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Impact of superplasticizer concentration and of ultra-fine particles on the rheological behaviour of dense mortar suspensions

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Abstract

This work aims at investigating the impact of the addition of superplasticizer and of ultra-fine particles, namely of silica fume and of precipitated titania, on the rheological behaviour of water-lean mortar pastes. The pastes are characterised in terms of their spread, their flowing behaviour and by means of performing a shear test, giving access to viscosity/shear gradient correlations. Adding superplasticizer is shown to shift the onset of shear thickening of the referring pastes to higher shear rates and to attenuate its otherwise rapid evolution, possibly by means of favouring steric particle–particle interactions. The workability of these mortars, which is characterised in terms of spread values and draining, is also improved. For the case of fly ash based mortars, adding ultra-fine particles is another way of (slightly) "retarding" shear thickening and of attenuating its evolution, possibly because of resulting in – on the average – lower hydrodynamic forces and reduced attractive Van der Waals interactions between particles. However, at the same time these mortars are characterised by a worsening in workability which is attributed to the huge amount of surface area provided by the ultra-fines.

Keywords: Mortar; Shear thickening; Workability; Superplasicizer; Ultra-fine particles; Steric interactions; Van der Waals interactions

1. Introduction

The rheological behaviour of construction materials such as concrete or mortar is particular decisive in terms of their workability, which is usually characterised by means of performing slump and/or spread tests [1]. These tests, however, only address a limited regime of shear rates, i.e. very low ones. Few investigations have focused at or at least included higher shear rates. Such rates can be attained in rheometers and may allow for characterising the impact of admixtures [2] or fine particles [3] by means of measuring the torque upon mixing. To the authors' knowledge, few or even none of these investigations primarily address themselves to the phenomena of shear thinning and shear thickening in freshly prepared construction materials such as mortar and/or concrete. Shear thickening may well occur upon mixing, provided that the hydrodynamic shear forces involved overcome repulsive forces due to interparticle potentials and Brownian motion [4]. Shear thickening is strongly unwanted as it may interfere with product quality and may even lead to damaging processing equipment.

The interplay between hydrodynamic forces, particle–particle interactions and rheological behaviour is manifold. It depends on parameters of the suspended phase(s) (i.e. phase volume, particle size (distribution) and shape) as well as on the suspending phase (i.e. viscosity) [5]. So far, studies aiming at improving the understanding of rheological phenomena have mostly focused on model systems, i.e. on particulate systems frequently synthesised via the Stöber synthesis and characterised by very narrow particle size distributions [4]. Applying index-matching and/or surface treatments [6] furthermore allows for limiting the impact of particle–particle interactions, i.e. of Van der Waals and/or of repulsive forces [7], respectively.

This work intends to turn towards dense suspensions, in particular towards mortar systems, for which understanding as well as controlling the rheological behaviour is of special

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importance to the construction industry: Mortars are characterised by wide particle size distributions and by diversity in terms of chemical composition. Their preparation leads to evolving particle–particle interactions, which furthermore complicates the situation. In a first step, this work aims at investigating the impact of the superplasticizer (SP) concentration and of adding of (ultra) fine particles on the rheological behaviour of the pastes. While the purpose of adding superplasticizers is mostly confined to improving deflocculation of the particles, thus to obtaining a better workability [1], the benefit of adding ultra-fine particles is more manifold. Besides altering rheological properties [3,8], i.e. the subject of this work, adding such particles may, in particular if being rich in SiO_2, also lead to significantly higher compressive strength values [9,10]. All pastes investigated within the frame of this work are characterised in terms of a spread, a funnel flow and a shear test — all together covering a range of shear rates of up to three decades.

2. Theoretical

Aiming at experimentally investigating the impact of admixtures and of fine particles on the rheological behaviour of mortar-like pastes, the theory discussed within the frame of this work is limited to what is necessary to understand the effects observed. The brief and strongly simplified theoretical part focuses on the onset of shear-thickening, as this phenomenon may be very critical in practical construction material related applications: If occurring, shear thickening tends to make effective mixing of ingredients difficult and may – due to its often sudden appearance – lead to damaging processing equipment.

The viscosity η of dense suspensions, such as of mortar, typically decreases with increasing shear rate up to a critical rate $\dot{\gamma}_C$ beyond which η starts to re-increase. $\dot{\gamma}_C$ separates the shear thinning from the shear thickening regime [11]. The order-to-disorder transition (ODT) theory developed by Hoffman [12,13] suggests that the initial lowering of the viscosity (shear thinning) is due to an ordering of the colloidal suspension into a layered structure which enables the particles to flow without collision. Shear thickening, observed at shear rates beyond $\dot{\gamma}_C$ is attributed to hydrodynamic forces which are assumed to become sufficiently strong to dislodge the particles from the layered structure, thereby disrupting it. The drastically increased number of collisions within the disordered state is claimed responsible for the often dramatic increase in viscosity. However, doubts with respect to the validity of this theory arose from observing both — suspensions that would shear thicken without layered structures ever being present and order to disorder transitions that would not result into thickening [6]. More recent findings propose that shear thickening is due to the formation of so-called hydro-clusters [6], and that it is not important of whether a layered structure is present or not as the transition to a state of hydrodynamic clustering may arise from a distorted colloidal fluid as well as from a shear ordered structure. The formation of these clusters implies that the stabilising forces (Brownian, electrostatic and/or steric) are dominated by the hydrodynamic forces and that the life time of the clusters exceeds the characteristic time of the flow convecting the particles apart [14].

Table 1
Fly ash based mortar formulations (1 l) with different SP concentrations (all data referring to masses are given in grams)

Component	Density/g/cm^3	fa SP 2.6	fa SP 1.9
Cement CEM I	3.13	117.9	118.3
Fly ash	2.51	562.1	563.9
Sand	2.7	1530.3	1535.2
Water	1	156.2	156.7
PCP (superplasticizer)	1.05	2.6	1.9

Table 2
Fly ash based mortar (1 l) with different ultra-fine particles (all data referring to masses are given in grams)

Component	Density/g/cm^3	fa SP 1.9	fa SP 1.9 SF	fa SP 1.9 TiO_2
CEM I	3.13	118.3	115.7	115.7
Fly ash	2.51	563.9	551.5	551.5
Silica fume	2.25	0.0	49.6	0.0
Precipitated titania	4.05	0.0	0.0	89.3
Sand	2.7	1535.2	1501.4	1501.4
Water	1	156.7	153.2	153.2
PCP(dry)	1.05	1.9	1.9	1.9

3. Experimental investigations

3.1. Materials

The first test series deals with the influence of a PCP-type superplasticizer (SP) on the rheological behaviour of a fly ash based mortar paste (Table 1).

The second experimental series aims at investigating the influence of ultra-fine particles. Two different mortar types are tested within this series: The first one is based on a cement/fly ash binder (Table 2), the second one on a classified cement/limestone filler (calcium carbonate) based binder (Table 3). Fig. 1 shows SEM-micrographs of the fly ash and of the limestone filler, respectively. The fly ash particles are nearly spherical in contradiction to the irregularly shaped limestone filler particles. They are, on average, also smaller than the calcium carbonate and contain a significant fraction of particles of the order of 1 μm and below.

Table 3
Calcium carbonate (limestone filler) based mortar (1 l) with different ultra-fine particles (all data referring to masses are given in grams)

Component	Density/g/cm^3	lf SP 2.5	lf SP 2.5 SF	lf SP 2.5 TiO_2
Classified CEM I	3.13	47.1	46.1	46.1
Limestone filler	2.73	671.4	657.7	657.7
Silica fume	2.25	0.0	46.2	0.0
Precipitated titania	4.05	0.0	0.0	83.1
Sand	2.7	1499.6	1468.8	1468.8
Water	1	172.3	168.8	168.8
PCP (dry)	1.05	2.5	2.5	2.5

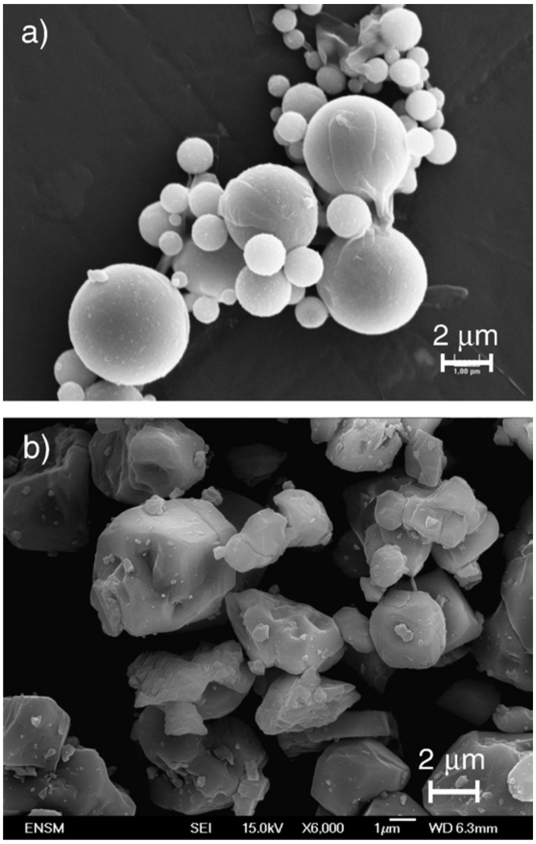

Fig. 1. SEM-micrographs of a) fly ash and b) limestone filler particles.

The classified cement, called C20 ($\rightarrow d_{\max} \approx 20$ µm) used in conjunction with the limestone filler was obtained from classifying the cement (CEM I) used in the fly ash based mortars with a Hosokawa Alpine classifier type 50 ATP. Fig. 2 depicts SEM-micrographs of the ultra-fine powders, i.e. of the silica fume and the precipitated titania, used to alter the rheological behaviour of the mortar pastes.

It is important to note that during each test series the amount of water and admixture is (nearly) kept constant. Minor differences result from adding the ultra-fine particles to the referring basic formula instead of replacing part of the filler (fly ash/calcium carbonate) – as usually done – in terms of volume.

3.2. Test details

Three tests, namely a spread, a funnel flow and a shear test, are performed twice (at different times) during each experiment in order characterise the rheological behaviour of the different mortar pastes. The mortar is prepared by mixing the components in a Perrier type mixer prior to carrying out these tests: The dry mixture is homogenised for 30 s before the water and admixture (SP) is added. A uniform paste was obtained by mixing according to the procedure outlined in Table 4. $t = 0$ is the moment when mixing has been accomplished.

The first rheological test performed is the spread test. A cone with a base and an upper diameter of 100 and 50 mm, respectively, a height of 150 mm, thus half of the values given in the norm NF EN 12350-2, is lifted to initiate the test. Delay times between the *end* of mixing and *initiation* of the test are given in Table 4 as well as in the referring figures. The spread of the approximately 687 ml of mortar involved is measured under four different angles ($\Delta\alpha \approx 45°$) after a relaxation period of 5 min following initiation. The relevant spread value obtained is the average value of the four individual measurements. The shear rate of the initial slump flow is of the order of 1 s^{-1} (Fig. 3) which is typical for concrete placement. However, it quickly decreases to around 0.1 s^{-1} (visibility limit) and below. When measuring the spread value 5 min after initiating the spread test, shear rates have usually decreased to values of no

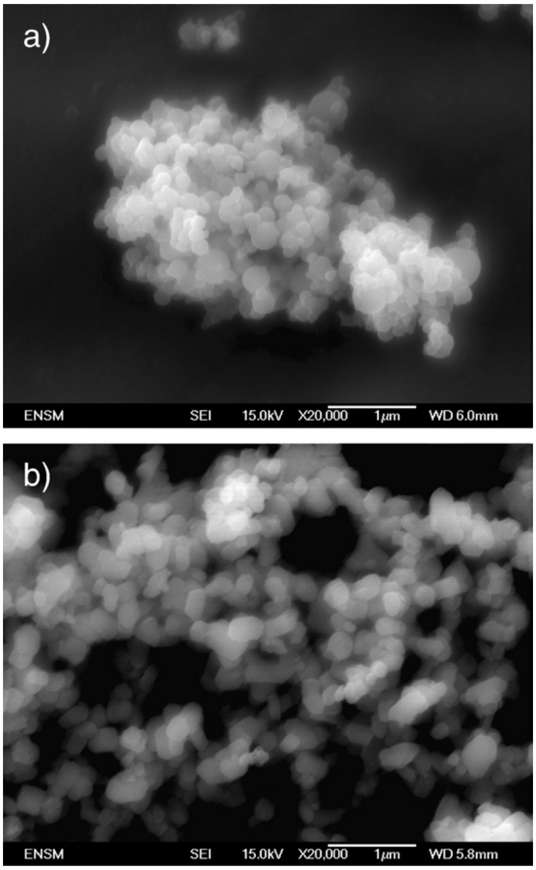

Fig. 2. SEM-micrograph of a) silica fume and b) precipitated titania particles.

Table 4
Test procedure

Base composition	fa	lf
Dry mixing	0:30 min	0:30 min
	introduction of water and admixture	
Wet mixing	3 min	4 min
End of mixing	$\rightarrow t=0$	$\rightarrow t=0$
Spread test (initiation)	$t=5$ min	$t=2$ min
Funnel flow test	$t=5{:}30$ min	$t=2{:}30$ min
Shear test		
Pre-homogenisation	–	$t=10{:}30$ min
First initiation	$t=18$ min	$t=13$ min
Homogenisation	$t=20{:}30$ min	$t=15{:}30$ min
Second initiation	$t=23$ min	$t=18$ min
Spread test (initiation)	$t=34$	$t=25$
Funnel flow test	$t=36$	–

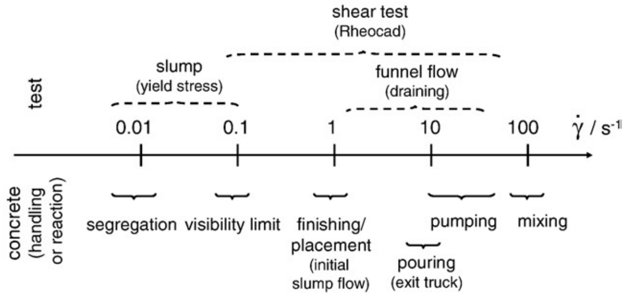

Fig. 3. Shear rates during different rheological tests and upon concrete handling.

more 0.01 s^{-1}. The spread values obtained at such low shear rates are believed to characterise more the yield stress, i.e. a threshold for shear, than any dynamic behaviour. Low spread values would then correspond to a high yield stress and vice versa.

The funnel flow test is carried out in parallel to the slump test. The principle of this test is to measure the time related to a quantified amount of draining (→draining time) of mortar from a ∅ 150 mm (→diameter of the filling opening) funnel. This funnel is 150 mm high and has a bottom opening of 26 mm from which the mortar is draining through a 40 mm long cylindrical outlet with the same inner diameter of 26 mm. The draining time is the time required for the surface level of the mortar to sink from a first marker located 12 mm below the funnel's filling opening to a second marker located 70 mm below the filling opening. This corresponds to a draining volume of approximately 623 cm^3. Typical shear rates upon draining from such a funnel lie between around 1 s^{-1} for viscous water lean pastes, similar or even dryer in comparison to those investigated here, and 40 s^{-1} for self-levelling concretes. The upper values of this range of shear rates is – upon concrete handling – typical for pumping, the lower values are close to those occurring upon finishing (Fig. 3).

The main shear test is performed on a Rheocad 400 (CAD Instrumentation) as shown in Fig. 4. The Rheocad is a mechanical computer-controlled device which allows for performing rheological measurements on viscous material such as mud, paints, gels, resins, polymers, mortar and cement paste. Within the frame of this study the Rheocad is used to determine the dynamic viscosity of mortar pastes with a maximum particle size of 4 mm within a wide range of shear rates: 1.8 l of mortar is poured into the bowl (Fig. 4b). The cap is clamped to the bowl which is subsequently mounted to the Rheocad. The cap disposes an inner stirrer with several wing-like mixing elements and an outer hook or semi anchor like stirrer. The inner stirrer turns clockwise and is essential for the measurement as it provides the momentum (i.e. the shear) to the mortar. The outer stirrer is additionally put into anti-clockwise operation for (re-)homogenising the mixture before (and/or after) a measurement. Homogenisation of the mortar may become necessary as the applied momentum, i.e. the centrifugal force, may lead to (partial) segregation of the mix. During measuring, the inner stirrer follows a well defined rotation cycle. Thereby, the torque is recorded as a function of the rotation velocity. Careful calibration of the system permits to transfer this correlation to a correlation between the dynamic viscosity of the mortar and the gradient of shear [15] which may cover a range between 0.1 and 60 s^{-1}. The upper limit of this range corresponds to the lower limit of values which typically occur upon concrete mixing.

In view of differences between the timing during experiments related to the fly ash (fa) and those related to the limestone filler (lf) based mortars direct comparison between these series should be avoided; however, this does not impose constraints concerning any conclusion regarding the impact of the ultra-fines added to the referring system.

4. Results and discussion

4.1. Influence of superplasticizer dosage

The results obtained from the shear test, the spread and the funnel flow tests carried out on the fly ash based mortar at two different admixture concentrations (Table 1) are depicted in Figs. 5 and 6, respectively.

The two admixture concentrations applied lead to shear gradient/viscosity correlations both characterised (Fig. 5) by initial shear thinning and an eventual onset of shear thickening. The curves shown in Fig. 5 are "up curves", i.e. obtained from increasing the shear gradient. The corresponding "down curves" of the shear tests performed within the frame of this study show slightly lower viscosity values, but are not visualised for readability reasons. At very low shear rates, i.e. for $\dot{\gamma} < \approx 0.3$ s^{-1}, the

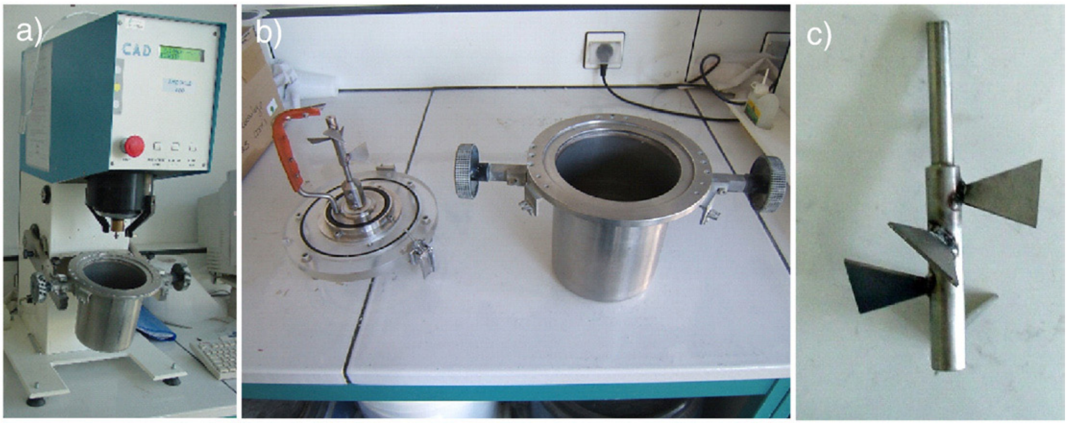

Fig. 4. a) Rheocad 400, b+c) stirrer(s) and b) bowl.

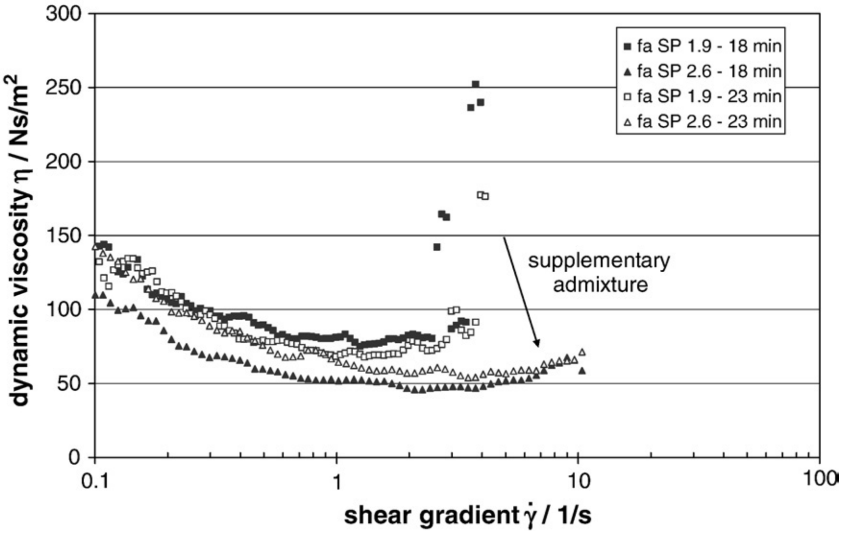

Fig. 5. Correlation between shear gradient $\dot{\gamma}$ and dynamic viscosity η for different admixture concentrations.

viscosity η is only slightly reduced if the (dry) admixture concentration is increased from 1.9 to 2.6 g per litre of mortar (Table 1). As $\dot{\gamma}$ increases, shear thinning starts to be slightly more pronounced for the mixture containing the higher admixture concentration, as η decreases a bit faster and to lower values. More important, however, are the shift of the critical shear rate $\dot{\gamma}_C$ towards higher values, i.e. from around 1.3 to 1.5 s^{-1} to between 2 and 5 s^{-1}, and the evolution of the correlation between η and $\dot{\gamma}$ within the shear thickening regime: Increasing the admixture concentration obviously retards and attenuates shear thickening. In fact, it facilitates placement and is in strong favour – if not even necessary – to mix, pump and pore this water-lean mortar type.

Retardation and attenuation are attributed to a better deflocculation and to a more complete and denser covering of the cement grains with the SP. An improved deflocculation leads to smaller “effective” particle sizes, i.e. to more individual (isolated) particles and to clusters containing less (non-dispersed) grains, and may therefore largely shift the onset of shear thickening towards higher shear rates [5]. In fact, the hydrodynamic force acting between two particles is – at a given shear rate and separation distance – less for smaller particles [4], so that higher shear rates may act until equilibrium between hydrodynamic and interparticle forces is eventually reached. However, the impact of the supplementary admixture is not only confined to hydrodynamic forces, but may also lead to an amplified steric contribution [7] to the repulsive particle–particle interactions: Stronger repulsive interactions resist hydrocluster formation up to higher shear rates and thus delay the onset of shear thickening. The increasingly dense arrangement of the superplasticizer is also likely to hamper mutual

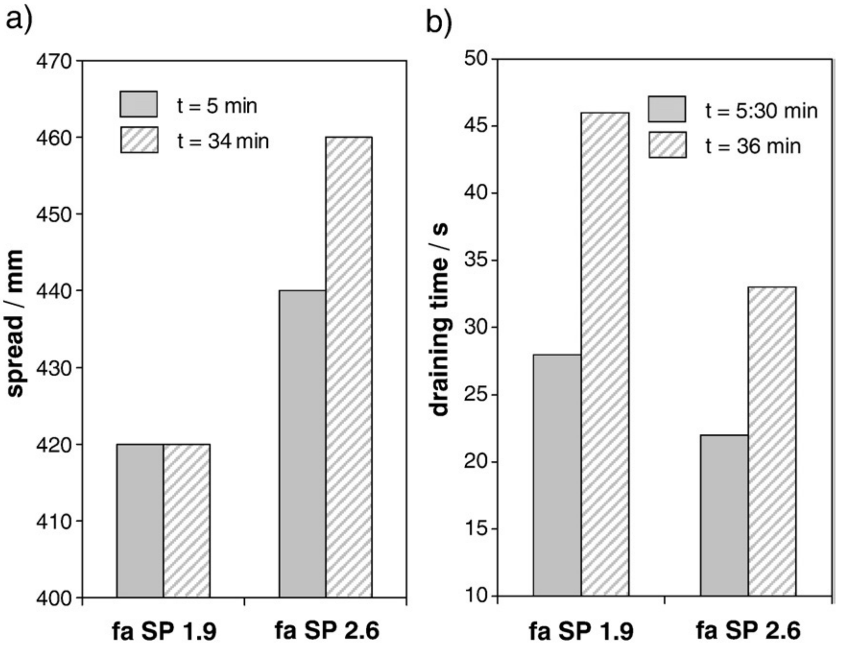

Fig. 6. a) spread and b) funnel flow test results for different admixture concentrations.

penetration of side chains and the related approaching of the particles. The observed significant attenuation of shear thickening may – in part – well be a consequence of this.

The results obtained from the spread and the funnel flow tests are shown in Fig. 6. The spread test is accompanied by very low shear gradients of 0.1 s^{-1} and significantly below. At such low shear rates the spread values obtained are believed to characterise the yield stress: High spread values indicate a lower yield stress, i.e. a less important threshold allowing for shear to occur. Here, the supplementary admixture leads to slightly elevated spread values as one would expect from a better deflocculation of the particles in the paste. In the funnel flow test, which is accompanied by shear gradients of at least 1 s^{-1} and above, shorter draining times generally indicate a lower viscosity of the paste. The draining time is several seconds shorter in the presence of supplementary admixture due to lower viscosity values obtained for the relevant range (Fig. 5). The remarkable increase of the draining time along the time axis is attributed to the ongoing hydration process, in particular of the C_3A-phases. Hydration of these phases is very water demanding and rapidly produces crystalline needle-like AFt-phases (ettringite) on the surface of the cement grains [16], so that the flowability of the paste worsens. Since the water to cement (+filler) ratio applied is as low as 0.23, evaporation may also be (in part) responsible for the increase of the draining times. In spite of the significant increase of the draining time, spread values remain nearly unchanged or even increase along time. This is attributed to the ongoing adsorption of the SP on the particle surface which balances or even outbalances the impact of the beginning hydration on the yield stress, i.e. on the threshold for shear.

4.2. Impact of ultra-fine particles

Silica fume and precipitated titania (Fig. 2) are added to a fly ash and to a calcium carbonate based mortar in order to investigate the impact of (ultra) fine powders on the rheological behaviour of the different pastes.

4.2.1. Fly-ash based mortar

The results of the shear, the spread and the funnel flow test referring to experiments carried out on the fly ash based mortar containing (ultra) fine SiO_2 (silica fume) and precipitated TiO_2-particles (Table 2) are shown in Fig. 7 ("up curves") and in Fig. 9, respectively.

All the different mortars applied lead to shear gradient/viscosity correlations which are characterised by initial shear thinning and an eventual onset of shear thickening. During the initial increase of the shear rate ($\dot{\gamma} < \approx 1$ s^{-1}) (Fig. 7) the dynamic viscosity of the mortars is – at the fist experimental run (t=18 min) – lowest in the absence of ultra-fine particles and highest in the presence of silica fume. This may be due to hydrogen bonds which are inherent to SiO_2-rich surfaces and capable of immobilising significant amounts of water [17]. As long as saturation with water has not been attained, strong capillary forces [18] have to be overcome upon mixing as well. Homogenisation of the mortar is proceeding along the shear test due to ongoing mixing. It reduces air intrusions, capillary forces and destroys hydrogen bonds and is assumed to be responsible for the converging behaviour of the correlations between η and $\dot{\gamma}$ at higher shear gradients. At later stages (2nd run), i.e. when homogenisation has mostly been attained, ultra-fine particles slightly reduce the viscosity of the paste in the shear thinning regime at moderate shear rates above 1 s^{-1}. However, this effect is less pronounced in comparison to when using supplementary admixture. It is also much less than what is observed in the shear thickening regime, where the impact of fine particles is strong and even appears to evolve with time. While the onset of shear thickening is only slightly retarded, i.e. to between 2 and 3 s^{-1}, which is somewhat less in comparison to when using supplementary admixture (Fig. 5), ultra-fine particles do in fact strongly attenuate shear thickening and may well be expected to facilitate mixing, pumping and pouring of water-lean mortar and concrete mixes. However, their impact on placement is probably little or may even be negative as shown by the elevated initial viscosity for low and moderate shear rates in the presence of silica fume.

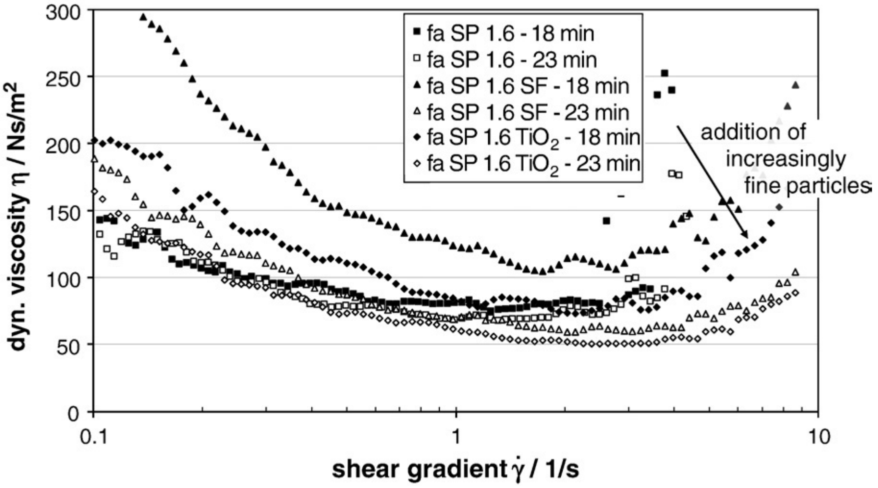

Fig. 7. Correlation between shear gradient $\dot{\gamma}$ and dynamic viscosity η for fly ash based mortars containing different (ultra) fine powders.

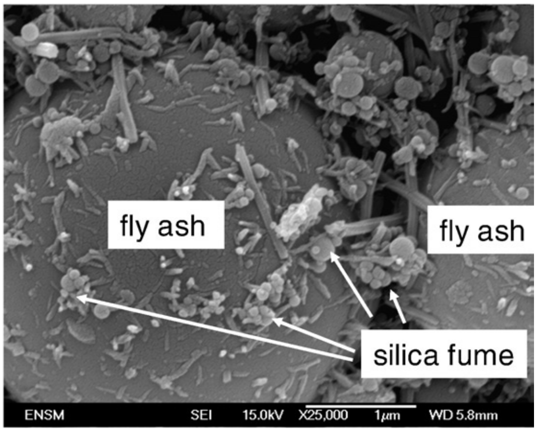

Fig. 8. SEM-microgaraph of a silica fume containing fly ash based mortar taken after 24 h of curing.

If adding fine particles to mortar mixtures one has to keep in mind the immense introduction of surface area involved. Less amount of admixture is therefore available per unit surface area so that steric particle–particle interactions are reduced, provided that saturation with superplasticizer is not or no longer attained. If steric interactions were the only active ones, repulsive interactions would diminish and the onset of shear thickening would occur at lower shear rates, which is in contrast to what is observed. However, adding fine particles also reduces the mean particle size and may therefore be expected to reduce the mean value of the hydrodynamic force acting between particles [4]. If – at a given shear rate – ultra-fine particles were decreasing the acting hydrodynamic force more significantly than the steric interactions one may expect a shift of the shear thickening regime towards higher shear rates.

However, in the prevailing mortar pastes particle–particle interactions are not necessarily confined to a steric nature, but may also (in part) originate from electrostatic and from Van der Waals interactions [7]. If Van der Waals interactions were playing an important role in a mortar paste containing no ultra-fine particles, adding such particles should significantly reduce said attractive interactions [19] and, as a consequence, increase the amount of the globally repulsive interaction. This would have a retarding impact on the onset of shear thickening, and may be also an attenuating effect on its evolution along $\dot{\gamma}$. Evidence suggesting that Van der Waals interactions may initially play an important role does in fact exist: Ultra-fine particles for which Brownian motion constitutes the dominant collision mechanism [20] generally tend to collide with significantly larger particles due to the elevated coagulation kernel [21]. In fact, SEM-micrographs (Fig. 8) of a mortar paste containing silica fume aggregates (Fig. 2a) taken 24 h after curing clearly show the attachment of numerous small silica fume aggregates on the surface of the much larger spherical fly ash particles.

The PCP-type superplasticizer applied leads to steric layers of the order of a few nm [22] so that ultra-fine particles may still act as a spacer between particles and consequently reduce the amount of the Van der Waals forces acting between neighbouring particles. The particular effective suppression of shear thickening observed if titania is added in place of silica fume may well be due to its open structure (Fig. 2b): Arranged in fluffy chains, titania aggregates may adjust separation distances between the large fly ash particles and the cement grains at the order of the referring primary particle size, i.e. between 50 and 100 nm. This separation distance is much more effective in reducing Van der Waals forces in comparison to when compact aggregates, such as the silica fume, with diameters of the order of 0.5 to 1 μm are used as a spacer [23].

The results obtained from the spread and the funnel flow tests are shown in Fig. 9. The measured spread is highest in the absence of ultra-fine particles. As the spread decreases from 420

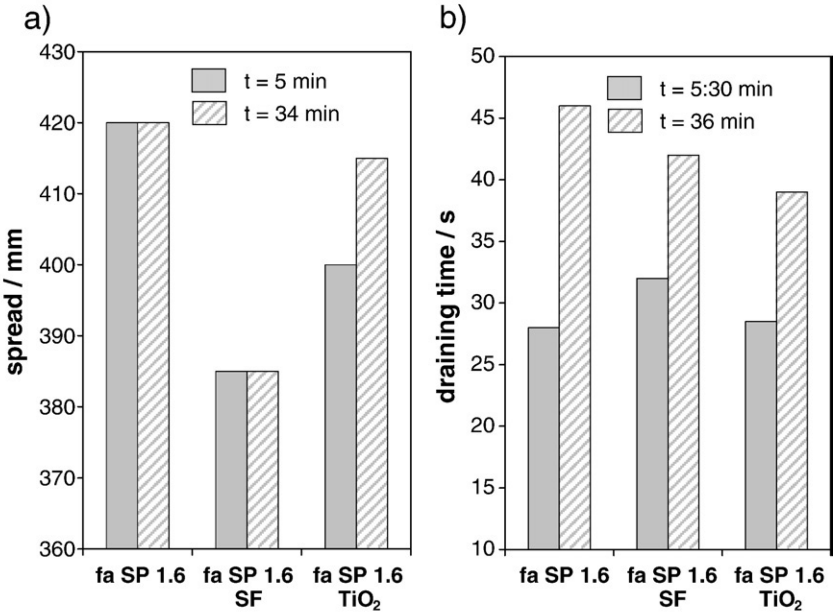

Fig. 9. a) spread and b) funnel flow test results for fly ash based mortars containing different (ultra) fine powder.

to 400 mm if titania is added to the mortar to 385 mm if silica fume is added one may conclude that the ultra-fine particles increase the yield stress, i.e. the threshold for shear. The behaviour observed may result from various reasons, such as from significant amounts of immobilised water (→hydrogen bonds) leading to higher effective solid volume fractions [17] and from strong capillary forces due to still incomplete homogenisation. Furthermore, adding ultra-fine particles to the mortar mixture (instead of replacing for example part of the filler, here fly ash) is responsible for a slight shift of the solid volume fraction towards higher values, so that a higher particle concentration suspension and potentially more viscous paste is generated. Finally one should also note that the huge amount of surface area which is provided by the ultra-fines is likely to reduce the amount of admixture per unit surface area so that Van der Waals based particle–particle attractions may eventually become increasingly important.

Similar results as in the spread test are obtained upon carrying out an initial funnel flow test. The draining time, which characterises the rheological behaviour at moderate shear rates, slightly increases from 28 s in the absence of ultra-fine particles to 28.5 s if the mortar contains titania. The increase is much more pronounced (32 s) if silica fume is added. The increase in draining time upon addition of the ultra-fines corresponds to an increasing viscosity and is attributed to the same reasons as the decrease in spread.

The spread values (i.e. yield stress) are either constant along time or do slightly increase. They are believed to strongly depend on the degree of dispersion of the particles in the paste, which is largely governed by the amount of adsorbed superplasticizer of the particle surface and can – depending on the adsorption kinetics – still evolve (improve) along time. Draining describes the viscosity of the paste at significantly higher shear rates and is believed to depend (far more than the yield stress) on parameters such as the water to cement (+filler) ratio and the form of the particles. In fact, crystalline needle like AFt-phases (ettringite) are rapidly formed along hydration. The corresponding reaction is very water demanding and further reduces the water contents of the already initially water lean paste.

4.2.2. Calcium carbonate (limestone filler) based mortar

The results of the shear, the spread and the funnel flow tests referring to the experiments carried out on the limestone filler based mortar (Table 3) are depicted in Fig. 10 (“up curves”), and Fig. 11, respectively. The main differences between mortars based on calcium carbonate and those based on fly ash (Table 2) are the significantly higher admixture concentration (2.5 instead of 1.9 g/l), a slightly higher water to cement+filler ratio (0.24 instead of 0.23 for the referring mixtures containing no ultra-fines), the incorporation of less, but far more reactive cement and the nature as well as the shape of the filler material (Fig. 1). There are also differences between the test procedures (Table 4) of which the initial homogenisation of the limestone filler based mortars performed prior to the first shear test is the most important one. All in all, these differences appear to have a major impact on the rheological behaviour of the referring pastes: As for the fly ash based mortars, thinning is initially observed with increasing shear (Fig. 10). However, in spite of the higher SP concentration, absolute values of η are at a higher level in comparison to when the mortar is based on fly ash which indicates a poorer workability. This may (in part) be due non-spherical shape of the abundant limestone particles (Fig. 1b).

Yet, limestone filler based mortars can be exposed to significantly higher shear-rates prior to the onset of shear thickening which in certainly in favour of mixing and pumping: $\dot{\gamma}_C$ is in fact not attained for shear rates up to 17 s^{-1}. Within this range of $\dot{\gamma}$, adding ultra-fine particles does not appear to be effective in terms of significantly altering the dynamic viscosity. In fact titania reduces η only marginally, while adding silica fume appears to slightly increase it. Any impact on mixing, pumping, pouring or placement of these mixes may therefore be assumed to be little.

The significant shift of $\dot{\gamma}_C$ for the limestone filler based pastes towards higher shear rates is assumed to be in part due to

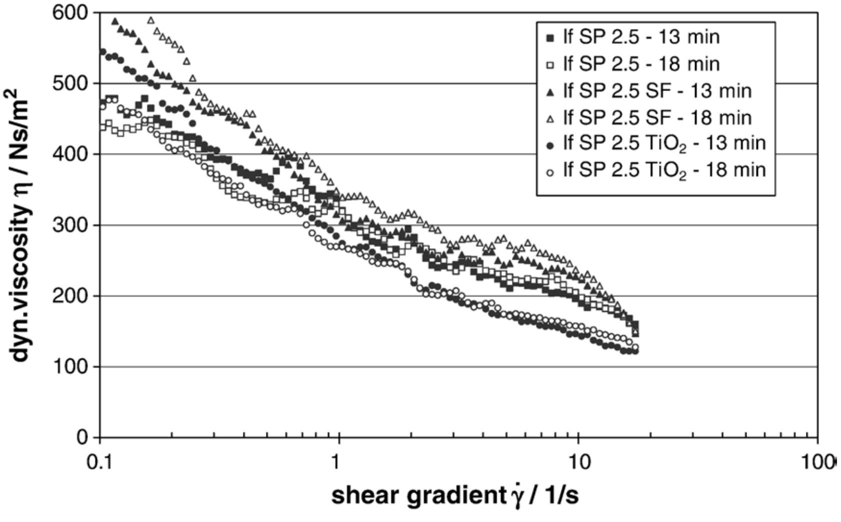

Fig. 10. Correlation between shear gradient $\dot{\gamma}$ and dynamic viscosity η for limestone filler based mortars containing different (ultra) fine powder.

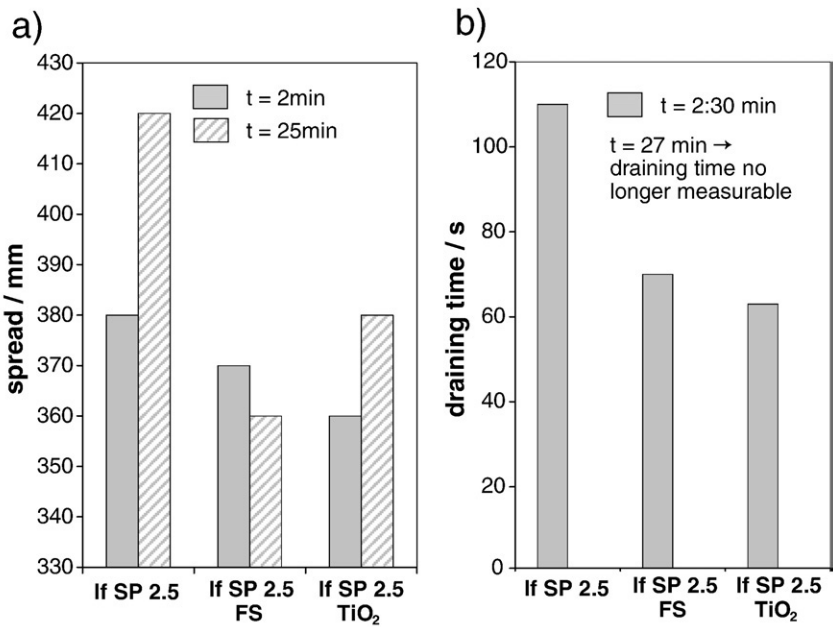

Fig. 11. a) spread and b) funnel flow test results for limestone filler-based mortars containing different (ultra) fine powder.

the elevated SP dosage. The elevated dosage leads to increased steric interactions and allows for stronger hydrodynamic forces, i.e. for higher shear rates [4] to act prior to the onset of thickening. However, it is also due to the significantly lower (BET) specific surface area of the calcium carbonate (0.7 m^2/g) in comparison to the fly ash (2.0 m^2/g) that the surface area related admixture concentration is higher. The lower surface area and the absence of the numerous hydrogen bonds, such as typical for the surface of the fly ash possibly reduce the amount of immobilised water [17], thus lead to a higher “effective” water content and to a retardation as well as to an attenuation of shear thickening [4].

The higher viscosity values inherent to the limestone filler based mortar pastes are assumed to be due to their high reactivity, i.e. to the faster hydration progression in comparison to the fly ash based paste. The elevated reactivity is attributed to the smaller grain size of the classified cement [24] and to the presence of the fine calcium carbonate particles [25,26].

The results obtained from the spread and the funnel flow tests are shown in Fig. 11. For the calcium carbonate based formulations the spread is again less in the presence of ultra fine particles. However, the effect is much less than observed for the fly ash based pastes. This in agreement with the nearly identical shear/viscosity correlations obtained for very low shear rates (Fig. 10). This nearly identical behaviour probably due to the largely increased dosage of superplasticizer in these formulations (Table 3) which provides good dispersion even in the presence of ultra fine, superplasticizer demanding particles. Merely the increase of the spread which is observed between the two reading points in the absence of ultra-fine particles is somewhat surprising. It is attributed to the ongoing adsorption of the superplasticizer on the surface of the particles. Note that the fist spread test is initiated only 2 min after mixing. If ultra-fine particles with a BET specific surface area of 20 m^2/g and more are present, much of the SP is adsorbed on the ultra-fines and no longer available for adsorption on the cement and on the calcium carbonate particles.

Due to the higher viscosity of the limestone filler based pastes, the draining time observed (Fig. 11b) is also much higher in comparison to the fly ash based pastes (Fig. 9b). At t=2:30 min, it is between 63 and 110 s, depending on the formulation of the mortar. Due to the presence of the air classified cement [24] and the fine limestone filler [25,26], the hydration progression of the limestone filler based mortars is possibly fast and assumed to be responsible for that the draining is no longer measurable once the second shear test has been performed. In view of the extreme sensibility of the draining time to the hydration progression, the slow draining of the calcium carbonate based formulations, as observed in particular in the absence of ultra-fine particles, may be a result of the formulation of this mortar (Table 3), i.e. of its (slightly) higher content of the very fast reacting cement and of the fine, hydration promoting calcium carbonate. Further work addressing this issue is certainly desirable.

5. Conclusions

The present study examines the influence of the addition of superplasticizer and of ultra-fine particles, i.e. silica fume and precipitated silica, on the rheological behaviour of water-lean mortar pastes. Three tests – a spread, a funnel flow and a shear test covering up to three decades of shear rates are performed in order to characterise the rheological behaviour of the different pastes.

Increasing the superplasticizer concentration is shown to be an effective means to improve the workability of water-lean mortar pastes, i.e. to shift the onset of shear thickening towards higher rates and to attenuate its evolution: Higher SP concentrations appear to augment its adsorption on the particle surface and thus to amplify steric, i.e. repulsive particle–particle interactions. This allows for easier mixing, pumping, pouring and placement of the referring pastes.

Ultra-fine particles are the source of huge amounts of additional surface area: The amount of SP per unit surface area decreases significantly and some of the water is possibly immobilized, so that the workability of the referring pastes, i.e. their behaviour upon placement, tends to be worse. Nevertheless, for the case of fly ash based mortars, adding ultra-fine particles is a way of (slightly) retarding shear thickening and of attenuating its evolution. This is in favour of mixing, pumping and pouring the referring product and is attributed to – on the average – lower hydrodynamic forces and to a decrease of the attractive Van der Waals interactions between particles. Water-lean mortars based on compositions of fine cement and ground calcium carbonate show particularly elevated viscosities and poor workability characteristics which are attributed to strongly accelerated hydration kinetics and to the non-spherical shape of the limestone filler.

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