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Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures

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Abstract

An experimental methodology to study the rheological response of superplasticised cement pastes subjected to temperatures ranging from 5 to 45 °C is presented. The content of a polycarboxylate-based superplasticiser (PC) and moment of its addition to the mix (direct or delayed) are investigated. A loop of shear rate ramps is applied to each sample in order to obtain information about apparent viscosities and yield stresses, as well as a measure of their thixotropic behaviour. Results from the experimental campaigns indicate PC saturation dosages depend only slightly on temperature. The evolution of yield stress and thixotropy with temperature shows inverted trends under some conditions.

Keywords: Rheology; Temperature; Cement paste; High-range water reducers; Polycarboxylate

1. Introduction

The flow properties of fresh concrete are affected by a large number of parameters, including not only cement content and composition and type and dosage of surfactant agents, but also composition, morphology and grain distribution of aggregates, environmental conditions, as well as the energy and sequence of mixing. Such a large variety of factors playing a significant role on concrete rheology lead to the inherent difficulty in comparing different sets of results from different laboratories and, consequently, the establishment of standard methods for the quantification of the rheological properties of cementitious materials in the fresh state.

One of the key issues in understanding the interactions between cement particles (or their hydrates) and surfactant agents such as superplasticisers is the influence of environmental temperature on the early stage evolution of cement pastes. This study aims at contributing to better understand the flow behaviour that superplasticised cement pastes exhibit under different temperatures by considering the process followed in their preparation, with special attention to the moment at which the superplasticiser is added to the mix. Different superplasticiser dosages and degrees of shearing are considered on delivering values of yield stress, apparent viscosity and thixotropy. In order to achieve this, a detailed experimental procedure has been designed as a basis for quantitative comparison for interlaboratory measurements.

Previous studies on this topic have addressed a variety of issues and used different techniques to carry out measurements of relevant properties. In the first comprehensive study on the influence of temperature on the flow properties of cement-based pastes, Jolicoeur et al. reported measurements of fluidity and rate of loss of fluidity of concentrated pastes ($w/c = 0.35$) at temperatures ranging from 0 to 40 °C [1]. Other parameters considered in their study were time after preparation of samples, dosage of a polynaphthalene sulphonated (PNS) superplasticiser and content of silica fume. Temperature was found to increase the fluidity of the pastes but tended to invert the trend when these incorporated silica fume. These results correlated to the adsorption ratio of the PNS. In addition, the concentration of non-adsorbed PNS correlated with fluidity beyond a threshold PNS dosage, suggesting that this fraction of the total admixture exerted a certain contribution to the overall fluidity [2]. Similar studies based on Marsh cone tests [3] were conducted by Roncero et al. for different types of superplasticisers based on

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polycarboxylate, polynaphthalene, polymelamine and a blend of the two latter [4–6]. Interestingly, in the range of 5 to 45 °C, they found that the saturation dosage, i.e. the superplasticiser dosage beyond which no significant increase in the fluidity is obtained, was independent of temperature. Also, correlation in the trends for cement, mortar and concrete pastes was observed. Results obtained with the Marsh cone, though, are purely qualitative since they are referred to the time that takes a fixed volume of the sample to empty the cone by the action of gravity. The interpretation of these results is limited, among other factors, because the shear rate at which the fluid is subjected is unknown and changing over the course of the test. Actually, different consistencies of the samples imply different shear rates. Thus, very fluid samples rapidly empty the cone experiencing high shear rates, whereas very viscous samples empty the cone at low shear rates. This should be taken into account when conducting comparative studies that involve non-Newtonian fluids.

Griesser et al. investigated the interactions between different types of cement and superplasticisers [7,8]. They studied the flow behaviour of cement, mortar and concrete pastes by means of a rotational viscometer that only allowed them to deliver data in units of torque. Therefore, the evaluation was made in terms of relative viscosity and relative yield value, as named by the authors. One of the main results reported in those studies is the effect of non-adsorbed superplasticiser and sulphate ions on the rheological responses observed at 8, 20 and 30 °C. The dependence of yield stress with temperature was found to be very specific to the combination of each type of cement and superplasticiser, although always uniform for each particular system. Yet, the content of tricalcium aluminate and sulphate alkalis in the cement had a predominant influence on the specific trend. On the other hand, apparent viscosity always decreased with temperature.

2. Experimental

2.1. Materials and equipment

Cement type I-52.5 R, distilled water and the commercial polycarboxylate-based superplasticiser (PC) Sika ViscoCrete 5-700® were used in all mixes. Cement was stored as received in plastic containers in the same room where the mixes were prepared. The composition and physical parameters of cement are given in Table 1. The admixture was supplied as a brown suspension with 38% of solid content and a density of 1090 kg·m^{-3}.

A Toni Technik 6902 mixer was used to prepare the cement pastes. This planetary mixer operates at two different gears: 140 rpm of revolving speed and 62 rpm of planetary speed, in the case of low gear, and 285 rpm of revolving speed and 125 rpm of planetary speed, in the case of high gear.

Rheological data were obtained with the coaxial cylinder viscometer VT 550 (Thermo Haake®). Profiled bob MV 2P (Haake®) and cup MVP (Haake®) were used in order to prevent possible slippage during the measurements. The dimensions of the bob and the cup were: h = 60.05 mm, R_i = 18.40 mm and h = 94.40 mm, R_o = 21.00 mm, respectively. Thus, the gap between them was 2.60 mm and the radii ratio was 1.14. The lateral surface of the bob and the cup contained 98 and 93 grooves, respectively. The grooves were 0.30 mm deep in the bob and 0.33 mm deep in the cup. The repeatability of the system was certified to be ±2% according to the manufacturer. The cup was fitted into a thermal vessel which was connected to a K10 thermostat (Haake®) operating at a precision of ±0.1 °C. Viscometer operation and measurements were computer-controlled using RheoWin 2.97 software (Haake®).

Table 1
Physicochemical characterisation of cement I-52.5 R

Chemical composition	Mass (%)
SiO_2	19.86
Al_2O_3	5.61
Fe_2O_3	3.40
CaO	62.38
MgO	2.14
SO_3	3.36
K_2O	0.97
Na_2O	0.15
Na_2O eq.	0.78
LOI	2.14
Bogue composition	**Mass (%)**
C_3S	50.86
C_2S	18.57
C_3A	9.13
C_4AF	10.34
Physical properties	
Blaine fineness	488 m^2/kg
2-day compressive strength	41.8 MPa
28-day compressive strength	63.6 MPa
Vicat initial setting time	85 min
Vicat final setting time	165 min

2.2. Conditions of preparation of mixes

Batches of 1.5 kg of cement pastes were prepared at a room temperature of 21 ± 1 °C, all of them at a water-to-cement ratio of 0.33. Two series of batches were prepared, each following a different mixing sequence concerning the introduction of the PC in the mixes, as described below. For both mixing procedures, the batches were prepared at PC dosages corresponding to 0.2%, 0.3%, 0.5%, 0.7%, 0.9% and 1.1% of solid content of the commercial suspension in relation to weight of cement (% sp/c). After overall 5 min of mixing at room temperature, over 80 mL of the batches were extracted from the mixer, of which 60 mL were used for each rheological test. The lapse between sampling from the mixer and the beginning of the test was 2 min. Different batches were prepared according to this procedure and measured at 5, 15, 25, 35 and 45 °C.

Cement was weighed with a precision of 0.1 g in a ceramic bowl and then transferred to the mixer cup. Water was weighed with a precision of 0.1 g in a 600-mL beaker. The necessary weight of superplasticiser suspension was introduced in a syringe as weighed by difference with a precision of 0.001 g.

The use of the syringe allowed to establish the actual dosages of superplasticiser with high accuracy and repeatability, something that is more difficult when this is not directly dissolved in the mixing water.

2.3. Mixing sequences

Two different methods of adding the superplasticiser have been used in this study. In the direct addition procedure, the commercial PC was diluted in distilled water and the resulting suspension was poured onto the cement in the mixer. 15 s later, a two-stage (low-speed and high-speed, 2.5 min each) stirring programme was applied to the mixes in order to produce homogeneous pastes for the rheological measurements.

In the delayed addition sequence, cement and distilled water were mixed for 2.0 min at low speed. The mixer was then stopped and the commercial PC was continuously spread onto the mix from the syringe. At the same time, special care was taken in assuring that the paste stuck at the walls and at the paddle of the mixer was scraped down to the bottom of the mixer cup. After 2.5 min of manual homogenisation of the superplasticiser in the paste, the mixer was restarted to apply a sequence consisting of 30 s of low speed stirring plus 2.5 min of high speed stirring.

Samples from both mixing sequences were introduced in the viscometer for rheological testing after 5 min of stirring in the mixer and 2 min of static hydration. In the case of delayed addition, 2.5 extra minutes were required to assure that all the mass of initial paste could be mixed with the superplasticiser introduced. A detailed scheme of the mixing sequences is given in Fig. 1.

2.4. Rheological measurements

Immediately after introduction in the viscometer, samples were subjected to a pre-shearing stage during 330 s at a shear rate of 5 s^{-1} in order to assure that thermal equilibrium between the paste and the vessel was attained. After 60 s at rest, a loop of shear rate ramps was applied including a linear 5-min upwards ramp from 0 to 100 s^{-1}, 60 s at maximum shear rate and an analogous downwards ramp from 100 s^{-1} to rest. This measurement programme is depicted in Fig. 2.

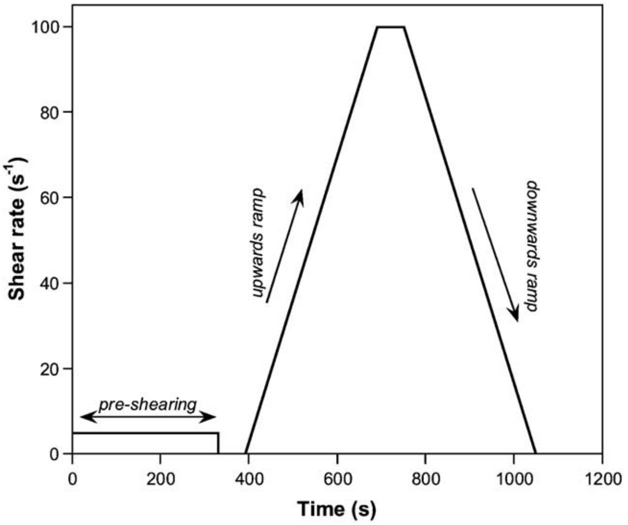

Fig. 2. Measurement programme applied with the VT 550 viscometer. Actual acquisition of data started with the upwards ramp, 60 s after the completion of a pre-shearing stage of 330 s at 5 s^{-1}. The ramps were scanned at a rate of 20 s^{-1}/min and recorded 263 data points each.

3. Results and discussion

3.1. Flow curves

The wide range of conditions tested in this work, especially of temperature and superplasticiser dosage, produced a variety of types of flow curves. The influence of temperature on the rheological behaviour of the pastes can be studied in plots of the variation of the shear stress as a function of increasing (upwards curve) and decreasing (downwards curve) shear rates applied to the samples (Fig. 3). It can be observed that, while viscosity

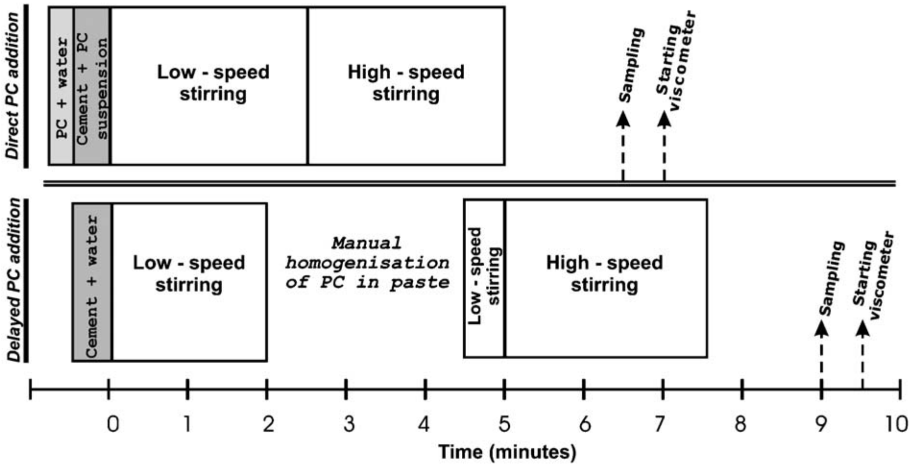

Fig. 1. Timing of the mixing sequences investigated. *Direct PC addition*: the commercial polycarboxylate is diluted in distilled water and the resulting suspension is poured on the cement powder prior to be subjected to stirring. *Delayed PC addition*: the commercial polycarboxylate is introduced in the mix after 2 min of pre-mixing cement and distilled water.

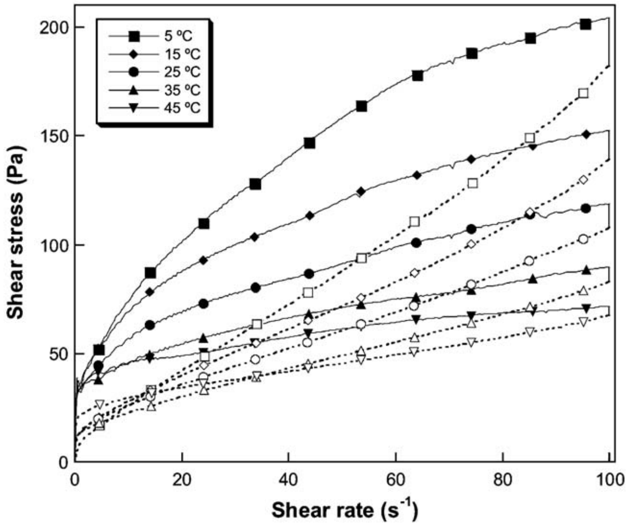

Fig. 3. Flow curves of samples prepared by direct addition of 0.3% of PC at 21 ± 1 °C and subsequently subjected to different temperatures. Upwards flow curves are depicted in solid lines and symbols; downwards flow curves are depicted in dashed lines and empty symbols.

(slope of the flow curves) is substantially affected by temperature in the studied range (5–45 °C), values of the yield stress (ordinate at zero shear rate) show little variation, especially in the case of upwards flow curves.

The high resolution of the rheometric tests carried out in this work reveal a complex rheological behaviour for some cement pastes. This was only observed in upwards flow curves, and may be a consequence of the extent and type of microstructure that forms during the stages previous to the application of the shearing loop. Such microstructure must be broken down to a large extent at the point of initiating the downwards ramp, since the profile of the downwards flow curves tends to be more linear. In general, the upwards flow curves exhibit a pseudoplastic behaviour, which is considered by some authors as a especial case of thixotropy in which breakdown and rebuilding of the structure occur simultaneously [9,10]. The fact that the apparent viscosity in such flow curves decreases with shear rate cannot be exclusively attributed to a shear thinning behaviour of the samples, but also to the structural breakdown that are undergoing during the test [11]. Either way, attempting to discriminate between the contributions of shear thinning and structural breakdown in the observed behaviour is beyond the scope of this work.

3.2. Apparent viscosity

In order to study the variation of apparent viscosity as a function of PC dosage and mixing sequence, values of apparent viscosity obtained from the upwards flow curves (η_{upw}) at a shear rate of $40\,\mathrm{s}^{-1}$ are plotted in Fig. 4. This shear rate has been arbitrarily chosen as representative of the value of η_{upw} measured at each temperature. It is well known that the delayed addition of superplasticisers in cement-based mixes (e.g. Fig. 1) enhances significantly the effectiveness of their dispersing power in comparison to the direct addition [12–15]. This is because in the latter a higher fraction of superplasticiser molecules becomes entrapped in early-forming hydrate layers and, consequently, lose their action as dispersing agents [16]. The molecular structure of polycarboxylate-based superplasticisers makes this difference in effectiveness less marked in comparison to other types of superplasticisers, namely, polynaphthalene or polymelamine sulphonate derivates. In this study, comparison between direct (Fig. 4a) and delayed (Fig. 4b) addition of the PC yields such an expected result, since the values of η_{upw} are lower in the latter procedure for most of the conditions tested, i.e. dosages above 0.2% and any temperature. The differences are more marked, though, as temperature and dosages of PC are lower (5–15 °C, below 0.5%). Note that both sets of data presented in Fig. 4 exhibit parallelism between η_{upw}–PC dosage curves for most of the PC dosages and temperatures tested. This evidences the chemical stability of these superplasticised cement suspensions in the time intervals used for the experiments. On the contrary, under conditions of low content of PC (0.2–0.3%) introduced in the mixes through

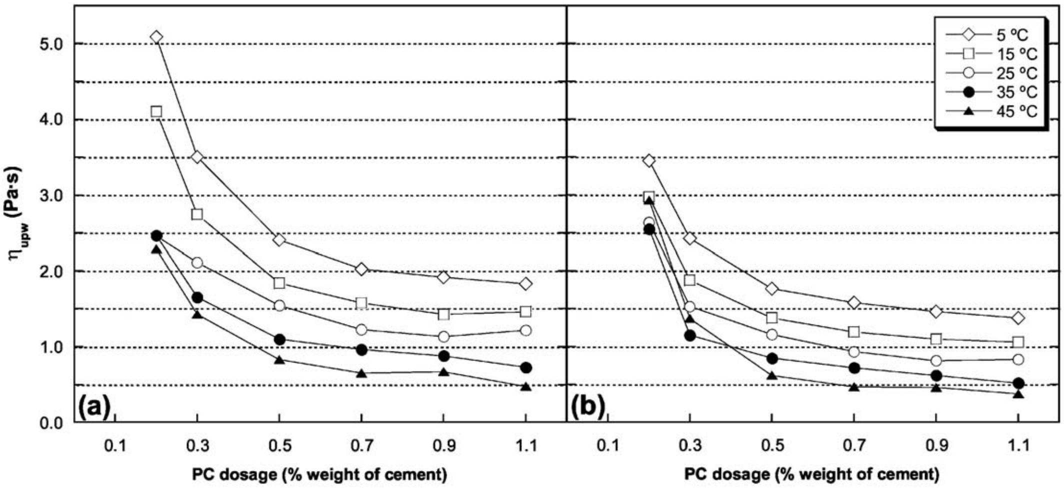

Fig. 4. Apparent viscosity at $40\,\mathrm{s}^{-1}$ from the upwards shear rate ramp as a function of PC dosage for mixes prepared by direct (a) and delayed (b) addition of PC and subjected to temperatures ranging from 5 to 45 °C during the rheological test.

delayed addition (Fig. 4b), the increase of temperature did not produce a monotonic decrease of η_{upw}, as expected for chemically stable suspensions, but rather inverted the trend up to the point of resulting in a net increase of η_{upw} for temperatures above 35 °C. This is indicative of a rapid growth of hydrates in the samples while the rheological test is run. This cross-over effect in the set of curves in Fig. 4b, as well as all the above-mentioned trends, remained the same for apparent viscosities calculated at any shear rate between 0 and 100 s^{-1}, although became more pronounced at low shear rates.

The forces to which samples are subjected during the measurement of upwards flow curves produce partial or total destruction of their microstructure. As a result of this, values of apparent viscosity measured under decreasing shear rate conditions (η_{dwn}; dotted curves in Fig. 3) are, in general, significantly lower than their equivalent η_{upw} at the same temperature and PC dosage, as evidenced in Fig. 5. On the other hand, for a given PC dosage, the effect of temperature seems less important for η_{dwn} than it was for η_{upw}. Interestingly, the above-mentioned cross-over effect is also present in the direct PC addition procedure, reaching values even higher than those of delayed PC addition (Fig. 5b) at temperatures of 35–45 °C and PC dosages of 0.2% and 0.3%. This indicates that the effect of shearing is not only to orientate the particles in suspension but also to break down the weak bonds between the particles forming agglomerates. The dissociation of the initial agglomerates produces finer ones and, therefore, a higher surface area exposed to the aqueous phase. When the concentration of superplasticiser in the aqueous phase of the suspensions (low dosages of PC) is insufficient in relation to the surface area to adsorb on, rapid hydration occurs at high temperatures and thus apparent viscosities increase.

3.3. Yield stress and saturation dosage

Determination of the yield stress (τ_0) of cement-based pastes is generally carried out by modelling the behaviour of flow curves (e.g. Fig. 3) and calculating the value for the shear stress at zero shear rate. However, this approach often yields to large discrepancies in the estimated value of τ_0 depending on the rheological model used [17,18].

The tests in this study cover a wide variety of conditions of temperature and dosages of superplasticiser. As it usually happens in attempting to quantify the behaviour of cement pastes, conventional rheological models are unable to provide comparable fits for different flow curves such as those shown in Fig. 3, especially at low shear rates. In view of this, and in order to provide a basis for comparison, τ_0 in this work is reported as the experimental shear stress value obtained at 1.2 s^{-1}. It has been reported that, for some systems, shear stress values measured by controlled-rate and controlled-stress techniques start to be coincident at 1.0 s^{-1} [19], as also suggested in our experiments at different temperatures (Fig. 6). This method of estimating τ_0 minimises the errors associated with the lack of sensitivity of rheological models at low shear rates and provides a physical (and not purely numerical) basis for comparison of the behaviour of cement pastes studied in this work; accordingly, it has been applied to the estimation of the static ($\tau_{0,s}$) and dynamic yield stress ($\tau_{0,d}$) values from upwards and downwards flow curves, respectively [20]. Thus, in Fig. 7, values of $\tau_{0,s}$ are plotted as a function of PC dosage, for different temperatures and for the two mixing sequences studied. Unlike values of apparent viscosity, $\tau_{0,s}$ is hardly affected by temperature, especially between 5 and 25 °C. Yet, the effect of delaying the addition of PC is again to lower the $\tau_{0,s}$ values, regardless of the temperature and PC dosage.

We can define *saturation dosage* (of superplasticiser) as the dosage beyond which higher contents of superplasticiser do not decrease the τ_0 value significantly. This parameter is important since an excess of superplasticiser can induce substantial retardation of the setting and bleeding. In this study, a saturation dosage of 0.7% (more clearly at temperatures between 5 and 25 °C) is observed for samples subjected to direct addition of superplasticiser (Fig. 7a), whereas for the delayed addition experiments (Fig. 7b) saturation occurs between 0.7% (at 45 °C) and 0.9% (5–25 °C). This dependence with temperature was not

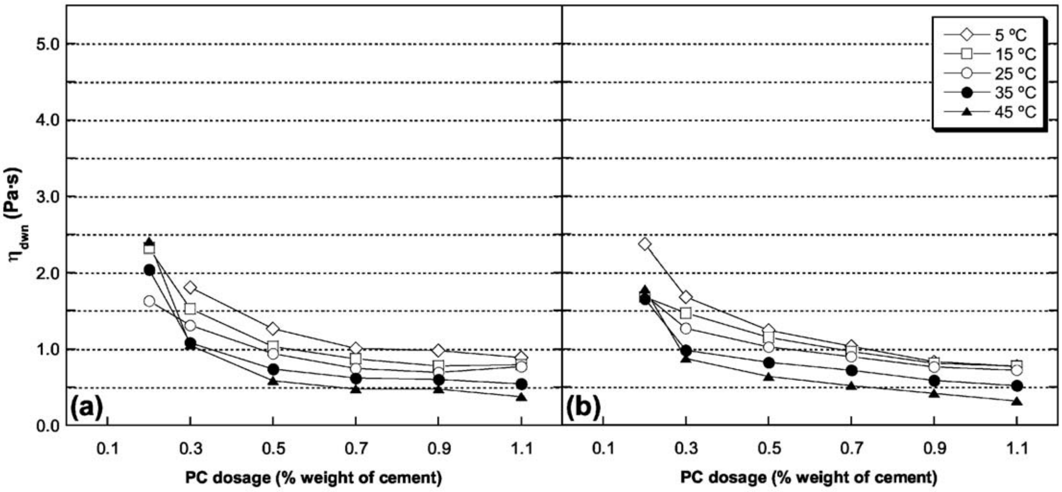

Fig. 5. Apparent viscosity at 40 s^{-1} from the downwards shear rate ramp as a function of PC dosage for mixes prepared by direct (a) and delayed (b) addition of PC and subjected to temperatures ranging from 5 to 45 °C during the rheological test.

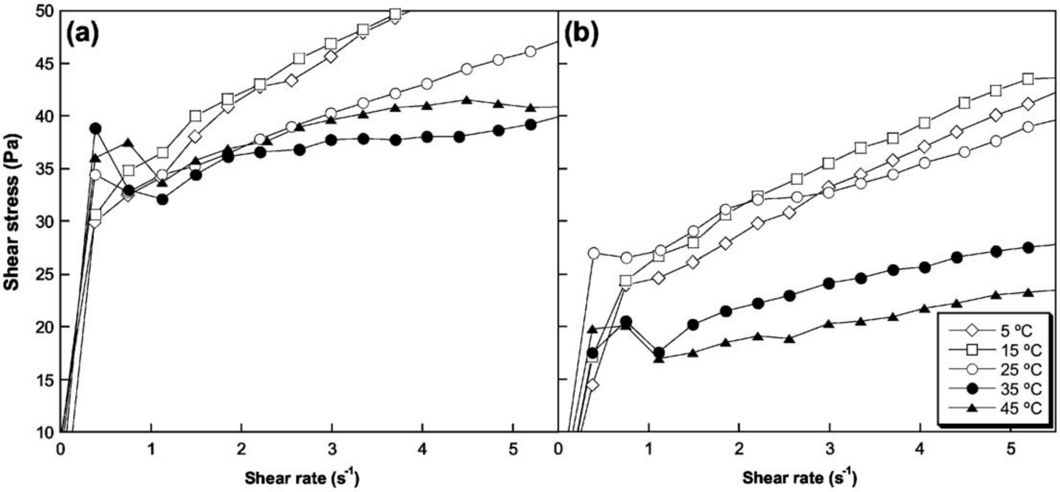

Fig. 6. Low shear rates section of flow curves corresponding to the upwards shear rate ramps in the designed measurement programme for pastes prepared by direct (a) and delayed (b) addition of 0.3% PC and subjected to temperatures ranging from 5 to 45 °C during the rheological test.

detected in previous studies where cement pastes were prepared following similar procedures but measurements were undertaken with the Marsh cone [4,6].

The dynamic yield stress is the yield stress value that remains in a material after having been sheared. In Fig. 8, values of $\tau_{0,d}$ are plotted as a function of PC dosage, for different temperatures and for the two mixing sequences studied. Both in the direct and in the delayed addition of PC, the $\tau_{0,d}$ values were always lower than equivalent $\tau_{0,s}$ values. The dependence of $\tau_{0,d}$ with temperature was similar to that for $\tau_{0,s}$. The abrupt increase in $\tau_{0,d}$ values at lower PC dosages is more marked, in relative terms, in the procedure of direct addition of PC.

The saturation dosage, as defined above, was around 0.5% for both procedures of addition of PC. This value was lower than those obtained from the determination of $\tau_{0,s}$, which ranged from 0.9% to 0.7% depending on the conditions tested. This indicates that, in spite of containing less PC, the effect of shearing is sufficient as to make extra addition of superplasticiser futile in terms of minimising $\tau_{0,s}$. Temperature did not affect the value of saturation dosage in any case. In addition, for PC dosages equal or higher than 0.5%, the $\tau_{0,s}$ values were close to zero. This indicates that the structure that may be formed by the particles of the suspension before the application of the shearing was destroyed to a large extent after the completion of the measurement programme. In particular, no structure could settle as shearing decreased through the downwards ramp in the scale of time of work.

3.4. Thixotropy

Some fluids subjected to a constant shear rate experiment a decrease in their viscosity with time toward an asymptotic value. If the material recovers its initial viscosity some time after the strain has ceased, this phenomenon is named thixotropy. Such fluids exhibit hysteresis in response to the application of a shear rate or shear stress loop. This property is

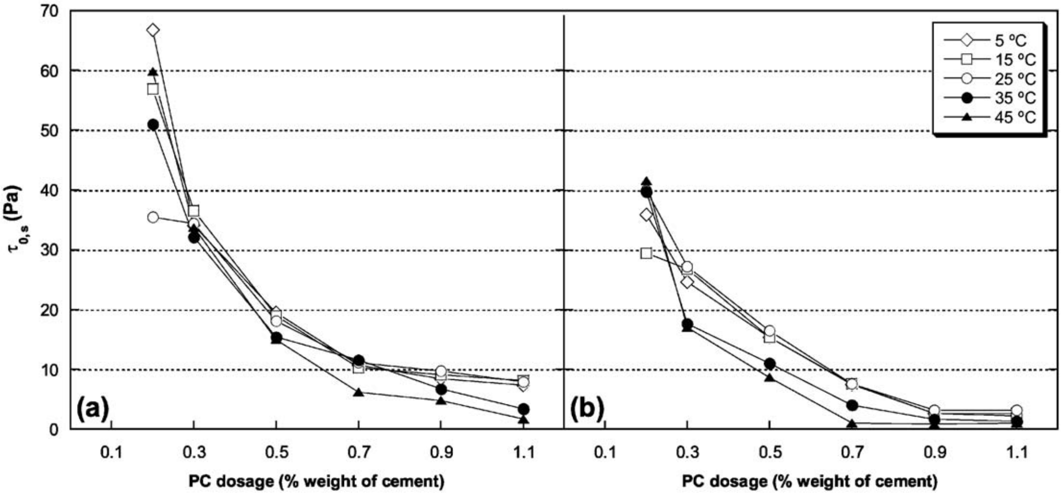

Fig. 7. Estimated static yield stress (from upwards flow curve) as a function of PC dosage for mixes prepared by direct (a) and delayed (b) addition of PC and subjected to temperatures ranging from 5 to 45 °C during the rheological tests.

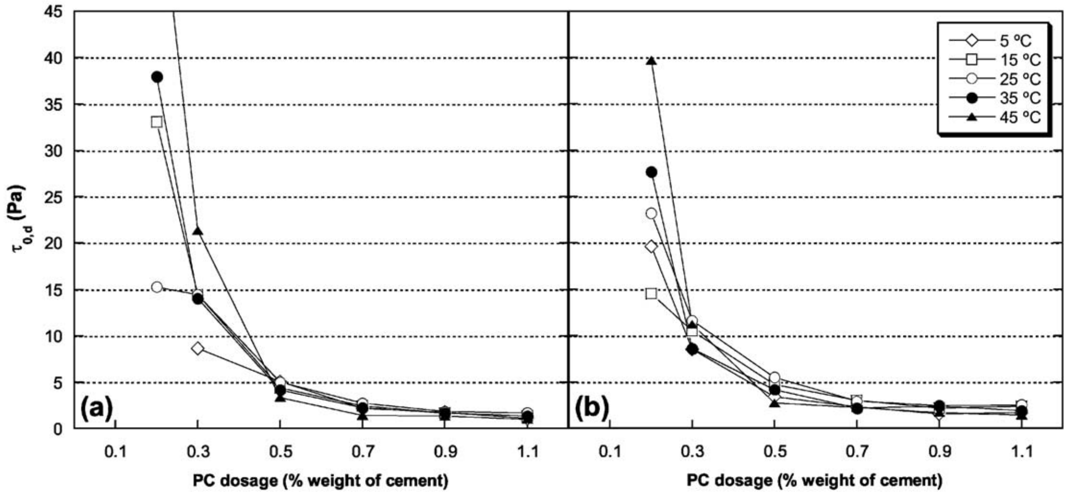

Fig. 8. Estimated dynamic yield stress (from downwards flow curves) as a function of PC dosage for mixes prepared by direct (a) and delayed (b) addition of PC and subjected to temperatures ranging from 5 to 45 °C during the rheological tests.

related to the degree of internal structure of the material. In comparative tests, it can even be interpreted in terms of the number and strength of the bonds, whichever their nature, between particles. Concentrated suspensions of agglomerates of solid particles in liquid media exhibit thixotropic behaviour [21]. The measurement programme designed in this work (see Fig. 2) also aims at establishing an arbitrary determination of the thixotropy of each paste and thus compare how structured are the mixes in relation to their variables of preparation and test conditions [22].

Fig. 9 shows the values of integrated areas enclosed between the upwards and downwards flow curves for different mixing sequences (direct and delayed addition) and dosages of PC at different temperatures. Thixotropy values were systematically lower in the delayed than in the direct addition procedure, evidencing a lower level of flocculation of cement particles in the former.

In accordance to the evolution of apparent viscosity and yield stress, for a fixed temperature, the effect of PC dosage was to diminish the value of the integrated area. More interestingly, for any fixed PC dosage, the effect of temperature was always to diminish this value. Note that this was not the case for the yield stress, which tended to be either temperature independent, in the range of medium and high PC dosages and temperatures up to 25 °C, or positively correlated with temperature, in pastes with low contents of PC.

These results suggest that two levels of microstructure can be considered: a first level corresponding to long-range interactions between neighbouring agglomerates and an internal level corresponding to the short-range interactions between particles forming agglomerates. Other factors aside, the τ_0 value seems to account for the long-range forces between agglomerates in suspension that have to be overcome in order to initiate the flow of the material. Under conditions of chemical stability of these concentrated suspensions, the magnitude of the long-range interactions remains unchanged between 5 and 25 °C, as suggested by the almost constant value of τ_0 throughout this range of temperatures. The decrease of τ_0 at high temperatures

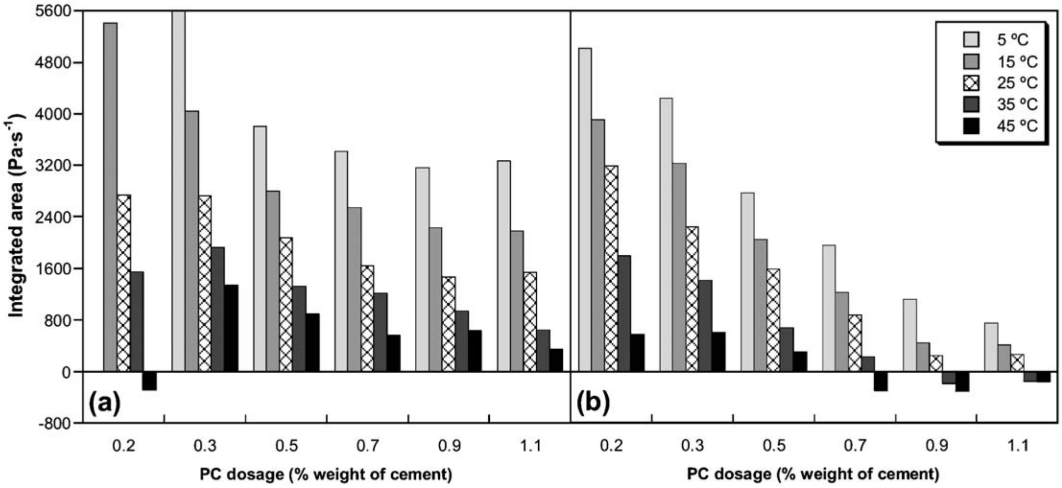

Fig. 9. Integrated area between flow curves as a function of PC dosage at different temperatures (of rheological test) for mixes prepared by direct (a) and delayed (b) addition of PC.

(35–45 °C) can be attributed to an increase in the Brownian motion of the particles, which partially weakens the interactions between agglomerates. In addition, this thermal agitation is also favoured by the decrease in the viscosity of the continuous phase. It is also possible that, in the transition from 25 °C to 45 °C, the chains of the adsorbed polymer might even undergo changes in their spatial conformation that could increase the steric component of the electrosteric repulsive potential—main mechanism of dispersion of polycarboxylate-based superplasticisers. On the other hand, as far as thixotropy is concerned, the monotonic decrease of the integrated area with temperature, already from 5 °C, is in agreement with mathematical models describing the mechanisms of dispersion between solid particles in colloidal systems [2]. According to this, temperature increases the electrosteric potential, which implies a lower level of association of particles (either single or agglomerates) and, therefore, a lower degree of thixotropy for the samples at the stage previous to the application of shearing. Then thixotropy tests allow to comparatively evaluate the extent of internal microstructure of these cement-based suspensions. Nevertheless, this interpretation from thixotropy tests can only be reliable under conditions of chemical stability of the samples, as discussed below. In the scale of time of this work (17.5 min of test), these conditions correspond to temperatures up to 25 °C and PC dosages of 0.5% or higher.

At PC dosages below 0.5% the increase of τ_0 with temperature is consistent with that reported by Lei and Struble for mixes without superplasticiser [23]. In this case, the interactions between agglomerates are governed by the chemical nature of the hydrates growing on their surfaces, which, as reported by these authors, are larger at higher temperatures as proved by scanning electron microscopy. These interactions are attractive and stronger than the interparticle interactions in suspensions stabilised by the action of superplasticisers. The fact that, even so, the value of the integrated area keeps on dropping with temperature in these conditions must be attributed to the ongoing hydration of cement particles during the test. As the test proceeds two competing mechanisms contribute to the instantaneous value of the recorded shear stress: the physical dissociation of agglomerates, which tends to diminish the rate of increase of the shear stress (pseudoplastic behaviour) and the ongoing hydration, which tends to increase the volume of the particles in suspension, as well as to reduce the volume of the aqueous phase, resulting in an increase of the actual volume fraction of the suspension and, consequently, raising the rate of increase of τ. At higher temperatures, the effect of the second mechanism becomes more notorious, up to the point that the τ values of some downwards flow curves are higher than those of the corresponding upwards ones, which explains the negative values of integrated area in Fig. 9. Therefore, under such conditions of low chemical stability of the suspension, thixotropy test is not indicating the degree of structure of the initial state of the sample but rather the extent of chemical change that this is undergoing. Whereas the yield stress is an absolute value of the stand-still state of a sample, thixotropy is the overall result of a dynamic process.

4. Conclusions

Under the wide range of conditions of work, flow curves recorded at high resolution exhibited a variety of complex behaviours, especially at low shear rates (below 20 s^{-1}), which made fitting with a unique rheological model inadequate. This fact prompted us to establish an alternative criterion for the estimation of the yield stress in which the first reliable data point that was common in all flow curves was considered as τ_0. The pseudoplastic behaviour of the flow curves was favoured at lower temperatures and PC dosages.

The sign of the evolution of the rheological parameters with temperature depended on the conditions of preparation of the mixes, especially on PC dosage. At dosages of 0.5% or higher, all cement suspensions were chemically stable in the scale of time of work. Thus, apparent viscosity decreased with PC dosage and linearly with temperature.

Under such conditions of stability, τ_0 was temperature independent between 5 and 25 °C, and higher temperatures tended to lower its value. On the contrary, at PC dosages below 0.5%, the temperature dependence of τ_0 evolved similarly to that of the apparent viscosity: decreasing between 5 and 25 °C but showing an incremental increase between 35 and 45 °C. The saturation dosage in terms of τ_0 was 0.7% regardless of the temperature when PC was directly added to the mixing water. Instead, in the delayed PC addition procedure, this value decreased from 0.9% to 0.7% as samples were subjected to higher temperatures.

Delaying the addition of the superplasticiser showed to reduce the absolute values of all rheological parameters measured in this work. Moreover, it allowed to reach τ_0 values closer to zero at any temperature provided that high contents of PC (0.7% and above) were added to the mixes.

Finally, an attempt to compare the level of microstructure of the mixes was made by integrating the enclosed area of the hysteresis loop of flow curves. The results indicated that the size of the agglomerates in suspension decreased with PC dosage. Likewise, the agglomerates were smaller in the delayed than in the direct PC addition procedure. The value of the integrated area decreased with temperature under any condition of preparation of the mixes, which contrasted with the invariability or increase of the τ_0 value under different conditions. Thus, τ_0 was attributed to be representative of the intensity of interactions between agglomerates in suspension before shearing, whereas the integrated area is more sensitive to the overall microstructure of the agglomerates. However, in potentially reactive systems, such as cement-based suspensions, the value of the integrated area has to be carefully interpreted, since high temperatures may promote rapid changes in the microstructure of the discrete phase as the rheological test proceeds. In such cases, this value may become less representative of the degree of initial microstructure of the sample.

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References

[1] C. Jolicoeur, J. Sharman, N. Otis, A. Lebel, M.-A. Simard, M. Pagé, The influence of temperature on the rheological properties of superplasticized cement pastes, in: V.M. Malhotra (Ed.), Superplasticizers and Other Chemical Admixtures in Concrete, ACI International, Farmington Hills, USA, 1997, pp. 379–405.

[2] J.A. Lewis, Colloidal processing of ceramics, J. Am. Ceram. Soc. 83 (2000) 2341–2359.

[3] N. Roussel, R. Le Roy, The Marsh cone: a test or a rheological apparatus? Cem. Concr. Res. 35 (2005) 823–830.

[4] J. Roncero, R. Gettu, L. Agulló, E. Vázquez, Flow behaviour of superplasticised cement pastes: influence of silica fume, Indian Concr. J. 76 (2002) 31–35.

[5] J. Roncero, R. Gettu, E. Vázquez, J.M. Torrents, Effect of superplasticizer content and temperature on the fluidity and setting of cement pastes, in: J. G. Cabrera, R. Rivera-Villareal (Eds.), The Role of Admixtures in High Performance Concrete, RILEM, Cachan, France, 1999, pp. 343–356.

[6] J. Roncero, Effect of superplastisizers on the behavior of concrete in fresh and hardened states: implications for high performance concrete. PhD dissertation, Universitat Politècnica de Catalunya, Barcelona, Spain, 2000.

[7] A. Griesser, F. Jacobs, F. Hunkeler, Influence of different super-plasticizers on the rheological properties of mortars, in: R.K. Dhir, P.C. Hewlett, M.D. Newlands (Eds.), Admixtures—Enhancing Concrete Performance, Thomas Telford, London, 2005, pp. 141–148.

[8] A. Griesser, Cement–superplasticizer interactions at ambient temperatures: rheology, phase composition, pore water and heat of hydration of cementitious systems. PhD dissertation, Swiss Federal Institute of Technology, Zürich, Switzerland, 2002.

[9] P. Coussot, Q.D. Nguyen, H.T. Huynh, D. Bonn, Viscosity bifurcation in thixotropic, yielding fluids, J. Rheol. 46 (2002) 573–589.

[10] N. Roussel, Steady and transient flow of fresh cement pastes, Cem. Concr. Res. 35 (2005) 1656–1664.

[11] G.H. Tattersall, B.P.F. Banfill, The Rheology of Fresh Concrete, Pitman Advanced Publishing, Boston, 1983.

[12] G. Chiocchio, A.E. Paolini, Optimum time for adding superplastizicer to Portland cement paste, Cem. Concr. Res. 15 (1985) 901–908.

[13] H. Uchikawa, D. Sawaki, S. Hanehara, Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement pastes, Cem. Concr. Res. 25 (1995) 353–364.

[14] I. Aiad, S.A. El-Aleem, H. El-Didamony, Effect of delaying addition of some concrete admixtures on the rheological properties of cement pastes, Cem. Concr. Res. 32 (2002) 1839–1843.

[15] I. Aiad, Influence of time addition of superplasticizers on the rheological properties of fresh cement pastes, Cem. Concr. Res. 33 (2003) 1229–1234.

[16] R.J. Flatt, Y.F. Houst, A simplified view on chemical effects perturbing the action of superplasticiser, Cem. Concr. Res. 31 (2001) 1169–1176.

[17] M. Nehdi, M.-A. Rahman, Estimating rheological properties of cement pastes using various rheological models for different test geometry, gap and surface friction, Cem. Concr. Res. 34 (2004) 1993–2007.

[18] A. Yahia, K.H. Khayat, Analytical models for estimating yield stress of high performance pseudoplastic grout, Cem. Concr. Res. 31 (2001) 731–738.

[19] G. Schramm, A Practical Approach to Rheology and Rheometry, Gebrueder Haake GmbH, Karlsruhe, 1994.

[20] C.W. Macosko, Rheology: Principles, Measurements, and Applications, VCH Publishers, New York, 1994.

[21] A. Potanin, Thixotropy and rheopexy of aggregated dispersions with wetting polymer, J. Rheol. 46 (2004) 1279–1293.

[22] D.A. Williams, A.W. Saak, H.M. Jennings, The influence of mixing on the rheology of fresh cement paste, Cem. Concr. Res. 29 (1999) 1491–1496.

[23] W.-G. Lei, L.J. Struble, Microstructe and flow behavior of fresh cement pastes, J. Am. Ceram. Soc. 80 (1997) 2021–2028.