

Effects of a strong polyelectrolyte on the rheological properties of concentrated cementitious suspensions

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Abstract

Strong polyelectrolytes, referred to as superplasticizers, are known to improve the initial fluidity of concentrated cement suspensions. To quantify how the polyelectrolytes affect the fluidity, we have studied the effect of a strong anionic polyelectrolyte, melamine formaldehyde sulfonate (MFS), on the zeta potential of cement particles and on the steady-shear and low-amplitude rheological properties of cement suspensions. Adsorption of low concentrations of MFS onto the cement particles leads to an inversion in the sign of the surface potential, causing the electrostatically flocculated particles to become electrostatically dispersed and giving rise to a corresponding decrease in the steady-shear viscosity and storage modulus. At an intermediate MFS concentration, the steady-shear viscosity and the storage modulus each display a minimum. This concentration corresponds to that at which the zeta potential becomes constant. Larger concentrations of MFS result in an increase in the viscosity and storage modulus, which is attributed to depletion flocculation. These results thus relate the interaction between particles to the suspension fluidity through the analysis on the surface potential of particles and microstructure of suspension.

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1. Introduction

The manufacturing of material composites from colloidal particle suspensions requires both sufficient fluidity of the suspension during flow and sufficient cohesiveness between the particles upon the cessation of flow to maintain the desired structural shape. Both the fluidity and the cohesiveness depend on the strength of the interactions between the colloidal particles. While fluidity is promoted by well-dispersed particles that are mutually repulsive, cohesiveness is promoted by particles that are attracted to each other. Hence, it is critical to achieve a balance between interparticle repulsion and attraction to optimize the competing requirements of fluidity and cohesiveness.

Polymeric stabilization of colloidal particles has been widely used to control the interactions between colloidal particles [1,2],

especially when the dispersions are subject to harsh processing conditions where the temperature and ionic strength are not constant. One example of this is the development of self-compacting engineered cementitious composites (SC-ECCs) [1,2]. SC-ECCs are designed to flow into a complex building structure without any extreme compaction, similar to self-compacting concrete [3], and to exhibit extremely ductile pseudo strain-hardening performance in the hardened state, similar to engineered cementitious composites (ECCs) [4]. Similar to typical cement suspensions, SC-ECC suspensions show a rapid increase in ionic strength as ionic species are released from the cement particle surfaces and a rise in temperature as the hydration reaction progresses between contact points between cement particles.

One type of polymer that has been widely used in cementitious materials is a strong anionic polyelectrolyte, referred to as a superplasticizer (SP). Common superplasticizers include sulfonated naphthalene formaldehyde and sulfonated melamine formaldehyde [3]. This type of polymeric admixture

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has been used since 1970s to increase the cement particle loading [3] as well as to improve the workability of fresh cementitious materials [6]. The polyelectrolytes are attracted to and consequently adsorb onto the cement particle phases that bear a surface charge opposite in sign to that of the polyelectrolyte, altering the surface potential of the particles [1,9]. This results in the dispersion of the particles that tend to aggregate due to strong electrostatic attraction between the oppositely charged phases, and subsequent reductions in the yield stress and viscosity [6,7].

However, these strong polyelectrolytes do not maintain the initial fluidity of a fresh cementitious suspension [10], which is necessary to achieve self-compactability [5]. The fast fluidity loss is primarily due to the increase in the ionic strength of the cementitious suspension, which leads to re-flocculation driven by van der Waals attraction. Since the strong polyelectrolytes do not provide significant steric repulsion to prevent this re-flocculation, copolymers such as weak or grafted polyelectrolytes have been developed to provide both electrostatic and steric—“electrosteric”—stabilization in a single molecular species [11–17]. The design of these copolymers must optimize the balance between electrostatic and steric stabilization to achieve a desired fluidity of the suspension. This design has been primarily based on trial and error modification of polymer structures, such as altering the length of the steric chains and the number of ionic groups on the backbone. However, it is necessary to first understand the individual roles of electrostatic stabilization and steric stabilization on fluidity prior to designing a copolymer that will provide the appropriate balance of both.

There have been a few studies related to the effects of strong polyelectrolytes on the zeta potential of particles, the subsequent interaction between the particles, the hydration process, and the suspension fluidity as quantified by the plastic viscosity, yield stress, and deformability (see, for example, Refs. [18–28]). A simple correlation of the amount adsorbed and the zeta potential to the interparticle forces as calculated for two-body interactions, however, does not always reflect the observed viscosity and yield stress, since the steady-shear deformation irreversibly disrupts the aggregated microstructure. Instead, low-amplitude oscillatory shear (LAOS) measurements are more appropriate to link the adsorption of the polyelectrolyte to the microstructural changes. While there have been studies on the LAOS behavior of cement pastes [27,28], no study has systematically addressed the effect of the superplasticizer on the microstructure and subsequent LAOS behavior.

In this paper, we focus on the role of electrostatic stabilization on cement suspension fluidity. The polyelectrolyte melamine formaldehyde sulfonate (MFS), a commercial SP used in the preparation of cementitious suspensions, was used as the electrostatic stabilizer in suspensions of Type I Portland cement. The amount of MFS adsorbed onto the cement particles is correlated to the measured zeta potential of the particles. Then, both steady-shear and low-amplitude oscillatory shear (LAOS) properties of suspensions of varying superplasticizer concentration are measured and correlated to the amount of MFS adsorbed and the zeta potentials. The steady-shear

properties were measured to characterize the response of the suspension microstructure to steady-shear (irreversible) deformation, while the LAOS properties were measured to quantify changes in the suspension microstructure with MFS and particle concentrations.

2. Experimental section

2.1. Materials

Type I ordinary Portland cement (LaFarge Cement Co., France) was stored in a dry environment until use. The superplasticizer, melamine formaldehyde sulfonate [MFS, molecular weight (MW)=20,000–30,000], was used as received in aqueous solution of 33 wt.% (W.R. Grace Chemical Co., Boston, MA). Unlike commercial air-entraining superplasticizers, MFS does not entrain air; thus, the rheological properties observed upon the addition of MFS can be attributed to the adsorption of the polymer onto the particles. De-ionized (DI) water was used in all suspensions.

Using a vibrating mixer, the cement particles were first mixed with DI water for 1 min to form a paste. Then, a known amount of the aqueous MFS solution was added to the cement paste and the paste was further mixed for 2 min. This sequential addition of water and the MFS solution was adopted to improve the uniformity of adsorption of MFS onto the cement particles, avoiding the fast stiffening of pastes caused by false setting [23,24]. The cement particle volume fractions varied from 0.46 [water/cement (W/C)=0.40] to 0.56 (W/C=0.25). The MFS concentration varied from 0% to 2.0% (w/w), based on the cement weight. At a given cement particle concentration, the minimum MFS concentration studied was that necessary to disperse the particles, and this concentration increased with increasing particle volume fraction. Likewise, the maximum MFS concentration studied was just less than that determined to lead to phase separation due to particle segregation.

2.2. Adsorption isotherm

The adsorption isotherm for MFS was quantified by ultraviolet (UV) spectroscopy (Varian Australia Ltd., Melbourne, Australia). Dilute cement suspensions were prepared with a constant particle concentration and varying MFS concentration following the mixing procedure detailed above. Then, the cement particles bearing adsorbed MFS were removed by centrifugation and the supernatant collected for UV analysis. The concentration of non-adsorbed MFS in the supernatant was calculated from measurements of the UV absorbancy at 490 nm, using a calibration curve established using MFS solutions of known concentrations.

2.3. Zeta potential measurements

The presence of adsorbed MFS alters the surface potential of the cement particles. To quantify this change, the zeta potential of the particles was measured as a function of MFS

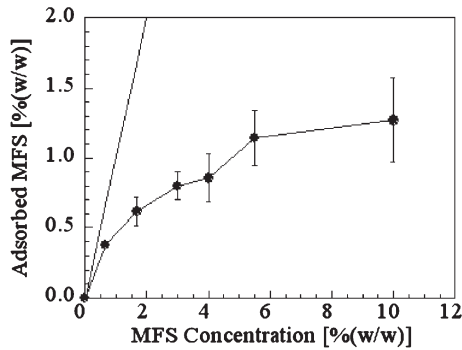


Fig. 1. Adsorption isotherm of MFS. —●—: actual, —: 100% adsorption of MFS assumed.

concentration (Zeta-meter Inc., Staunton, VA). Cement suspensions with a constant particle concentration and varying MFS concentrations were prepared and then diluted with DI water for the zeta potential measurements. It was assumed that MFS did not desorb following this dilution, based on no observed change in the suspension pH upon dilution. The velocity of the particles under an applied voltage was measured, from which the electrophoretic mobility u (velocity/electric field) was calculated. The mobilities were converted to zeta potentials using the Helmholtz–Smoluchowski equation:

$$\zeta = \frac{\eta u}{\epsilon} \quad (1)$$

where ζ is the zeta potential, η is the fluid viscosity, and ϵ is the dielectric permittivity. Eq. (1) is valid for $\kappa a > 100$, where κ^{-1} is the Debye length of the particles, and a is the particle radius.

2.4. Rheological measurements

The steady-shear and low-amplitude oscillatory shear (LAOS) properties of the suspensions were measured using a controlled-strain rheometer (CS-50, Bohlin Instruments, Gloucestershire, England). The rheometer was equipped with a concentric cylinder geometry with a gap spacing of 1.4 mm, and the sample temperature was kept constant at 25 ± 1 °C. To eliminate the dependence of the microstructure on shear history, a pre-shear was applied to the samples prior to the rheological measurements. This pre-shear consisted of subjecting the samples to a shear rate of 150 s^{-1} for 30 s, followed by a rest time of 3 min prior to the steady-shear measurements and 10 min prior to the LAOS measurements.

During the steady-shear measurements, the shear stress was measured as a function of shear rate ranging from 0.00146 to 146 s^{-1} , from which the suspension viscosity was calculated. During the LAOS measurements, the storage modulus (G') and the loss modulus (G'') were measured as a function of frequency (from 0.01 to 0.1 Hz) and as a function of time (at 1 Hz) within the linear viscoelastic region (LVR). The critical strain marking the end of the LVR was determined to be approximately 1×10^{-4} , and was noted to decrease with increasing particle concentrations. Since the storage modulus becomes relatively independent of frequency for frequencies greater than 1 Hz,

1 Hz was selected as the frequency at which the time-dependence of the microstructural changes was characterized.

3. Results and discussion

3.1. Adsorption isotherm

Shown in Fig. 1 is a plot of the MFS adsorption isotherm. The amount of MFS adsorbed increases more rapidly at low MFS concentrations, followed by a relatively smaller increase in the adsorbed amount up to the plateau. The particle surfaces were saturated with approximately 1.2% MFS based on particle weight, which required the addition of MFS of 6.0% . Also shown in Fig. 1 is a straight line that corresponds to 100% adsorption of the MFS molecules. The difference between this line and the actual adsorption isotherm gives the amount of non-adsorbed MFS chains. There is a more significant increase in the concentration of non-adsorbing MFS chains for MFS concentrations above approximately 1.0% .

According to observations made by Blank et al. [8] and Uchikawa et al. [23], most of the MFS chains adsorb onto the positively charged interstitial phases due to electrostatic attraction. The reduction in the adsorption efficiency of MFS reflects not only steric hindrance effects of molecules already adsorbed but also the gradual decrease in the electrostatic attraction between the interstitial phases and MFS.

3.2. Zeta potential measurements

Cement particles are composed of interstitial phases with a positive potential ranging from 20 to 40 mV and of silicate phases with a negative potential of approximately -10 mV [9]. The positive potential on the interstitial phases results from the preferential adsorption of Ca^{2+} or $\text{Ca}(\text{OH})^+$ onto the hydrated calcium sulfoaluminate or ferrite components. In contrast, the less hydrated silicate (SiO_4^{4-}) components have a lower affinity for the calcium and thus remain negatively charged. The measured zeta potential thus represents the composite potential of the particle surface.

Fig. 2 shows that the adsorption of MFS significantly alters the zeta potential of the cement particles at a constant pH of 12 . At this pH, the bare cement particles have a

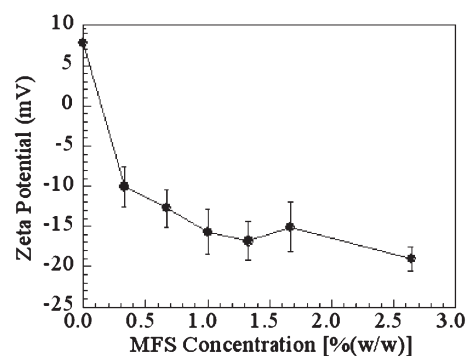


Fig. 2. Effect of MFS concentration on the zeta potential of the cement particles (pH=12).

positive zeta potential of approximately 8 mV, which is in agreement with other studies [9]. The addition of 0.33% MFS changes the zeta potential to approximately -10 mV, suggesting that the adsorption of MFS onto the positively charged interstitial phase neutralizes this phase. The zeta potential continues to become more negative upon increasing the MFS concentration up to 1.0%. The changes in the zeta potential become less significant at MFS concentrations greater than 1.0%, which is attributed to the smaller increase in the adsorbed amount of MFS at these concentrations. Indeed, the zeta potential profile mirrors the adsorption isotherm for the MFS.

3.3. Rheological properties of polyelectrolyte-free cement suspensions

The steady-shear properties of cement suspensions in the absence of MFS are shown in Fig. 3a for particle volume fractions of 0.46 ($W/C=0.40$) and 0.49 ($W/C=0.35$). The shear viscosity is larger at the higher particle concentration for all shear rates. It is not possible to measure the rheological properties of the suspensions prepared without MFS for particle concentrations larger than 0.49 because of the extensive flocculation of the particles and subsequent large suspension viscosity.

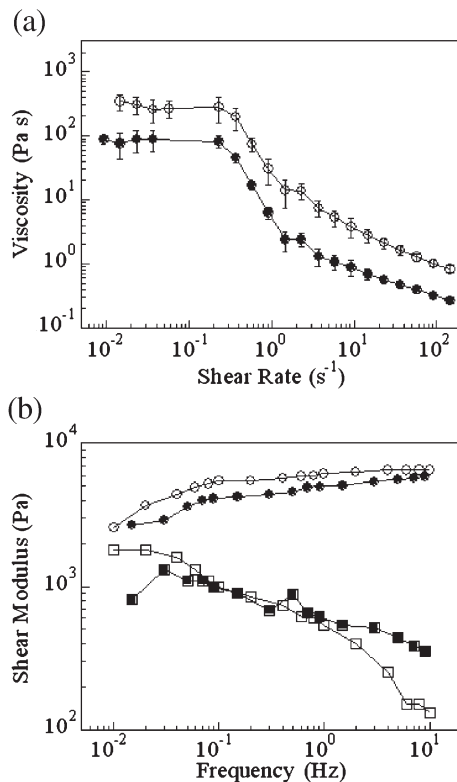


Fig. 3. Rheological properties of cement suspensions in the absence of MFS. (a) Steady shear properties: ●, $\phi_{\text{cement}}=0.46$, ○, $\phi_{\text{cement}}=0.49$. (b) Low-amplitude oscillatory shear properties: ●, storage modulus at $\phi_{\text{cement}}=0.46$; ■, loss modulus at $\phi_{\text{cement}}=0.46$; ○, storage modulus at $\phi_{\text{cement}}=0.49$; □, loss modulus at $\phi_{\text{cement}}=0.49$.

At shear rates less than 0.3 s^{-1} , a Newtonian plateau is observed. In this region, the local break-up rate of the microstructure by the shear deformation is comparable to the microstructural growth or recovery rate due to flocculation, so that the overall resistance to flow is constant. In the intermediate shear rate region (0.3 to $\sim 2 \text{ s}^{-1}$), the rate at which the microstructure is destroyed is greater than the rate of growth of the microstructure, leading to a significant decrease in the viscosity and a continuous decrease in the flocculated domain size is also expected. Such flow behavior is commonly seen in polymer-stabilized suspensions [29]. At shear rates greater than 3 s^{-1} , the shear stress increases with increasing shear rate, leading to a slower reduction in the viscosity with increasing shear rate. The decrease in viscosity in this region is attributed to a further reduction in the flocculated domain size.

To characterize the flocculated microstructure prior to plastic yielding, low-amplitude oscillatory shear measurements were conducted. The storage modulus (G'), which characterizes the elastic (reversible) storage of energy, and the loss modulus (G''), which characterizes the dissipation of energy, were measured as a function of the frequency of the periodic deformation. As the frequency increases, the structure is less able to dissipate the energy and the storage modulus becomes independent of frequency, responding like an elastic solid. The storage modulus measured at such high frequency is related to the strength of flocculation, especially when strong interparticle forces, such as van der Waals or electrostatic forces, are present in the suspension [30]. As shown in Fig. 3(b), the storage modulus increases with frequency, approaching a constant value of the modulus at higher frequencies. In contrast, the loss modulus decreases over all frequencies. The storage modulus is always greater than the loss modulus, regardless of the particle concentration. In addition, the storage modulus is greater for the suspension with the larger particle concentration. These trends show that the cement suspensions behave as solid-like viscoelastic materials, suggesting the presence of a strongly flocculated microstructure in which the particles are interconnected. It is the break-up of this microstructure that leads to the decrease in viscosity noted in the intermediate shear rate region.

3.3.1. Steady-shear properties of cement suspensions containing MFS

The effect of MFS on the steady-shear viscosity of cement suspensions is shown in Fig. 4. In this figure, the low-shear (0.06 s^{-1}) and high-shear (23.3 s^{-1}) viscosities are shown as a function of MFS concentration for particle concentrations ranging from 0.46 to 0.56.

At a particle volume fraction of 0.46, a slight decrease in the low-shear viscosity is noted upon the addition of 0.17% MFS, while no significant change in the high shear viscosity is observed. At a particle concentration of 0.49, a small reduction in the viscosity at both shear rates is observed upon the addition of MFS at 0.17%. The larger MFS concentrations used at the higher particle concentrations of 0.51 and 0.53 led to a greater than one order of magnitude decrease in the low-

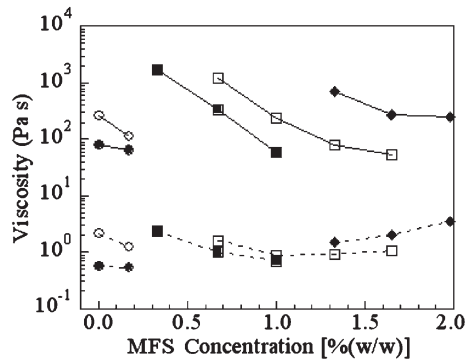


Fig. 4. Effect of MFS concentration on the steady shear viscosity measured at a shear rate of 0.06 s^{-1} (—) and a shear rate of 23.2 s^{-1} (---); \bullet , $\phi_{\text{cement}} = 0.46$, \circ , $\phi_{\text{cement}} = 0.49$, \blacksquare , $\phi_{\text{cement}} = 0.51$, \square , $\phi_{\text{cement}} = 0.53$, \blacklozenge , $\phi_{\text{cement}} = 0.56$.

shear rate viscosities. At the particle concentration of 0.53, the low-shear viscosity becomes relatively constant at MFS concentrations of 1.33% and greater, and the high-shear viscosity becomes relatively constant at MFS concentrations of 1.0% and greater. Finally, at a particle concentration of 0.56, a smaller change in low-shear viscosity is observed while the high-shear viscosity increases with increasing MFS concentration.

The suspension viscosities correlate well with the changes in the particle zeta potentials. As shown earlier, the zeta potential decreases up to a MFS concentration of 1.0%, and then is relatively constant for larger MFS concentrations. With consequently little change in the interparticle forces and hence the aggregate domain size at the larger MFS concentrations, it is not unexpected that the viscosities become relatively constant. The increase in high-shear viscosity for a particle concentration of 0.56 is likely due to depletion flocculation [30], which will be discussed later.

3.3.2. LAOS properties of cement suspensions containing MFS

As shown earlier, increasing the cement particle concentration in the absence of MFS leads to an increase in the storage modulus. It is of interest is how the addition of MFS to the suspensions modulates the increase in the moduli.

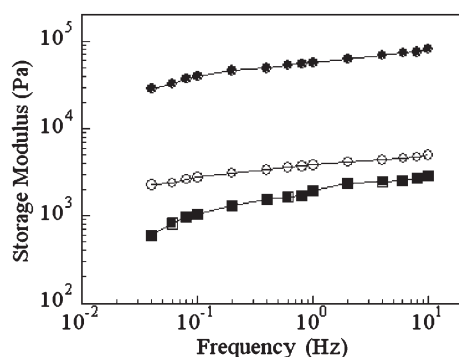


Fig. 5. Effect of MFS concentration on the low-amplitude oscillatory shear flow properties of cement suspensions at $\phi_{\text{cement}} = 0.51$: \bullet , MFS 0.33% (w/w), \circ , MFS 0.67% (w/w), \blacksquare , MFS 1.00% (w/w).

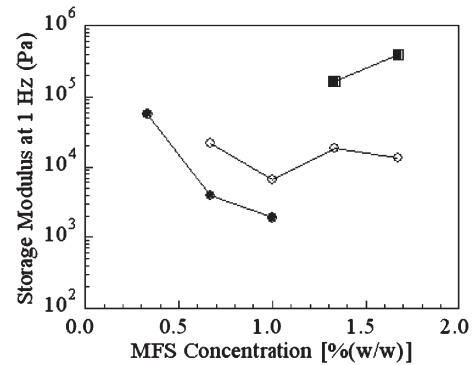


Fig. 6. Effect of MFS concentration on storage modulus of cement suspensions at various particle concentrations: \bullet , $\phi_{\text{cement}} = 0.51$, \circ , $\phi_{\text{cement}} = 0.53$, \blacksquare , $\phi_{\text{cement}} = 0.56$.

Shown in Fig. 5 are the LAOS results of cement suspensions stabilized by MFS at a particle concentration of 0.51. Irrespective of the MFS concentration, the storage moduli increase with frequency and the rate of increase decreases at higher frequencies. At each frequency, the storage moduli decrease with increasing MFS concentration. As observed in Fig. 2, the zeta potential becomes more negative with increasing MFS concentration. This leads to an increase in the electrostatic repulsion between the particles, in turn enhancing the stability of the suspensions and decreasing the storage moduli.

The effect of MFS concentration on the storage moduli at a frequency of 1 Hz is shown in Fig. 6 for particle concentrations of 0.51, 0.53, and 0.56. Similar to the viscosity results, the storage modulus does not always decrease with increasing MFS concentration. At a particle concentration of 0.51, increasing the MFS concentration leads to a continuous decrease in the storage modulus. At a particle concentration of 0.53, the modulus does not decrease monotonically with increasing MFS concentration, however. Instead, the modulus displays a minimum at a MFS concentration of 1.0% and is approximately the same at MFS concentrations of 1.33% and 1.67%. At a particle concentration of 0.56, the storage modulus increases upon increasing the MFS concentration from 1.33% to 1.67%. Recall that at this particle concentration the high-shear viscosity also increased with increasing MFS concentration. These increases in the viscosity and shear modulus imply that additional flocculation develops in spite of the electrostatic dispersion of the flocculated particles due to the absorbed MFS. It is likely that this additional flocculation results from particle attraction induced by the non-adsorbed MFS chains (i.e., depletion flocculation), since the concentration of non-adsorbed MFS chains increases at larger MFS concentrations (Fig. 1).

The moduli were also measured as a function of time at a frequency of 1 Hz. This measurement provides information about how rapidly the flocculated structure forms in the suspensions following the breakdown of any existing structure by the pre-shear [31]. In general, the rate of increase in the storage modulus becomes greater after 30 min, irrespective of

the MFS concentration. The dependence of the storage modulus on time t can be expressed using the following:

$$\text{For } t \leq 30 \text{ min: } G'(t) = G_0' + \alpha t$$

$$\text{For } t > 30 \text{ min: } G'(t) = G_1' + \beta t \quad (2)$$

where G_0' is the storage modulus at 0 min, G_1' is the storage modulus at 30 min, and α and β are the growth rates (kPa/min).

The values of α and β as a function of MFS concentration are given in Table 1 for particle concentrations of 0.51 and 0.53. At a particle concentration of 0.51, increasing the MFS concentration to 1.0% markedly reduces the rate of growth of the modulus. At a particle concentration of 0.53, increasing the MFS concentration up to 1.0% also decreases the rate of growth of the storage modulus. Further increases in the MFS concentration above 1.0% tend to increase the growth rates.

3.3.3. Significance of the optimal MFS concentration

The data presented above emphasize the importance of determining the optimal MFS dosage to achieve the desired fluidity and cohesiveness in a cement suspension, balancing electrostatic dispersion with depletion flocculation. To determine this dosage, it is necessary to determine how the addition of the polyelectrolyte affects both the steady-shear ('fluidity') and LAOS ('cohesiveness') properties of the suspension.

While there are similarities between the zeta potential, steady-shear, and LAOS data, there are also contrasts that are interesting to note. For example, adding 0.33% MFS to the cement suspensions increased the dispersion of the flocculated particles, as illustrated by the reductions in the viscosity and storage modulus. However, the *magnitude* of the zeta potential (not the sign) did not significantly change upon adding this concentration of MFS. Consequently, based on a simple Derjaguin–Landau–Verwey–Overbeek (DLVO) analysis of colloidal particle interactions we would not expect a change in the electrostatic repulsion between the particles and likewise in the resulting dispersion of the particles. It is important to remember that the cement surfaces have both positively charged interstitial phases and negatively charged silicate phases. In the absence of MFS, the oppositely charged phases are electrostatically attracted. As noted earlier, MFS adsorbs preferentially on the interstitial phases. At the MFS concentration of 0.33%, the MFS likely neutralizes the interstitial phases and the measured

zeta potential of -10 mV is attributed solely to the silicate phases. While the magnitude of the zeta potential is similar to that measured in the absence of MFS, oppositely charged phases on the particle surfaces no longer exist and the primary electrostatic interaction is altered from attraction to repulsion. This leads to the observed increase in the dispersion of the particles.

Increasing the MFS concentration leads to a decrease in the viscosity and storage modulus for MFS concentrations up to that corresponding to the zeta potential plateau (1.0%), where a minimum is observed in both the viscosity and modulus. In this region, the increase in the amount of MFS adsorbed enhances the electrostatic repulsion between the particles.

While MFS concentrations greater than 1.0% did not give rise to any significant change in the zeta potential, the high-shear viscosity, the storage modulus, and the moduli growth rates increased with increasing MFS concentration. As stated earlier, this is likely due to the additional particle attraction induced by the presence of non-adsorbing MFS chains in the suspension medium. This depletion flocculation is most evident at the largest particle concentration, for which the interparticle spacing is the smallest.

Finally, note that an increase in the storage modulus is still observed even at the 'optimal' MFS dosage of 1.0%, accounting for the fast fluidity loss of cement suspensions dispersed by a superplasticizer like MFS. This indicates that strong interparticle forces induce re-flocculation between the cement particles, which were initially well dispersed by MFS. This is attributed to the increase in the ionic strength of the suspending medium, which compresses the adsorbed polyelectrolyte layers and weakens the electrostatic repulsion [32], allowing van der Waals attraction to dominate the interparticle interactions. To maintain particle dispersion and suspension fluidity, it is necessary to introduce an additional stabilization method that is insensitive to solution ionic strength, such as a nonionic polymer. This is the focus of a subsequent article [33].

4. Conclusions

The adsorption of a strong polyelectrolyte such as melamine formaldehyde sulfonate (MFS) inverts the sign of the surface potential on cement particles from positive to negative, with the magnitude of the negative potential increasing and then becoming constant with increasing MFS concentration. This sign inversion in the zeta potential causes the electrostatically flocculated cement particles to be electrostatically dispersed. This is shown by the reductions in the low-shear viscosity and the storage modulus upon the addition of MFS. At the MFS concentration at which the zeta potential becomes constant, the high-shear viscosity and the storage modulus display a minimum. Further increases in MFS concentration lead to increases in the high-shear viscosity and storage modulus, indicative of depletion flocculation caused by excess MFS in solution. These results illustrate the importance of determining the optimal concentration of a superplasticizer such as MFS to achieve both fluidity and cohesiveness in a cement suspension.

Table 1
Effect of MFS concentration on storage moduli growth rates quantified with α and β

Cement particle concentration (ϕ_{cement})	$W_{\text{MFS}}/W_{\text{cement}}$ (%)	α (kPa/min)	β (kPa/min)
0.51	0.33	2.9	19
	0.67	0.3	10
	1.00	0.3	4.2
0.53	0.67	1.6	12
	1.00	0.6	3.9
	1.33	0.8	4.6
	1.67	1.2	8.7

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