0.35$, $\phi = 0.47$) presheared at varying hydration times. The large symbols (● and ■), indicate the initial elastic modulus values measured immediately after preshear for ordinary and white cement, respectively. The calorimetry data (dashed curve) is replotted on the secondary y-axis for comparison.

suspensions that were hydrated for varying times before disrupting the evolving particle network under high shear. The initial G'_i values depended strongly on PAA/PEO concentration ranging from ~ 1000 to ~ 1 Pa at respective PAA/PEO concentrations of $0.2w^*$ and w^* ($t = 5$ min). These observations reflect the dramatic improvement in stability imparted with increasing PAA/PEO addition. In their initial quiescent state, both systems experienced a rapid buildup in G' as a function of hydration time (see first curve in each plot). However, on disrupting the particle network at short hydration times (<1 h), remarkable differences were observed between the $G'(t)$ evolution of ordinary and white portland cement–PAA/PEO suspensions. The ordinary portland cement–PAA/PEO suspensions exhibited an order of magnitude or higher decrease in G'_i at $0.2w^*$ and w^* , respectively, when the hydration time increased from 5 min to 1 h. Even more striking, at w^* , this system experienced a gel-to-fluid transition that resulted in a cessation of the G' evolution under quiescent conditions until hydration times of nearly 24 h were reached. At the onset of the acceleratory period (~24 h), the particle network reformed within

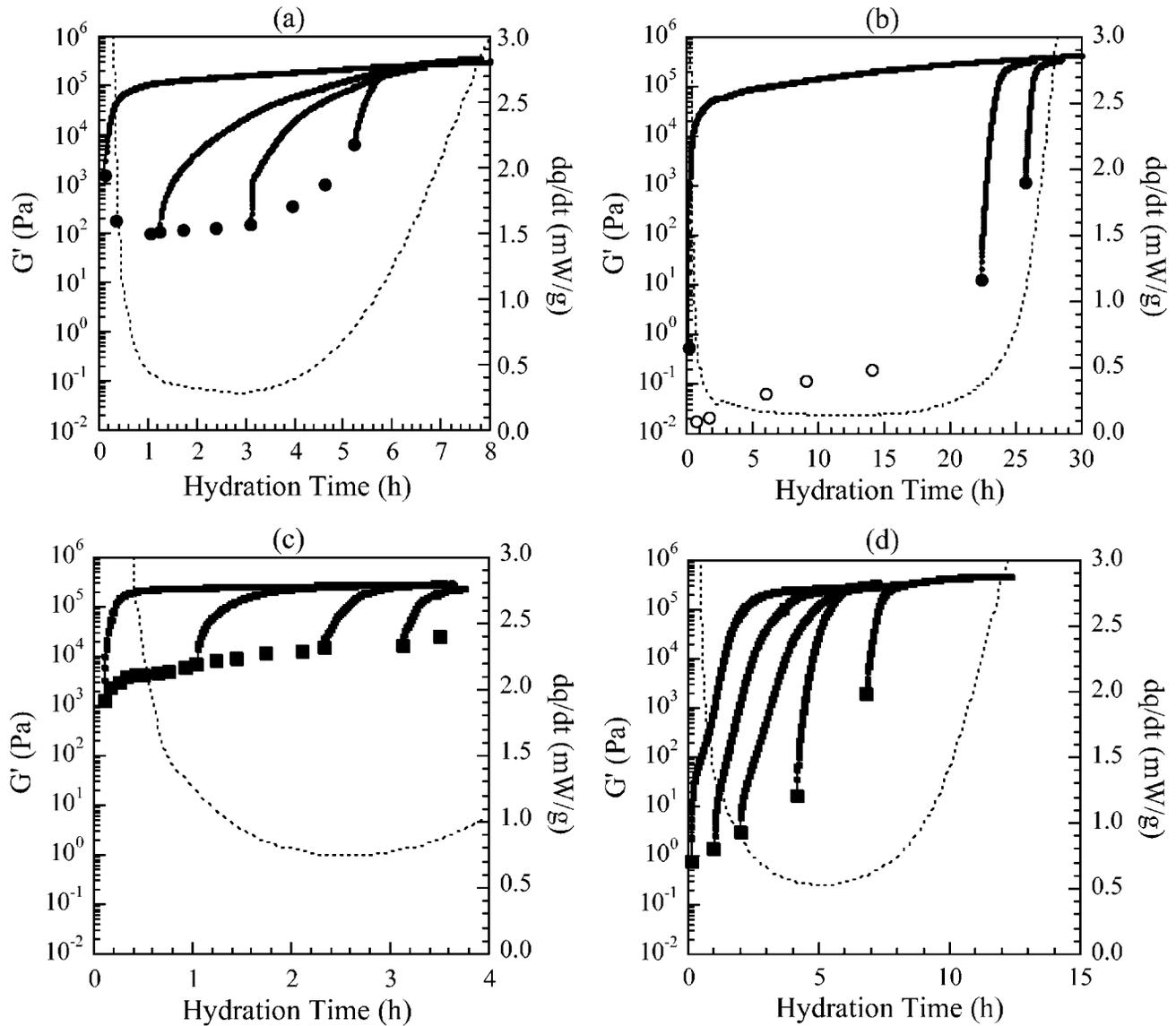


Fig. 6. Elastic modulus as a function of time for cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$) of varying cement composition and PAA/PEO concentration, presheared after varying hydration times: (a) ordinary cement, $0.2w^*$, (b) ordinary cement, w^* , (c) white cement, $0.2w^*$, and (d) white cement, w^* . The large symbols (\circ , \bullet , and \blacksquare), indicate the initial elastic modulus values measured immediately after preshear for ordinary and white cement, respectively. (Note, open and filled symbols indicate fluid- and gel-like behavior, respectively.) The calorimetry data (dashed curve) are replotted on the secondary y-axis for comparison.

the cement suspension leading to the reappearance of a gel-like response. In sharp contrast, white portland cement–PAA/PEO suspensions exhibited a gel-like response over all hydration times irrespective of PAA/PEO concentration. Interestingly, at hydration times beyond 1 h, G'_i increased exponentially for all cement–PAA/PEO systems studied until ultimately the particle network could no longer be disrupted under high shear. Initial set is defined when there is no longer any recovery in G'_i as compared with the plateau modulus value of $\sim 10^5$ Pa.

IV. Discussion

Our observations reveal that the rheological property evolution of cement–PAA/PEO suspensions depends strongly on cement composition. This is particularly evident at short hydration times (<1 h), where the cement particle surface and solution chemistry are rapidly evolving. The gel-to-fluid transition observed for ordinary portland cement–PAA/PEO suspensions formulated at the critical PAA/PEO concentration (w^*) was a remarkable finding and would not have been uncovered without the dynamic probe of

suspension structure offered by our $G'(t)$ approach. Despite substantial differences in their early $G'(t)$ response, the evolution of the initial G'_i , measured on disrupting the cement–PAA/PEO suspensions under high shear, followed an exponential dependence at longer hydration times (>1 h). Here, we discuss the origins of the $G'(t)$ behavior for pure cement pastes and cement–PAA/PEO suspensions with an emphasis on how the cement composition influences hydration phenomena and, thus, interparticle forces and initial setting behavior.

(1) Ordinary and White Portland Cement Pastes

Pure cement pastes exhibited nearly identical $dq(t)/dt$ responses and $G'(t)$ evolution at short hydration times (<1 h); however, compositional variations between the two cements influenced the solution composition, which led to significant differences in their ionic strength. Interestingly, the G'_i values measured on disrupting the ordinary portland cement paste network actually decreased by a factor of 2 at short hydration times. This observation suggests a weakening in the van der Waals interactions between cement particles under high ionic strength conditions. This observation is

supported by recent theoretical calculations by Prieve and Russel²⁵ that indicate both the range and magnitude of van der Waals forces are diminished under such conditions.

Both cement pastes exhibited $G'(t)$ behavior that was fully reversible until the onset of the acceleratory period at ~ 2 h. Beyond this hydration time, the pastes stiffened irreversibly; i.e., their particle network could no longer be disrupted under high shear. This transition is of interest, because it generally coincides with initial setting due to the nucleation and growth of calcium silicate hydrate (C-S-H) resulting from C_3S hydration.⁵ The observed stiffening strongly suggests that there is a fundamental change in the type of bonding between cement particles beyond this critical transition time. We attribute this to solid bridge formation at the contact points between particles within the flocculated network, which is in good agreement with the hypothesis proposed by Lei and Struble.⁵

(2) Ordinary and White Portland Cement–PAA/PEO Suspensions

Cement–PAA/PEO suspensions exhibited dramatic differences in their solution conductivity and $G'(t)$ evolution at short hydration times (< 1 h) as a function of cement composition, even though their affinity toward PAA/PEO adsorption and their $dq(t)/dt$ responses were nearly identical. The solution conductivity measurements revealed two important differences between these systems. First, the solution conductivity was nearly twice as high for the ordinary portland cement relative to the white portland cement–PAA/PEO system, which can be understood given the differences in their solution composition described above. Second, there was a nearly fourfold increase in the characteristic hydration time, τ_c , between ordinary ($\tau_c = 5.6$ h) and white ($\tau_c = 1.3$ h) portland cement suspensions, respectively. These values likely stem from differences in the rate of early hydration product formation between the two cements due to their different C_3A content.

The $G'(t)$ evolution observed for cement–PAA/PEO suspensions at short hydration times (< 1 h) depended strongly on both cement composition and PAA/PEO concentration. Not surprisingly, the addition of PAA/PEO species yielded improved stability for both the ordinary and white portland cement suspensions. Their enhanced stability led to a significant decrease in the initial G'_i value measured at 5 min of hydration, i.e., an order of magnitude lower for $0.2w^*$ and 4 orders of magnitude lower for w^* suspensions relative to initial values measured for the pure cement pastes. In the quiescent state, both cement–PAA/PEO suspensions exhibited a dramatic rise in G' with increasing hydration time. Interestingly, however, the ordinary portland cement suspensions exhibited further improvements in stability when their particle network was subsequently disrupted under high shear. For example, the G'_i value measured for suspensions ($0.2w^*$ PAA/PEO) was about an order of magnitude lower after 1 h of hydration than that observed initially (at 5 min). Even more striking, the G'_i value measured for suspensions (w^* PAA/PEO) was about 2 orders of magnitude lower after 1 h of hydration than that observed initially (at 5 min). Moreover, these systems became fully stabilized as evidenced by a gel-to-fluid transition. In sharp contrast, such changes in G'_i values and, hence, stability were not observed for the white portland cement–PAA/PEO suspensions at either PAA/PEO concentration. Without the dynamic probe of suspension structure offered by our $G'(t)$ approach, these remarkable observations would not have been uncovered.

To explain our findings, we must explore why hydration phenomena diminish interparticle attractions in the ordinary portland cement system. This appears to stem primarily from differences in the solution ionic strength (or conductivity) between the two cements. van der Waals attractions between cement particles are weakened with increasing ionic strength, as discussed above. As the initial system stability improves from the pure paste to w^* suspensions, the extent to which the G'_i value decreases at short hydration times also increases. Differences in their initial stability reflect a transition from particles flocculating in a deep primary

(pure pastes) or secondary minima ($0.2w^*$ suspensions) to those flocculating in a shallow secondary minimum (w^* suspensions). While the former two systems exhibit a modest additional improvement in stability at short hydration times, they remain in the gelled state due to the dominance of van der Waals attractions. In the latter case, little change in the interparticle attraction is needed to fully stabilize the system, i.e., a reduction in well depth by only a few kT . Because the solution ionic strength in the white portland cement pastes and suspensions is nearly 4 times lower than that observed for the ordinary portland cement system, less weakening of the van der Waals attractions between particles is expected.

At longer hydration times (> 1 h), the cement–PAA/PEO suspensions exhibit a rise in G'_i proportional to $\exp(t/\tau_c)$, which persisted until the onset of the acceleratory period, as shown in Fig. 7. Characteristic hydration times (τ_c) of 5.6 and 1.3 h were determined for ordinary and white portland cement suspensions, respectively, from the solution conductivity measurements. This dependence is significant, because it establishes a link between the rheological and hydration behavior of cement–PAA/PEO suspensions through τ_c as well as the generality of this relationship for portland cements of varying composition. However, due to significant variations in G'_i at short hydration times, these data could not be fitted by the exact equation $G'_i = G'_{i,0} \exp(t/\tau_c)$, which is a no adjustable parameter fit reported previously by Kirby and Lewis.⁴ This equation is only valid for white portland cement PAA/PEO (w^*) suspensions.

Another important finding was that the value of τ_c was independent of the PAA/PEO concentration for a given cement system. This is of particular interest for the ordinary portland cement–PAA/PEO suspensions, as they resided in both the fluid (at $0.2w^*$) and gel (at w^*) states under our experimental conditions. Clearly, in the fluid state, the observed G'_i evolution cannot be related to microstructural changes (e.g., bond strength increase) stemming from formation of a particle network, as their interparticle interactions are repulsive in nature. Therefore, one must view the observed elastic response in the context of related work conducted on concentrated colloidal fluids.²⁶ In such systems the measured G' reflects a loss of particle mobility at high solids loading; i.e., the particles cannot move rapidly with respect to each other without generating lubrication forces opposing an applied shear.²⁶ As a result, G' increases with the frequency of applied shear and with increasing colloid volume fraction. At a constant

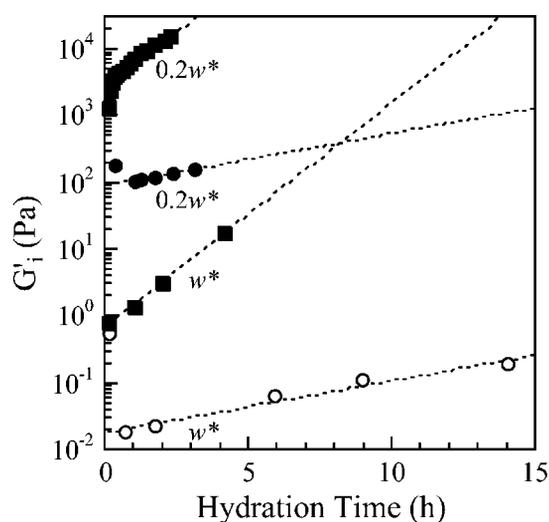


Fig. 7. Semilog plot of the initial elastic moduli (measured after preshearing the suspensions at intermittent hydration times) plotted as a function of hydration time for ordinary (\circ , \bullet) and white (\blacksquare) portland cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$). (Note, open and closed symbols indicate liquid- and gel-like behavior, respectively.) The dashed lines were determined using $G'_i(t) \sim \exp(t/\tau_c)$ where $\tau_c = 5.6$ and 1.3 h for ordinary and white portland cement–PAA/PEO suspensions, respectively.

frequency (1 Hz), Raynaud *et al.*²⁷ show that only a modest change in the solid volume fraction of a colloidal fluid is required to produce a significant rise in G' . In cement systems, solid hydration products, such as ettringite, calcium aluminate sulfate monohydrate, and calcium sulfate dihydrate form in solution, thereby increasing the solid volume fraction. Such products are known to have deleterious effects on the flow behavior of cement–PAA/PEO suspensions, especially when the C_3A /gypsum content is high.¹ Since all of these species grow in a preferred, crystallographic direction that results in rodlike morphology,^{28,29} they can occupy large excluded volumes giving rise to significant increases in the shear elastic modulus. Therefore, we propose that the main contribution of hydration to the evolution of G'_i beyond the deceleratory period is the creation of new solids. Given the analogous rise in G'_i with increasing hydration time observed for both ordinary portland cement–PAA/PEO suspensions, we believe that the behavior of each system stems from the same origin. This finding is significant, because it contradicts our earlier hypothesis that such changes mainly reflect an increase in bond strength within the particle network.⁴ This new interpretation is further supported by our recent observations that PAA/PEO comb polymers are highly robust dispersants, whose stabilizing ability is insensitive to pH and ionic strength changes.³⁰

After the onset of the acceleratory period, G'_i increased sharply for all cement–PAA/PEO systems. The ordinary portland cement suspensions (at w^*) experienced a fluid-to-gel transition that coincided with this onset, indicating the reformation of a particle network. This particle network could be partially disrupted under high shear well into the acceleratory period of hydration, but ultimately it stiffened irreversibly ($t \sim 30$ h). The other suspensions also stiffened irreversibly near the onset of the acceleratory period, though some differences were observed due to variations in their degree of aggregation as well as to the rate of hydration product formation during the acceleratory period, as indicated by the area under the $dq(t)/dt$ curves. In all cases, irreversible stiffening, which coincided with initial setting, was attributed to solid bridge (C–S–H) formation at the contact points between particles within the flocculated network.

V. Conclusions

We have studied the rheological property evolution and hydration behavior of ordinary and white portland cement (type I) pastes and concentrated cement–PAA/PEO suspensions. Cement composition had a marked effect on the elastic property evolution ($G'(t)$) and hydration behavior in the presence of PAA/PEO comb polymers, even though their affinity to adsorb such species was nearly identical. Both ordinary and white portland cement pastes exhibited G'_i values of $\sim 10^4$ Pa and fully reversible $G'(t)$ behavior until the onset of the acceleratory period ($t \sim 2$ h), where the pastes stiffened irreversibly. In contrast, cement–PAA/PEO suspensions (at w_{crit}) exhibited G'_i values of ~ 1 Pa and $G'(t)$ behavior comprised of both reversible and irreversible features. Interestingly, ordinary portland cement–PAA/PEO suspensions experienced a fluid-to-gel transition on high shear mixing at short hydration times (< 1 h), and the particle network did not rebuild until ~ 24 h of hydration. In sharp contrast, white portland cement–PAA/PEO suspensions remained weakly gelled throughout the initial stage of hydration even after high shear mixing. Such differences were a remarkable finding, and would not have been uncovered without the dynamic probe of suspension structure offered by our $G'(t)$ approach. At longer hydration times (> 1 h), both ordinary and white cement–PAA/PEO suspensions exhibited $G'_i(t) = G'_{i,0}(t) \exp(-t/\tau_c)$ with τ_c values of 5.6 and 1.3 h, respectively. Our observations suggest that hydration phenomena impact interparticle forces during early stage hydration and, ultimately, lead to initial setting through the formation of solid bridges at the contact points between particles within the gelled network.

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References

- H. F. W. Taylor, *Cement Chemistry*, 2nd ed. Thomas Telford Publishing, London, U.K., 1997.
- J. A. Lewis, H. Matsuyama, G. Kirby, S. Morissette, and J. F. Young, "Polyelectrolyte Effects on the Rheological Properties of Concentrated Cement Suspensions," *J. Am. Ceram. Soc.*, **83** [8] 1905–13 (2000).
- V. Tohver, J. E. Smay, A. Braem, P. V. Braun, and J. A. Lewis, "Nanoparticle Halos: A New Colloid Stabilization Mechanism," *Proc. Natl. Acad. Sci. U.S.A.*, **98** [16] 8950–54 (2001).
- G. H. Kirby and J. A. Lewis, "Rheological Property Evolution in Concentrated Cement–Polyelectrolyte Suspensions," *J. Am. Ceram. Soc.*, **85** [12] 2989–94 (2002).
- W.-G. Lei and L. J. Struble, "Microstructure and Flow Behavior of Fresh Cement Paste," *J. Am. Ceram. Soc.*, **80** [8] 2021–28 (1997).
- L. Nachbaur, J. C. Mutin, A. Nonat, and L. Choplin, "Dynamic Mode Rheology of Cement and Tricalcium Silicate Pastes from Mixing to Setting," *Cem. Concr. Res.*, **31**, 183–92 (2001).
- D. C. Darwin and E. M. Gartner, "Cement Admixture Product," U.S. Pat. No. 5 665 158, 1997.
- A. Arfaei and N. H. Milford, "Hydraulic Cement Additives and Hydraulic Cement Compositions Containing Same," U.S. Pat. No. 4 960 465, 1990.
- N. Q. Dzuy and D. V. Boger, "Yield Stress Measurement for Concentrated Suspensions," *J. Rheol.*, **27** [4] 321–49 (1983).
- N. Q. Dzuy and D. V. Boger, "Direct Yield Stress Measurement with the Vane Method," *J. Rheol.*, **29** [3] 335–47 (1985).
- A. E. James, D. J. A. Williams, and P. R. Williams, "Direct Measurement of Static Yield Properties of Cohesive Suspensions," *Rheol. Acta*, **26**, 437–46 (1987).
- H. A. Barnes, "The Vane-in-Cup as a Novel Rheometer Geometry for Shear Thinning and Thixotropic Materials," *J. Rheol.*, **34** [6] 841–67 (1990).
- N. J. Alderman, G. H. Meeten, and J. D. Sherwood, "Vane Rheometry of Bentonite Gels," *J. Non-Newtonian Fluid Mech.*, **39**, 291–310 (1991).
- R. Buscall, J. I. McGowan, and A. J. Morton-Jones, "The Rheology of Concentrated Dispersions of Weakly Attracting Colloidal Particles With and Without Wall Slip," *J. Rheol.*, **37** [4] 621–41 (1993).
- H. A. Barnes, "A Review of the Slip (Wall Depletion) of Polymer Solutions, Emulsions, and Particle Suspensions in Viscometers: Its Cause, Character, and Cure," *J. Non-Newtonian Fluid Mech.*, **56**, 221–51 (1995).
- P. V. Liddell and D. V. Boger, "Yield Stress Measurements with the Vane," *J. Non-Newtonian Fluid Mech.*, **63**, 235–61 (1996).
- J. A. Yanez, T. Shikata, F. F. Lange, and D. S. Pearson, "Shear Modulus and Yield Stress Measurements of Attractive Alumina Particle Networks in Aqueous Slurries," *J. Am. Ceram. Soc.*, **79** [11] 2917–24 (1996).
- E. J. Gartner, J. F. Young, D. A. Damidot, and I. Jawed, "Hydration of Portland Cement," pp. 57–108 in *Structure and Performance of Portland Cement*. Edited by J. Bensted and P. Barnes. E&FN Spon, New York, 2002.
- R. Kondo and M. J. Daimon, "Early Hydration of Tricalcium Silicate: A Solid Reaction with Induction and Acceleration Periods," *J. Am. Ceram. Soc.*, **52** [9] 503 (1969).
- R. Kondo and S. Ueda, "Kinetics of Hydration of Cements," *Int. Symp. Chem. Cem.*, **5th**, 203–55 (1969).
- J. N. Israelachvili, *Intermolecular and Surface Forces*. Academic Press, New York, 1992.
- D. Bonen and S. L. Sarkar, "The Superplasticizer Adsorption Capacity of Cement Pastes, Pore Solution Composition, and Parameters Affecting Flow Loss," *Cem. Concr. Res.*, **25** [7] 1423–34 (1995).
- S. Jiang, B.-G. Kim, and P.-C. Aitcin, "Importance of Adequate Soluble Alkali Content to Ensure Cement/Superplasticizer Compatibility," *Cem. Concr. Res.*, **19**, 71–78 (1999).
- B.-G. Kim, S. Jiang, C. Jolicœur, and P.-C. Aitcin, "The Adsorption of PNS Superplasticizer and Its Relation to Fluidity of Cement Paste," *Cem. Concr. Res.*, **30**, 887–93 (2000).
- D. C. Prieve and W. B. Russel, "Simplified Predictions of Hamaker Constants from Lifshitz Theory," *J. Colloid Interface Sci.*, **125** [1] 1–13 (1988).
- R. L. Larson, *The Structure and Rheology of Complex Fluids*. Oxford University Press, New York, 1999.
- L. Raynaud, B. Ernst, C. Verge, and J. Mewis, "Rheology of Aqueous Latices with Adsorbed Stabilizer Layers," *J. Colloid Interface Sci.*, **181**, 11–19 (1996).
- F. Kreppelt, M. Weibel, D. Zampini, and M. Romer, "Influence of Solution Chemistry on the Hydration of Polished Clinker Surfaces: A Study of Different Types of Polycarboxylic Acid-Based Admixtures," *Cem. Concr. Res.*, **32**, 187–98 (2002).
- E. Hekal and E. A. Kishar, "Effect of Sodium Salt of Naphthalene-Formaldehyde Polycondensate on Ettringite Formation," *Cem. Concr. Res.*, **29**, 1535–40 (1999).
- G. H. Kirby, D. J. Harris, Q. Li, and J. A. Lewis, "Poly(acrylic acid)–Poly(ethylene oxide) Comb Polymer Effects on BaTiO₃ Nanoparticle Suspension Stability," *J. Am. Ceram. Soc.*, **87** [2] 181–86 (2004). □