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Rheology of cementitious paste with silica fume or limestone

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Abstract

The rheological behaviour of cementitious pastes where cement has increasingly been replaced by densified silica fume (SF), untreated SF or limestone has been studied. The effect of SF on the flow resistance, taken as the area under the flow curve, was found to depend on the dispersing ability of the plasticizer as illustrated by pastes with naphtalene sulphonate-formaldehyde condensate (SNF) and polyether grafted polyacrylate (PA).

The gel strengths increased with increasing SF replacement of cement independently of plasticizer type. The cementitious gel strength was, however, depending on the type of SF since pastes with densified SF developed lower gel strengths than pastes with untreated SF. This phenomenon was attributed to agglomerates in the densified SF which remained unbroken by the mixing and measurement sequence.

Both flow resistance and gel strength decreased with increasing limestone replacement. Thus, silica fume may have an advantage over limestone filler as stabilizing agent for self-compacting concrete preventing segregation upon standing and reduced form pressure due to a more rapid gel formation.
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Keywords: Flow resistance; Gel strength; Limestone; Rheology; Silica fume

1. Introduction

The objective of the present study was in relation to self-compacting concrete (SCC) technology to investigate the effect of silica fume (SF) and limestone filler on rheology of cementitious binders plasticized by a polyether grafted polyacrylate superplasticizer (PA) recommended for SCC and compare the performance with SNF. SF is focused on since it is used by the Norwegian SCC technology for stabilisation, while other countries rather use high amount of fillers like limestone. The approach was fundamental by keeping the volume fraction of solids constant within each series and replacing cement with same volume of SF or limestone. In this way it should be easier to see effects of fineness, particle packing and surface chemistry. Parts of the present study has been presented in a pervious publication by Justnes and Vikan [1] where the rheological measurements mainly were characterized by the Bingham model. This paper addresses new means of analysing the rheological behaviour of cementitious paste, namely flow resistance as the area under the flow curve and gelling rate from oscillation measurements, as well as gel strength.

Reported research on the effect of SF on paste rheology seems limited, while contradictory results can be found for concrete [2,3]. Zhang and Han [4] investigated the effect of a number of fine mineral admixtures on cement paste rheology using the Casson equation. They used $w/(c+s)=0.25$, 10% SF and 5% superplasticizer and found that both Bingham viscosity and yield point *decreased* relative to pure cement paste. Park et al. [5] found on the other hand for cementitious pastes with constant water to binder ratio of 0.35 and 2 wt.% polynaphtalene sulphonate based plasticizer that the yield stress and plastic viscosity from the Bingham model steeply *increased* with increasing SF replacement. Cyr et al [6] focused on the shear thickening effect of superplasticizers on cement pastes with and without mineral additives using the Herschel-Bulkley equation. They tested 10 and 25% SF replacing cement, varied w/b while keeping the superplasticizer dosage constant (3%), and found that SF leads to a small shear thinning. Salem [7] investigated the rheology of OPC–SF system, but with high SF replacement rates of 10, 20, 30 and 50% and high $w/(c+s)$ of 0.6 and 0.8. He found increasing hysteresis in up/down flow curves with SF dosages as a sign of thixotropy. The high dosages found in

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literature are surprising realizing that modern concrete technology seldom uses more than 10% SF of cement mass.

2. Experimental

A rapid portland cement (CEM I 42,5 RR) was used with composition 61.98% CaO (C), 20.15% SiO_2 (S), 4.99% Al_2O_3 (A), 3.36% Fe_2O_3 (F), 3.55% SO_3 ($\overline{S}$), 2.36% MgO, 1.08% K_2O and 0.42% Na_2O. This corresponds to the potential minerals 45.7% C_3S, 23.3% C_2S, 7.5% C_3A and 10.2% C_4AF and 7.7% $C\overline{S}$ according to Bogue calculations. The loss of ignition (LOI) was 1.34%, the specific density 3.12 g/cm^3 and the specific surface 546 m^2/kg according to the Blaine method.

Densified and untreated SF was obtained from the ferrosilicon manufacturer Elkem ASA Materials, Kristiansand, Norway, and both consisted of 94.7% SiO_2 with a specific surface of 22 000 m^2/kg (N_2 adsorption, BET).

High purity limestone powder (98–99% $CaCO_3$) with a Blaine specific surface of 486 m^2/kg from Franzefoss, Norway, was used. The particle size distributions of cement, densified and undensified SF, and limestone were measured with a COULTIER LS 230 and plotted in Fig. 1. All powders were dispersed by ultrasound.

Two different plasticizers were tested. The superplasticizer sodium naphthalene sulphonate-formaldehyde condensate (SNF) was of the type Mighty 150 produced by Kao, Japan, a solution with 42% solids. The super-plasticizer (PA) was a polyacrylate grafted with polyether named RN-15 by Rescon-Maipei, Norway. It contained 20% solids and a viscosifying agent based on water soluble cellulose derivate. The viscosifyer is added to the polyacrylate in order to increase the viscosity of the water phase and thus stabilize the paste. The plasticizer dosage was kept constant to 1.32% SNF and 0.79% PA (lower dosage than for SNF due to higher efficiency) of dry powder mass for all mixes.

Cement pastes (150 ml) were made with a constant total particle volume fraction of 0.442, corresponding to about $w/c = 0.40$ without mineral replacement, and with SF replacing cement in volume increments of 0.01 from 0.00 to 0.06 (corresponding to mass SF of total powder from 0.0 to 9.9%, alternatively from 0.0 to 13.6 vol.%). The blending was performed in a high shear mixer by adding solids to the water and mix for 0.5 min, resting for 5 min and blending again for 1 min. The admixtures were either added in the water first (momentary addition) or added to the paste after 5 min resting period (delayed addition).

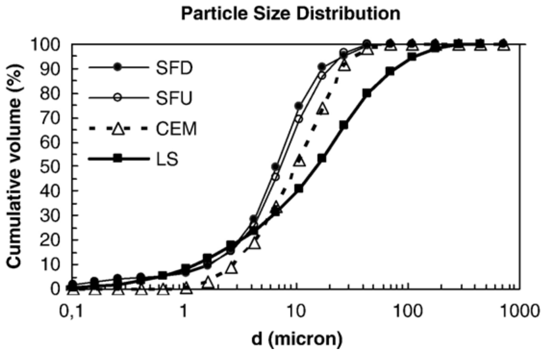

Fig. 1. Particle size distribution of the densified SF (SFD), undensified SF (SFU), cement and limestone.

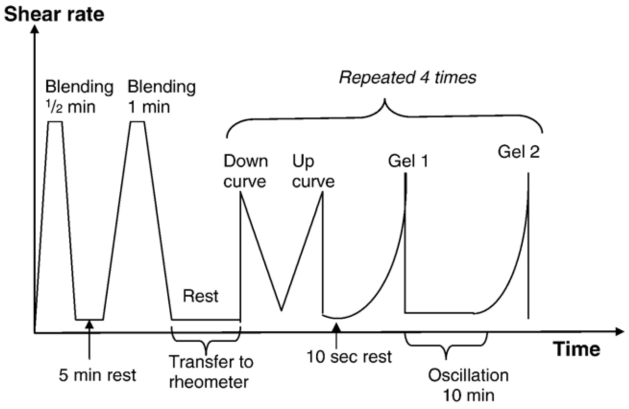

Fig. 2. Flow chart of the measurement sequence.

The rheological parameters were recorded by a parallel plate (1 mm gap, upper plate serrated to 150 μm depth) rheometer MCR 300 produced by Physica. The measurement sequence was started when the paste was 20 min old from the first contact with water and repeated 4 times to monitor time dependencies. All pastes with PA included all the following intervals and lasted 25 min. Measurements done on pastes with SNF were 5 min shorter since the first gel strength measurement was omitted. Elapsed time from water addition to the first measurement sequence was, however, equal for all pastes:

- Stress (τ) — shear rate ($\dot{\gamma}$) curve with linear sweep of $\dot{\gamma}$ from 200 down to 2 s^{-1} in 30 points lasting 6 s each (down-curve).
- Stress (τ) — shear rate ($\dot{\gamma}$) curve with linear sweep of $\dot{\gamma}$ from 2 up to 200 s^{-1} in 30 points lasting 6 s each (up-curve).
- 10 s resting as 5 points lasting 2 s each with no recording.
- Shear rate ($\dot{\gamma}$) – stress (τ) curve with logarithmic sweep of τ from typically 0.2 to 50 Pa (may vary) in 46 points lasting 5 s each to measure gel strength after 10 s rest.
- Oscillatory time sweep with 30 points lasting 20 s each with amplitude $\gamma = 0.1\%$ and angular frequency $\omega = 6$ s^{-1} measuring storage and loss moduli G' and G".
- Shear rate ($\dot{\gamma}$) – stress (τ) curve with logarithmic sweep of τ from 0.5 to 200 Pa (range may vary) in 60 points lasting 5 s each to measure gel strength after 10 min rest (i.e. oscillation).

The mixing and measurement sequence is illustrated in Fig. 2.

Rheological data were extracted from the down-curve. Homogeneous pastes were ensured by the shearing action of higher rates before the rate range of the calculations. Additional shearing of the pastes was, moreover, provided by the last gel strength measurement in each interval.

3. Results and discussion

3.1. Paste composition concept

The volume concentration of solids was kept constant throughout the test series since the apparent viscosity, $\eta \approx \tau/\dot{\gamma}$,

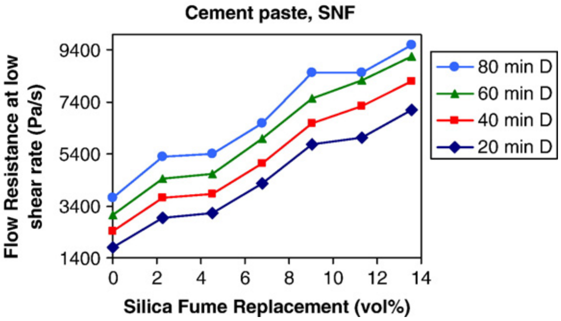

Fig. 3. Flow resistance as a function of undensified silica fume replacing cement and time (20 min between each interval) derived from low shear rate range (43–9 s^{-1}). 1.32% dry SNF superplasticizer was added by mass of powder (D=delayed plasticizer addition).

of slurries is a function of the volume concentration of solids, φ, according to the Krieger-Dougherty equation [8]:

$$\frac{\eta}{\eta_c} = \left(1 - \frac{\varphi}{\varphi_m}\right)^{-[\eta]\varphi_m} \tag{1}$$

where η_c is the viscosity of the continuous phase (1 mPa·s for water at 20 °C), φ_m is the maximum volume concentration of solids (about 0.65) and $[\eta]$ is the intrinsic viscosity of the suspension given by

$$[\eta] = \lim_{\varphi \to 0} \frac{\frac{\eta}{\eta_c} - 1}{\varphi} \cong 5 \tag{2}$$

3.2. Rheological model

The rheological measurements showed that the Bingham model was not suitable to model the data since cement pastes often exhibited shear thinning or shear thickening behavior. The Herschel–Bulkley model was, moreover, not suitable since it provided negative yield stresses [9]. The area under the flow curve measured at medium (152–118 s^{-1}) and low (43–8.8 s^{-1}) shear rate range was therefore chosen as an alternative rheological parameter to correlate with the paste characteristics. The medium shear rate range is relevant for mixing while the low is relevant for pouring concrete. The flow resistance will always be a positive value and not depend on curve shape. Furthermore, the choice between two parameters for correlation, as for the Bingham model, can be omitted. The area is obtained by multiplying the average yield stress,τ, with average shear rate, $\dot{\gamma}$, in each shear rate step, and it will have the unit Pa/s or W/m^3 (i.e. the power required to move a volume unit of paste in the prescribed manner).

Table 1
Flow resistance (FR) of cementitious pastes with undensified SF and 1.32% SNF (added with mix water)

SF (vol.%)	Interval	FR Medium shear rate range (Pa/s)	FR Low shear rate range (Pa/s)
0.00	1	9948	5851
2.26	1	8552	5652
4.52	1	11182	6507
6.79	1	14083	7546
0.00	2	10900	6264
2.26	2	9585	6209
4.52	2	12049	7105
6.79	2	14729	8527
0.00	3	12148	7050
2.26	3	11182	6809
4.52	3	13073	7416
6.79	3	13403	8075
0.00	4	13004	7648
2.26	4	12457	7399
4.52	4	13784	8226
6.79	4	11266	7333

Table 2
Gel strength (Pa) measured after 10 min oscillation for cementitious pastes with 1.32% SNF as a function of undensified SF replacement and time

	Gel strength (Pa)			
SF	Int. 1	Int. 2	Int. 3	Int. 4
(vol.%)	20 min	40 min	60 min	80 min
0.00	>120	>120	>120	>120
2.26	220	130	160	220
4.52	140	180	230	230
6.79	190	290	>300	280

3.3. Effect of silica fume on the rheological properties of cementitious paste

Flow resistance at low shear rate range for cement pastes with 1.32% delayed SNF addition is depicted as a function of undensified SF replacement in Fig. 3 while obtained results for pastes with immediate SNF addition are listed in Table 1. The flow resistance is seen to increase with increasing SF replacement independently of shear rate range confirming the findings of Park et al. [5].

Table 2 recites the results from gel strength measurements for the same pastes performed after 10 min rest (i.e. oscillation). The substantial increased gel strength with increasing SF

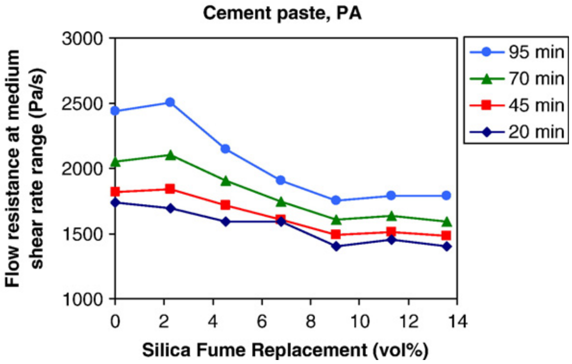

Fig. 4. Flow resistance as a function of undensified silica fume replacing cement and time (25 min between each interval) derived from medium shear rate range (152–118 s^{-1}). 0.79% dry PA was added by mass of powder.

Table 3
Gel strength (Pa) measured after 10 min oscillation for cementitious pastes with 0.79% PA as a function of undensified SF replacement and time

SF	Gel strength (Pa)			
	Int. 1	Int. 2	Int. 3	Int. 4
(vol.%)	20 min	45 min	70 min	95 min
0	46	39	43	49
2.26	43	41	46	61
4.52	58	49	52	69
6.79	61	55	52	61
9.05	67	56	52	59
11.31	92	76	71	92
13.57	103	87	87	109

replacement seen in Table 2 can be explained by the ionisation of SF surface due to the high pH and possible bridging with polyvalent cations like calcium (i.e. precursor to pozzolanic reaction) (Eq. (3)) and/or water uptake by the formation of CSH via a silica gel intermediate [10].

$$2{\equiv}\text{Si–OH} + \text{Ca}^{2+} + 2\text{OH}^{-} = {\equiv}\text{Si–O}^{-+}\text{Ca}^{+-}\text{O–Si}{\equiv} + 2\text{H}_2\text{O} \qquad (3)$$

Fig. 4 illustrates that the flow resistance *decreases* with increasing content of undensified SF when PA is added as plasticizer. The effect of SF on the rheology is thus dependent on the dispersing ability of the plasticizer. The flow resistances given in Figs. 3–4 and the gel strengths given in Tables 2 and 3 illustrate that PA has a much stronger dispersing ability than SNF. Thus, agglomerates of cement and silica fume are better dispersed and prevented from reforming after shear mixing. Thus, provided that the agglomerates are dispersed by the high shear blending and the plasticizer, small, spherical SF particles (average 0.15 μm) are able to pack in the gaps between relatively large cement grains (average 10 μm) which would otherwise be filled with water [11]. Such entrapped water would not contribute to the fluidity of the paste. The ball-bearing effect of rather spherical small particles on the irregular cement grains would also enhance the dispersion of the paste.

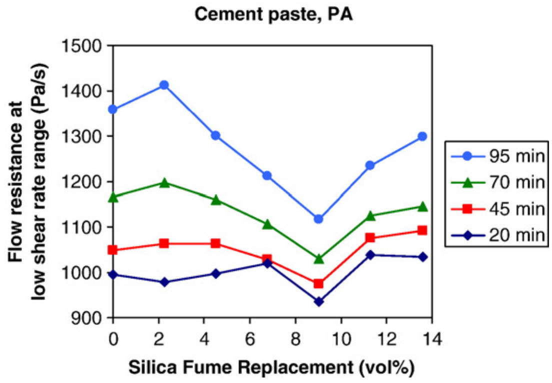

Fig. 5. Flow resistance as a function of undensified silica fume replacing cement and time (25 min between each interval) derived from low shear rate range (43–9 s^{-1}). 0.79% dry PA was added by mass of powder.

Table 4
Gel strength after 10 min rest (i.e. oscillation), τ_{10}, and flow resistance (FR) values of cementitious paste (w/c=0.40) with 0.79% PA

SF (vol.%)	Measurement interval	FR (medium) (Pa/s)	FR (low) (Pa/s)	τ_{10} (Pa)
0.00	1	1736	995	46
13.57	1	1405	1035	103
13.57 d	1	1697	1034	65
0.00	2	1919	1048	39
13.57	2	1481	1091	87
13.57 d	2	1803	1116	61
0.00	3	2053	1166	44
13.57	3	1593	1145	87
13.57 d	3	2113	1318	69
0.00	4	2436	1357	49
13.57	4	1791	1298	109
13.57 d	4	2564	1653	130

The plasticizer was added with the mixing water. Undensified and densified (d) silica fume are compared for 0 and 13.6 vol.% SF as a function of time.

Sellevold and Radjy [12] found similarly that the effect of SF was depending on the plasticizer dosage: The concrete water demand increased with the SF content when no plasticizer was added. However, no additional water was required to maintain the slump of a plasticized concrete as the content of SF increased. The water demand decreased, moreover, with increasing plasticizer dosages.

Fig. 5 illustrates that the flow resistance in the low shear rate range reaches a minimum at 9.05% SF replacement whereupon it is increasing probably due to gelling. The trends of flow resistance in the medium and low shear rate ranges coincide with the trends of the plastic viscosities and yield stresses respectively, derived from the Bingham model by Justnes and Vikan [1].

Increased flow resistance with increasing time can be explained by surface hydration of the cement grains that leads to increased volume fraction of solids (φ in Eq. (1)) in a twofold manner; removing liquid water and creating solid hydrates. For instance, 3% degree of hydration will increase apparent viscosity from 42.5 to 51.8 mPa·s (=cP) according to Eq. (1) (22% increase) when average density of hydration products is assumed to be 2.67 kg/m^3 and that 40% water is bound per anhydrous cement reacted (probably higher since ettringite dominates the early reactions) [13].

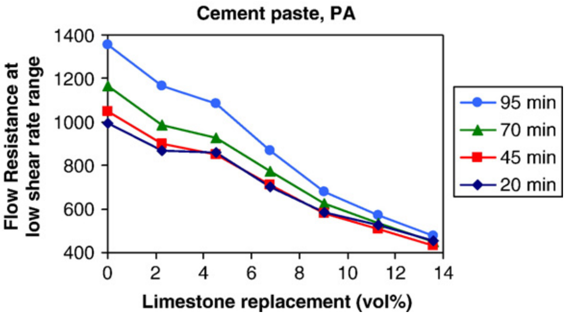

Fig. 6. Flow resistance at low shear rate range (43–9 s^{-1}) as a function of limestone replacement and time. 0.79% dry PA was added by mass of powder.

The influence of delayed PA addition (D), and densified SF (d) versus untreated SF, on measured gel strength can be seen in Table 4. The reduction in gel strength due to densification of SF (see $\tau_{10\ \mathrm{min}}$) may be due to unbroken SF agglomerates. Thus, there may be fewer outer boundary sites that can be bridged by Ca^{2+}.

3.4. Influence of limestone on the rheological properties of cement pastes

Fig. 6 shows flow resistance curves from the low shear rate range for cement pastes with 0.79% PA as a function of limestone replacement and time. Graphs from the medium shear rate range were omitted since the trends were similar to the ones found in the low shear rate range. Fig. 6 shows decreasing flow resistance with increasing limestone replacement which together with Fig. 7 indicates that the limestone particles disperse the cement particles more efficiently than SF or that less gel is formed due to coarser grains and lack of silanol groups. Limestone has a surface area of 486 m^2/kg which is considerably smaller than the surface area of SF which is 22,000 m^2/kg. The ball-bearing effect and packing of limestone between the cement particles is therefore not as efficient as for the smaller and more spherical SF particles. The dispersing ability of limestone is thus probably caused by lower reactivity than cement and less gel formation than SF.

Fig. 7 illustrates that limestone is not contributing to gelling. The graphs illustrate that the gel strength is nearly independent of limestone replacement until 8 vol.% whereupon it is decreasing. It is interesting to notice that the gel strength has an increasing tendency for limestone replacement up to 9.5% in the 4th measurement interval (114 min after water addition). These results indicate that limestone filler disperses the cement grains and that it may act as nucleation sites when the hydration sets in as proposed by Gjørv and Løland [14].

Finally, attempts were made to estimate gelling rate using the G' evolution (storage modulus) in the oscillation period and extrapolate it in time to the actual τ_{10} measurement. The procedure is described in detail elsewhere [15], but the results are plotted in Fig. 8. With the potential errors of disturbing the gel during the oscillation period, the plot show a steady increase of gelling rate with increasing silica fume replacement and a steady decrease with increasing limestone replacement. The differing trends for the flow resistance as a function of SF and limestone replacement may thus be caused by the different gelling tendencies of the two materials. Silica fume may as a consequence be advantageous as a stabilizing agent for self-compacting concrete preventing segregation upon standing and reduce formwork pressure due to faster formation of stronger gel compared to concrete binders with limestone.

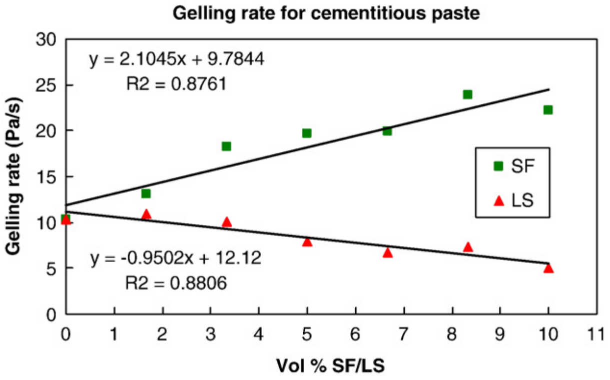

Fig. 8. Gelling rates of cementitious pastes as a function of undensified silica fume and limestone replacement. 0.79% dry PA was added by mass of powder.

4. Conclusions

The influence of SF replacement on the flow resistance depended on the plasticizer type: The flow resistance increased with increasing silica fume replacement when SNF was added as a plasticizer and decreased when PA was added. Increased flow resistance and gel strength with SF replacement using SNF may be caused by early gel formation due to water binding by SF or the ionisation of SF surface due to the high pH and possible bridging with polyvalent cations like calcium. Decreased flow resistance with increasing SF replacement using PA might be caused by the dispersing power of the plasticizer coupled with SF particle packing between cement grains displacing water or by a ball-bearing effect of silica spheres.

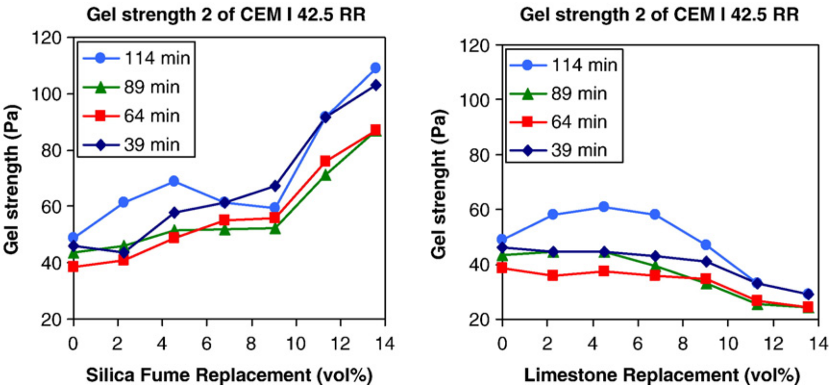

Fig. 7. Gel strength built up after 10 min rest (i.e. weak oscillation) as a function of undensified SF and limestone dosage and time (25 min intervals). 0.79% dry PA was added by mass of powder.

The measured gel strengths were lower for mixes with densified SF versus untreated SF. This effect was attributed to unbroken agglomerates in the densified SF.

The flow resistance was found to decrease when limestone replaced cement. Measured gel strengths were, moreover, markedly lower than for pastes with SF. These results indicate that limestone particles disperse the cement particles more efficiently than SF or that less gel is formed for limestone replaced cement pastes than for SF replaced pastes. The “bridging effect” of Ca is probably also absent due to coarser grains and no silanol groups. Silica fume may thus be advantageous as stabilizing agent for self-compacting concrete preventing segregation upon standing and reduced form pressure due to a more rapid gel formation.

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