Influence of high mixing intensity on rheology, hydration and microstructure of fresh state cement paste

Dongyeop Han

Engineering Research Institute, Seoul National University, Seoul, South Korea

Raissa Douglas Ferron (**corresponding author:** rferron@mail.utexas.edu)

Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin, Texas, U.S.

Abstract

From both the fundamental and applied points of view, there is a growing interest in characterizing the rheological properties of concentrated suspensions, such as cement paste. When a cement paste is sheared, its intrinsic network structure will respond to the shear induced stresses. The influence of mixing intensity on the rheological properties of fresh state cement paste is studied. The results showed that contrary to what is popularly believed, when subjected to a high mixing intensity the rheological properties of cement paste can increase once a certain threshold mixing intensity is achieved. This increase in rheological properties was associated with changes in the chemical nature and physical nature of the cement pastes.

Keywords: mixing, rheology, microstructure, hydration, cement paste

1. Introduction

Due to the development of highly flowable concrete and increased use of chemical admixtures, renewed interest in predicting and understanding the rheological behavior of concrete has occurred. In its fresh state, concrete can be considered a suspension consisting of sand and gravel particles suspended in a paste matrix [1,2]; however, even the paste matrix is heterogeneous, comprised of cement particles and hydrates in a pore solution. As a result, the macroscopic flow behavior and rheological properties of

concrete are highly impacted by the inherent structure of the paste matrix. The factors affecting the rheological properties of pastes can be broadly separated into two categories: non-hydrodynamic factors and hydrodynamic factors. Non-hydrodynamic factors include interactions affects arising from colloidal forces and in the case of cementitious materials, hydration effects. Hydrodynamic effects are due to interactions resulting from non-colloidal origins between the suspending medium and the particles [3–5]. Particulate suspensions, such as cement paste, are complex rheological materials whose material properties are dependent upon its processing, especially the mixing process. Understanding the effect of the mixing forces on cement paste is essential to understanding the rheological properties of cement paste [6,7]. Yet the majority of the research on rheological behavior of cement paste has focused on the effect of mixture ingredients and far fewer have focused on the process used to prepare the cement pastes for evaluation. Studying the cement paste phase to gain insight into concrete behavior is common practice; as such it is important to consider how the behavior cement paste is affected by the mixing process.

In 2011, a new standard, ASTM C1738, was introduced for preparation of cement pastes. This standard uses a high shear mixer for preparation of cement pastes and was motivated from the work of Helmuth et al. [8] who suggested that high mixing intensity (≥ 4000 rpm) is needed to mimic the mixing energy of cement paste within concrete. Helmuth et al. [8] showed that the correlations between stiffening behavior of concrete prepared in the field and that of cement paste prepared in the lab were dependent on the mixing energy used to prepare the pastes. Good agreement between the stiffening behavior of concrete and pastes mixed using a high shear mixer was seen when the temperature during the high shear mixing process was controlled. However, the shear rate that is experienced by the paste matrix within concrete will depend on the processing stage (e.g. casting, mixing, etc.), as well as the actual mixture composition. For example, Helmuth et al. [8] estimated the shear rate within the paste matrix for a lean concrete mixture during mixing to be 2000 s^{-1} , whereas, the shear rate for a rich concrete paste during mixing was estimated to be 500 s^{-1} . Similarly, Roussel [9] estimated the shear rate applied to cement paste is approximately 5 times higher than the shear rate applied to concrete in the case of ordinary concrete,

whereas it is only approximately 2.5 times higher than the shear rate applied to concrete in the case of SCC. Both works highlight the important role that mixture composition plays on shear rates generated in the pastes and illustrates that as the lubrication layer around the aggregates increases, shear rates in the paste matrix decreases. This implies that a lower mixing speed is needed when mixing cement paste to replicate the mixing that occurs in a rich concrete or SCC than what would needed to replicate the mixing of a lean concrete. Regardless of the composition of the mixture, it is often assumed that as more power is inputted during mixing that a weakening of the internal structure and a reduction in the rheological properties of the mixture will occur. Yield stress is inversely related to slump (slump flow), and thus increasing the mixing power of a cement paste should correspond to an increase in the slump (slump flow) behavior of the paste. However surprisingly the opposite behavior has also been reported in cement paste, mortars and concrete. Rupnow [10] observed a decrease in the temporal evolution of plastic viscosity in pastes prepared with a Hobart and high-shear mixer (maximum mixing speed in both were 285 rpm). However, Helmuth [8] reported higher rates of increase in the yield stress of pastes initially mixed with a high-shear mixer than those initially mixed with Hobart mixer. Similarly, Han and Ferron [11] observed a considerable increase in the rheological properties of cement pastes prepared using a high shear mixer versus those prepared using a Hobart mixer.

Further research on the microstructure and rheological properties of fresh state cement paste under high mixing intensity conditions is needed to understand how this affects the fresh state behavior of cement-based materials. The aim of this paper is to examine the influence of high shear mixing on the rheological properties and fresh state microstructure of Portland cement pastes. The fresh state microstructure was assessed with a focused beam reflectance measurement (FBRM) [12–14] device. The results obtained are then discussed on the basis of hydration kinetics and a shear-based agglomeration model, and a mechanism is proposed to explain the effect of high shear mixing on the rheological behavior and microstructural development of the pastes.

2. Experimental plan

2.1. Materials and mixture proportions

All cement pastes mixtures were prepared using deionized water and a cement conforming ASTM C150 Type I and Type II specifications. The chemical composition of the cement is shown in Table 1. Based on the cement mill sheet [15], the Blaine fineness was 401 m²/kg and specific gravity was 3.15. A polycarboxylate-based superplasticizer (herein referred to as “SP”) conforming to ASTM C494 [16] Type A and F was employed in many of the mixtures; the specific gravity of the SP was 1.064 [17]. The dosage of SP was set to 0.2% by mass of the cement; the volume of mixing water was corrected to account for the SP when SP was used. The mixture proportions of the pastes evaluated are provided in Table 2; four different cement pastes with three different solid contents were evaluated. The mixture proportions in Table 2 are expressed for one liter paste; however, for the actual preparation of the cement paste samples, 0.25 L of cement pastes was prepared.

2.2. Sample preparation

The mixing protocol for the cement pastes is shown in Figure 1. A Chandler 3060 high shear mixer was used to prepare the pastes (see Figure 2a for a picture of the mixing blade geometry). As shown in Figure 1, six key steps were conducted to homogenize the pastes. A relatively low mixing speed (500 rpm) was selected for the second step so that differences in the magnitude of the initial mixing intensity and secondary mixing intensity on the rheological behavior of the pastes could be examined. Five different mixing speeds (1000, 2000, 4000, 8000, and 12000 rpm) were selected for Steps 4 and 6. A maximum mixing speed of 12000 rpm was selected since this was the maximum mixing speed specified in the 2011 and 2013 versions of ASTM C1738 [18] (note, the ASTM C1738 procedure has been revised and in 2014 standard the maximum speed is 10,000 rpm). The first four steps should be sufficient to homogenize the pastes, but Step 6 was included to evaluate the influence of additional mixing time on the paste since

additional mixing is often conducted on high performance cementitious materials [19]. During the mixing process, the mixing speeds were maintained at the pre-set speeds with a control unit. The Chandler high shear mixer was equipped with a water bath. This water bath circulated water around the mixing container and allowed for the temperature of the cement paste to be controlled during mixing. The unit was set to maintain a temperature of 15 ± 2.0 °C. This was sufficient to maintain limit the temperature variations in pastes prepared at 1000, 2000, and 4000 rpm and the final temperature of these pastes after mixing (i.e., after Step 6) was 24 ± 2.0 °C. However, even with the water bath system, a 10.0 °C temperature increase was measured between the temperature of the mixing water before Step 1 and the temperature of the paste after Step 6 (data not shown) for the pastes prepared at 8000 and 12000 rpm during preliminary testing. Therefore, to counteract this temperature increase, in addition to setting the water bath unit to 15 ± 2.0 °C, the temperature of the mixing water was chilled to 15 ± 2.0 °C prior to mixing. With these treatments, the temperature of the pastes mixed at 8000 rpm and 12000 rpm after mixing was approximately 24 ± 2.0 °C.

2.3. Experimental methods

2.3.1. Rheology

To evaluate the properties of fresh state cement pastes, flow curve rheological test were conducted using with a commercial rheometer (Anton Paar MCR 301). The rheometer was equipped with a solvent trap to prevent excessive evaporation during the tests and a Peltier setting controlled the temperature of the samples at 23 ± 1 °C. A concentric cylinder geometry was used; inner diameter of cup and outer dimension of bob were 28.9 mm, and 26.6 mm.

Prior to conducting the flow curve test, a 0.1 s^{-1} preconditioning process was applied for 30 seconds (which was enough time to reach a steady state shear stress condition), followed by 30 seconds of resting. In order to obtain the flow curve, the shear rate was stepped-down from 50 s^{-1} to 10 s^{-1} in increments of 10 s^{-1} (see Figure 3). Each shear rate was maintained for 60 seconds since this was determined to be a

sufficient amount of time to achieve a steady-state shear stress for each shear rate. The data was recorded every second and the last 10 data points at a given shear rate were averaged to represent the average resultant shear stress at that shear rate. According to Ferraris et al. [20], the range of typical shear rate experienced by cement paste in concrete during the placing process is 10 or 20 s⁻¹. Since some of the flow curves displayed non-linear behavior, the apparent viscosity at 20 s⁻¹ of shear rate (see equation 1) was used to characterize the mixtures. The apparent viscosity, μ_{app} , was defined as:

$$\mu_{app} = \frac{\tau_{20\text{ s}^{-1}}}{20\text{ s}^{-1}} \quad (1)$$

where $\tau_{20\text{ s}^{-1}}$ is the average resultant shear stress at 20 s⁻¹ of shear rate.

2.3.2. Fresh State Particle Size Measurements

A focused beam reflectance measurement (FBRM) system was used to evaluate the in-situ particle conditions of the cement pastes [17, 26, 31, 35] and to gain insight about the fresh state microstructure of cement paste. The basic FBRM process involves scanning the suspension at 2 m/s with a rotating laser beam and measuring the time duration of the reflected laser from the particles in the scanning path. The time duration of the reflected light coupled with information regarding the scanning velocity of the laser is then used to obtain the chord length of the particles/agglomerates¹. The chord length of the particle is the length from one edge to the opposite edge on the scanning path rather than the diameter of the particles. Information about the number of chord counts per second, as well as the actual length of the chords, is recorded.

Figure 4 presents a schematic of the FBRM set-up. As can be seen in the figure, the FBRM set-up includes a beaker that contains the sample, the FBRM probe, and an impeller. After preparing the paste

¹ In this paper, aggregation and agglomeration will be used interchangeable. Agglomeration is the general process that describes the formation of particles collecting to form a cluster. An agglomerate is a cohesive mass consisting of two or more primary particles.

in the high shear mixer, a portion of the paste was transferred to the FBRM beaker. To minimize the effect of sedimentation on the data, the paste was agitated with the impeller, and the probe was inserted into the sample face to the direction of flow at a downwards angle [12]. Three different agitating speeds (150, 300, and 450 rpm) were used to examine how the agitation speed affected fresh state microstructural behavior and agglomeration strength among the particles. Measurements were recorded every 10 seconds, and each test was performed for 30 minutes. Estimating the shear rates of samples in mixing vessels is not trivial, however using a vane approximation (see Equation 2) [24], an indication of the magnitude of the shear rate applied to the sample in the FBRM container at the different mixing speeds was estimated (see Table 3).

$$\dot{\gamma} = 2R_b R_c \Omega / (R_c^2 - R_b^2) \quad (2)$$

where R_b is the radius of the vane (in this case the radius of the FBRM impeller), R_c is the radius of the cup (in this case the radius of the FBRM sample container), and Ω is the angular velocity of the vane.

From Figure 4, it can be seen that $R_b = 25\text{mm}$ and $R_c = 32.5\text{mm}$.

2.3.3. Calorimetry

In order to determine the heat signature of the pastes, after preparing the cement pastes with the Chandler high shear mixer, 20 g of the cement paste was placed in a 3114/3236 TAM Air Thermal, Thermometric AB Isothermal Calorimeter for 20 hours. For each mixture, at least two replicates were tested. The heat of hydration curves in Figure 14, 15, and 16 are based on the results of a representative sample from each mix, while the data in Tables 4, 5, and 6 are based on the average of the samples.

2.3.4 Flame photometry

Flame photometry was used to gain insight about the pore solution chemistry, particularly the potassium and sodium concentration since they contribute significantly to the ionic strength of the pore solution and

previous work [25] has shown that microstructural rebuilding (i.e. thixotropy) was strongly impacted by these ions [26]. After 045 pastes were prepared (see Section 2.2), a 100 g. sample of fresh state cement paste was put through a Buckner funnel in order to extract the pore solution. A 0.50 μm filter paper was use to extract the pore solution. Extraction was conducted by vacuum filtering using the process described by Hema [27]. During the extraction process, 25 ml of deionized water was poured on top of the cement paste and the obtained pore solution was diluted to 0.2 % (w : w) with deionized water to the detectable range (0 to 199.9 ppm for sodium, and 0 to 9.99 ppm for potassium [28]) of a Cole Parmer Dual Channel Flame Photometer (Model 2655-10).

3. Results and Discussion

3.1. Rheological properties

Figure 5 shows the apparent viscosity values at 20 s^{-1} , and Figure 6 presents the flow curves for the cement paste. The various curves in each sub-plot of Figure 6 correspond to the final mixing speeds that were used to prepare the paste. As expected, the apparent viscosities increased as the solid volume increased. As the solid content increases, particle-to-particle interactions are likely to increase, and the increased interactions among the particles results in an increased resistance to flow [1, 28, 36]. The apparent viscosity values were lower for the 045_SP paste than for the 045 cement paste. This is attributed to the electrosteric hindrance effects from the polycarboxylate-based SP [32,33], and it has been shown that incorporating polycarboxylate--based SP tends to result in weaker agglomerates which can be easily broken down by shear [21,34].

Higher mixing energy has been associated with cement paste with lower viscosities and increased fluidities [6,35–37]. In Figure 5, it was seen that when the sample preparation mixing speed increased from 1000 rpm to 4000 rpm, the apparent viscosity did not increase (it generally decreased or remained the same for all the mixtures). However, when the mixing speed increased above 4000 rpm, various

behaviors were observed. Between 4000–8000 rpm, the apparent viscosity was relatively unchanged for the mixtures without SP; however, a considerable increase in the apparent viscosity values were seen in the pastes containing SP as the sample preparation mixing speed increased from 8000 rpm to 12000 rpm. Hence it appears that mixing speeds within a range of 1000 rpm to 4000 rpm is sufficient to disperse the cement particles and that above a threshold mixing speed increasing the speed no longer results in decreasing the viscosity of the cement paste. Cement pastes are often characterized as being Bingham fluids [30], however it can be seen that when the sample preparation mixing speed increased above a certain threshold a shift towards shear-thinning behavior occurred in some of the cement pastes. For the pastes examined in this research, the threshold speed occurred between 4000 rpm and 8000 rpm for the majority of cement pastes (see Figure 6).

3.2 Microstructural change of cement paste

Figures 7, 8, 9, and 10 display the results of the FBRM experiments and shows how agglomeration evolved over time when samples were prepared using different sample preparation speeds and different FBRM agitation speeds. It can be seen that in all cases, the global behavior of the samples trended towards agglomerate breakup when the agitation speed used during the FBRM experiment increased and as the agitation speed increased generally the chord length of cement pastes decreased. As seen in Figures 7, 8, 9, and 10, at agitation speeds of 150 and 300 rpm, the mean chord length of the cement pastes prepared with a final mixing speed of 12000 rpm was generally greater than cement pastes prepared with a final mixing lower than 8000 rpm. However, as the FBRM agitation speed increased to 450 rpm (see plot c in Figures 7, 8, 9, and 10), the chord length of the cement pastes prepared using a final preparation speed of 12000 rpm was often comparable to those prepared with lower sample preparation mixing speeds. The results illustrate the dynamic nature of agglomerate resilience. Samples prepared with the faster sample preparation speeds contained microstructures with larger agglomerates; this may be due to

stronger interparticle bonds and/or faster rates of agglomeration. Regardless of the mechanism inducing the formation of the agglomerates, it can be seen that these large agglomerates were able to resist breakdown under the lower FBRM agitation speeds of 150 rpm and 300 rpm, but when enough power is applied to the system even those agglomerates can be ruptured.

Inspired by an approach described by Jarvis et al. in which the relationship between particle size and velocity gradient is used to determine a shear-based agglomeration strength [38], the slope of the average chord length-FBRM agitation speed curve (see Figure 11) is used as a measure to estimate the overall strength of the microstructure. The curves shown in Figure 11 represent three theoretical examples of a mixture that was prepared using three different sample preparation speeds (A, B, and C) and evaluated using the FBRM technique (note, the mixture composition and the FBRM testing approach is the same in the three examples). For ease of reading, we will refer to the mixture by the sample preparation speed that was used to prepare it (e.g. mixture “B” is the mixture that is prepared using sample preparation speed B). As the agitation speed increased from “1” to “2”, the average chord sizes of all the mixtures decreased. Mixture “A” had the largest initial average particle chord length of the three samples and its final average chord length was the same as mixture “B”; whereas mixture “C” had a slope that is equivalent to mixture “B”, but the average particle chord length of mixture C was smaller than that of mixture “B”. Since the slope of mixture “B” is the same as mixture “C” the microstructural response of these two mixtures to the agitation is similar, which suggests that the mixtures have equivalent agglomeration strength. However, since the average chord length of mixture “B” is greater than that of mixture “C”, the microstructure of mixture “B” is comprised of larger agglomerates than mixture “C”; thus the overall state of agglomeration is considered to be higher than that of mixture “C”. Mixture “A” initially has agglomerates that are larger than the other two mixtures, however, as the agitation speed increased, the agglomerate size of mixture “A” decreased to an agglomerate size similar to mixture “B”. Thus, the agglomeration strength of mixture “A” was weaker than mixture “B”, and this is manifested by the slope of the curve represented by mixture “A” curve being steeper than that of the curve represented

by mixture “B”. The sign of the slope indicates whether breakdown or agglomeration is occurring, where negative signs represent breakdown/disaggregation has occurred. The absolute magnitude of the slope is used to determine the agglomeration strength, and in the case of a negative slope higher values are associated with lower agglomeration strengths (i.e. weaker systems). Based on this concept, the agglomeration strength of the pastes was calculated by determining the slope of the line passing through the average chord length-FBRM agitation speed plot at 150 rpm and 450 rpm.

Figure 12 shows the agglomeration strength of each cement paste as calculated and expressed in Figure 11. It is readily apparent that the cement paste prepared at higher mixing speeds had weaker agglomeration strength. Furthermore, agglomeration strength decreased as the distance between agglomerates increased, regardless of whether this increased spacing was caused by reducing the number of particles in the system (e.g. compare 042 and 045 mixtures) or via polymeric dispersion (e.g. compare the 045 and 045_SP mixtures). Combining the FBRM chord length results (Figures 7, 8, 9, and 10) and the agglomeration strength results (Figure 12), it is concluded that the cement paste prepared with very high mixing speeds contained larger agglomerates than their counterpart pastes prepared at the lower mixing speeds, however these agglomerates were relatively weak. The results are consistent with work by Ferron [25] that showed that agglomeration strength decreased as agglomerate size increased.

3.3 Changes in the chemical environment of cement paste

The rheological properties of cement paste are influenced by its microstructure [6,21,39,40], thus when a cement paste is prepared at different mixing speeds, changes are likely to occur to its microstructural state. Agglomerates form not only because of hydration but also due to thixotropy and interparticle forces from the colloidal nature of the finest cement particles [41]. The agglomeration of cement particles can be considered as two different types [26]: coagulation and flocculation. Coagulation refers to a relatively strong and irreversible agglomeration between multiple cement particles (such as those that may occur due to hydration or very strong interparticle forces of attraction), while flocculation is considered as a

relatively weak and reversible agglomeration (such as those that may form due to the thixotropic phenomena). The ionic concentration influences the thickness of electrical double layers of the particles [42]. The Debye-Hückel length ($1/\kappa$) equation represents the thickness of the double layer (Equation 2) [26,43]:

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon \epsilon_0 RT}{2F^2 I}} \quad (3)$$

where ϵ_0 is the permittivity of the vacuum, ϵ is the dielectric constant (relative permittivity) of the dispersion medium, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and I is the ionic strength. As the ionic concentration is increased, the thickness of electrical double layers decreases, which can result in increased/stronger agglomeration.

Figure 13 shows an illustration depicting how a high sample preparation mixing intensity may result in increasing agglomeration of cement particles. First, breakdown of cement particles occurs due to the mixing process, thereby increasing the specific surface area in contact with the mixing water. As the specific surface area increases, the ionic concentration of cement paste increases due to an increasing rate of ionic dissolution from the surface of the cement particles [26,44]. This increased ionic concentration reduces the thickness of the diffused layers of the electric double layer on the cement particles, which facilitates agglomeration of cement particles [30, 40, 42]. Thus, it is likely that varying the mixing speed can also result in changing the chemical nature a mixture and that these changes will impact agglomeration kinetics. To investigate this, additional experiments were conducted to examine whether changes in hydration mechanism or concentration of ions in the pore solution occurred when pastes were prepared with different mixing intensities.

The cement pastes were prepared using the protocol shown in Figure 1 and the hydration kinetics of the samples were monitored for 20 hours after initial contact of the cement with the mixing water. Figure 14 shows that as the final sample preparation mixing speed increased, cement hydration was accelerated and the overall heat evolved during this time period increased (see Figure 15); this

phenomenon occurred regardless of whether the mixture contained superplasticizer or not. Further analysis of the heat of hydration curves (see Tables 4, 5, and 6) elucidates that the end of the acceleration period was more sensitive to the applied mixing speed than the end of the induction period. Hydration kinetics prior to the induction period is controlled by dissolution of ions from the cement grains [46], whereas the acceleration period is controlled by nucleation and growth of C-S-H [47]. Nucleation is a diffusion controlled process. Thus the results suggest that C-S-H formation was modified (e.g. via the rate at which C-S-H is formed and/or the structural arrangement/porosity) since such changes can affect the rate at which ions diffuses through the hydrate. This is in agreement with the results of Juilland et al. [47] who observed a faster rate of hydration in cement pastes that were prepared at 1200 rpm versus those prepared at lower intensities (specifically 500 rpm and hand mixed). It was postulated that this behavior was due an increased dissolution rate of ions from the surface of cement particles caused by the mechanical action of mixing densifying the C-S-H nuclei. Additionally, it cannot be ignored that the formation of the hydration products from the aluminate phases, such as ettringite, will also be occurring during this time period. Similar to the impact of mixing on the silicate phases, it is likely that the increased mixing intensity will also impact the formation of hydrates precipitating from the aluminate phases. Ettringite has a considerable impact on the rheological behavior and stiffening of fresh cement pastes [40,48]. As such, changes in ettringite size, morphology, or amount is also likely to have a considerable effect on rheological behavior. Work conducted by Dalas et al. [49] on model system paste mixtures showed that inclusion of polycarboxylate resulted in increasing the specific surface area of ettringite in mixtures containing the polycarboxylate admixture as compared to mixtures not containing polycarboxylate admixtures. Results by Ng et al. [50] also suggests that increased ettringite formation occurred during the early stages of hydration in pastes containing polycarboxylate admixtures as compared to neat paste. Furthermore, polycarboxylate admixtures are prone to generating air bubbles within the paste matrix and air will also affect rheological properties [51,52]. Thus, the greater sensitivity to mixing intensity seen in the plasticized mixtures as compared to the non-plasticized mixtures could be

due to the polycarboxylate-based admixture inducing changes within the paste that modified the fundamental rheological response of the paste systems. Generally, an increase in hydration rate is associated with an increase in the early strength development (which is one of the reasons why cement fineness has decreased over the years) [53,54]. However, in many applications, minimizing the initial heat release is preferred in order to limit the development of thermal stresses which can cause early-age cracking. Further work is needed in order to investigate the extent to which mixing intensity influences properties, especially with respect to strength, capillary porosity and shrinkage development.

From Figure 16 (a), it can be seen that for the cement paste prepared at a final mixing speed of 1000 rpm, inclusion of the superplasticizer had a slight retardation effect. Interestingly, the delaying effect of superplasticizers was compensated by increasing the final mixing speed (compare Figures 16 (a), (b), and (c)). Retardation of cement hydration due to superplasticizers has been commonly reported, and could be due to adsorption of the polymer molecules of the superplasticizer onto cement particles inhibiting subsequent topochemical reactions from occurring [50,55–59] and/or an increase in the time needed to reach the percolation threshold due to the particles being initially dispersed further apart from the superplasticizer [53]. It was seen that the apparent viscosity of the *045_SP* mixture was lower than of the *045* mixture (see Figure 5) at all the sample preparation mixing speeds that were used in this research. However as the sample preparation speed increased the difference between the apparent viscosity of the *045* and *045_SP* decreased, which indicates that the cement-SP interaction has been affected.

The pore fluid of cement is comprised of several ions (primarily, Na^+ , K^+ , OH^- , Ca^{2+} and SO_4^{2-}) [60]. As depicted in Figure 13, an increase in the ion concentrations of the pore fluid may contribute to the acceleration behavior and particle agglomeration behavior observed in the pastes that were prepared using the higher final mixing speeds. In order to examine whether this could be the case, the concentration of alkali was measured using flame photometry. It can be seen that the potassium and sodium concentrations of the cement paste prepared with final mixing speed of 12000 rpm was higher than other cement pastes prepared with lower final mixing speeds (see Figure 17). Thus the results are in

agreement with the hypothesis that the increased mixing intensity increased the early-age dissolution process. The increased ion concentration in the mixture prepared at 12000 rpm when compared to mixtures prepared at the lower mixing intensities is likely caused by increased deagglomeration of the cement grains due to initial rupturing of the flocs. This deagglomeration could then heighten the accessibility of the alkali ions to the pore solution. Increase soluble alkali content has been shown to increase the rheological properties of pastes [61-62]. This is consistent with the trend seen in Figure 18, in which the mixture containing the highest measured alkali ions displayed the greatest apparent viscosity. Ferron [25] showed that SP demand was strongly correlated to the potassium and sodium concentrations in the pore solution, which suggests that for the paste presented in Figure 17 that mixing at 12000 rpm may necessitate more superplasticizer to achieve a target fluidity condition than mixing at 4000 rpm.

4. Conclusion

The results of this study contributes to our understanding of the mechanisms affecting the rheological behavior of cement pastes due to changes in the mixing speed. It was determined that after a certain mixing speed threshold, the rheological properties of fresh state cement paste increased. The results showed that pastes prepared at higher mixing speeds exhibited a larger mean chord size and higher rheological properties than their counterpart pastes prepared at lower mixing speeds. This trend was amplified in pastes containing superplasticizer. Changes in the physical and chemical nature of the pastes occurred when the mixing speed varied. Based on an agglomeration strength analysis using in-situ particle size measurements, pastes that were prepared with high mixing speeds contained larger agglomerates that were more weakly linked together than pastes prepared at lower sample preparation speeds. This behavior was associated with changes in chemical reactions in the cement pastes, specifically with regards to hydration kinetics and soluble alkali concentration. As the mixing speed increases,

increases in hydration kinetics and alkali content of the pore solution occurred. Such changes will likely lead to a decrease in the thickness of the diffuse double-layer and promote agglomeration.

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Table 1. Oxide composition of cement [15]

Items	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O _e
Amount (%)	20.7	4.5	3.3	65.1	1.4	2.6	0.50

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Table 2. Mixture proportions for cement paste. c/p refers to solid content volume and is the volume of cement per volume in paste, whereas w/c refers to the water-to-cement ratio and is based on the mass of cement versus the mass of water.

Code*	c/p (by volume)	w/c (by mass)	SP	Quantity for 1 liter of paste		
				Cement (g)	Water (g)	HRWR (g)
042	0.42	0.44	None	1323.000	580.000	-
045				1417.500	550.000	-
045_SP	0.45	0.39	Yes	1417.500	547.336	2.835
047_SP	0.47	0.36		1480.500	527.217	2.961

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Table 3. Estimated shear rate applied in the FBRM set-up

FBRM agitation speed (rpm)	Estimated shear rate (s^{-1})
150	59
300	118
450	177

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Table 4. Influence of mixing speed on the time at which the of induction period ended

Pastes	Mixing speeds				
	1000 rpm	2000 rpm	4000 rpm	8000 rpm	12000 rpm
<i>045</i>	78 ± 4 min.	72 ± 4 min.	67 ± 5 min.	64 ± 3 min.	63 ± 3 min.
<i>045_{SP}</i>	87 ± 3 min.	83 ± 3 min.	78 ± 5 min.	74 ± 2 min.	69 ± 5 min.

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Table 5. Influence of mixing speed on the time at which the acceleration period ended

Pastes	Mixing speeds				
	1000 rpm	2000 rpm	4000 rpm	8000 rpm	12000 rpm
<i>045</i>	398 ± 2 min.	413 ± 0 min.	391 ± 0 min.	339 ± 1 min.	334 ± 0 min.
<i>045_{SP}</i>	455 ± 1 min.	455 ± 0 min.	428 ± 0 min.	377 ± 7 min.	331 ± 0 min.

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Table 6. Influence of mixing speed on the slope of acceleration period of cement paste (slope = tangent)

Pastes	Mixing speeds				
	1000 rpm	2000 rpm	4000 rpm	8000 rpm	12000 rpm
<i>045</i>	2.72 ± 0.00	2.80 ± 0.02	2.97 ± 0.00	3.40 ± 0.00	3.71 ± 0.01
<i>045_{SP}</i>	2.57 ± 0.18	2.81 ± 0.16	3.27 ± 0.01	3.95 ± 0.00	4.40 ± 0.03

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Figure(s)

Figure 1. Mixing protocol to prepare cement pastes. Mixing speeds for Steps 4 and 6 ranged from 1000, 2000, 4000, 8000, and 12000 rpm.

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(a) Mixer blade assembly

(b) High shear mixer connected to water circulation system

Figure 2. Chandler 3060 mixer system used to prepare cement pastes (a) blade set (b) mixer connected to water circulation system

Figure 3. Applied shear rate protocol for flow curve measurement

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Figure 4. Schematic of FBRM test set up

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Figure 5. Influence of mixing speed and cement pastes on the apparent viscosity at 20 s^{-1} of shear rate (the data points were obtained by average of two representative flow curve tests)

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(a) 042

(b) 045

(c) 045_SP

(d) 047_SP

Figure 6. Influence of mixing speed on flow curve behaviors depending on different cement pastes

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(a) FBRM observation speed:150 rpm

(b) FBRM observation speed:300 rpm

(c) FBRM observation speed:450 rpm

Figure 7. Influence of final mixing speeds on particle chord length under different agitation speeds for 042 paste

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Figure 8. Influence of final mixing speeds on particle chord length under different agitation speeds for 045 paste

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Figure 9. Influence of final mixing speeds on particle chord length under different agitation speeds for 045_SP paste

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Figure 10. Influence of final mixing speeds on particle chord length under different agitation speeds for 047_SP paste

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Figure 11. Schematic depicting how agglomeration strength of the cement agglomerates can be estimated using average particle chord length and agitation speeds from FBRM experiments

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Figure 12. Estimated agglomeration strength in different pastes prepared at different final mixing speeds (Negative values indicates aggregate break-down whereas positive values indicate aggregate build-up.)

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Figure 13. Schematic view of the hypothesis

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(a) 045

(b) 045_SP

Figure 14. Influence of the final mixing speeds on rate of heat evolutions of cement pastes

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(a) 045

(b) 045_SP

Figure 15. Influence of the final mixing speeds on cumulative heat of hydration of cement pastes

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59

(a) 1000 rpm

(b) 4000 rpm

(c) 12000 rpm

Figure 16. Influence of mixing speeds on compensating the delaying effect of SP in cement pastes

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Figure 17. Influence of applied final mixing speeds on the concentration of alkalis from the fresh state 045 mixture

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(a) K^+

(b) Na^+

Figure 18. Relationship between ionic concentrations of alkali ions and apparent viscosity of 045 mixture