

# Rheological Property Evolution in Concentrated Cement–Polyelectrolyte Suspensions

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**We have studied the rheological property evolution and hydration behavior of pure white portland cement (Type I) pastes and concentrated cement–polyelectrolyte suspensions. Polyelectrolyte species have a marked effect on the initial stability, elastic property evolution ( $G'(t)$ ), and hydration behavior of this cement system. Pure cement pastes exhibited an initial  $G'$  value 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–polyelectrolyte suspensions exhibited initial  $G'$  values of  $\sim 1$  Pa and  $G'(t)$  behavior comprised of both reversible and irreversible features. Their initial  $G'$  values, measured after disrupting the particle network under high shear conditions, grew exponentially with hydration time, where  $G'_i = G'_{i,0} \exp(t/\tau_c)$  and  $\tau_c$  corresponds to the characteristic hydration time determined from calorimetry measurements. Our observations of these cement–polyelectrolyte systems 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 on concrete mixing and placement. Cement pastes consist of multiphase particles with a broad size distribution ( $\sim 1$ – $100 \mu\text{m}$ ) suspended in an aqueous medium. Particle interactions are dominated by long-range van der Waals attractive forces, which must be overcome through the introduction of electrostatic, steric, or other repulsive forces<sup>1</sup> to yield the desired degree of colloidal stability. Lewis *et al.*<sup>2</sup> have recently studied the effects of polyelectrolyte additions on the initial stability and flow behavior of concentrated cement suspensions. Such species, commonly known as superplasticizers, impart electrosteric stabilization to the system. Their observations revealed that concentrated cement suspensions exhibited strong shear thinning flow behavior in the absence of polyelectrolyte species. However, on the addition of a critical concentration of such species, i.e., sulfonated naphthalene formaldehyde condensate (SNF) and carboxylated acrylic esters (CAE), the suspensions exhibited a nearly Newtonian response. Those observations were in good agreement with interparticle force calculations, which predicted that cement particles (mean diameter  $\sim 10 \mu\text{m}$ ) would flocculate into a strong, primary minimum in the

absence of polyelectrolyte additions, whereas they would flocculate into a shallow, secondary minimum in the presence of such species.

The influence of colloidal forces on the rheological property evolution of concentrated cement suspensions remains a subject of debate. Two competing views have emerged regarding the origin of initial setting behavior in pure cement systems.<sup>3,4</sup> Lei and Struble<sup>3</sup> proposed that initial setting primarily involves a transition from a particle network dominated by colloidal forces to one held together by solid bridges arising from the precipitation of hydration products at regions of interparticle contact. Nachbaur *et al.*<sup>4</sup> proposed that initial setting is driven solely by long-range van der Waals interactions between cement particles, and that such interactions undergo little change as hydration proceeds. Both research groups have studied the rheological property evolution of pure portland cement suspensions with a water/cement ( $w/c$ ) ratio of  $\sim 0.45$  during initial hydration (0–2.5 h). Lei and Struble measured the yield stress behavior and critical strain of such pastes and correlated the observed changes to their corresponding microstructural evolution. In contrast, Nachbaur *et al.*<sup>4</sup> measured the elastic modulus ( $G'$ ) evolution by performing a series of strain, stress, and time sweeps.

The selection of pure cement suspensions or model systems based on tricalcium silicate for fundamental studies of rheological property evolution makes it difficult to discern between colloidal interactions and hydration phenomena. These highly attractive systems exhibit behavior similar to that of attractive (nonreactive) colloidal suspensions; i.e., they undergo a fluid-to-gel transition above a critical colloid volume fraction ( $\phi_{\text{gel}}$ ).<sup>5–9</sup> Accompanying this transition, a marked rise in  $G'$  (or yield stress,  $\tau_y$ ) with time is observed. For nonreactive colloid suspensions, the transition solely reflects microstructural changes stemming from increased particle–particle bond density; i.e., their bond strength remains constant with time, while the bond density increases as a result of particle diffusion and rearrangement. Rueb and Zukoski<sup>7</sup> have shown that the  $G'(t)$  evolution of colloidal gels follows a first-order kinetic process, i.e.,  $G'(t) = G'_{\text{eq}}[1 - \exp(-\alpha t)]$ , where  $G'_{\text{eq}}$  is the elastic modulus of the gel at equilibrium and  $\alpha$  is a parameter describing the rate of gelation. A hallmark of (nonreactive) colloidal gels is that their  $G'(t)$  evolution should be completely reversible on fully breaking down particle–particle contacts under high shear and allowing them to reform under quiescent conditions (see Fig. 1).<sup>10</sup> One can therefore probe hydration effects on bond strength (i.e., arising from changes in solution chemistry or solid bridge formation) by measuring irreversible changes in  $G'(t)$  evolution for reactive cement suspensions.

Here, we investigate the rheological property evolution and hydration behavior of concentrated cement suspensions in the absence and presence of polyelectrolyte species. We show that polyelectrolyte species have a dramatic effect on the initial stability and elastic properties of concentrated cement suspensions as well as on their hydration behavior, as characterized by  $G'$  and calorimetry measurements. We further show that the  $G'(t)$  evolution of pure cement pastes is reversible until the onset of the acceleratory period, where the particle network can no longer be disrupted under high shear conditions. In sharp contrast, the  $G'(t)$  evolution of cement–polyelectrolyte suspensions was more complex, exhibiting both reversible and irreversible features. Our

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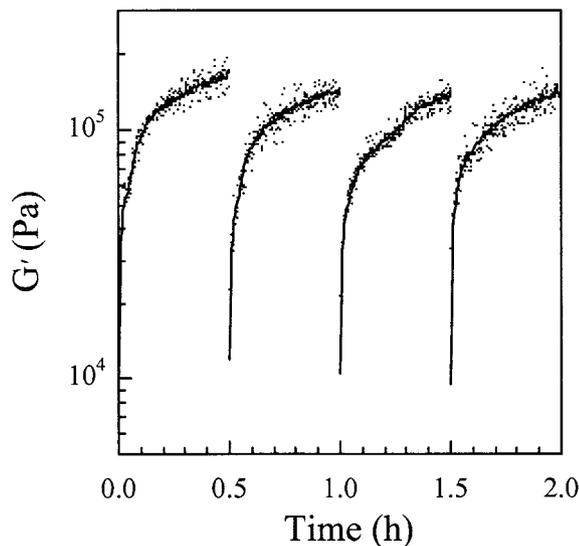


Fig. 1. The elastic modulus versus time for nonreactive, colloidal gels ( $\phi_{\text{Al}_2\text{O}_3} = 0.45$ )<sup>10</sup> presheared on aging at varying times.

observations indicate that the colloidal interactions between polyelectrolyte-stabilized cement particles are influenced by hydration phenomena, and that, ultimately, both pure cement pastes and superplasticized-cement suspensions experience initial setting that is likely induced by solid bridge formation at the particle-particle contacts within the gelled network.

## II. Experimental Procedure

### (1) Materials System

An ASTM Type I white portland cement (Lehigh Portland Cement Co., Yorktown, PA) was used in this study. The cement composition shown in Table I was determined by X-ray fluorescence and Bogue analysis.<sup>11</sup> The cement powder had a specific surface area of 2.0 m<sup>2</sup>/g as determined by BET (Model ASAP 2400, Micrometric, Norcross, GA), a mean particle size of 7.2  $\mu\text{m}$ , and a particle size distribution ranging from 0.2 to 20  $\mu\text{m}$ , as determined by particle size analysis (Model CAPA-700, Horiba, Ltd., Tokyo, Japan).

Two polyelectrolytes served as superplasticizers in this study: (1) sulfonated naphthalene formaldehyde condensate, SNF (Kao Chemical Co., Tokyo, Japan) and (2) a carboxylated acrylic ester

copolymer,<sup>12,13</sup> CAE (W. R. Grace & Co., Cambridge, MA). SNF is depicted as a homopolymer with one ionizable sulfonate group ( $\text{SO}_3^-$ ) per monomer unit. CAE superplasticizers are comb copolymers with a backbone consisting of poly(acrylic acid) (PAA), which has one ionizable carboxylate group ( $\text{COO}^-$ ) per monomer unit, and randomly grafted, poly(ethylene oxide) (PEO) based "teeth." The average molecular weights of SNF and CAE were determined from gel permeation chromatography to be 5400 and 15 200 g/mol, respectively. Their respective critical concentrations ( $\Phi^*$ ) required to promote stabilization (as evidenced by the onset of Newtonian behavior) of concentrated cement dispersions were found to be 25 mg of SNF/(g of cement) and 4 mg of CAE/(g of cement) through adsorption isotherm measurements (see Ref. 2).

### (2) Calorimetry and Conductivity Measurements

Calorimetry and suspension conductivity measurements were conducted to characterize cement hydration behavior. Concentrated suspensions ( $\phi_{\text{cement}} = 0.474$ ) were prepared with a water-cement ( $w/c$ ) ratio of 0.35 (by weight) by adding the appropriate amount of cement to an aqueous stock solution of varying polyelectrolyte concentration. Each suspension was 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 suspension conductivity was measured as a function of time for cement-polyelectrolyte suspensions prepared at their respective critical polyelectrolyte concentrations and continuously stirred.

### (3) Rheological Measurements

Oscillatory shear measurements were conducted on concentrated cement 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).<sup>14-22</sup> The suspensions were prepared by adding an appropriate amount of cement powder to aqueous stock solutions of varying polyelectrolyte 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<sup>-1</sup> applied for  $\sim 60$  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 time at a constant strain of roughly 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<sup>-1</sup> for 60 s. Their modulus data were then collected following the same procedure outlined above for the fresh pastes. By tracking the elastic property evolution in this manner, we could separate the observed  $G'$  evolution into both reversible and irreversible components, thereby allowing us to assess the relative influence of colloidal forces and hydration phenomena, respectively.

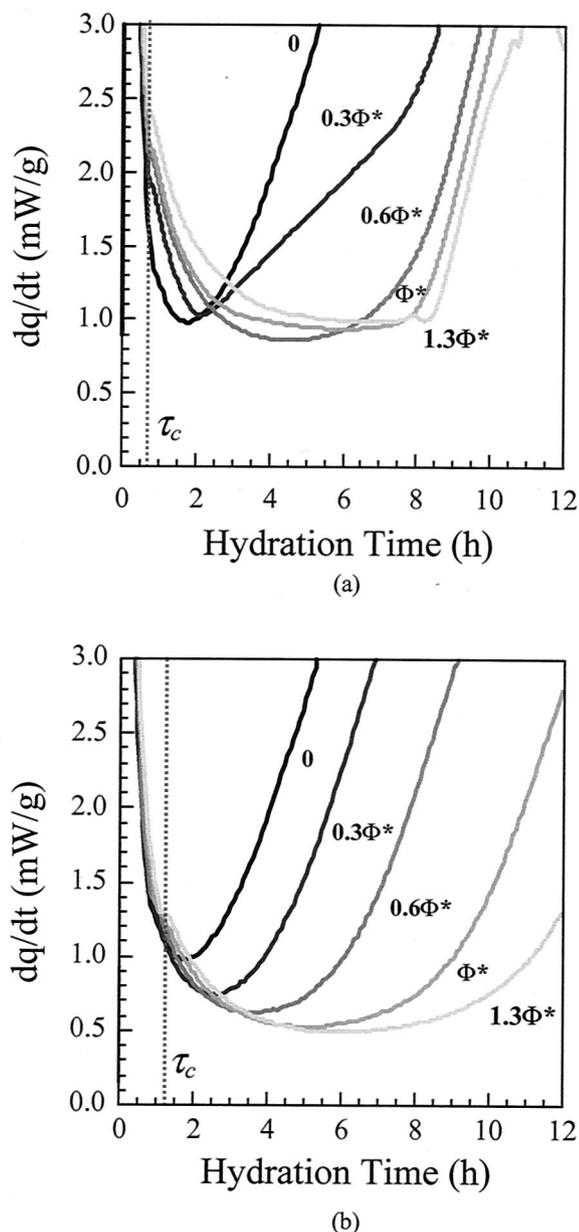
## III. Results

### (1) Hydration Behavior of Cement-Polyelectrolyte Suspensions

The rate of heat evolution ( $dq/dt$ ) as a function of hydration time is shown in Fig. 2 for concentrated cement suspensions of varying polyelectrolyte concentration. These curves are divided into three regions of hydration behavior: (1) deceleratory period, (2) induction period, and (3) acceleratory period.<sup>11,23-26</sup> At short hydration times, all curves collapsed onto a single curve, i.e.,  $dq(t)/dt$  was independent of polyelectrolyte concentration for a given cement-polyelectrolyte system. Beyond a characteristic hydration time ( $\tau_c$ ) of 37 and 80 min for SNF and CAE, respectively, the  $dq(t)/dt$

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

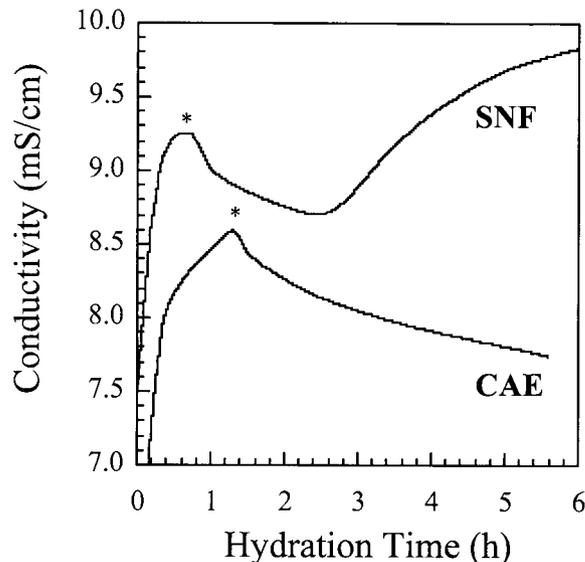
Component	Composition
Chemical composition	
SiO <sub>2</sub>	21.7
Al <sub>2</sub> O <sub>3</sub>	4.9
Fe <sub>2</sub> O <sub>3</sub>	0.32
CaO	65.5
MgO	1.8
K <sub>2</sub> O	0.22
Na <sub>2</sub> O	0.23
SO <sub>3</sub>	3.4
LOI	1.4
Phase composition	
C <sub>3</sub> S	58.7
C <sub>2</sub> S	18.0
C <sub>3</sub> A	12.4
C <sub>4</sub> AF	1.0
Gypsum	7.3



**Fig. 2.** Plots of the rate of heat evolution ( $dq/dt$ ) versus hydration time for concentrated cement suspensions ( $w/c = 0.35$ ) of varying normalized concentration of (a) SNF and (b) CAE. The dashed lines indicate the characteristic hydration times,  $\tau_c$ , of  $\sim 37$  min and  $\sim 80$  min for cement–SNF and cement–CAE suspensions, respectively.

response exhibited a strong dependence on polyelectrolyte concentration. The time required to achieve a minimum in  $dq/dt$  as well as the onset of the acceleratory period increased with increasing polyelectrolyte concentration. Interestingly, SNF additions had a less systematic effect on this behavior (especially at  $0.3\Phi^*$ , which exhibited anomalous behavior), relative to CAE additions. The anomalous behavior observed at  $0.3\Phi^*$  may reflect the sensitivity of the aluminat–sulfate reactions to SNF concentration as shown previously.<sup>27–30</sup>

The conductivity of cement–polyelectrolyte suspensions is shown as a function of hydration time in Fig. 3. These results were corrected by subtracting out the background conductivity associated with nonadsorbed polyelectrolyte species.<sup>2</sup> The conductivity is directly related to ionic strength of the solution in which the cement particles are suspended. The conductivity was observed to increase rapidly at short hydration times ( $\sim 3.5$  and 30 min for SNF and CAE, respectively) followed by a more modest increase until a maximum value was obtained at their respective characteristic



**Fig. 3.** Plot of conductivity as a function of time for concentrated cement suspensions ( $w/c = 0.35$ ) at the critical concentration ( $\Phi^*$ ) of (a) SNF and (b) CAE. (Note: The asterisks denote their respective characteristic hydration times,  $\tau_c$ .)

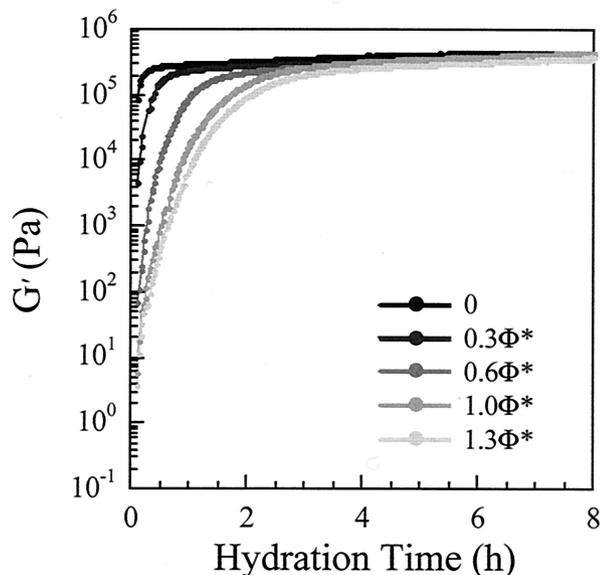
hydration times. Beyond  $\tau_c$ , the conductivity decreased for both cement–polyelectrolyte systems. For the cement–SNF suspensions, the conductivity was observed to increase once again at the onset of the induction period.

## (2) Rheological Behavior of Cement–Polyelectrolyte Suspension

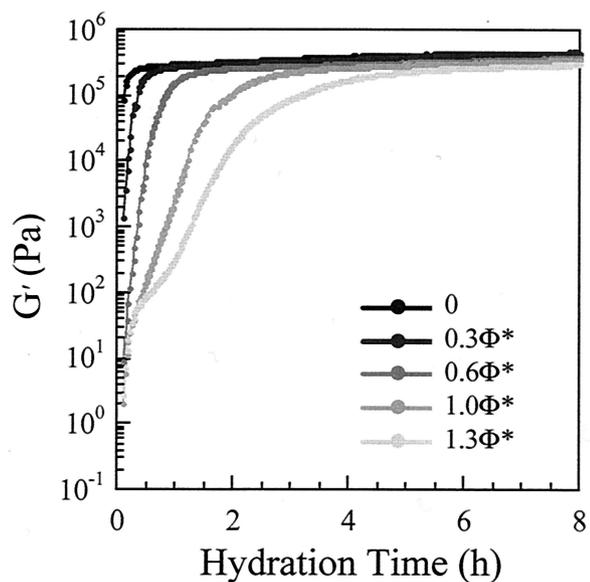
The elastic modulus ( $G'$ ) as a function of hydration time for concentrated cement suspensions of varying polyelectrolyte concentration are shown in Figs. 4(a) and (b) for SNF and CAE, respectively. The initial rise in elastic modulus with time was quite rapid for the pure cement suspensions, and appeared to approach a plateau  $G'$  value after  $\sim 2$  h of hydration. Although  $G'$  continued to rise on further hydration, instrument limitations hindered our ability to make accurate measurements in this region.<sup>4</sup> For the cement–polyelectrolyte suspensions, two key differences were observed. First, the initial  $G'$  values ( $G'_i$ ), acquired 6.5 min after initial cement contact with water, decreased by several orders of magnitude with increasing polyelectrolyte concentration, as shown in Fig. 5.  $G'_i$  values of roughly 2–4 Pa were obtained at the critical polyelectrolyte concentration (expressed in terms of a normalized value,  $\Phi/\Phi^* = 1$ ), which remained constant above this concentration range. Their initial rise in elastic modulus with time also decreased with increasing polyelectrolyte concentration. Similar behavior was observed for suspensions at the same normalized SNF and CAE concentration ( $\Phi/\Phi^* \leq 1$ ).

The  $G'$  evolution of pure cement pastes hydrated at varying times is shown in Fig. 6(a). Three curves are presented corresponding to cement pastes that were hydrated for 0, 0.5, and 1 h, respectively, before disrupting the evolving particle network under high shear conditions. Their  $G'_i$  values were found to be  $\sim 30$  kPa independent of hydration time ( $t < 2$  h). At the onset of the acceleratory period ( $\sim 2$  h), these pastes could no longer be broken down under the application of high shear.

The  $G'$  evolution of concentrated cement–polyelectrolyte suspensions hydrated at varying times is shown in Figs. 6(b) and (c) for SNF and CAE polyelectrolytes, respectively. Several curves are presented in each plot corresponding to cement pastes that were aged from 0 to 7 h before disrupting the evolving particle network under high shear conditions. The SNF- and CAE-stabilized suspensions exhibited low  $G'_i$  values ( $\sim 1$  Pa) in the absence of aging, i.e., several orders of magnitude below the value of 30 kPa observed for pure cement pastes. The rise in the  $G'_i$  as



(a)



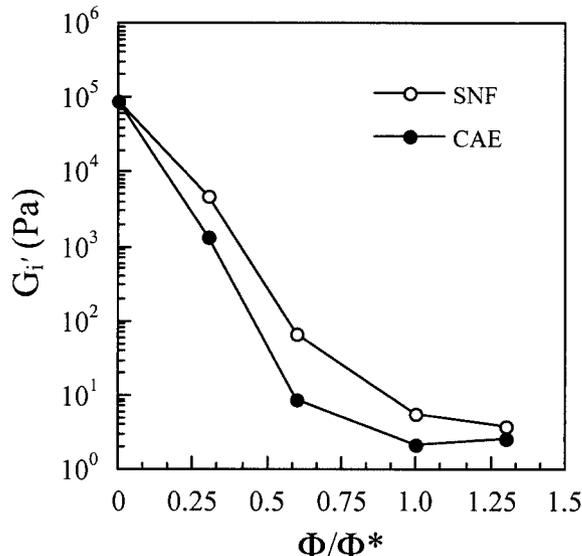
(b)

**Fig. 4.** Semilog plots of the elastic modulus ( $G'$ ) versus hydration time for concentrated cement suspensions ( $w/c = 0.35$ ) of varying normalized polyelectrolyte concentration of (a) SNF and (b) CAE.

a function of hydration time was more pronounced in the presence of SNF additions, as compared with CAE additions. Although the reversible nature of both systems diminished as hydration proceeded in this region, there was still significant recovery of  $G'_i$  compared with the “plateau” modulus of  $\sim 300$  kPa. Beyond the onset of the acceleratory period ( $\sim 7.5$  h) for the cement–SNF system, the gelled network could no longer be broken down under the application of high shear. In contrast, the gelled network continued to display some reversibility well into the acceleratory period for the cement–CAE system.

#### IV. Discussion

We observed significant differences between the  $G'(t)$  evolution of pure white portland (Type I) cement pastes, cement–polyelectrolyte suspensions, and nonreactive colloidal gels. Such differences arise primarily because of hydration phenomena, e.g., ion



**Fig. 5.** Semilog plot of initial elastic modulus as a function of normalized polyelectrolyte concentration for concentrated cement suspensions ( $w/c = 0.35$ ) with SNF and CAE additions.

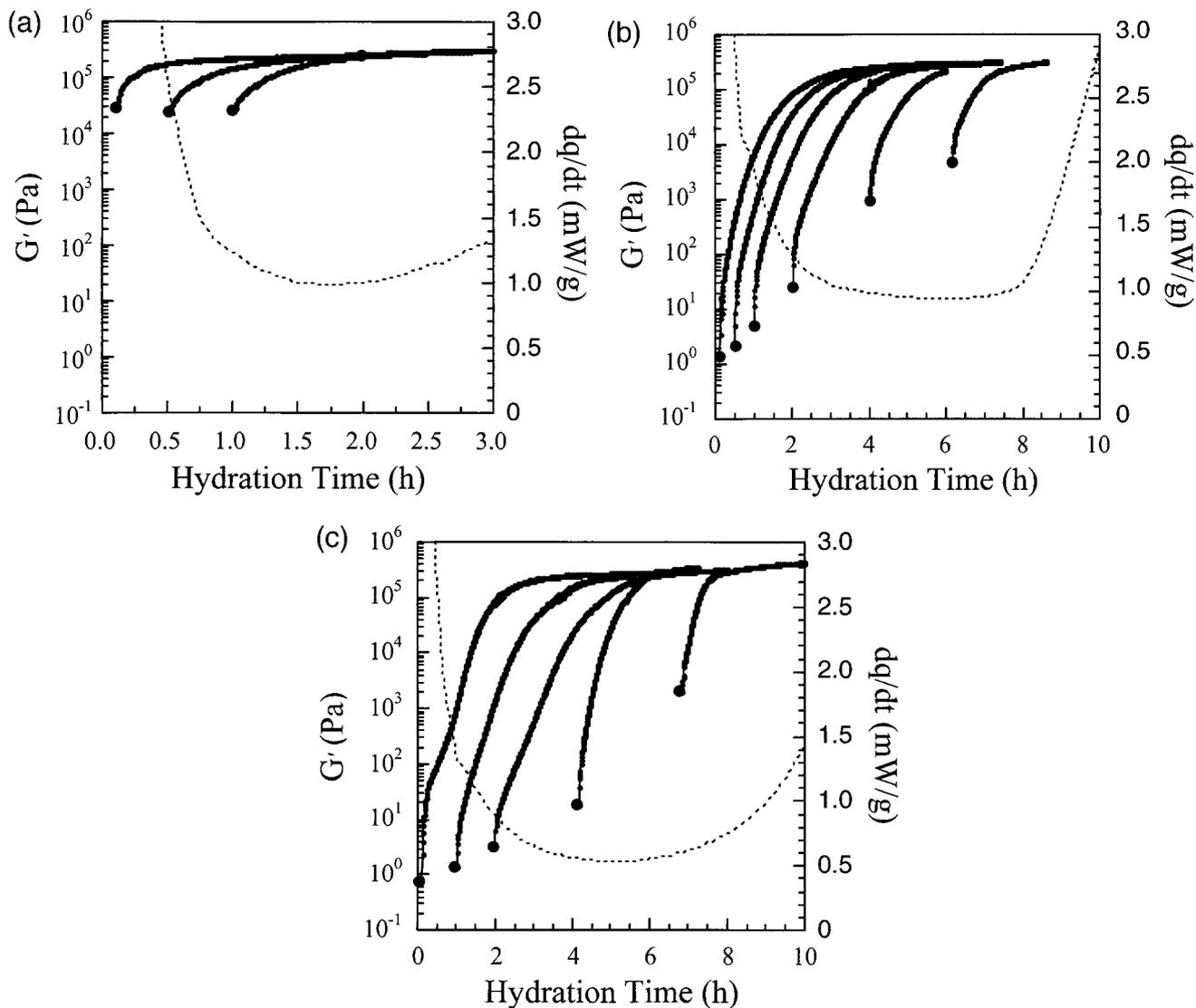
dissolution and hydration product formation, which induce irreversible changes in  $G'(t)$  behavior as a function of increasing hydration time. Here, we discuss the origin of the  $G'(t)$  behavior observed for such systems, with an emphasis on the relative contributions of colloidal forces and hydration phenomena.

The  $G'(t)$  evolution observed for pure cement pastes was completely reversible during initial hydration ( $t < 2$  h), where  $G'_i$  remained constant when the particle network was disrupted under high shear. The magnitude of  $G'_i$  ( $\sim 30$  kPa) reflects the fact that cement particles aggregate into a deep primary minimum in pure cement pastes, as predicted by Lewis *et al.*<sup>2</sup> Such systems appear to be insensitive to changes in ionic strength during initial hydration, because of the weak electrostatic contribution to the interparticle pair potential. At the onset of the acceleratory period, the  $G'(t)$  behavior of pure cement pastes becomes fully irreversible, i.e., the particle network could no longer be disrupted under high shear. This observation strongly suggests that there is a fundamental change in the type of bonding between particles beyond this critical transition time. We attribute this to solid bridge formation at the contact points between particles within the flocculated structure, which is in good agreement with the hypothesis proposed by Wei and Struble.<sup>3</sup>

The  $G'(t)$  evolution of cement–polyelectrolyte suspensions differed dramatically from that observed for pure cement pastes. First, the  $G'_i$  values (acquired at  $\sim 6.5$  min of hydration) were several orders of magnitude below that found for the pure cement pastes at the same  $w/c$  ratio of 0.35. This observation reflects the improved stability imparted by the presence of polyelectrolyte species. Second, the reversible nature of the  $G'(t)$  curves diminished with increasing hydration time in a systematic fashion. We observed an exponential rise in  $G'_i$  (measured on network disruption under high shear conditions) as a function of hydration time during the deceleratory and induction periods (see Fig. 7), which is given by

$$G'_i = G_{i,0}' \exp(t/\tau_c) \quad (1)$$

where  $G'_i = G_{i,0}'$  at  $t = 0$  min and  $\tau_c$  is the characteristic hydration time of 37 and 80 min for SNF and CAE, respectively. This expression is significant because there are no adjustable parameters, i.e.,  $\tau_c$  is equivalent to the characteristic hydration time observed from the calorimetry and conductivity results establishing sole dependence of the exponential rise in  $G'_i$  on changes induced by early hydration phenomena. Although this establishes a strong link between early stage hydration and rheological



**Fig. 6.** The elastic modulus as a function of time for (a) pure cement pastes, (b) cement–SNF, and (c) cement–CAE suspensions ( $w/c = 0.35$ ) presheared at varying hydration times. The large, filled circles indicate the initial elastic modulus values measured immediately after preshear. The calorimetry data (dashed curve) is plotted on the secondary  $y$ -axis for comparison.

property evolution for white portland cement–superplasticizer suspensions, the generality of this result for other cement systems has yet to be established.

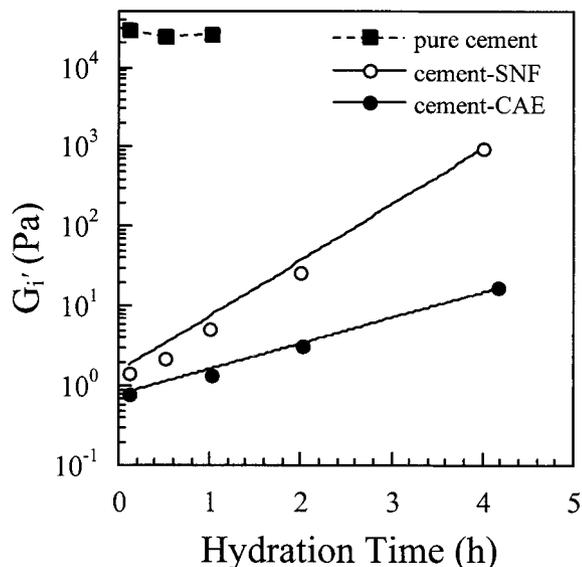
The low  $G'_i$  values observed initially for the cement–polyelectrolyte suspensions is indicative of particle flocculation in a weak, secondary attractive minimum. Thus, unlike pure cement pastes, superplasticized cement suspensions are far more sensitive to changes in interparticle forces arising from hydration phenomena. Two possible factors may contribute to our observations: first, increased ionic strength as a result of cement particle dissolution may lead to enhanced attractions between cement particles with adsorbed polyelectrolyte layers, and second, the formation of hydration products may further promote such attractions by “burying” the adsorbed species. It is well known that the electrostatic repulsions between charged segments along the polyelectrolyte backbone or adjacent adlayers are screened in conditions of high ionic strength, effectively mitigating electrosteric repulsive forces between cement particles.<sup>31–35</sup> This effect intensifies in the presence of multivalent ions in solution, such as found in cement pore solutions.<sup>34,36,37</sup> The formation of a thin hydration product layer on the particle surfaces during early hydration may partially “bury” the polyelectrolyte adlayer, further diminishing the electrosteric repulsive forces between cement particles.<sup>38–41</sup>

The reversibility of the  $G'(t)$  behavior was completely lost near the onset of the acceleratory period for the cement–polyelectrolyte

suspensions. For the cement–SNF suspensions,  $G'(t)$  became fully irreversible just after the onset of the acceleratory period, whereas a more gradual loss of reversibility was observed for cement–CAE suspensions. We attribute such differences primarily to the rate at which hydration products form during the acceleratory period as indicated by the sharpness in rise of  $dq/dt$  with time in Fig. 2 for these two systems. This observation suggests that polyelectrolyte architecture and chemistry play an important role in determining the initial setting behavior of cement pastes. We plan to address such effects for CAE-based superplasticizers in a companion paper.

## V. Conclusions

We have studied the rheological property evolution and hydration behavior of pure white Portland (Type I) cement pastes and concentrated cement–polyelectrolyte suspensions. Polyelectrolyte species were found to have a marked effect on the initial stability, elastic property evolution ( $G'(t)$ ), and hydration behavior of these cement systems. Pure cement pastes exhibited an initial  $G'$  value of  $\sim 10^4$  Pa and fully reversible  $G'(t)$  behavior when the particle network was disrupted under high shear conditions. The observed  $G'(t)$  behavior at short times ( $< 2$  h) was driven solely by interparticle forces. However, at the onset of the acceleratory



**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 pure cement pastes, cement-SNF and cement-CAE suspensions. The solid lines were determined using Eq. (1), where  $\tau_c = 37$  min and 80 min for SNF and CAE, respectively. (Note: The dashed line only serves to guide the eye.)

period, these pastes stiffened irreversibly because of hydration effects. In sharp contrast, cement-polyelectrolyte suspensions exhibited initial  $G'$  values of  $\sim 1$  Pa. Their  $G'(t)$  behavior displayed both reversible and irreversible features, with the latter stemming from hydration effects. Our observations strongly suggest that hydration phenomena both impact colloidal forces during early stage hydration and, ultimately, lead to initial setting via solid bridge formation at the contact points between particles within the gelled network. The measurement of multiple  $G'(t)$  curves acquired on disrupting the particle network at intermittent hydration times proved to be an effective approach for distinguishing between colloidal interactions and hydration phenomena in these complex, reactive systems.

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