

Cement paste yield stress and self-compacting mortar stability

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ABSTRACT

Self-compacting concrete (SCC) has been extensively used because of its high-performance. This is mostly due to the integral stability of its components predominantly driven by the cement paste rheology and influences the viscosity of the overall suspension. Referring to Stokes law, solid particles exerting downward forces sink through the liquid phase only once the drag force fails. This work argues that the stability of self-compacting cement mortar does not only depend on the overall viscosity of the cement suspension but also on the yield stress of the suspending medium, the cement paste. Rheological measurements in shear steady mode, conventional column apparatus and total organic carbon measurements were done. Results showed that, cement mortars with higher yield stress pastes exhibited more stable suspensions while those with lower yield stresses resulted in unstable mortars with higher segregation. No correlation was found between rheological parameters and bleeding of cement pastes and corresponding cement mortars.

1. Introduction

Self-compacting concrete is a multiphase material, and its mechanical stability can be investigated on different levels depending on the physical interaction of interest. At mortar scale, the suspension is mainly constituted by the cement paste referred to as the liquid medium and sand as suspended particles or solid medium. Static segregation in cementitious systems adheres to Stokes's Law and adjusting the rheological properties of cement mortar is critical in achieving stable mixes [1]. For any suspended aggregate to not settle through the liquid medium, the gravitational force must be equal to the upward forces (drag or buoyancy forces). Static segregation appears mostly after casting and consists of suspended particles sinking in the suspending medium. On the other hand, bleeding is the formation of a layer of water on top of the cement system surface resulting from excessive mixing water.

Stolz and Masuero [2] have found that the rheology of mortars is strongly controlled by the degree of aggregate compaction in the system. Within this context, the viscosity of the overall system would be the most affected according to the Dougherty constitutive model. In other investigations, the rheology of the suspending media has been shown to play a critical role in the stability of cement systems. For instance, Yahia et al. and Roussel [3,4] found that the rheology of cement mortar could be tailored to achieve the desired segregation resistance of SCC mixes. Similarly, Westerholm et al. [5] studied the structure composition of the mortar phase in SCC systems and found that, the yield stress of cement

mortar increased as the fine fractions within increased while insufficient and uneven dispersion of the fines fraction led to an increase in void contents, causing excessive bleeding of SCC mixes. This would probably be explained by the fact that fine grains embedded in the cement paste provide more contact sites between them due to a higher specific surface area resulting in a strong network with considerable yield stress values. This is because the internal particles network of cement pastes is primarily affected by colloidal, and particle contact interactions [6]. On the other hand, interstitial voids within the grain network would serve as channels through which excess mixing water reaches the upper surface of the suspension resulting in bleeding.

Although work has been done attempting to shed light on the stability of cement systems, the subject remains an ongoing research topic in the concrete field. Even though it has been agreed that understanding the rheology of a cement system is crucial for ensuring a stable mix, debates persist on determining which rheological parameters are responsible for mix stability. For Leemann and Winnefeld [7] the viscosity of cement paste should be enhanced using viscosity modifying agents to prevent segregation and bleeding of cement systems while Roussel [4] clearly showed the importance of rheological performances of different phases in a multiphase suspension to assure concrete stability. He further determined their respective yield stress performances to avoid migration and settlement of aggregates. These approaches have to do with the interpretation of Stokes law that attributes particle settlement to differences in densities and viscosity of the suspending

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medium in the suspension phases. Tregger et al. [8] and Abeyrwan [9] on the other hand reported that increasing simultaneously both the viscosity and yield stress of cement systems, positively affects its segregation behaviour. In another investigation, Perrot et al. [10] attempted to establish the relationship between the stability and flow behaviour of cement systems. They found that there was no direct relationship between yield stress and bleeding but that there was a strong correlation between the plastic viscosity values and their bleeding indexes. In contrast, Rubio-Hernández et al. [11], Abebe and Lohaus [12] noticed that there was no relationship between yield stress of cement mortars and aggregate settlement for dynamic segregation. This could probably be due to induced turbulent flow and continuous shearing in which case Stokes-Law cannot be used as it is only relevant for laminar flow systems.

Undoubtedly, understanding the rheology of the suspending media is key when attempting to achieve stable cement suspensions. However, it is now confirmed that physical and chemical characteristics of the cement powder used can alter the rheological behaviour of a fresh cement systems. This becomes more pronounced in the presence of superplasticisers that contain chemical group functions necessary for cement compatibility [13–16]. These researchers pointed out the ability of cement adsorption behaviour depending on the superplasticiser molecular structure and weight. They further suggested that the fluidity of cement pastes is somewhat the result of adsorbed and non-adsorbed superplasticiser molecules. On one hand, the adsorbed superplasticiser favours the production of hydrates [17,18] that results in a more fluid system keeping the concrete fresh for a longer period. On the other hand, non-adsorbed superplasticiser plays the role of lubricant together with trapped waters in the system augmenting thus the fluidity of the overall network. In practice, different polymers are used either individually or in association with other polymers. Bessaies et al. [19] warned that when more than one polymer is used in cement pastes, competitive adsorption occurs which results in other polymers being ineffective during the adsorption process.

It is evident that numerous investigations have been conducted to assess the rheology of the overall cement system mixes, its stability, and their factors. However, less attention has been paid to developing relationships between the rheology of the liquid phase and the overall stability of cement systems especially under no shear stress conditions. It is possible that segregation performances of cement suspensions could be improved proportionally with enhancements of rheological behaviours of their suspending phases. Hence, this study investigates the effect of yield stress and viscosity of cement pastes on the static segregation and bleeding of corresponding self-compacting cement mortars.

2. Experimental program

2.1. Materials

2.1.1. Sand

A blend of two crystalline Silica sands was used in this study as recommended by Zeghichi et al. [20] to ensure favourable results by having acceptable proportions of fine and coarse particles. The blended sand consisted of a 50% split of the two sands to fall within the SANS 1083 grading limits as shown in Fig. 1.

2.1.2. Cement

Three different cements of type CEM I 52.5N were used. They were manufactured by the same company at three different plants. Table 1 provides their chemical characteristics as obtained using X-ray fluorescence (XRF). The cements had different oxides that resulted in different cement phases such as aluminate content able to influence SP adsorptions. Physical characteristics are presented in Table 2.

2.1.3. Superplasticisers

Two types of SP's were used to produce the SCC mortar, namely SP1 and SP2. The SP's were individually optimised and thereafter blended in different proportions to produce SP3 used at an optimum dosage of 0.9%. This enabled different yield stress values of cement pastes to be obtained so that their impact on the stability of the corresponding SCCM could be evaluated. The two SPs are polycarboxylate-based and consist of acrylic polymers with distinctive features as indicated in Table 3 and

Table 1
Chemical analysis of the cements.

PARAMETER:	INFORMATION		
Chemical Oxides (%)	Sample Reference		
	CEMENT A	CEMENT B	CEMENT C
SiO ₂	23.14	20.28	20.40
Al ₂ O ₃	3.28	4.26	4.55
Fe ₂ O ₃	4.43	2.55	2.68
Mn ₂ O ₃	0.13	0.12	0.57
TiO ₂	0.41	0.28	0.31
CaO	62.64	64.80	61.79
MgO	1.50	0.91	2.51
P ₂ O ₅	0.07	0.11	0.04
SO ₃	2.46	2.45	3.35
Cl	0.00	0.00	0.00
K ₂ O	0.47	0.67	0.20
Na ₂ O	0.26	0.16	0.05
LOI	1.75	2.25	3.43
Total	100.5	98.8	99.9

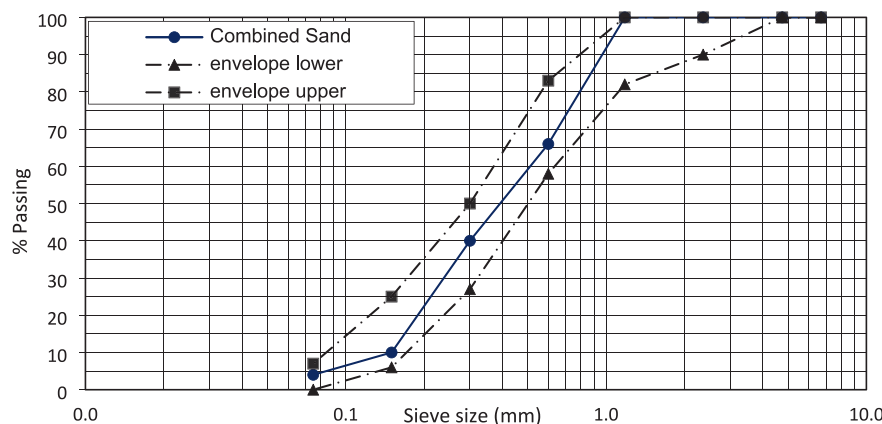


Fig. 1. Sand optimization in relation to SANS 1083 grading boundaries.

Table 2
Physical characteristic of the cements.

PARAMETER:	INFORMATION		
Physical Testing	Sample Reference		
	CEMENT A	CEMENT B	CEMENT C
Relative Density	3.09	3.15	3.12
Specific Surface, cm ² /g	3800	4300	4100
Standard Consistency, %	28.0	27.6	28.0
Initial Set Min	180	130	100
Final Set Min	195	150	120
32 μm Residue, %	15.6	23.2	9.5
45 μm Residue, %	5.3	10.3	2.2
90 μm Residue, %	0.2	0.8	0.1
212 μm Residue, %	0.0	0.1	0.0

Table 3
Physical and chemical characteristics SP1.

Superplasticiser SP1	
Consistency:	Liquid
Colour:	Amber
Density according to ISO 758 (g/m ³):	1.08 ± 0.02 at +20 °C
Main action:	increased workability and/or reduction of mixing water and rapid development of mechanical strengths at early ages and at T > 15 °C
Classification according to EN 934-2:	high range water reducing, hardening accelerating, superplasticiser, tables 3.1, 3.2 and 7
Classification according to ASTM C494:	type F and type C
Classification according to ASTM C1017:	type I
Chlorides soluble in water according to EN 480-10 (%):	<0.1 (absent according to EN 934-2)
Alkali content (Na ₂ O equivalent) according to EN 480-12 (%):	<3.0
pH content according to ISO 4316:	6.5 ± 1.0
Molecular weight	42.000

Table 4
Physical and chemical characteristics SP2.

Superplasticiser SP2	
Consistency:	liquid
Colour:	amber
Density according to ISO 758 (g/cm ³):	1.07 ± 0.02 at +20 °C
Main action:	increase workability and/or reduction of mixing water and slump retention over long periods
Classification according to EN 934-2:	set retarding, high range water reducing, superplasticiser, tables 11.1 and 11.2
Classification according to ASTM C494:	type G
Classification according to ASTM C1017:	type II
Chlorides soluble in water according to EN 480-10 (%):	<0.1 (absent according to EN 934-2)
Alkali content (Na ₂ O equivalent) according to EN 480-12 (%):	<2.5
pH according to ISO 4316:	6.0 ± 1.0
Molecular weight	40.000

4. These SPs had different adsorption abilities based on their group function such as SP1 having a longer side chain and higher molecular weight than SP2.

The mix design at mortar scale provided in Table 5 was done as suggested by Su et al. [21] and recommended by the EFNARC [22] and Table 6 shows the corresponding cement paste mix design.

Table 5
Cement mortar mix design.

Units	w/c	Water	Cement	Admixture	Sand
kg/m ³	0.40	181	463	4.163	922

Table 6
Cement paste mix design.

Units	w/c	Water	Cement	Admixture
g	0.4	11.7	30	0.09

All mix design parameters were kept constant throughout the experiments. Table 7 highlights the blending fractions of the two reactant SPs to yield the product SP3. This was done to assess possible improvements in the effectiveness of the SP. Besides, this helps obtaining cement pastes with different yield stress values at equal optimum SP dosage. Values on the horizontal axis of the graphs for all results in this article indicate the SP2 fraction in the SP3 dosage.

2.2. Experimental procedure and testing

The optimum dosage of 0.9% for SP3 was the average value of individual optimum SP values for the three cements used. These values were obtained by measuring the spread value of SP for different dosages. The optimum dosage was the one above which increasing the dosage does not provide any change in mortar spread. The mini-slump flow test was carried out to assess the flowability of the SCCM as the suspension with two mediums, sand as the solid phase and cement paste as the liquid phase. The stability assessment of the mortar was evaluated using the mini-column segregation and bleeding test. Rheological measurements were carried out to evaluate the yield stress and plastic viscosity of cement pastes as suspending medium of different cement mortars. The Total Organic Carbon (TOC) was used to measure the adsorption behaviour of the SP on cement particles. All results which had discrepancies greater than 10 mm for the mini-slump flow and greater than 20% for the stability tests were repeated as suggested by [23]. An error analysis was conducted for all test results using the standard deviation over the square root of the of the number of tests.

2.2.1. Segregation test

The column apparatus was manufactured using the ASTM C1610-06 standard [24] guidelines, but with similar sizes as used by Mahdikhani & Ramezani pour [25]. The column was placed on a level table and the cement mortar sample poured to full height. The mortar was left for 15 min to settle, the top section removed after 15 min and washed in a 300 μm sieve for 1 min followed by the mortar in the bottom section. The material retained in the sieves was then labelled in containers and placed in the oven to dry for 24 h at 110 °C. All steps after the resting period (15 min) were done within 20 min as prescribed by the ASTM C1610-06 standard [24]. The Static Segregation was then calculated using Equation (1):

Table 7
SP3 mix proportions of SP1 and SP2 as reactants at the optimum dosage of 0.9%.

Mix Proportions (%)	SP2 fraction	SP1 (g)	SP2 (g)	Total SP3 (g)
10%/90%	10%	11.7	1.3	13
20%/80%	20%	10.4	2.6	13
30%/70%	30%	9.1	3.9	13
40%/60%	40%	7.8	5.2	13
50%/50%	50%	6.5	6.5	13
60%/40%	60%	5.2	7.8	13
70%/30%	70%	3.9	9.1	13
80%/20%	80%	2.6	10.4	13
90%/10%	90%	1.3	11.7	13

$$SI = 2 \left[\frac{M_{bot} - M_{Top}}{M_{bot} + M_{top}} \right] \times 100 \tag{1}$$

where;

SI- Segregation Index (%), M_{bot} - Oven dried mass of the bottom sample (g), M_{Top} - Oven dried mass of the top sample (g).

2.2.2. Mini-slump test spread flow

There is currently no referenced standard method for conducting the mini-slump flow test [26]. However various studies including [27,28] have supported both the application of the mini-slump cone method and its credibility for assessing the spread flow of different cementitious materials. The mini cone (Base diameter = 38 mm; Top diameter = 19 mm and height of 57 mm) was positioned at the centre of a plexiglass baseplate with negligible friction. After the sample temperature was measured it was poured into the cone and left to rest for 30 s while cleaning any spilt mortar on the plate. The cone was lifted in one motion and the timer started immediately when the cone was lifted from the plate. Two perpendicular diameters were measured, and the average recorded. The yield stress was then calculated using Equation (2) as proposed by Roussel and Coussot [28];

$$\tau_y = \frac{225 \rho g V^2}{128 \pi^2 R^5} \tag{2}$$

where; ρ - density of sample (kg/m^3), τ_y - yield stress (Pa), V- volume of cone (m^3), R- spreading diameter (mm), g- acceleration due to gravity (m/s^2).

Only 4 mixes when using Cement B and C did not meet the criteria set out by Roussel and Coussot [28].

2.2.3. Bleeding test

A simplified method to assess bleeding using a plastic cylinder was used as per ASTM C 940-98a standard [28] and applied by Ji et al. [30,31]. A labelled 1000 ml cylinder was lubricated and placed on a level table. Approximately 800 ml (± 10 ml) of the cement mortar sample was poured into the cylinder. The actual volume and time were recorded. The top of the cylinder was covered with filter paper to prevent evaporation. Measurements were recorded at 15 min intervals for the first hour and at 60 min intervals thereafter for 3 h from the first reading [29]. The degree of bleeding was then calculated using the Equation (3) [31]:

$$B = \frac{V_w}{V_1} \times 100 \tag{3}$$

where; V_1 - volume of the mortar sample at the start of test (ml), V_w - volume of bleed water at the end (ml), B- final bleeding (%).

2.2.4. Rheometer measurements

The SCCP yield stress and viscosity were evaluated by fitting the Bingham model (Equation (4)) on the down curves from flow curves obtained from rheological data executed in shear mode using an Anton Paar MCR 51 Rheometer. The rheometer was equipped with sandblasted parallel plate system with a 0.6 mm gap, which was approximately ten times larger than the biggest cement particle size. The measurement cycle was set at 300 s divided equally for the downward and upward curves. The shear rate for both the downward and upward curves was from $0.1 s^{-1}$ to $100 s^{-1}$ before a pre-shearing period of 10 s at $100 s^{-1}$. After calibration, the sample was poured on the lower plate and the top plate lowered for testing.

Bingham:

$$\tau = \tau_y + \eta_p \dot{\gamma} \tag{4}$$

where; τ ; shear stress (N/m^2), τ_y ; yield stress (N/m^2), η_p ; plastic viscosity ($N/m^2.s$).

$\dot{\gamma}$; shear rate (s^{-1}).

2.2.5. Adsorption measurements

Superplasticiser adsorption was also assessed to determine the amount of superplasticiser adsorbed by the cement particles in the cementitious solutions. This was done by calculating the Total Organic Carbon (TOC) content present in the cement suspensions. The superplasticiser adsorption was then calculated by the subtracting the amount of carbon left in the supernatant (the amount of carbon in the cement paste sample less the amount of carbon present in the cement only sample) from the original amount of carbon (amount of carbon present in the superplasticiser solution only), after the sample was centrifuged at 5000 rpm.

2.3. Sample preparation

The mixing of the SCCM was done using an industrial 10 l capacity 3 speed dough mixer. A similar technique has been used in different investigations [32,33,34] for cement sample mixing. The cement and sand were first poured into the mixing bowl and mixed for 3 min to assure material homogeneity. Next, the superplasticized water was added and mixed for 3 min. After this, the mixing process was stopped, and the bowl was scraped off by hand to remove all the unmixed cement. The mixer was switched on again for additional 2 min and completely stopped after 9 min for testing.

The representative cement paste samples of the corresponding cement mortar mixes were vigorously mixed by hand until homogeneous cement pastes were obtained using deionised water [32,35]. Manual mixing seemingly provided consistent paste especially as required sample quantity for this experimental was small. The sample was then transferred to the rheometer using a laboratory spoon.

3. Results and discussion

3.1. Effect of SP3 on self-compacting mortar rheology

For cement suspensions in general, two important criteria need to be met; adequate flowability and negligible segregation. Yield stress and viscosity play an essential role in the flow behaviour of cement suspensions. Petrou et al. [36] deemed the estimation of the yield stress from the mini-slump test as one way in which mortar rheology can be tailored to achieve a consistent stability. The effectiveness of blending SPs on the flowability of SCCM was investigated using the mini-slump cone. Mortar yield stress values of product SP (SP3) expressed in SP2 fractions at optimum dosage are presented in Fig. 2. For all cements, increasing the SP2 fraction within the blended SP, significantly decreased the cement mortar yield stress values.

Each cement reaches its optimum value at different blending

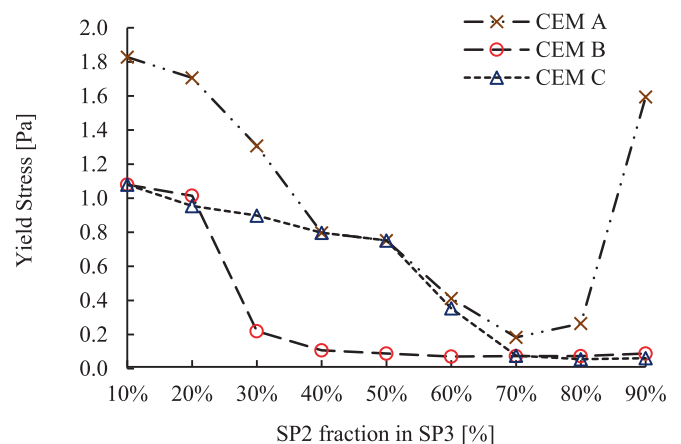


Fig. 2. The effect of blended SP3 at optimum dosage of 0.9% on cement mortar yield stress using three different cements.

fractions. CEM A and CEM C reached their optimum values only at higher SP2 fractions (70%) compared to CEM B (50%). This behaviour could be attributed mostly to the chemical functions of reactant SPs [12–14]. Polymers in SP1 had longer side chains and a higher molecular weight than SP2. According to Winnefeld [13], superplasticisers with shorter side chains have better adsorption ability compared to those with longer side chains. It is therefore understood that, at low SP2 fractions, adsorption properties of SP3 are dominated by the lower adsorption properties of reactant SP1. Alternatively, the cement-SP interactions could also explain the observed behaviour of SP3 on the cements used. The cement aluminate, calcium sulphate phases and Blaine value significantly influence the adsorption properties of a given superplasticiser during the hydration processes [18]. CEM A with both a lower C₃A content and Blaine value availed insufficient surfaces ready to adsorb SP molecules and interact with mixing water thus resulting in higher yield stress values compared to other cements. However, the discrepancy observed beyond 70% SP2 fraction for CEM A could not be explained and this requires further investigations.

3.2. Effect of the cement paste rheological parameters on corresponding SCCM stability

3.2.1. Cement paste yield stress and mortar static segregation

At concrete scale, cement mortar is the suspending medium which sustains coarse aggregates in the cement system to assure homogeneity of the mix. Similarly, at mortar scale cement paste assures homogeneity and stability of the mix by exhibiting consistent rheological behaviour. SCCM stability was assessed and associated to respective cement paste rheological performances. Each reactant fraction with the SP3 provided a cement paste system with a specific yield stress value. According to results shown in Fig. 3, cement mortars with low yield stress cement

pastes resulted in cement systems with higher segregation index values. In other words, increasing the SP2 content within the blended SP3 decreased the suspending medium yield stress thus, resulting in higher segregation index values of the SCCM. At microstructural level the yield stress of cement paste is a true indicator of the strength that the system exhibits. Solid migrations within a liquid result from the balance between the drag force as offered by the liquid phase and gravity as experienced by solid particles [37]. Since at mortar level, aggregates are supported by cement paste in a form of a “net”, it is thus understood that, if its bearing forces are lower compared to that of sand particles, the later will sink through resulting in segregation.

This was in line with the findings of Petrou et al. [36] in their investigation on aggregate settlement. Low yield stresses in self-compacting cement systems emanate from dispersing forces and steric hindrance caused by admixtures which result in denser particles settling and pushing the liquid upwards. As the yield stress reaches its lowest value due to greater superplasticiser adsorption, forces exerted by denser particles become dominant resulting in settling. This leads to a highly fluid system with a greater segregation index value. Similar observations have been reported in different investigations [4,7,23].

In all cases, CEM A and CEM C performed robust interactions in the presence of SP3 at 0.9% optimum dosage compared to CEM A. At all SP2 fractions up to 60%, the two cements (CEM A, CEM C) provided more stable mortar systems, while with CEM B only up to 20% SP2 fraction stable mortars were obtained.

3.2.2. Cement paste yield stress and mortar bleeding

Fig. 4 presents the relationship between cement paste yield stress and bleeding of the corresponding cement mortar. No bleeding was noticed in all cement mortars except CEM C mortar with cement paste yield stress values below 0.3 Pa. Consequently, no correlation could be

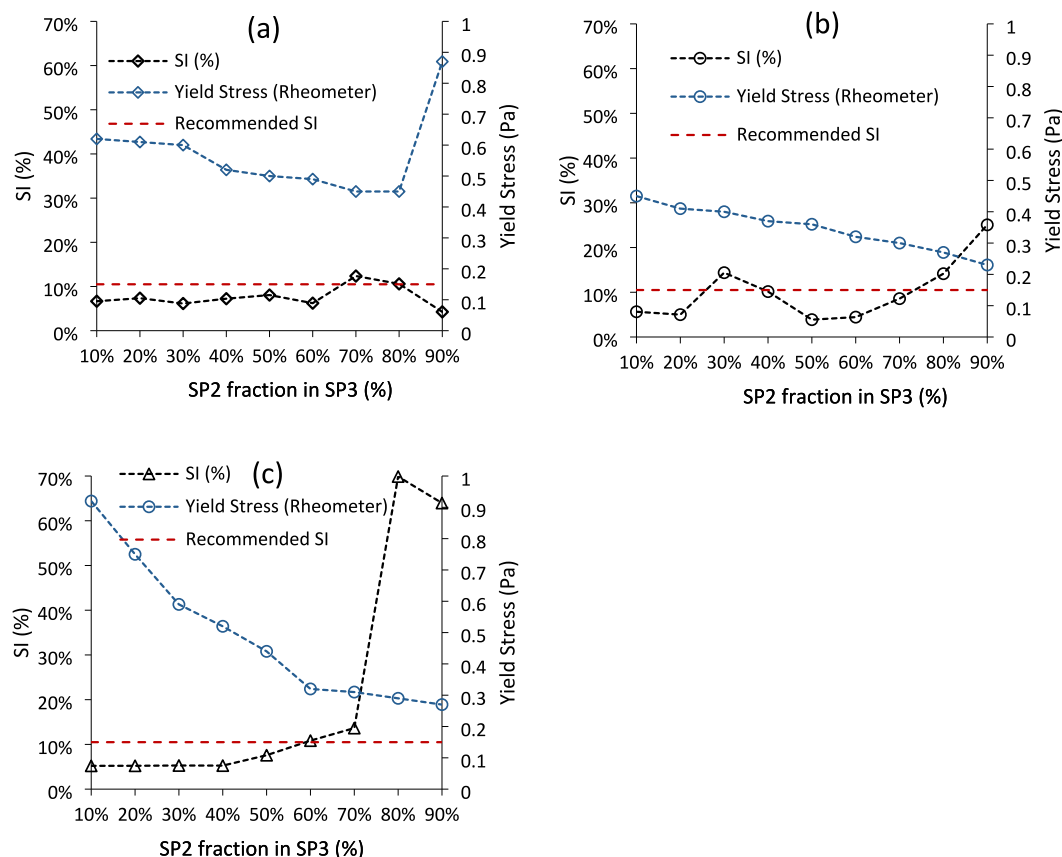


Fig. 3. Relationship between cement paste yield stress values and segregation indexes of corresponding SCCM in relation to the recommended SI value (15%) by Libre et.al [22] (a) CEM A, (b) CEM B and (c) CEM C.

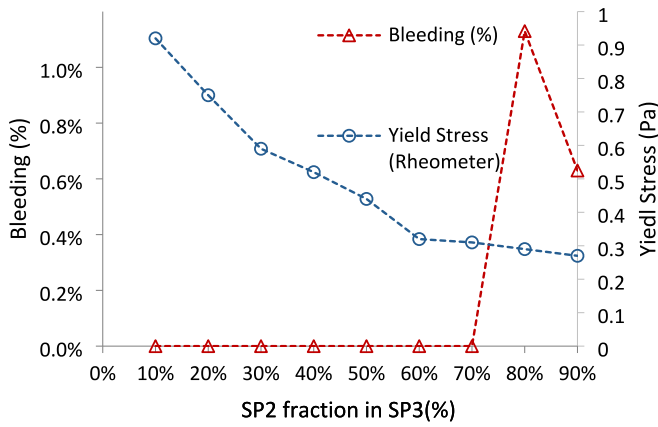


Fig. 4. Relationship between cement paste yield stress values and bleeding of the corresponding SCCM for Cement C.

established between the cement paste yield stress and bleeding values. Bronk et al. [38] admitted that the correlation between yield stress and bleeding of cement suspension is indirect since the two parameters are from different mechanisms. Yield stress results from colloidal interactions whereas bleeding results from a competition between colloidal forces and gravity in such a way that cement suspensions will not bleed if colloidal forces prevail over gravity forces. In other words, bleeding is a consequence of consolidation and sedimentation at suspending medium level depending on the suspension w/c ratio [39]. Colloidal forces depend on the interparticle distance and the average diameter of grains or surface area. It is thus suspected that cement mortars didn't bleed due to the fact the consolidation mechanism, or the yield stress development of cement paste occurred faster so that cement particles could not allow water migration to the surface. These observations agree with those of Perrot et al. [10] who attempted to establish a correlation between mortar yield stress values and their respective bleeding indexes. Their study demonstrated that bleeding in mortar systems was not a direct function of their yield stress values. Some cement mortars with lower yield stress values experience no bleeding while some with higher values exhibited bleeding and vice versa.

The occurrence of bleeding in CEM C mortar could therefore be associated to apparent microstructural sedimentation at paste level that prevailed over consolidation mechanisms of the cement paste translated by low yield stress values.

3.2.3. Cement pastes plastic viscosity and mortar static segregation.

The plastic viscosity values of the cement pastes are presented in Fig. 5 and their effects on cement mortar segregation indexes in Fig. 6. It

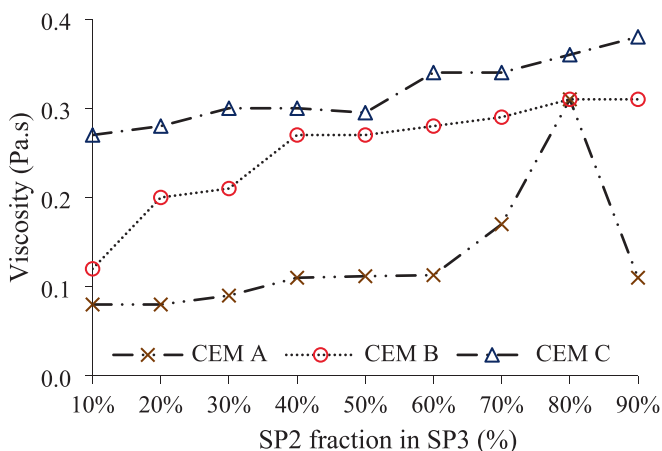


Fig. 5. The effect of SP3 at optimum dosage on cement paste plastic viscosity.

is apparent that, increasing the SP2 fraction within SP3 at optimum dosage increases the plastic viscosity of cement paste mixes for all cements. This can be attributed to the adsorption property of SP3 on cement particles as effected by the presence of the SP2 fraction. In general, at low SP2 fractions, SP3 adsorption is low as illustrated in Fig. 7 resulting in large amounts of free SP within the cement paste that decreased the viscosity of the cement paste. Of course, it is agreed that un-adsorbed SP increases the viscosity of cementitious materials, but this is true mostly for systems with low water – binder ratios. However, in high w/c ratio mixes, excess SP within the interstitial solution increases the packing density and the water film thickness of pastes decreasing therefore the viscosity of the suspension [40]. The packing density of a suspension is ultimately improved by efficiently rearranging solid particles within the system. Conservatively, it is assumed that SP in cementitious systems disperses cement agglomerates yielding a network with smaller particles easily rearranged in an optimum manner and so improving the packing density of the cement system. The dispersion of cement agglomerates within the system is generally followed by the release of trapped water that increases the thickness of film water around solid particles. This reduces the friction between particles within the network and consequently decreases the viscosity of the cement system. However, this phenomenon depends on the w/c ratio. Cement systems with a low w/c ratio has a particle network with smaller spaces, entanglements of un – adsorbed SP within the interstitial solutions increases its viscosity and affects the overall viscosity of the system without significant improvement of its packing density. For cement systems with a high w/c ratio with appreciable interparticle spaces, SP agglomerates from excess SP increases the packing density while trapped water from the dispersion effect of adsorbed SP increases the film thickness and decreases the viscosity of the system.

Within these conditions, the yield stress of the cement system remains high due to insufficient particle dispersion. It was also clear that cement mortar segregation index values were proportional to cement pastes viscosity values. Increasing the cement paste viscosity value resulted in cement mortars with higher segregation index values. These results are in contrast with the findings by Tregger et al. [7] and Yan et al. [1] although most of investigations were executed at mortar scale.

It is therefore understood that the ability of cement mortar to segregate cannot only be defined by the plastic viscosity parameter of a given cement system. Achieving a stable cement mortar system requires a balance between both cement paste yield stress and viscosity values since segregated cement mortar systems are either the result of the presence of a high plastic viscosity or low yield stress cement paste within the system. Although it is of great interest to determine the sweet spot of these rheological parameters, that is the value of cement paste yield stress and plastic viscosity that simultaneously provide a stable mortar, it was not within the scope of this work. However, researching this would be of great interest.

3.3. Adsorption of superplasticiser on cement particles

The performance of superplasticisers depends on how much adsorption occurs between the polymers and the cement particles resulting in different physical interaction phenomena such as steric hindrance and electrostatic repulsion that contribute to the dispersion of cement particles within the solution.

Fig. 7 shows the adsorption behaviour of SP3 on all cements. These measurements were done at optimum dosage of SP3 and therefore the saturation state of the SP on cement particle was not thus checked. Results were reported to support the performance of SP3-cement interactions on the rheological behaviour of cement systems. The yield stress development of cement is a function of many parameters including the hydration of early reactive phases such as aluminate and silicate, cement characteristics and superplasticiser dosage [41]. The high yield stress and low plastic viscosity values of cement paste systems in the presence of low SP2 fractions within SP3 are thus justified by the

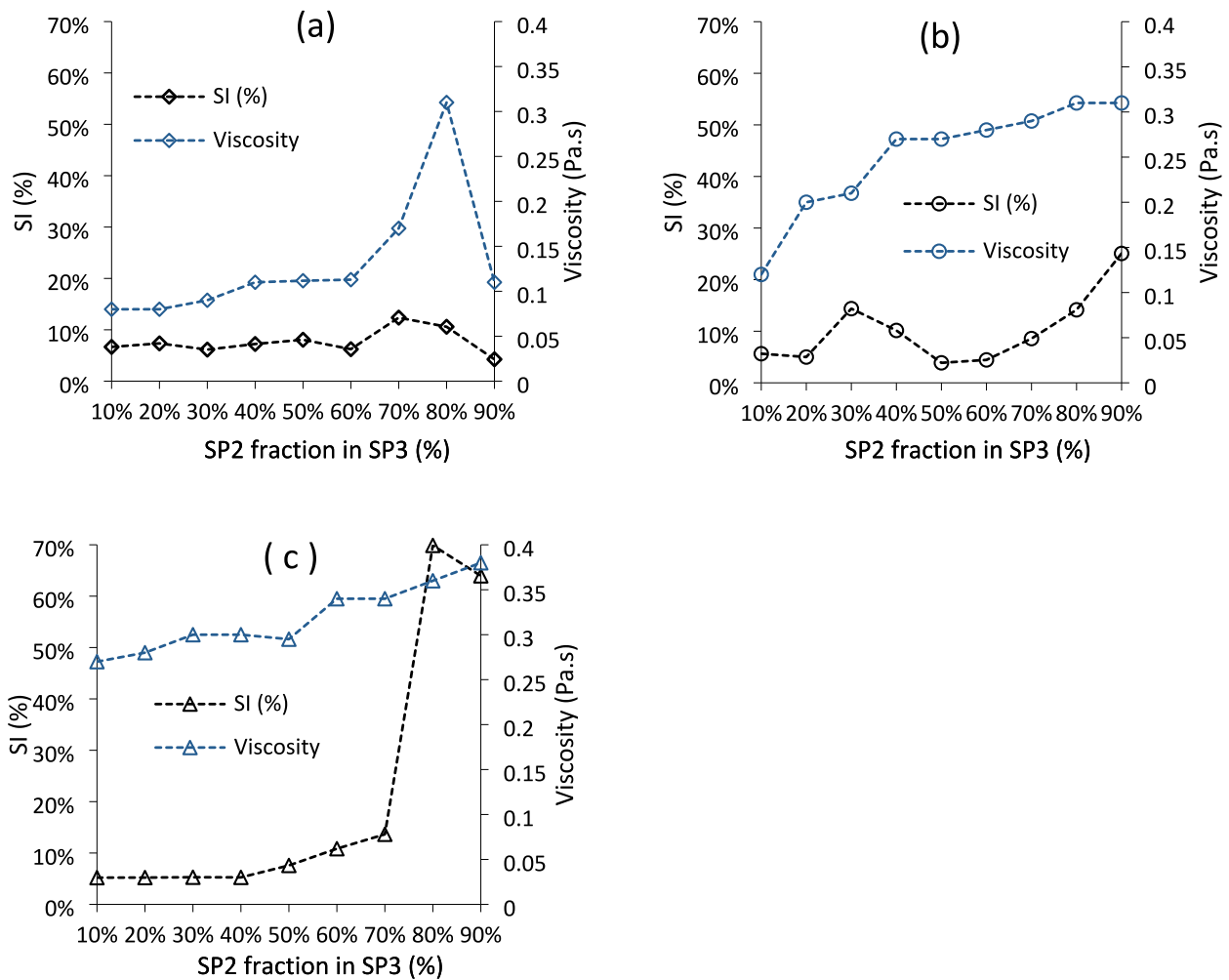


Fig. 6. The effect of cement paste viscosity on corresponding cement mortar segregation (a) CEM A; (b)CEM B; (c) CEM C.

low superplasticiser adsorption behaviour experienced at these blended SP proportions [15]. In particular, the SP adsorption seemed to increase with increase SP2 fraction for CEM A while for CEM B and CEM C this was only observed at low SP2 fractions up to 40%. Further increases of SP2 fractions did not affect the adsorption ability.

It is assumed that these adsorption properties are related to the group function of each SP blend as highlighted in section 3.2 and reported in [13,15].

SP1 had long and thin polymers while SP2 had shorter and thicker side chains which could have resulted in delayed adsorption onto the cement particles. Moreover, SP2 had a lower molecular mass than SP1 which resulted in an interesting combination as shorter chains and greater molecular mass of polymers are much more effective with regard to adsorption according to Feng et al. [15].

4. Conclusion

The effect of yield stress and viscosity of cement paste on the static segregation and bleeding in cement mortar systems were investigated in this study by blending two superplasticisers at varying fractions in the presence of three different cements. This allowed producing cement pastes with different yield stress values which were used to assess the stability of corresponding cement mortar systems. Cement system stability was measured at mortar scale while their rheological and adsorption behaviour at cement paste scale. Cement mortar systems stability were associated to their cement paste rheological performances. These rheological performances were mostly related to the

chemical and physical properties of materials used that defined their interactions within the system. Results, of this study confirmed the following;

1. It is possible to improve the effectiveness of SPs by blending two different SPs. However, it is advised that this blending be done after reactant SP optimisations. This is to assure that they are operating at their individual maximum effectiveness. In general, it was observed that increasing the SP2 fraction within the blended SP3 enhanced its dispersion ability, thereby reducing the yield stress value of the cement system.
2. The mechanism defined in this research work for mortar stability could be extended on concrete level for industrial use by considering aggregate effects and ambient temperature during placement. This enables admixture companies to produce more effective SPs for SCC manufacturing with possibilities to contain production costs based on SP blending.
3. The adsorption ability of superplasticiser products largely depends on the group function of reactant SPs and the characteristics of cements used. Low SP3 adsorption occurred at low SP2 fractions due to their shorter side chains and lower molecular weight that slowed down the adsorption property of SP on cement particles as opposed to SP1 with long side chain and heavy molecular weight that favours faster SP adsorption. This determined the rheological behaviour of different cement pastes in the presence of the blended SP. High yield stress and low plastic viscosity cement pastes were therefore obtained at low SP2 fractions.

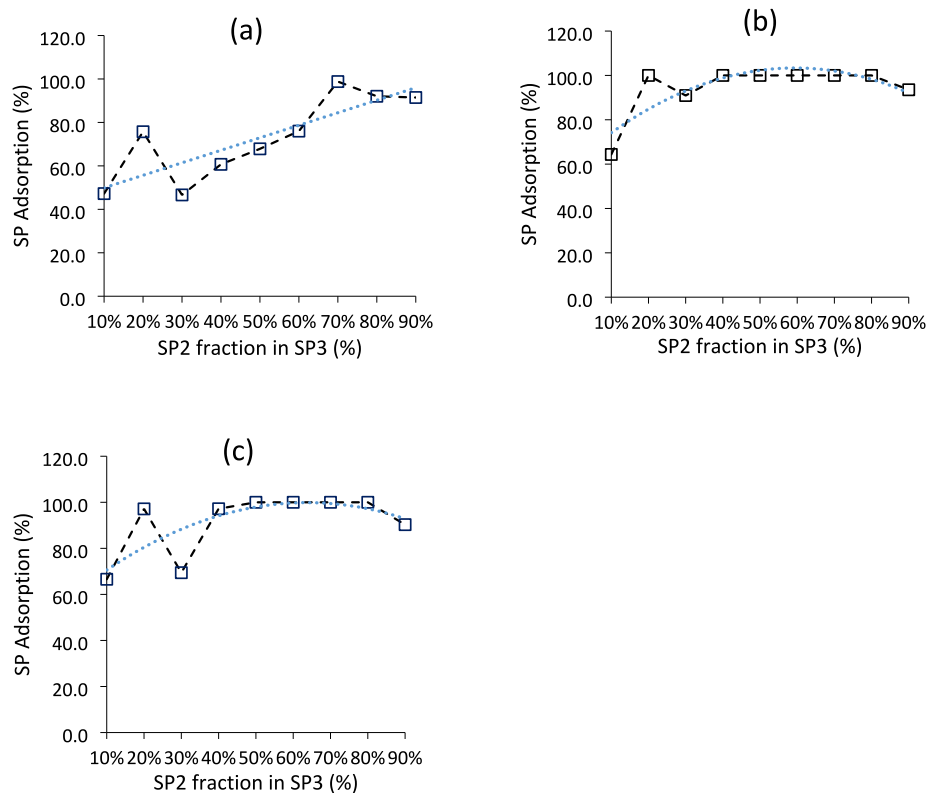


Fig. 7. Adsorption of superplasticizer at optimum dosage of 0.3% on cement; (a) CEM A; (b) CEM B; (c) CEM C.

- Cement mortars with high yield stress cement pastes resulted in more stable cement system with lower segregation index values while those with low yield stress values resulted in unstable cement systems with higher segregation indexes. It is however suggested that the overall stability of a cement mortar system cannot be defined by only considering one rheological parameter (plastic viscosity) as proposed currently in the literature, but both yield stress and viscosity should be considered and tailored for a desired mortar stability.
- The bleeding of cement mortar was found to not directly depend on the rheological performance of corresponding cement paste and was presumably associated to physical interactions that take place within the overall system during the cement hydration processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

- W. Yan, W. Cui, L. Qi, Effect of aggregate gradation and mortar rheology on static segregation of self-compacting concrete, *Constr. Build. Mater.* 259 (2020), 119816.
- C.M. Stolz, A.B. Masuero, Influence of grains distribution on the rheological behavior of mortars, *Constr. Build. Mater.* 177 (2018) 261–271.
- A. Yahia, M. Tanimura, Y. Shimoyama, Rheological properties of highly flowable mortar containing limestone filler-effect of powder content and w/c ratio, *Cem. Concr. Res.* 35 (3) (2005) 532–539.
- N. Rousset, A Theoretical Frame to Study Stability of Fresh Concrete, *Mater. Struct.* 39 (1) (2007) 81–91.
- M. Westerholm, B. Lagerblad, J. Silfwerbrand, E. Forssberg, Influence of fine aggregate characteristics on the rheological properties of mortars, *Cem. Concr. Compos.* 30 (4) (2008) 274–282.
- J. Zhu, X. Shu, J. Tang, T. Li, Q. Ran, J. Liu, Effect of microfiners from manufactured sand on yield stress of cement paste, *Cement Build. Mater.* 267 (2021), 120987.
- N. Tregger, A. Gregori, L. Ferrara, S. Shah, Correlating dynamic segregation of self-consolidating concrete to the slump-flow test, *Constr. Build. Mater.* 28 (1) (2012) 499–505.
- Abeyruwan, H. 2016. Yield Shear Stress of Cementitious Mortar for Self-Compacting Concrete. The 7th International Conference on Sustainable Built Environment, (December).
- A. Leemann, F. Winnefeld, The effect of viscosity modifying agents on mortar and concrete, *Cem. Concr. Compos.* 29 (5) (2007) 341–349.
- A. Perrot, T. Lecompte, H. Khelifi, C. Brumaud, J. Hot, N. Rousset, Yield stress and bleeding of fresh cement pastes, *Cem. Concr. Res.* 42 (7) (2012) 937–944.
- F.J. Rubio-Hernández, J.F. Velázquez-Navarro, L.M. Ordóñez-Belloc, Rheology of concrete: A study case based upon the use of the concrete equivalent mortar, *Materials and Structures/Materiaux et Constructions* 46 (4) (2013) 587–605.
- Y.A. Abebe, L. Lohaus, Rheological characterization of the structural breakdown process to analyze the stability of flowable mortars under vibration, *Constr. Build. Mater.* 131 (2017) 517–525.
- F. Winnefeld, S. Becker, J. Pakusch, T. Götz, Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems, *Cem. Concr. Compos.* 29 (4) (2007) 251–262.
- E. Janowska-Renkas, The effect of superplasticizers' chemical structure on their efficiency in cement pastes, *Constr. Build. Mater.* 38 (2013) 1204–1210.
- H. Feng, L. Pan, Q. Zheng, J. Li, N. Xu, S. Pang, Effects of molecular structure of polycarboxylate superplasticizers on their dispersion and adsorption behavior in cement paste with two kinds of stone powder, *Constr. Build. Mater.* 170 (2018) 182–192.
- K. Matsuzawa, D. Shimazaki, H. Kawakami, E. Sakai, Effect of non-adsorbed superplasticizer molecules on fluidity of cement paste at low water-powder ratio, *Cem. Concr. Compos.* 97 (June 2018) (2019) 218–225.
- H.K. Choudhary, A.V. Anupama, R. Kumar, M.E. Panzi, S. Matteppanavar, B. N. Sherikar, B. Sahoo, Observation of phase transformations in cement during hydration, *Constr. Build. Mater.* 101 (2015) 122–129.
- M. Liu, J. Lei, L. Guo, X. Du, J. Li, The application of thermal analysis, XRD and SEM to study the hydration behavior of tricalcium silicate in the presence of a polycarboxylate superplasticizer, *Thermochim Acta* 613 (1) (2015) 54–60.
- H. Bessaies, J. Hot, R. Baumann, N. Rousset, Cement & Concrete Composites Consequences of competitive adsorption between polymers on the rheological behaviour of cement pastes, *Cem. Concr. Compos.* 54 (2014) 17–20.
- L. Zeghichi, Z. Benghazi, L. Baali, The effect of the kind of sands and additions on the mechanical behaviour of S, C. C. *Physics Procedia* 55 (2014) 485–492.

- [21] N. Su, K.-C. Hsu, H.-W. Chai, A simple mix design method for self-compacting concrete, *Cem. Concr. Res.* 31 (12) (2001) 1799–1807.
- [22] EFNARC. 2005. *The European Guidelines for Self-Compacting Concrete. The European Guidelines for Self Compacting Concrete*, (May): 63.
- [23] N.A. Libre, R. Khoshnazar, M. Shekarchi, Relationship between fluidity and stability of self-consolidating mortar incorporating chemical and mineral admixtures, *Constr. Build. Mater.* 24 (7) (2010) 1262–1271.
- [24] ASTM C1610. ASTM C1610M-06: Standard Test Method for Static Segregation of Self-Consolidating Concrete Using Column Technique. West Conshohocken (PA): ASTM International; 2006.
- [25] M. Mahdikhani, A.A. Ramezani-pour, New methods development for evaluation rheological properties of self-consolidating mortars, *Constr. Build. Mater.* 75 (2015) 136–143.
- [26] Z. Tan, S.A. Bernal, J.L. Provis, Reproducible mini-slump test procedure for measuring the yield stress of cementitious pastes, *Materials and Structures/Materiaux et Constructions* 50 (6) (2017) 1–12.
- [27] A. Bouvet, E. Ghorbel, R. Bennacer, The mini-conical slump flow test: Analysis and numerical study, *Cem. Concr. Res.* 40 (10) (2010) 1517–1523.
- [28] N. Roussel, P. Coussot, “Fifty-cent rheometer” for yield stress measurements: From slump to spreading flow, *J. Rheol.* 49 (3) (2005) 705–718.
- [29] ASTM C940. ASTM C940-98a(2003): Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory. West Conshohocken (PA); ASTM International; 1998.
- [30] Y. Ji, Z. Sun, X. Jiang, Y. Liu, L. Shui, C. Chen, Fractal characterization on pore structure and analysis of fluidity and bleeding of fresh cement paste based on 1H low-field NMR, *Constr. Build. Mater.* 140 (2017) 445–453.
- [31] Y. Ji, Z. Sun, X. Yang, C. Li, X. Tang, Assessment and mechanism study of bleeding process in cement paste by 1H low-field NMR, *Constr. Build. Mater.* 100 (2015) 255–261.
- [32] A. Bahurudeen, A.V. Marckson, A. Kishore, M. Santhanam, Development of sugarcane bagasse ash based Portland pozzolana cement and evaluation of compatibility with superplasticizers, *Constr. Build. Mater.* 68 (2014) 465–475.
- [33] H. Toutanji, C. Goff, K. Pierce, H. Fares, Using aggregate flowability testing to predict lightweight self-consolidating concrete plastic properties, *Cem. Concr. Compos.* 62 (2015) 59–66.
- [34] S.K. Ling, A.K.H. Kwan, Adding ground sand to decrease paste volume, increase cohesiveness and improve passing ability of SCC, *Constr. Build. Mater.* 84 (2015) 46–53.
- [35] P. Juilland, A. Kumar, E. Gallucci, R.J. Flatt, K.L. Scrivener, Effect of mixing on the early hydration of alite and OPC systems, *Cem. Concr. Res.* 42 (9) (2012) 1175–1188.
- [36] M.F. Petrou, B. Wan, F. Gadala-Maria, V.G. Kolli, K.A. Harries, Influence of mortar rheology on aggregate settlement, *ACI Struct. J.* 97 (4) (2000) 479–485.
- [37] Y. Cai, Q.-F. Liu, L. Yu, Z. Meng, Z. Hu, Q. Yuan, B. Šavija, An experimental and numerical investigation of coarse aggregate settlement in fresh concrete under vibration, *Cement Concrete Compos.* 122 (2021), 104153.
- [38] T. Bronk, M. Haist, L. Lohaus, The Influence of Bleeding of Cement Suspensions on Their Rheological Properties, *Materials (Basel)* 13 (2020) 1609.
- [39] T.S. Tan, T.H. Wee, S.A. Tan, C.T. Tam, S.L. Lee, A consolidation model for bleeding of cement paste, *Adv. Cem. Res* 1 (1) (1987) 18–26.
- [40] J. Liu, K. Wang, Q. Zhang, F. Han, J. Sha, J. Liu, Influence of superplasticizer dosage on the viscosity of cement paste with low water-binder ratio, *Construction and building materials* 149 (2017) 359–366.
- [41] A. Bognera, J. Link, M. Baum, M. Mahl, M. Macherb, T. Gil-Diaz, J. Lützenkirchen, T. Sowoidnich, F. Heberling, T. Schäfer, H.M. Ludwige, F. Dehna, H.S. Müllera, M. Haist, Early hydration and microstructure formation of Portland cement paste studied by oscillation rheology, isothermal calorimetry, 1H NMR relaxometry, conductance and SAXS, *Cement Concrete Res.* 130 (2020).