Optimization of superplasticizer dosage for cementitious suspension involved in high shear applications

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The dosage of superplasticizer (SP) plays a vital role in influencing the behaviour of fresh concrete through cementitious paste. For optimizing the SP dosage, generally empirical tests like mini-slump and Marsh cone are adopted. However, they do not capture the requirement of suitable SP dosage for processes involving high shear energy like pumping. Recent studies have shown that SP, especially polycarboxylate ether/esters (PCE)-based, influences the shear thickening behaviour of cement-based pastes. The addition of PCE at higher dosage, decreases the apparent viscosity by de-flocculation of cement paste. However, at increased shear forces, the reaggregation results in early onset of shear thickening and also increases its intensity, thus affecting the pumping process. On the other hand, the commercially available, site-specific PCE and the prescriptive SP dosages complicate the problem. The above problem necessitates the need to understand the mechanism behind the action of PCE on shear thickening of cement pastes experiencing high shear energy process. In this regard, it is rational to optimize the SP dosage based on shear rates (corresponding to applications) through rheological studies rather than empirical tests.

Keywords: Cementitious suspension, high shear energy, rheological studies, shear thickening, superplasticizer optimization.

ESTIMATION of pumping pressure is typically based on design charts. However, the traditional design charts have their own limitations, due to the increased use of chemical admixtures that can produce more flowable concrete mixtures. Continuous efforts over a century have improved the guidelines to design pumpable concrete. These advances are supported largely by trial and error approaches from the field. Likewise, based on experimental observations, design charts were used for predicting pumping pressure[1–3]. These design charts consider numerous parameters to predict concrete pumping pressure, among which either the spread or slump is considered to be the origin of the chart. In the past decade, usage of these charts with spread or slump was done successfully. However, the use of highly flowable concretes such as self-compacting concrete (SCC) in construction, necessitates modification in pressure prediction[4]. Pumping pressure required for flowable mixtures that have higher spread or slump values should be low according to the design charts. Instead, pumping of flowable mixtures possibly may require relatively higher pressure than conventional vibrated concrete (CVC), as observed in practice[5,6]. It is well known that the slump can be varied by adjusting water to binder (w/b) ratio or paste volume or by modifying gradation of aggregates. The above variations produce a simultaneous change in both yield stress and viscosity, hence justifying the usage of slump or spread as a good indicator for pumping. Recent advancements in chemical admixtures such as superplasticizers (SPs) and viscosity modifiers could fine-tune either yield stress or viscosity separately, raising the need for optimizing both parameters during the process of pumping. Moreover, SPs have become an integral part of modern concrete; especially, in high shear processes like pumping.

Methodology for optimizing superplasticizer dosage: needs a relook?

In most of the studies, optimization of SP dosage is carried out in the respective cement paste rather than on concrete. This is because the action of SPs on concrete is on the interface of cement particle and water. Further, concrete test demands materials, energy, time and space[7]. Moreover, the paste phase in concrete controls the flowability and cohesion of concrete[8]. Consequently, the concrete flowability can be studied by examining effect of SPs on paste. Some convenient and simple tests to study the effect of SPs on cement based suspensions are the Marsh cone test, flow spread and mini-slump test[8–12]. The Marsh cone test and mini-slump test can be used as an indication to identify the flow time and yield stress of cement paste respectively, with respect to different SP dosages[13,14]. Viscosity of the paste can be indirectly related to flow time obtained from the Marsh cone. Higher the flow time, higher is the viscosity of the cement paste.

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Percentage increase in SP dosage decreases the flow time of cement paste. There is a break point beyond which there will not be any significant reduction in flow time. This corresponds to saturated SP dosage based on the Marsh cone test. Objectively, this can be determined by flow time curve obtained for paste at different SP dosage[15]. Aïtcin[16] proposed a method for determining the optimum dosage of SP using the Marsh cone. In this method, for a given *w*/*c* ratio with different dosages of SP, the flow time has to be measured at 5 and 60 minutes. The dosage at which the two curves intersect corresponds to the optimized dosage. Gomes *et al.*[15] proposed a criterion for the optimization of SP dosage based on an experimental study. The dosage at which the log flow time versus SP dosage curve exhibits an internal angle of 140° ± 10° was identified as the optimized dosage. There are some problems in using these criteria for optimization of SP dosage. Sometimes, the flow-time curve does not exhibit an internal angle of 140° ± 10° at any point, and the 5th and 60th minute curves may not intersect at all. Further, an analytical method was developed to relate flow time with viscosity of cement paste. However, it was applicable only to cement paste with flow times higher than 15 sec and without yield stress[7,11]. Deformation of cement paste can be estimated by mini-slump test; the effect of SP dosage on yield stress can also be better understood using mini-slump test[11,17,18]. Although the basic principle followed is lower the yield stress of the paste, higher is the spread and vice versa, Ferraris *et al.*[19] found a weak correlation between mini-slump value and yield stress. Moreover, the empirical experiments could identify saturated and optimum SP dosages based on certain conditions/applications; their validity is limited for other conditions. Especially, the optimum dosage obtained cannot be used for obtaining predictive behaviour of a broad range of cement and SP combinations. Since the mini-slump test is scaled-down (paste) test[20] and is performed at low shear rates[21,22], the requirement of SP dosage will be higher, leading to possible segregation or retardation in concrete. This could be attributed to the particles in the suspension which are highly flocculated at low shear rates, needing higher SP dosage in order to disperse them thoroughly. On the other hand, mixing, spraying and pumping involve high shear rates (1–100 s^{-1}). At high shear rates, the particles in the suspension will be in a dispersed state requiring lesser amount of SP dosage to disperse the particles completely. Therefore, further increase in SP dosage results in increased shear thickening intensity at higher shear rates due to reaggregation of the particles in the suspension. This scenario can be captured precisely using rheological studies alone. Before understanding the suitable testing methodology for optimization of SP, it is desirable to understand the science behind the inter-particle interactions, interactions of cement with SP, and shear thickening phenomenon with respect to shear rate.

Inter-particle forces and their influence on state of cementitious suspension

SP affects the rheology of cement-based suspensions. It is widely accepted that yield stress of the suspension is an important rheological parameter that can be altered by SPs. Recent studies have shown that the SP affects apparent viscosity of the suspension as well[23,24]. Substantial changes brought about by SPs in the rheological behaviour of cement-based suspensions are due to the modification of inter-particle forces[25]. Stability of cement-based suspension is due to the balance between attractive van der Waals forces and electrostatic forces. In water, cement surfaces are charged due to the dissociation of surface groups or specific ion adsorption. Charged surface results in the distribution of ions at the interface that can be well described by a double-layer model. This can be distinguished by a stern zone and a diffuse zone. The stern zone consists of counter-ions unaffected by Brownian motion immobilized by the particle surface. The diffuse zone consists of mobile ions which have the same charge as that of the particle surface. Distribution and concentration of ions are higher at the surface and decrease in the bulk solution (diffuse zone). Increase in distance from the particle surface results in decrease in the concentration of ions in the bulk solution, thus decreasing electrostatic forces. Thickness of the diffuse zone is given by Debye length or decay length denoted as k^{-1}, within which the repulsive potential is significant. According to the continuum theory, electrical potential decays exponentially with respect to distance as shown in eq. (1).

$$\psi_{\mathrm{ES}} = \psi_0 \mathrm{e}^{-\mathrm{kx}}, \tag{1}$$

where ψ_0 is the surface potential.

Debye length or decay length is given in eq. (2).

$$k^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 k_{\mathrm{B}} T}{e^2 \sum_i c_i Z_i^2}}, \tag{2}$$

where ε is the relative dielectric constant of water, ε_0 the permittivity of vacuum, k_{B} the Boltzmann constant, T the absolute temperature, e the charge of an electron and c is the bulk concentration of the ith electrolyte of valence z.

Overlap of double layer takes place as two identical charges approach each other. This results in excess ionic concentration between the two approaching surfaces that enhances the osmotic pressure, consequently diluting the ions between the surfaces by drawing water from the bulk. Increase in ionic concentration in bulk results in effective screening of surface charges, thereby decreasing the range of electrostatic repulsion (i.e. Debye length decreases). This is the case with cement-based suspensions, in which ionic concentration of bulk solution is of the order of 100–200 mM (ref. 26). Effective increase in ionic concentration of bulk solution in cement-based suspension results in reduced effectiveness of repulsive potential to a very short distance, consequently increasing the attractive potential. In addition, ionic concentration of a cement-based suspension cannot be approximated to fixed values due to its inherent nature, where hydration of cement-based suspension results in additional attractive forces by ion correlation. With respect to increase in time, attractive forces between negatively charged C–S–H particles increases due to the presence of divalent calcium ions[27,28]. Total potential energy shows maxima, and minima, since van der Waals attraction and electrostatic repulsion are a function of separation distance between the particles. At zero separation distance, the attractive van der Waals forces reach infinity; nevertheless, electrostatic repulsion remains finite according to eqs (3) and (4) below. The total interaction energy prevailing under this condition is called primary minimum.

$$F_{\mathrm{vd}W} \cong -A\left(\frac{\overline{a}}{12h^2}\right), \tag{3}$$

where F_{vdw} is the van der Waals force, A the Hamaker constant, $\overline{a}$ the harmonic average radius and h is the distance between particles.

$$F_{\mathrm{ES}} \cong -2\pi\varepsilon\varepsilon_0\overline{a}\psi_{\mathrm{ES}}^2\frac{k\mathrm{e}^{-kh}}{(1+\mathrm{e}^{-kh})}, \tag{4}$$

where F_{ES} is the electrostatic repulsive force, ε the relative dielectric constant of water, ε_0 the permittivity of vacuum, $\overline{a}$ the harmonic average radius and ψ_{ES} is the zeta potential.

At short separation distance, attractive forces dominate resulting in flocculation. As the separation distance increases, the balance between attractive force and repulsive force varies resulting in different scenarios (flocculation and de-flocculation). This depends upon ionic strength of the suspension and electrostatic potential. At low ionic strength, the Debye length increases thus resulting in significant repulsive force, as separation distance between particles decreases further, resulting in enhanced repulsive force and an energy barrier. Stability of the suspension increases with increase in magnitude of this energy barrier. Under certain circumstances, the particles in the suspension overcome this energy barrier resulting in a primary minimum, where the particles stick together. As the ionic strength of the suspension increases, Debye length decreases. Thus, the magnitude of repulsive force decreases significantly as a consequence, the suspension flocculates. At even higher ionic strength, inter-particle force will be always attractive resulting again in a flocculated state of the suspension.

Effect of ionic strength and superplasticizers on the behaviour of cement-based suspensions with respect to applied shear rate

In case of cement based suspensions, due to their high ionic strength, they will remain almost flocculated. Thus, for cement based suspensions, SPs plays a vital role in de-flocculating the particles in the suspension by different mechanisms. Therefore, SPs are synthesized in such a way that on adsorption they provide net repulsive forces.

As soon as shear forces start acting on the particles, the cement-based suspensions begin to flow. The magnitude of shear force increases, surpassing attractive forces between particles, resulting in a dispersed suspension. Extent of dispersion depends upon the relative prevalence of shear forces with respect to attractive forces. Initially, due to high attractive forces cement particles flocculate, thus resulting in localized higher effective volume fraction compared to sum of the volume of individual particles. Flocculates include the volume of water between the particles, consequently showing higher viscosity and yield stress. The shear forces increase resulting in deflocculation of suspension thereby reducing the effective volume fraction. Consequently, viscosity of the suspension decreases. Further, increase in shear forces result in reaggregation of the particles in the suspension due to a phenomenon called hydro-clustering[29,30]. This is due to excessive viscous dissipation of cement particles in the suspension as the shear force increases, in turn resulting in dominance of net attractive forces over other forces. This leads to increase in viscosity of the suspension, thus displaying shear thickening behaviour[31].

On the other hand, cement-based suspensions with SPs result in net repulsive forces, thus dispersing the suspension and increasing the initial state of de-flocculation. This reduces localized initial effective volume fraction, thus decreasing yield stress and viscosity. Even though with respect to increase in SP dosage yield stress and viscosity of the suspension decrease, intensity of shear thickening increases and onset of shear thickening behaviour shifts to lower shear rates. Further, increase in shear rate displays substantial increase in viscosity of cement-based suspensions, thus displaying a strong shear thickening behaviour. Such behaviour decreases the efficiency of the mixing and pumping process, where applied shear force is higher[32]. Although shear thickening behaviour was observed for suspension with poly carboxylic-based (PCE) SPs, similar behaviour was not observed with poly-naphthalene sulphonate (PNS) and poly-melamine sulphonate (PMS)[33]. This shows that behaviour of suspension with PCE is highly related to the mechanism by which PCE-based SPs act on the cement-based suspension.

Mechanism of superplasticizers and their relevance to shear thickening behaviour

Invariably, with respect to increase in shear forces, shear thickening behaviour can be observed in any suspension[30]. Several studies have shown that a PCE-based cement suspension undergoes relatively higher shear thickening and onset of shear thickening at lower shear rates[33–35]. This necessitates to understand the fundamental manner in which the PCE-based SPs act on cement-based suspensions. In general, repulsive forces in cement-based suspensions with SPs arises due to electrostatic repulsion and steric repulsion. For a PCE-based SP, the latter dominates, while for a PNS and PMS-based SP the former dominates.

PCE-based SPs consists of carboxylic groups in their main chain, grafted with polyethylene oxide (PEO) side chains. PCE molecules get ionized once they come in contact with the highly alkaline cement suspension. Ionized PCE molecules constitute deprotonated carboxylic groups that get adsorbed on the surface of the cement particles by electrostatic interaction, thereby hindering flocculation of cement particles. Although flocculation of cement particles is hindered by electrostatic repulsion, presence of side chains extends the range of repulsive forces to several hundred nanometres, which is of only few nanometres in case of cement suspension with PNS- and PMS-based SPs[25]. Therefore, increase in inter-particle space is the highest for the cement-based suspension with PCE SPs, thus reducing the viscosity of the suspension more effectively. Nonetheless, as the shear rate increases viscous dissipation between particles overcomes repulsive forces, thus resulting in hydro-clustering. PCE SPs that are strongly adsorbed to the surface of cement particles remain intact thereby increasing localized effective volume fraction, thus resulting in higher shear thickening. Further, gradual shift in onset of shear thickening to low shear rate for a suspension with PCE SP could be due to the highly dispersed initial state in which the applied shear forces are not required to de-flocculate the suspension. Instead, the highly deflocculated state increases the viscous dissipation, thereby reducing the shear energy required for the formation of hydro-clusters, resulting in early onset of shear thickening.

Although this phenomenon could be identified as the major reason for shear thickening of a suspension with PCE-based SPs, no supporting experimental evidences could be found. Above all, versatility in designing PCE-based SPs for a specific application enhances problems related to applications that involves increased shear rate. In order to understand this in better way, it is necessary to evaluate the influence of PCE architecture on cement-based suspensions at higher shear rates. Therefore, in most of the cases where the cement-based suspension undergoes higher shear forces require SP dosage lower than those obtained by empirical tests such as the Marsh cone and mini-slump. The optimum range of SP dosage obtained using the empirical test is decided based on flow initiation due to gravity (in case of mini-slump) and flow time obtained (in case of the Marsh cone) for low yield stress fluids. In the above tests, shear forces experienced by the suspension are very low. Hence the state of the suspension is controlled only by the van der Waals attractive forces, resulting in higher optimized dosage than required. This could be attributed to the inadequate shear forces to create additional repulsion that could increase the need of SP for dispersion. On the other hand, at higher shear rates, shear forces contribute towards de-flocculation of the suspension in addition to the electrostatic repulsion and steric repulsion, thus resulting in relatively lower range of SP dosage. Therefore, if the optimum range of SP dosage obtained based on empirical tests (the Marsh cone and mini-slump) were used, due to higher SP dosage, the onset of shear thickening shifts to low shear rate. Further, intensity of shear thickening increases due to increase in localized effective volume fraction. In order to validate the proposed hypothesis, an experimental study was performed.

Experimental study

An experimental study was carried out in order to understand the variation in optimized SP dosage determined by mini-slump test[36,37] and rheological examination (Figure 1)[38]. Ordinary Portland cement 53 grade (OPC) complying with IS 269 (2015)[39] and a PCE-based SP with a specific gravity of 1.071 (at 25°C) were used. A specific mixing protocol was followed out using a planetary mixer in order to homogenize the mixture (Table 1). The study was carried out according to the protocol given in Figure 1 and Table 1 for the selected combinations (Table 2).

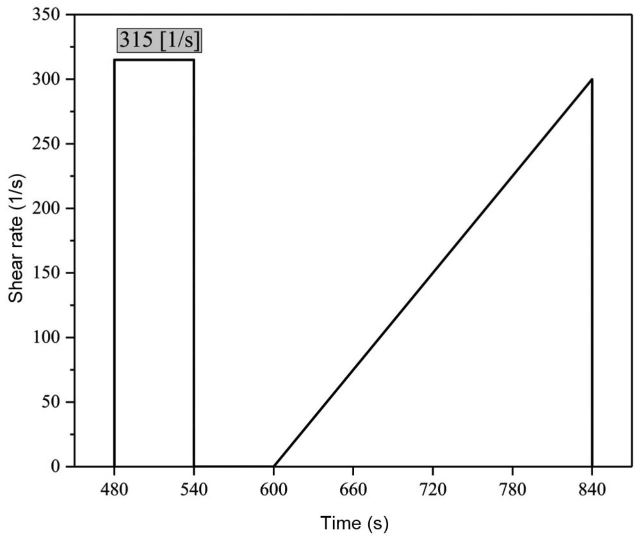

Figure 1. Rheological protocol used in the present study.

Table 1. Stepwise experimental study and description with the corresponding time period

Description	Individual time period (s)	Cumulative time period (s)
Dry mixing	120	120
Adding 80% of water and mixing in a planetary mixer (agitator speed – 107 rpm; attachment speed – 61 rpm)	60	180
Manual homogenization (scrapping the sides and bottom of the bowl)	60	240
Adding 20% of water with prescribed superplasticizer (SP) dosage and mixing (agitator speed – 107 rpm; attachment speed – 61 rpm)	60	300
Manual homogenization (scrapping the sides and bottom of the bowl)	60	360
Mixing (agitator speed – 107 rpm; attachment speed – 61 rpm)	120	480
Rheological study		
Pre-shear at 315 s^{-1}	60	540
Rest	60	600
Linear shear until it reaches the corresponding maximum shear rate (up to 300 s^{-1}; up-curve)	240	840
Mini-slump test		
Pouring suspension in mini-slump apparatus followed by tamping on the top surface of the apparatus to remove any air voids in the suspension	60	Poured at tenth minute after mixing 660
Removing the apparatus and allowing the suspension to flow (due to gravitational effect)	60	720

Table 2. Mini-slump values for different superplasticizer dosage (ordinary Portland cement 53 grade at 0.40 water/binder ratio)

SP dosage (% bwob*)	Mini-slump spread (mm)
0.0	76
0.1	105
0.2	135
0.3	151 (initiation of bleeding)

*By weight of binder (liquid).

Results and analysis

Table 2 shows the results of the mini-slump test. The dosage corresponding to a maximum spread without bleeding was identified as the criterion for fixing the optimum SP dosage. A plot was drawn between mini-slump spread and SP dosage (Figure 2). From Figure 2, it can be observed that the spread increases with increase in SP dosage up to 0.2%, beyond which the paste shows mild bleeding (initiation). Therefore, 0.2% of SP dosage was considered as optimum for the suspension according to the mini-slump spread.

Table 3 shows the results of the rheological examination. SP dosage beyond a certain limit may result in shear thickening (increase in apparent viscosity) of the cementitious suspension. The shear thickening of the suspension leads to blockage of concrete inside the pipe. Therefore, it is important to identify onset of shear thickening (point at which the apparent viscosity reaches the minimum value beyond which it starts increasing), and reduce the intensity of shear thickening as well. In the present study, intensity of shear thickening was calculated as follows.

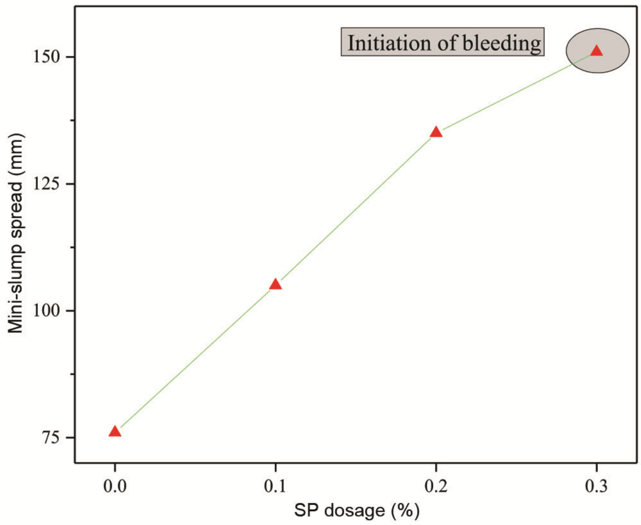

Figure 2. Mini-slump spread values of ordinary Portland cement 53 grade at 0.40 water/binder ratio.

$$\text{Intensity of shear thickening (\%)} = \frac{\eta_{\max} - \eta_{\min}}{\eta_{\min}} \times 100, \tag{5}$$

where $\eta_{\max}$ is the apparent viscosity of the suspension at the shear rate of interest, and $\eta_{\min}$ is the minimum apparent viscosity of the suspension.

From Figure 3 *a*, it is clear that for a given shear rate, the onset of shear thickening decreases with increase in SP dosage. Based on eq. (5), the intensity of shear thickening was calculated at different shear rates (100, 200 and 300 s^{-1}). From Figure 3 *b*, it can be observed

Table 3. Optimization dosages and possible working shear rates

SP dosage optimization method	Optimum SP dosage (%)	Suitability of optimum SP dosages for processes with shear rates (s^{-1})
Mini-slump test	0.2	All ranges (usually less than 1)
Rheological test	0.3	<32
	0.2	<62
	0.1	<215

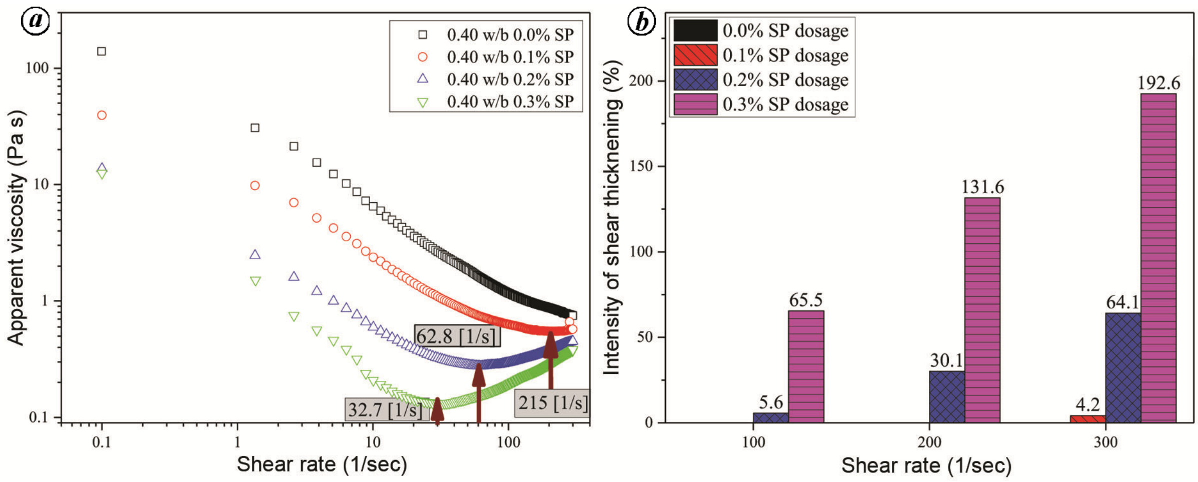

Figure 3. ***a***, Apparent viscosity of suspension (0.40 w/b ratio). ***b***, Shear thickening intensity at different shear rates.

that, for 100 s^{-1} shear rate, the intensity of shear thickening remains zero (since onset is observed at 215 s^{-1}) for 0.0% and 0.1% SP dosage. However, when the dosage of SP is increased to 0.2% the intensity of shear thickening is 5.6% (shear thickening onset at 62.8 s^{-1}) and at 0.3% SP dosage the intensity of shear thickening is 65.5% (shear thickening onset at 32.7 s^{-1}). At 200 s^{-1}, similar trend is observed with higher intensities for 0.2% and 0.3% SP dosage. At 300 s^{-1}, even for 0.1% SP dosage, shear thickening intensity is evident. Tables 2 and 3 show the results of the empirical (mini-slump test) and rheological studies.

From Table 3, it is clear that for different SP dosages, the working range of shear rates are different. For example, for a process involving shear rates more than 62 s^{-1}, it is not desirable to use 0.2% SP dosage, due to possible shear thickening. From this observation, it is evident that optimization using empirical test may not be suitable for all practical applications. Hence, it is rational to use rheological studies for the targeted applications with specific shear rates. Based on such studies, the SP dosage corresponding to a shear rate beyond which the cementitious suspension exhibits shear thickening behaviour is identified as the criterion for fixing the optimum dosage of SP.

Conclusion

Processing concrete at high shear forces result in its behavioural change from shear thinning to shear thickening. Shear thickening behaviour results in increased apparent viscosity. Even though addition of SP decreases apparent viscosity by de-flocculation, at increased shear forces reaggregation occurs earlier, especially for PCE-based SPs. This results in a gradual shift and increase in apparent viscosity to low shear forces, in turn resulting in the onset of shear thickening at low shear rates and increasing the intensity of shear thickening. On the other hand, optimized dosages of SP obtained from simple empirical tests (the Marsh cone and mini-slump) are for specific conditions and usually such dosages are higher than required, resulting in possible segregation and retardation. Additionally, versatility in designing PCE-based SPs for a specific application drastically changes shear thickening behaviour. Therefore, there is a need for understanding the mechanism by which SPs act at high shear forces. Further, for processes with high shear forces such as pumping and mixing, optimization of SPs dosage must be carried out based on rheological studies rather than adopting the optimized dosage obtained from empirical tests.

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