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Effect of silica fume and slump-retaining polycarboxylate-based dispersant on the development of properties of portland cement paste

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ABSTRACT

This paper investigates the effect of silica fume (SF), a slump-retaining polycarboxylate ether (PCE) dispersant, and their combinations, on the fresh and hardened properties of ordinary portland cement paste. The investigated properties include hydration kinetics, rheological properties (i.e., plastic viscosity and yield stress), setting time, and compressive strength. Cement was partially replaced by SF at mass substitution levels of 0%, 10%, 20%, and 30%. The PCE dosages included 0%, 0.6%, 1.2%, 1.8%, and 2.4%, by mass of the binder. The results indicate that SF accelerates cement hydration rates and reduces the time of initial/final setting in relation to its content in the paste. This is due to the provision of additional C-S-H nucleation sites on SF surfaces. However, when PCE is present, such enhancement induced by SF is suppressed. In addition to enhancing cement hydration rate, SF reduces inter-particle spacing, thus amplifying rheological properties. In contrast, PCE reduces viscosity and yield stress. Both SF and PCE reduce 1-day compressive strength due to the effects of cement dilution (caused by SF) and the suppression of early-age hydration kinetics of cement (caused by PCE). The 7-day compressive strength, however, are broadly the same among the binary pastes; this is because the acceleratory and retarding effects of SF and PCE, respectively, are less pronounced at later ages. Finally, robust correlations between hydration kinetics, rheological properties, and compressive strength evolution are established. Those correlations can provide a basis for optimizing binder formulation and proportioning of high/ultra-high performance concrete.

1. Introduction

The fresh and hardened properties of cement paste dictate the properties of concrete, and are largely dependent on the development of the paste's microstructure as hydration of cement progresses [1]. Silica fume (SF) and slump-retaining polycarboxylate ether (PCE) superplasticizers have been used to improve the fresh and hardened properties of cement paste, especially in the context of designing high- and ultra-high-performance concrete [2–5].

The beneficial effect of replacing cement with SF on the mechanical strength and durability of cement paste are well-documented in literature [6–8]. Such enhancement in properties is attributed to two mechanisms. First, the very fine SF particles serve as fillers in the cement paste, providing additional sites for C-S-H[1] nucleation, and, thus, accelerating the hydration kinetics of cement [9–11]. This is known as the "filler" effect, which operates predominantly at early-ages when the rate of cement hydration is high. Second, and at later ages, SF undergoes a chemical reaction with portlandite (CH), typically referred to as the pozzolanic reaction, which leads to the precipitation of pozzolanic calcium-silicate-hydrate (C-S-H). Such formation of pozzolanic C-S-H improves the solid-to-solid phase connectivity within the paste's microstructure, which, in turn, manifests as improvement in properties, including higher strength and enhanced durability [12–19]. Due to the relatively low reactivity of SF compared with cement, the pozzolanic reaction is typically slow, and, thus, anecdotally considered a secondary mechanism [9,18–20] with limited impact on hydration kinetics and property development within the first 7 days of hydration.

In addition to the favorable effects on hardened properties, SF – on account of the fineness of its particles – improves the particle packing density of the paste [21]. However, in cementitious environments, the

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[1] As per the standard cement-based notation: C = CaO, A = Al_2O_3, F = Fe_2O_3, S = SiO_2, T = TiO_2, \$ = SO_3, H = H_2O, an. $\bar{C}$ = CO_3.

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fine SF particles are highly susceptible to agglomeration due to the large magnitude of the Van der Waals forces, especially when the SF content is high (i.e., replacement level ≥ 20% by mass, which can cause significant reduction in inter-particle spacing at the time of mixing and, thus, amplifies the Van der Waals interactions). Such agglomeration of SF particles may have adverse effects on the hydration kinetics, rheological properties, and development of mechanical properties [9,22]. Firstly, the agglomeration of SF particles results in a disproportionately smaller enhancement in cement hydration kinetics in relation to area increment. This is because of large reduction in the exposed surface area of SF particles, thus rendering it unavailable for heterogeneous nucleation of C-S-H. Secondly, the agglomeration of SF particles may lead to poor rheological properties, especially in the case of high-performance concrete that typically has a high SF content (i.e., 10%-to-25% by mass) [23–28]. For example, past studies have shown that in the absence of a superplasticizer (also referred to as dispersant), the yield stress and plastic viscosity of cement paste increase with SF content [29]. Poor or uncontrolled fresh properties may significantly diminish hardened properties, and compromise acceptance of the material in concrete construction [17,26].

To alleviate the effect of particle agglomeration and to improve workability of ready mix concrete, PCE superplasticizers (e.g., precast-type or slump-retaining PCE) – wherein each molecule has a comb-shaped architecture – are used as dispersants in systems made with SF. The backbone (i.e., comprised of polyacrylic or polymethacrylic polymers) of the PCE adsorbs onto cement particulates [9,30]; while the side chains (i.e., comprised of polyethylene oxide), which are oriented outward into the solution, act to disassemble the flocculated/agglomerated particles [31,32]. Experimental studies on cementitious pastes with various water-to-binder ratios (w/b) have demonstrated that PCE improves the dispersion of cement particles and reduces the viscosity by increasing the packing density and water film thickness in the paste [33,34]. Although some PCEs improve the overall rheological behavior of the paste, the hydration of cement can be suppressed by slump-retaining PCE [35,36]. This can be attributed to the adsorption of the PCE molecules onto cement surfaces, which inhibits surface dissolution and the formation of product nucleation sites [9,31,32,37–44]. Similar to cement particles, the surface charge of SF particles – in cementitious environments – is positive due to the enrichment of adsorbed Ca^{2+} species onto negatively charged silanolate groups of its surface [2]. As such, the retarding PCE molecules adsorb onto SF surfaces as well [9], and aids in the dispersion of SF particles [45]. Therefore, the adverse (i.e., hydration-retarding) effect of the PCE on cement hydration could be mitigated by adding SF, which provides additional surfaces for PCE absorption, and, as such, reduces PCE adsorption on cement surfaces [46,47]. However, the adsorption of PCE on SF surfaces blocks nucleation sites provided by the SF particles [47], and, therefore, diminishes its filler effect. Based on these results, it can be said that SF and slump-retaining PCE have competing effects – wherein the replacement of cement by SF produces reactivity enhancement, and the addition of PCE suppresses hydration [9,18,19,30–32,48,49]. Nevertheless, there is no consensus on how the combination of SF and PCE affects the development of fresh and hardened properties of cement paste. Knowledge of fundamental mechanisms of cement hydration, rheological properties, setting, and strength development in the presence of both SF and PCE is vital to determine the optimum amounts of SF and PCE for high- and ultra-high performance concrete.

In this study, experimental investigations on key properties of cement paste were carried out, including isothermal calorimetry for hydration kinetics, determination of rheological properties, thermogravimetric (TG) analyses for phase quantification, setting time measurement, and mechanical strength evaluation. A wide range of slump-retaining PCE dosages (0–2.4%, by mass of binder) and SF replacement levels (0–30%, by mass of binder) were investigated. Correlations between the hydration kinetics and rheological properties, setting time, and mechanical strength were established for optimizing binder formulation and proportioning of high and ultra-high performance concrete.

Table 1
Chemical composition of cementitious materials.

Phases	Cement	Silica fume
Oxides (XRF results)	Mass%	Mass%
SiO_2	19.8	95.5
Al_2O_3	4.5	0.7
Fe_2O_3	3.2	0.3
CaO	64.2	0.4
MgO	2.7	0.5
SO_3	3.4	–
Na_2O equivalent	–	0.4
Loss of Ignition (LOI)	2.6	1.0
Crystalline phases (QXRD results)	Mass%	Mass%
Alite (C_3S)	61	
Belite (C_2S)	8	–
Aluminate (C_3A)	6	–
Ferrite (C_4AF)	9	–
Gypsum (C$.2H)	3.4	–

2. Materials and experimental program

2.1. Materials

A Type I ordinary portland cement (OPC) and a commercially-available SF product were used in this study. Their chemical compositions were determined using X-ray fluorescence (XRF) and quantitative X-ray diffraction (QXRD) techniques. The results are listed in Table 1. The particle size distributions (PSDs) of OPC and SF were determined using the static light scattering (SLS) method, and the results are plotted in Fig. 1. The median particle size (d_{50}, μm) of the cement and SF was determined as 9.98 μm and 0.23 μm, respectively. By factoring the density (i.e., 3150 $kg\,m^{-3}$ for cement and 2250 $kg\,m^{-3}$ for SF), the total specific surface areas (SSAs, $m^2 \cdot kg^{-1}$) of the cement and SF were calculated according to the PSDs as 380 $m^2\,kg^{-1}$ and 18,200 $m^2\,kg^{-1}$, respectively. A slump-retaining PCE dispersant that has a solid mass content of 23% and a density of 1050 $kg\,m^{-3}$ was used. The molecular architecture of the comb-shaped PCE polymer consists of a polymethacrylic backbone (14.1 nm) with grafted poly (ethylene oxide) side chains (25.1 nm).

All pastes were prepared at a constant liquid-to-solid ratio (l/s) or w/b of 0.45, by mass. To investigate the effect of SF on the properties of

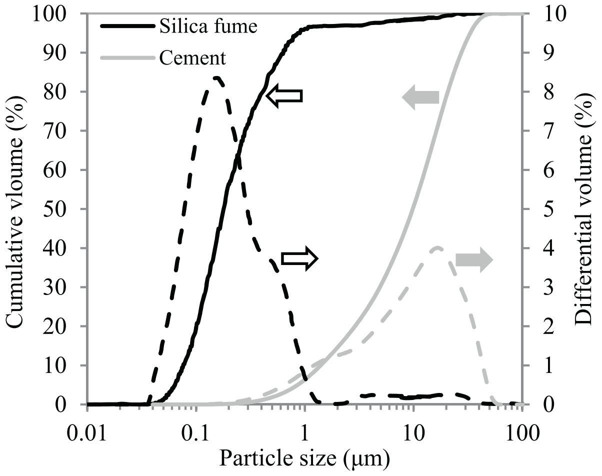
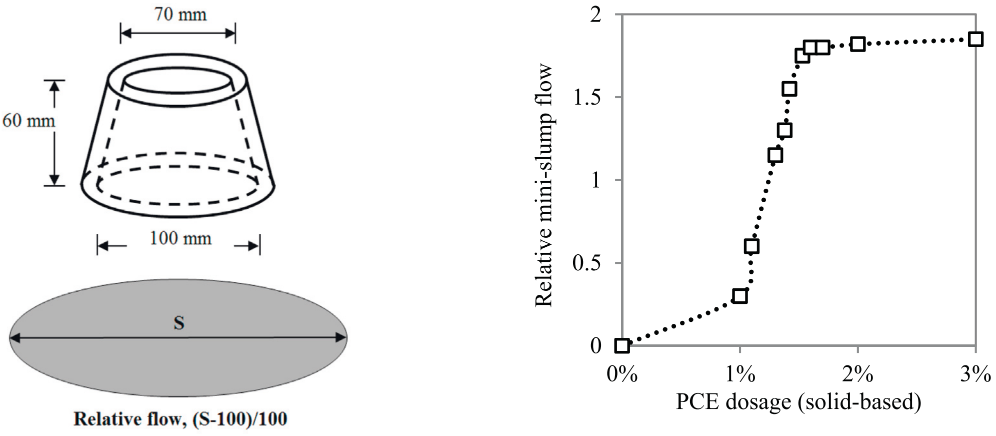


Fig. 1. Particle size distributions of the cement and silica fume. The highest uncertainty was 6% based on six replicate measurements.



(a) (b)

Fig. 2. (a) Dimensions of the mini-slump cone, and (b) relative flow of the slump of a binary paste prepared with 30% SF and different dosage of PCE.

the paste, cement was partially replaced by SF at 0%, 10%, 20%, and 30%, by mass. To determine the upper bound of the slump-retaining PCE content for paste with w/b of 0.45, the effect of PCE on mini slump spread value of paste was investigated. The dispersant was added to the mixing water at dosages of 0%, 0.6%, 1.2%, 1.8%, and 2.4%, respectively, by mass as liquid of the binder (i.e. 0%, 0.14%, 0.36%, 0.42%, and 0.56%, respectively, by mass as solid of the binder). The upper bound (2.4%) of the PCE dosage was determined by mini-slump flow test to correspond to the saturation point (i.e., beyond this point, increase of PCE content does not change spread of the slump flow) of the paste made with w/b of 0.45.

The mini-slump flow tests of binary pastes prepared with different dosages of PCE were conducted in the following three steps in accordance with ASTM C 230/C 230 M [50]: (1) pour the paste into a mini-slump cone to its full capacity without any mechanical consolidating (i.e. the paste is self-consolidating), as illustrated in Fig. 2(a); (2) lift the cone after 30 s (sec) to allow the paste to spread; (3) measure the maximum diameter of the paste spread circular in two perpendicular directions. The measured spread is then used to calculate the relative mini-slump flow that is defined as (S-100)/100, where S (unit: mm) is the spread value, and the cone's bottom diameter is 100 mm. Fig. 2(b) shows the testing results of the binary paste containing SF at 30% mass replacement level. The paste's flowability increases with the PCE dosage until the dosage reaches 2.4% of the mass of the binder. Beyond this critical dosage (2.4%), further increments in PCE dosage do not change the flowability. Thus, this critical dosage is referred to as the saturation point of the test mixture. The same test was conducted for all the binary pastes to determine the saturation points of PCE dosage and ensure homogenous dispersion of all the investigated paste mixtures. To ensure homogenously dispersion of all investigated pastes, the upper bound of PCE dosage was determined to be 2.4% of the mass of the binder. The lower PCE dosages correspond to 25%, 50%, and 75% of the maximum dosage (i.e., 2.4% $_{\text{mass}}$ of the binder), respectively.

2.2. Experimental program

All pastes were prepared and tested at room temperature (23 ± 2 °C). In each batch, 600 mL of paste mixture was mixed using a 5.6-L Hobart mixer. The following mixing procedure was followed: (1) mix dry cementitious materials at 1 rps (revolutions-per-second) for 1 min; (2) introduce well-mixed water/PCE solution and mix at 1 rps for 20 s and then at 4 rps for 30 s; (3) scrap materials sticking at the mixing bowl's bottom for a duration of 30 s; and (4) mix the mixture at 4 rps for 1 min. Special care was taken to ensure homogeneity of the paste (i.e., complete wetting of the solids with DI-water).

After mixing, the heat of hydration of each paste was monitored for up to 96 h (4 days) using an isothermal conduction calorimeter (Calmetrix I-CAL 8000) that was programmed to maintain the sample at a constant temperature (20 ± 0.1 °C).

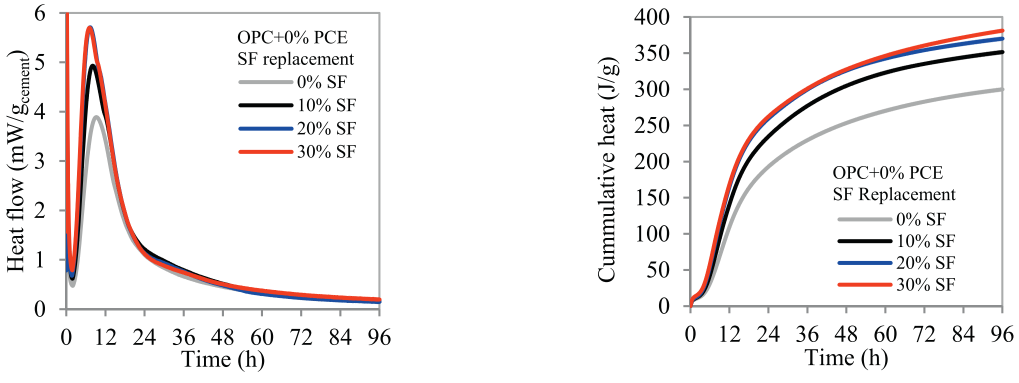
A SDT600 thermogravimetric analyzer (TGA) was used to identify and measure the quantities of phases present at different hydration times. The temperature and mass sensitivity of the analyzer are 0.25 °C and 0.1 μg, respectively. Hydration was arrested at a given age (i.e., 1 day and 7 days) by crushing the hydrated paste into grains smaller than 5 mm, and submerging them in isopropanol for 24 h. The samples were then oven dried at 85 °C, after which they were finely powdered using an agate mortar and pestle. The powder samples were heated under N_2 purge at a flow rate of 100 mL min^{-1} and a heating rate of 10 °C·min^{-1} in pure aluminum oxide crucibles over a temperature range of 30 °C–1000 °C. Mass loss (TG) and the differential mass loss (DTG) patterns were used to quantify the amount of CH and calcite (if any may have formed due to carbonation of C-S-H and CH) present in the system. For these phase quantifications, well-established methods detailed in prior studies [51,52], were used.

The rheological properties of the pastes were tested using a co-axial rheometer (ConTech 6 viscometer) at 70 min after initial water contacting with the cementitious materials. The measurements were subjected to pre-shear at a rotational velocity of 0.5 rps for 25 s, followed by a stepwise reduction in rotational velocity from 0.5 rps to 0 rps. The yield stress (τ_0) and plastic viscosity (μ_p) were calculated using the Bingham fluid model [53], as shown in equation (1).

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{1}$$

where $\dot{\gamma}$ denotes the shear rate. Replicate measurements using at least three separately mixed paste batches, were carried out for each mixture, and the rheological measurements were determined for each of these mixtures. The coefficients of variation were in the range of 5% for τ_0 and 8% for μ_p across all samples.

The initial and final setting times of the pastes were evaluated in accordance with ASTM C191 [50]. Compressive strengths was evaluated at 1, 4, and 7 days, using 50 mm cube specimens in accordance with ASTM C 109 [50]. The specimens in molds were immediately covered with wet burlaps and plastic sheets and demolded after 1 day, and then cured in lime-saturated water at 23 ± 1 °C until the time of testing. Three samples were replicated in each test. The coefficient of variation for the compressive strength was found less than ± 5%.



(a) (b)

Fig. 3. (a) Heat flow rates and (b) cumulative heat of OPC replaced by SF at different percentages with 0% PCE. The measurement uncertainty is ± 2%. The l/s for all pastes is 0.45.

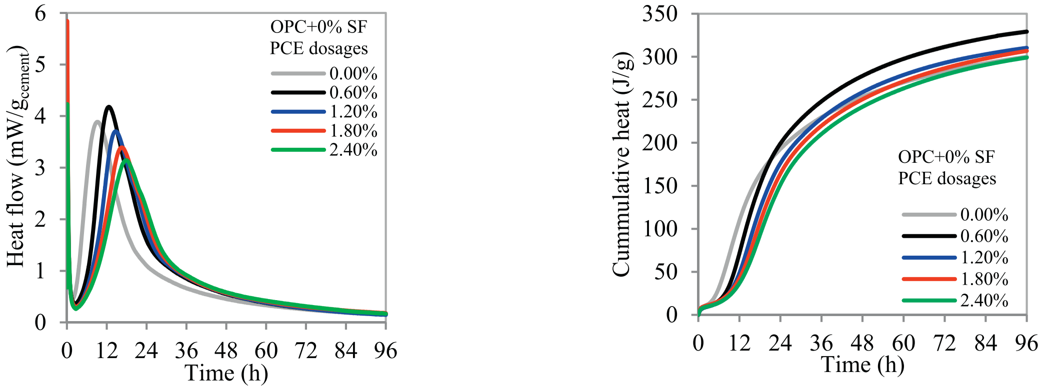
3. Results and discussions

3.1. Hydration kinetics of plain and binary pastes

Fig. 3 shows the effect of SF on cement hydration kinetics. As the SF content increases, the heat evolution curves are shifted leftward (Fig. 3(a)), indicating that both the slope of the acceleration regime (i.e., the period between the induction period and the main hydration peak) and the peak heat flow rate are increased. Also, the cumulative heat release increases with SF replacement levels (Fig. 3(b)). These reactivity enhancements are attributed to the filler effect of SF. More specifically, the addition of very fine SF (Fig. 1) particles provides additional nucleation sites for the heterogeneous nucleation of C-S-H, and, thus, promotes the hydration kinetics of cement. However, the acceleratory effect of SF becomes less pronounced as the replacement level increases from 20% to 30%. This is attributed to two mechanisms: (1) the agglomeration of SF particles reduces their exposed surface area and hinders the heterogeneous nucleation of C-S-H [1,17,54–58]; (2) the nucleation site is saturated as to the surface area provided by SF exceeds, by far, the number density of C-S-H nuclei formed at prevalent levels of cement content [9]. Because of the fine size (d_{50} = 0.23 μm) of the SF particles, the effects of particle agglomeration are expected to be more dominant compared with that of nucleation site saturation [9].

The slump-retaining PCE used in this study suppresses cement hydration kinetics in both plain and binary paste systems increasingly with its dosage (Fig. 4(a)). The addition of the PCE delays the onset of the acceleration, and this results in prolongation of the induction period. This retarding effect of the slump-retaining PCE propagates beyond the induction period, resulting in delayed occurrence of the main hydration peak and suppressed values of peak heat flow rate. The retardation induced by the slump-retaining PCE is because of the adsorption of PCE molecules on the surfaces of cement and SF particles. Such adsorption inhibits surface dissolution and product nucleation sites, thus resulting in suppression of the overall hydration kinetics [34,45]. It is important to note that the effect of the slump-retaining PCE used in this study on the overall heat release at later ages (Fig. 4(b)) is less pronounced. This is because in pastes provisioned with the PCE, the post-peak deceleration is slower as compared with equivalent pastes that are devoid of the PCE (Fig. 4(a)); as such, PCE-containing pastes react faster at later ages), and are able to recoup the loss in early-age reactivity.

The competing effects of PCE and SF on cement hydration rates are shown in Fig. 5. Here, key calorimetric parameters, extracted from heat evolution profiles of plain and bended pastes, are shown. The calorimetric parameters provide quantitative description of changes in hydration kinetics in response to SF and PCE additions. At any given PCE dosage, the time corresponding to the main hydration peak decreases significantly, and following an approximately linear relationship, with SF replacement level (Fig. 5(a)). This is attributed to additional heterogeneous nucleation of C-S-H on the SF surfaces via the filler effect [9]. However, such enhancements in reactivity becomes less pronounced when SF is greater than 20%; as stated previously, this is due to effects of agglomeration and nucleation site saturation [9]. The time of occurrence of the peak increases, and the peak heat flow rate



(a) (b)

Fig. 4. (a) Heat flow rates and (b) cumulative heat release of plain paste system (0% SF) at different slump-retaining PCE dosages. The measurement uncertainty is ± 2%. The l/s for all pastes is 0.45.

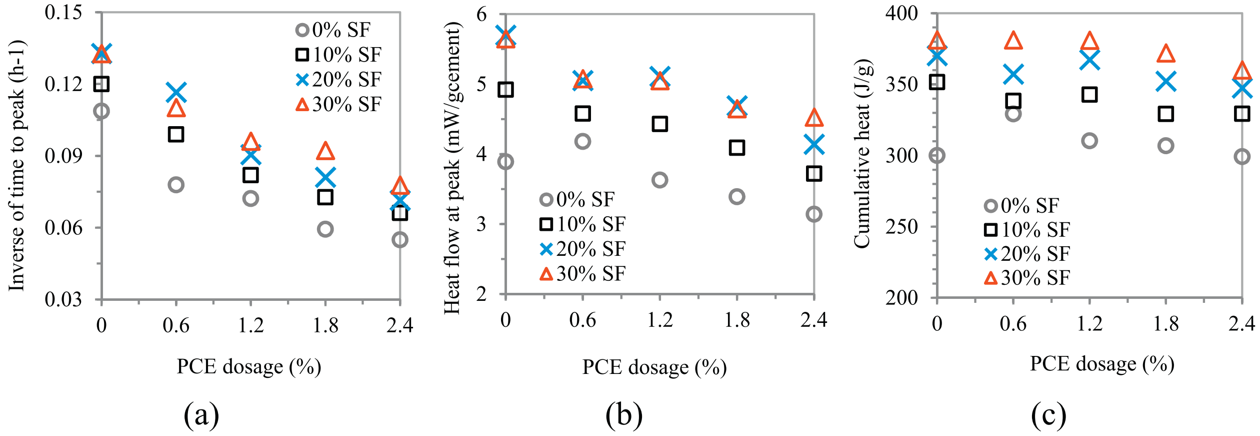


Fig. 5. (a) Inverse of time to the main hydration peak, (b) heat flow rate at the main hydration peak, and (c) cumulative heat release at 96 h of hydration of plain and binary pastes with different slump-retaining PCE dosages extracted from the calorimetry profiles. The measurement uncertainty is ± 2%. The l/s for all pastes is 0.45.

(Fig. 5(b)) decreases, with PCE. Furthermore, it is noted that, in both plain and binary pastes, the cumulative heat release at 96 h decreases with PCE dosage (Fig. 5(c)). This suggests that inhibition of dissolution and nucleation sites, as caused by the slump-retaining PCE, are carried over to later-ages, but becomes less pronounced. As stated previously, this is expected because in PCE-containing pastes the post-peak hydration kinetics are superior compared with those prepared without PCE; as such, at later-ages, the cement in pastes ends up hydrating to more or less the same extent regardless of the PCE dosage. Lastly, it is noted that in binary pastes – regardless of the PCE dosage – the cumulative heat release at 96 h increases with SF replacement level. This is because the fraction of SF's surface area, which is unaffected by PCE adsorption, is still able to offer additional sites for heterogeneous nucleation of C-S-H; this counteracts not only the retarding effect of PCE but also the effect of cement dilution (i.e., less cement in paste due to partial replacement by SF), and produces higher heat compared with the plain system.

To validate the hypotheses made in the preceding paragraphs, the portlandite contents of the pastes, as measured using the TG methods, are shown in Fig. 6. The portlandite contents of both plain and binary pastes at 1 day decline monotonically with PCE dosage (Fig. 6(a)). These results are in very good agreement with those shown in Figs. 4 and 5, and confirm that PCE suppresses cement hydration in relation to its dosage. However, at given PCE dosage, portlandite contents in binary pastes remain consistently similar to that in the plain system (Fig. 6(a)). This is because of the filler effect of SF. Specifically, the fraction of SF's area – which is unaffected by PCE adsorption – is still able to serve as a filler and offer additional sites for heterogeneous nucleation of C-S-H; this supersedes the retarding effect of slump-retaining PCE and the effect of cement dilution, and produces commensurable portlandite content as compared with the plain system. Equivalent portlandite contents in binary pastes also suggests that the pozzolanic activity of SF – in which SF reacts with portlandite to form pozzolanic C-S-H – is negligible within the first 24 h of hydration; similar trends in portlandite contents, for equivalent [cement + SF + PCE], were also reported in our previous study [9]. To better understand this, let us consider equations (2) and (3) which show hydrolysis (i.e., the first step of SF's dissolution) and pozzolanic reaction of SF, respectively:

$$\equiv \text{Si–O–Si} \equiv \; + \; \text{H–OH} \rightarrow \; \equiv \text{Si–OH} \tag{2}$$

$$\equiv \text{Si–OH} \; + \; \text{Ca(OH)}_2 \rightarrow \text{C–S–H} \tag{3}$$

In the binder-water system (especially at pH ≪ 13.0), the Si–O bond of SF is difficult to rupture owing to its higher bond energy [17]; thus, the process shown in equation (2) is slow, and, as such, pozzolanic reaction (equation (3)) is limited at early ages [11]. In addition, when SF replacement level is high (i.e. SF ≥ 20%), particle agglomeration significantly reduces the effective surface area, thus further reducing pozzolanic reaction with CH [9,11].

At 7 days of hydration, the trends in portlandite contents are

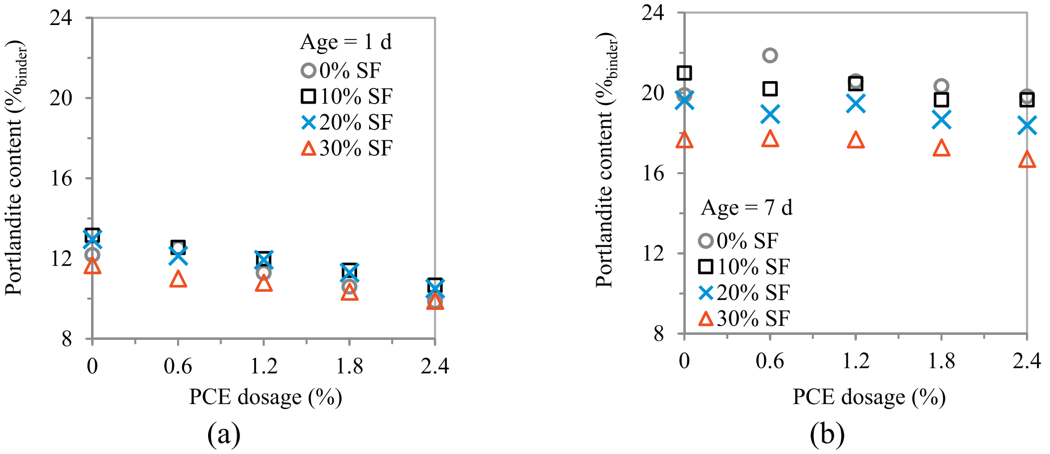


Fig. 6. Portlandite contents (by mass % of the binder, i.e., dry paste) in plain and binary pastes: (a) after 1 day of hydration, and (b) after 7 days of hydration, determined from DTG analyses. The l/s for all pastes is 0.45. The highest uncertainty in phase quantifications by DTG is ± 4%.

different from those observed at 1 day (Fig. 6(b)). Foremost, it is observed that the slump-retaining PCE has negligible effect on portlandite content of a given paste (either plain or binary) at 7 days; for example, in the [cement + 30% SF] paste, the 7-day portlandite contents do not change significantly with PCE dosage. These results are in very good agreement with the results shown in Fig. 5(c), wherein it is shown that the later-age cumulative heat release does not change significantly with PCE dosage. When combined, these results strongly suggest that the early-age retardation caused by PCE does propagate to 7 days, but the retarding effect is progressively contracted after the main hydration peak and, ultimately, becomes insignificant at later-ages (i.e., age ≥ 4 days). Going back to Fig. 6(b), it can be seen that SF has a more pronounced effect on portlandite content at 7 days. Here, the portlandite contents decrease with increasing SF replacement levels. The decrease in portlandite content – in relation to SF content – is attributed to combined effects of cement dilution (i.e., less cement in [cement + SF] paste) and the pozzolanic activity of SF. It is pointed out that the effect of cement dilution exists at early-ages too, but they do not reflect in the measurements of heat or of portlandite contents because they are superseded by the acceleratory filler effect of SF. At later-ages, when SF's filler effect no longer plays a major role, the pozzolanic effect of SF (which results in consumption of portlandite) and the effect of cement dilution become relatively more pronounced and, consequently, manifest as smaller portlandite contents in the cement + SF paste systems.

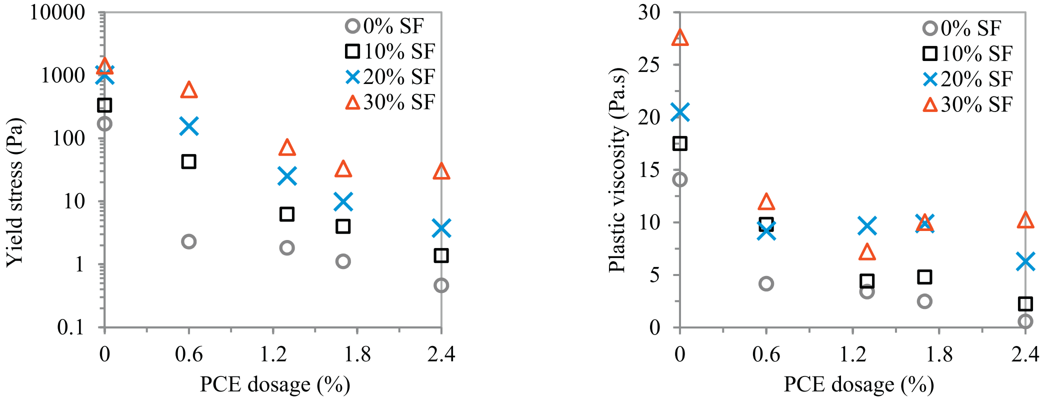
3.2. Rheological properties

In this study, the yield stress and plastic viscosity at 70 min after water addition were investigated to evaluate the influence of SF and PCE. Results obtained from the tests are plotted in Fig. 7(a) and (b). Both the yield stress and plastic viscosity increase with SF content. For pastes prepared without PCE, as the SF content increased from 0 to 30%, the yield stress increased from 170 Pa to 1420 Pa (by 735%, see Fig. 7(a)); the plastic viscosity increased from 14 Pa s to 28 Pa s (by 100%, see Fig. 7(b)). This is hypothesized to be due to the combined effect of two mechanisms that are operating simultaneously. The addition of SF promotes cement hydration by providing additional surface area for nucleation of C-S-H. In addition to bolstering C-S-H nucleation, SF imparts profound effects on the dispersion and packing of particles (i.e., average inter-particle spacing) in the paste. The addition of fine SF particles reduces inter-particle spacing and the content of free water in the paste (i.e., due to water adsorption on SF surfaces). Reduced inter-particle spacing leads to higher inter-particle friction. Due to the combined effects of enhanced C-S-H nucleation and higher inter-particle friction, the paste's shear resistance is amplified, thus increasing the yield stress and plastic viscosity [59]. In contrast to the response of [cement + SF] pastes, the rheological properties of PCE-containing plain pastes decrease with the dosage of PCE. In plain pastes, as the PCE dosage increased from 0 to 0.6%, the yield stress reduced from 170 Pa to 0.46 Pa (by 99.7%, see Fig. 7(a)); the plastic viscosity reduced from 14 Pa s to 0.56 Pa s (by 96.0%, see Fig. 7(b)). This is because, the hydration kinetics are suppressed in the presence of PCE. In addition, the slump-retaining PCE enhances particle dispersion, increases inter-particle spacing, enhances free water content in the paste, and, thus, reduces inter-particle friction. Due to the combined effects of suppressed hydration of cement and reduced inter-particle friction, the yield stress and plastic viscosity of pastes are reduced [16]. In cement + PCE + SF systems, PCE and SF have competing effects. PCE decreases, whereas SF increases the rheological properties.

3.3. Setting time

The measured initial and final setting times of plain and binary pastes with different PCE dosages are presented in Fig. 8(a) and (b), respectively. Both the initial and final setting times decrease and increase with SF content and PCE dosage, respectively, approximately in linear fashion. The underlying mechanisms are associated with the effects of SF and PCE on the amount and connectivity of hydrates. The addition of fine SF particles provides larger surface area that facilitates the nucleation and precipitation of hydration products, thus bolstering the growth of hydrates and increasing their connectivity within the microstructure. This manifests as shorter times of initial and final setting of the pastes. The addition of PCE suppresses the formation of product nuclei and its subsequent growth; these effects act to impoverish the connectivity of the hydration products, thus resulting in prolongation of the initial and final setting times [60,61]. In pastes containing both SF and PCE, the acceleratory and retarding effects of SF and PCE, respectively, compete, and produce a composite response.

An interesting observation is that, at higher PCE dosages, the reductions in the final setting times – as induced by SF – are less pronounced as compared to those prepared at low PCE dosages (i.e., at equivalent but high PCE dosages, final setting times of binary pastes are similar to those of plain pastes). More specifically, and as shown in Fig. 8(b), as the SF content increases from 0 to 30%, the final setting time is reduced from 460 min to 330 min (by 28%) for the paste without any PCE, and from 720 min to 660 min (by 8%) for the paste with 2.4% PCE. This convergence of the final setting times at higher PCE dosages is because of the competing acceleratory and retarding effect of SF and PCE, respectively. More specifically, at low PCE dosages, the acceleratory effect of SF is more dominant than the retarding effect of PCE; as such, large reductions in final setting times occur with increasing SF replacement level. However, at higher PCE dosages, the enhanced



(a) (b)

Fig. 7. Rheological properties of the investigated cement paste at 70 min after water addition: (a) yield stress; (b) plastic viscosity. The highest uncertainty of rheological properties quantification is ± 2%.

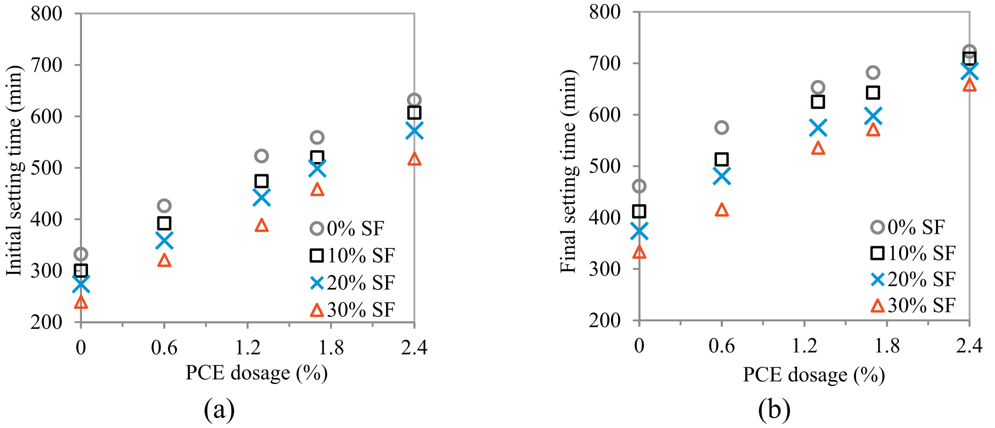


Fig. 8. Setting times: (a) initial setting time; (b) final setting time.

adsorption of PCE molecules on the surfaces of SF particles suppresses the acceleratory filler effect of SF; as such on the setting times of binary pastes are more similar to those of plain paste [62].

3.4. Compressive strength

Fig. 9(a) and (b) show the compressive strengths of plain and binary pastes at 1 and 7 days, respectively. The 1-day compressive strength decreases with SF content (Fig. 9(a)). However, at 7 days, the difference between plain and binary paste systems is significantly reduced, regardless of PCE content (Fig. 9(b)). The mechanisms by which SF causes alteration in strength gain at early age and later ages are slightly different.

The 1-day and 7-days strength reduces with increase in SF replacement level, which is primarily because of reduction in the cement content of the paste. Such dilution of cement content leads to reduced amount of C-S-H, increased porosity, and, thus, lower strength. In addition to the effect of cement dilution by SF, other mechanisms play a role in reducing the 1-day strength. Within the first day of hydration, the pozzolanic reaction of SF is very slow due to the slow dissolution kinetics of SF [63] – and, therefore, the formation of pozzolanic C-S-H is limited. However, at 7 days of hydration, the pozzolanic reaction of SF starts to accelerate [17], and, therefore, more pozzolanic C-S-H is produced and porosity is reduced. Notably, pastes prepared with low SF content and low PCE dosage exhibit higher 1-day and 7-day strength than the control system. This is due to sufficient cement content in the pastes, suitable content of PCE (i.e. ≤ 0.6%) which enhances particle dispersion, and formation of pozzolanic C-S-H. However, at high SF replacement levels (i.e. ≥ 20%), the agglomeration of SF particles adversely affects its filler effect and pozzolanic activity, thus disallowing large fraction of SF's surface area to partake in formation of C-S-H and pozzolanic C-S-H. Such reduction in the reactivity of SF makes the effect of cement dilution more pronounced, and causes higher porosity in the system [64]. Also, at high SF replacement levels, due to severe agglomeration of SF particles, even high PCE dosages are inadequate to alleviate particle agglomeration – this diminishes the filler and pozzolanic effect of SF.

In the presence of PCE, it is observed that when 10% of SF is incorporated, slightly higher strength is obtained compared with that of plain paste at low PCE dosage (i.e., ≤0.6%). This is because the cement content of paste is high, and the low dosage of PCE is able to alleviate – at partially – agglomeration of SF particles without significantly retarding the reaction. However, at high SF replacement levels, SF particles agglomerate extensively; PCE provides some relief from agglomeration, but does not necessarily increase “exposed surface area” of SF particles [9]. Specifically, the adsorption of PCE molecules on the cement and SF particles' surfaces hinders their ability to serve as nucleation sites for C-S-H and suppresses the hydration kinetics of cement; these retarding effects increase progressively with PCE dosage [65]. As a result, the 1-day compressive strength of binary pastes – including those provisioned with PCE – are consistently lower than the plain pastes. However, at 7 days, the fraction of SF's surface, which is still exposed to the solution, is able to exert filler effect and participate in the pozzolanic reaction with portlandite; these effects contribute to the strength-gain of the paste [9,57,66]. When these competing effects of PCE and SF are consolidated, it is noted that at 7 days, regardless of the

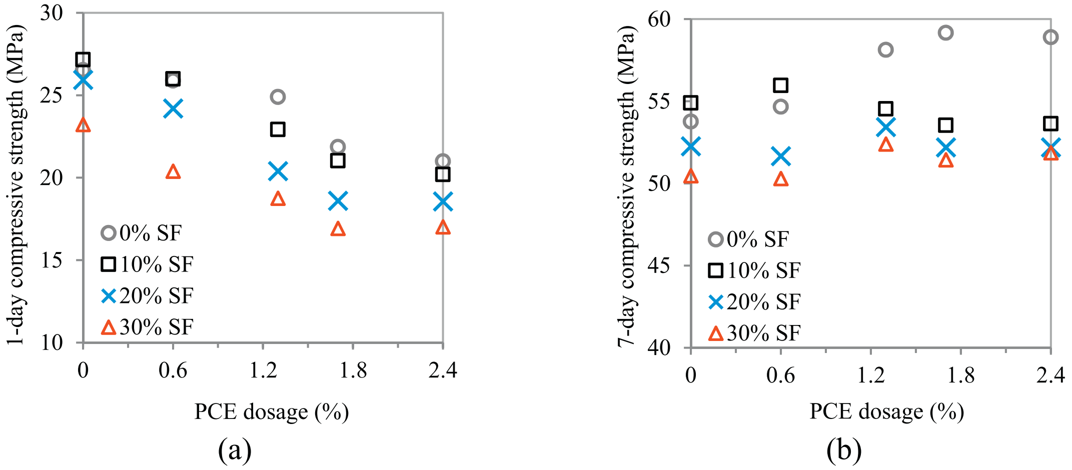


Fig. 9. Relationship between the compressive strength and PCE dosage at: (a) 1 day; (b) 7 day of hydration.

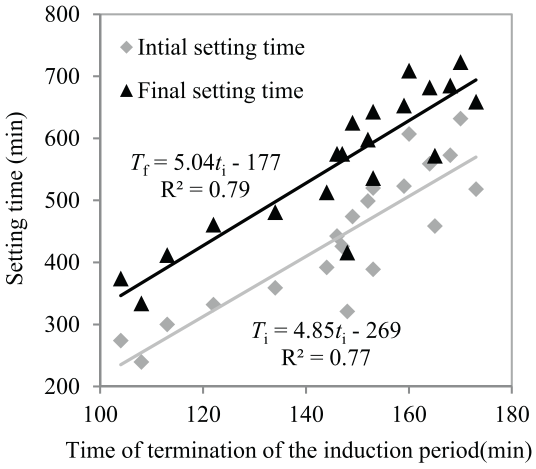


Fig. 10. Correlations between initial and final setting times and time of termination of the induction period for heat flow curves of all investigated mixtures.

PCE dosage, all binary pastes develop broadly similar strengths (i.e., within ± 5 MPa of each other).

4. Correlations between hydration kinetics and property development

The initial setting time (T_i) and final setting time (T_f) are correlated with the time (t_i) of the termination of the induction period, as shown in Fig. 10. Both the initial and final setting times increase with the time of termination of the induction period. This is because the hydration product starts to precipitate (in large amounts) and the connection between hydrates begins to build when the induction period is terminated. The relationship between the setting time and termination of the induction period is broadly linear (see equations highlighted in Fig. 10), and serves as simple means to predict the initial and final setting times of the pastes by merely using the heat evolution profiles as input.

The relationship between the time (t) corresponding to the main hydration peak and the rheological properties at 70 min after water addition is shown in Fig. 11(a) and (b). Both the yield stress and plastic viscosity at 70 min decrease with the time corresponding to the main hydration peak. A shorter time of occurrence of the main hydration peak implies faster formation of hydration products and, thus, faster transition from slurry to plastic state. The faster growth of C-S-H, turns the soft interaction among cementitious particles into more rigid interactions in shorter time, and, consequently, results in higher rheological properties.

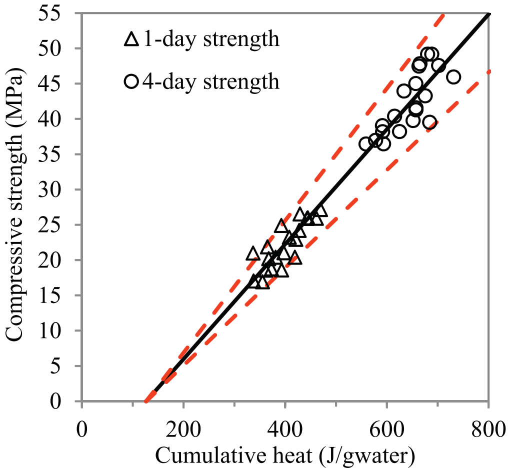
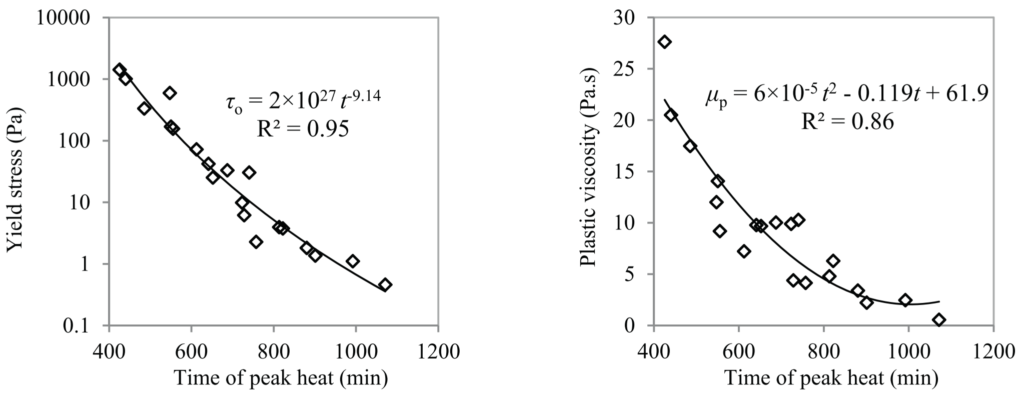


Fig. 12. Correlations between the compressive strength and J/g_{water} (cumulative heat release normalized by initial water content) at1 day and 4 day. The solid-black line represents linear best fit line with 15% bounds placed on either side (dashed-red lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 12 plots the 1-day and 4-days compressive strengths against the corresponding cumulative heat of hydration. The cumulative heat of hydration is normalized by the water content of the paste, in order to factor in the (initial) capillary porosity of the system. In the literature, several researchers have shown that the compressive strength of cementitious systems is linearly correlated with the water-normalized heat release, as both parameters directly result from the hydration of cement, and, therefore, are indicative of the extent of cement hydration that has occurred in the system [67–69]. In this study, this correlation was examined for pastes prepared with SF and the slump-retaining PCE. As shown in Fig. 12, a monotonic linear relationship is established between compressive strength evolution and cumulative heat release. The majority of data points lies within the ± 15% bound of the linear best fit line (solid-black line in Fig. 12). A linear correlation of this nature is significant in that, it suggests that irrespective of the contents of the paste (i.e., content of SF and/or PCE), measures of heat release can be used for apriori estimation of the evolution of mechanical properties in these pastes.

5. Conclusions

Based on investigations conducted in this study, the following



(a) (b)

Fig. 11. Relationships between rheology properties and hydration kinetics of all the investigated mixtures: time at main peak heat vs. (a) Yield stress, (b) plastic viscosity determined at 70 min after water addition.

conclusions can be draw:

(1) Partial replacement of cement by SF results in enhancement of cement hydration kinetics. These reactivity improvements are associated with SF's filler effect, that is, provision of product nucleation sites on extra surface area provided by SF. However, because of the agglomeration of SF particles, hydration enhancements become less pronounced at high SF replacement levels.
(2) In presence of slump-retaining PCE, which was used in this study, hydration of cement is suppressed in proportion to PCE dosage. This is due to adsorption of PCE molecules onto cementitious particles, resulting in blocking of dissolution and C-S-H nucleation sites.
(3) Both yield stress and plastic viscosity increase with SF content and decrease with PCE dosage. The addition of SF promotes cement hydration and reduces inter-particle spacing, thus augmenting plastic viscosity and yield stress. In contrast, the presence of slump-retaining PCE decelerates the cement hydration, increases inter-particle spacing, and reduces inter-particle friction, thus reducing plastic viscosity and yield stress.
(4) Both the initial and final setting times decrease, broadly in a linear fashion, with the SF content and increase with the PCE dosage. SF promotes formation of hydration products and increases solid-to-solid phase connectivity compared with plain system, thus shortening both the initial and final setting times. The slump-retaining PCE tends to suppress formation of product nuclei, and disrupts connectivity of hydration products, thus delaying the initial and final setting times.
(5) The strength at 1 day decreases with SF content and PCE dosages due to the effects of cement dilution (further aggravated by low pozzolanic activity of SF and agglomeration of SF particles) and hydration-retarding effect of slump-retaining PCE. However, at 7 days, the difference in strength between plain and binary pastes is significantly smaller. This is mainly because pozzolanic reaction of SF starts to dominate strength-gain in the paste.
(6) Hydration kinetics was found to correlate well with initial/final set times, rheological properties, and compressive strength. Such correlations can provide a reliable basis for prediction of key engineering properties, and facilitate formulation of pastes containing SF and PCE for high performance concrete with optimized hydration reactivity, rheology, setting, and compressive strength.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cemconcomp.2019.03.021.

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