Experimental investigation and theoretical modeling of silica fume activity in concrete

Vagelis G. Papadakis*

Danish Technological Institute, Building Technology Division, Concrete Centre, Gregersensvej, Taastrup, Denmark

Abstract

Silica fume was used as additive in mortar, replacing part of the volume of either Portland cement or aggregate. In a series of experiments, the development of the strength, porosity, bound water, and calcium hydroxide content was measured. The silica fume addition in both cases gave higher strengths than the control mixture. The bound water content and porosity were finally the same as for the control mixture in the case of the aggregate replacement. On the basis of the experimental results, the chemical reaction of the silica fume in hydrating cement is proposed. Using this equation and the cement hydration reactions, quantitative expressions for estimation of the chemical composition, porosity, and, indirectly, strength and durability of a silica fume–concrete are proposed. © 1999 Elsevier Science Ltd. All rights reserved.

Pozzolanic materials have long been used as Portland cement additives or as active additions in concrete [1,2]. Among these supplementary cementing materials are industrial by-products such as condensed silica fume, known simply as silica fume (SF) or microsilica, from electric arc furnaces producing silicon and ferrosilicon alloys. SF belongs to the category of highly pozzolanic materials because it consists essentially of silica in noncrystalline form with a high specific surface, and thus exhibits great pozzolanic activity (reaction with calcium hydroxide). It is mainly used to improve the mechanical properties and the durability of concrete [2–6].

The literature is rich in papers dealing with pozzolanic materials [1,2,5], such as SF, in concrete and their mechanical and physical properties. What is lacking, however, is a theoretical description of the pozzolanic activity in concrete including identification and kinetics of the chemical reactions, quantification of the reaction products, and determination of the concrete porosity and microstructure. It also must be emphasized that, although numerous papers refer to general improvement of the concrete properties using pozzolans, it is not clear what material is replaced in the concrete mixture when a pozzolan is added. When water is replaced by a pozzolan, the improvement is obvious. The situation is not clear when aggregates or cement, or both, are replaced by a pozzolan in a given concrete volume.

This work aims at filling this gap in the case of SF, presenting a quantitative prediction of the SF addition effect on important physical, chemical, and mechanical characteristics of the SF concrete and contributing to the elucidation of its role in concrete performance and durability.

1. Experimental

1.1. Experimental program

An experimental program was developed to determine the pozzolanic activity of the SF (products and reaction stoichiometry) and its influence on the main properties of concrete. The program included measurements of $Ca(OH)_2$ (CH), bound H_2O (H), porosity, pore volume distribution (PVD), heat development, compressive and flexural strength, and microscopic observations on cement and SF–cement pastes and mortars. It is assumed that the conclusions on mortar and paste also are applicable to concrete.

1.2. Materials

SF from Elkem Materials A/S, Norway, was used. A rapid Portland cement was used (400 m^2/kg Blaine's fineness). Normal graded sand (2670 kg/m^3 density) and a common plasticizer were used for mortar preparation. The physical and chemical characteristics of the materials are given

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* Current address: Orfeos 25, GR-17564, Paleo Faliro, Athens, Greece.

Table 1
Physical and chemical characteristics of cement and silica fume

	Cement	SF
Physical properties		
BET specific surface (m^2/g)	1.3	18
Particle mean diameter (μm)	14.0	0.36
Density (kg/m^3)	3130	2260
Chemical analysis (%)		
SiO$_2$	20.10	90.90
Al$_2$O$_3$	4.25	1.12
Fe$_2$O$_3$	3.49	1.46
CaO	63.20 (1.48 free)	0.69 (0.024 free)
SO$_3$	2.88	0.38
Loss on ignition	0.86	3.00
Mineralogical characteristics		
Insoluble residue (%)	0.14	62.85
Glass phase	—	96

in Table 1. Representative samples of cement and SF were examined using a scanning electron microscope (SEM). Cement particles (Fig. 1) have an irregular polygonal shape. SF particles are too small to be observed in detail by SEM; however, it is observed that they form spherical agglomerates of 10 μm in diameter.

1.3. Mixture proportions and specimen preparation

To obtain a rigorous comparison between different mixtures, a common basis was selected: the volume unit of the fresh or hardened concrete or mortar (1 m^3). If a material is added to this unit, e.g., SF, then an equal volume of another component must be removed to keep the same total volume and a common comparison basis. Two cases were selected: SF to replace aggregates, and SF to replace cement.

Mortar specimens were used for mechanical properties and heat measurements. The mixture proportions are summarized in Table 2. In the control specimen, the water-to-cement ratio (W/C) was 0.5 and the aggregate-to-cement ratio (A/C) was 3. When SF replaces volume of aggregate, three contents of SF were selected: 5%, 10%, and 15% addition to the cement weight giving specimens SFA1, SFA2, and SFA3, respectively. In all these specimens, the cement

and water contents were kept constant and equal to those of the control. For cement replacement by SF, the same contents were selected: 5%, 10%, and 15% replacement of the control cement weight giving specimens SFC1, SFC2, and SFC3 respectively. In all these specimens, the water content was kept constant and equal to that of the control. Due to the lower density of SF relative to the cement density, an extra small volume was created and it replaced the aggregate.

Each mixture was prepared in a mixer of 10-L total capacity. The dry materials were mixed for 2 min. Then the water was added, containing the plasticizer (0.5% by weight of the cement plus SF) and the mixing was continued for an additional 2 min (representing the practice). The specimens for strength measurements were cast in 40 × 40 × 160-mm steel molds. Twenty-one such prisms were prepared for each mixture. All specimens were vibrated for 20 s on a vibration table and then covered to minimize water evaporation. The molds were stripped after 24 h, and the specimens immersed in water (CH-saturated) at 20°C until testing.

The precise measurement of important characteristics for the understanding of the SF activity led to the preparation of the same mixtures as above, but without aggregate. These samples represent the paste matrix of the previous mortar specimens. The preparation of these paste specimens is part of the experimental procedure (gravimetrical) for the determination of the quantities required. The pastes were cast in preweighed plastic containers. First the cement (10 g) and SF (0.5, 1, or 1.5 g) were added. These materials were mixed by hand using a microspatula for 2 min; then the water was added (5 g) and the fresh paste was mixed for an additional 2 min. The container was hermetically sealed and the weight was recorded. A high accuracy (±1 mg) balance was used. One day after the casting, 1 mL of water was added, and the containers were placed in a room at 20°C prior to testing.

1.4. Strength measurements

Strengths were measured at ages of 3, 14, 28, 49, 91, 182, and 364 days. For each test, three specimens from each mixture were removed from the water, their flexural strengths
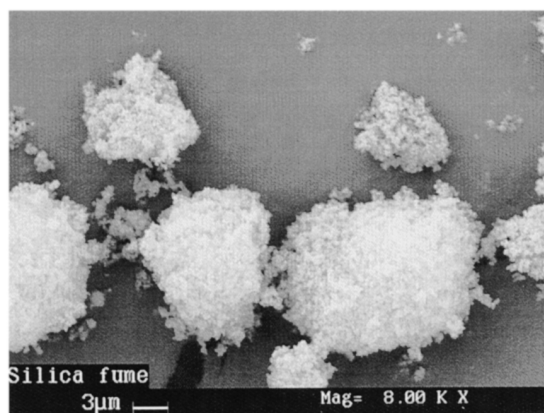

Fig. 1. SEM micrographs (8000×) of Portland cement (left) and silica fume (right).

were measured, and the six half prisms obtained were tested for compressive strength. The mean value of these measurements was used. The main problem in comparisons between mixtures was the varying air content of the specimens, which itself creates differences in strength. To solve this problem, the density of all specimens was first determined using a gravimetrical method. Knowing the zero-air content density of the saturated specimens, the air content can be calculated from their relative difference. Then all the strength results were converted to refer to the control air content (3.3%), by a procedure described elsewhere [7].

1.5. Heat development experiments

In this study, semiadiabatic calorimetry was used. The mixture preparation was similar to that for strength measurements. The specimens were cast in tin cylinders of 150-mm diameter and 300-mm height. The exact time of water addition into the mixer and the mortar weight were recorded. The cylinders were placed immediately after casting into special vessels with insulated walls. The surrounding air temperature was kept constant at 20°C. A thermocouple was placed in the middle of the sample, and the temperature was recorded every 15 min. The increased temperature during the test significantly accelerates the hydration. Knowing the specific heat of the sample, the measured temperature rise is converted to the equivalent amount of heat developed.

1.6. CH-content, H-content and, porosity measurements

The SF–cement pastes were analyzed for CH-content, chemically bound H_2O content (hereafter referred to as H-content), and porosity at 3, 7, 14, 28, 49, 112, 182, and 364 days after casting. For each test, the specimen was stripped, placed in a preweighed glass mortar, and pulverized. The mortar with the material was placed in an oven at 105°C until the weight was constant. These weight indications were sufficient for the determination of the H-content and porosity [7]. The paste properties were reduced to the corresponding mortar specimen volume multiplying by the appropriate paste volume/ mortar volume fraction.

For the determination of CH-content, a sample of the oven-dried powder was examined by a combination of two techniques: quantitative X-ray diffraction analysis and thermal evolved gas analysis. A procedure that makes a correction for the concurrent dehydration of other compounds while CH is dehydrating was followed [8].

1.7. Microscopic observations

Samples of SF–cement pastes, dried at 105°C and covered by a carbon layer, were examined by SEM and energy dispersion X-ray analysis (EDX).

2. Results and discussion

2.1. Strength measurement results

The results (reduced to a common air content, 3.3%) from compressive strength measurements on control and SFA (SF replaces aggregate) mortars are presented in Fig. 2a. A significant increase in SFA specimen strengths is observed compared with the control, from the beginning of hy-
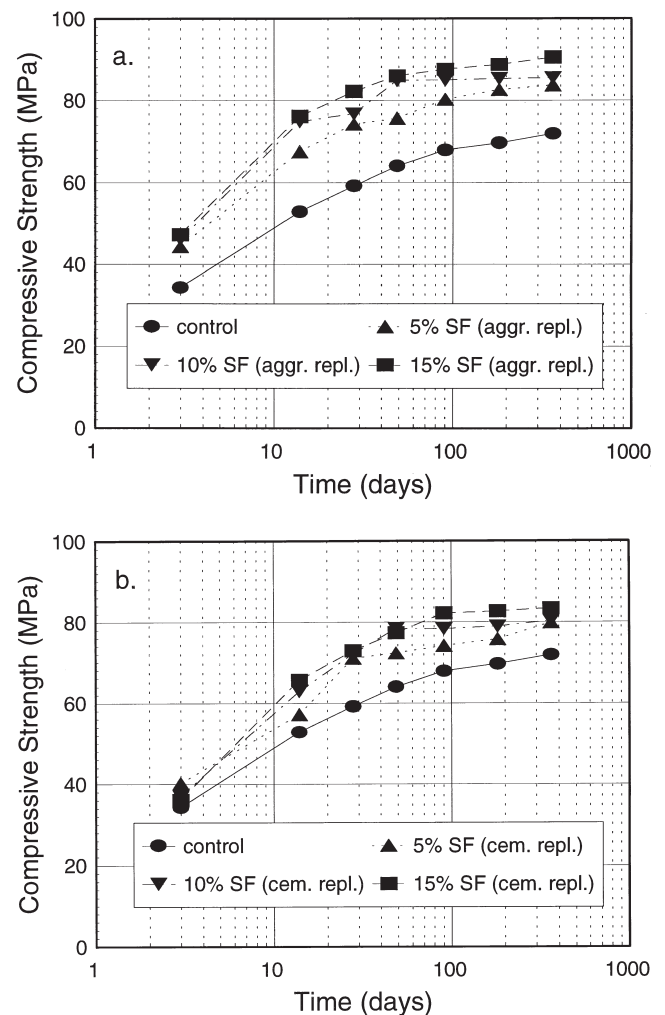

Fig. 2. Compressive strength development of mortars when SF replaces (a) aggregate (5%, 10%, and 15% addition to the cement weight) and (b) cement (5%, 10%, and 15% cement replacement).

Table 2
Absolute and relative mixture proportions for mortar specimens

Specimen	C	W	P	A	W/C	P/C	A/C
Control	514.6	257.4	0.0	1543.8	0.50	0.00	3.00
SFA1	514.6	257.4	25.7	1513.4	0.50	0.05	2.94
SFA2	514.6	257.4	51.5	1483.0	0.50	0.10	2.88
SFA3	514.6	257.4	77.2	1452.6	0.50	0.15	2.82
SFC1	488.8	257.4	25.7	1535.3	0.527	0.053	3.14
SFC2	463.1	257.4	51.5	1526.9	0.556	0.111	3.30
SFC3	437.4	257.4	77.2	1518.4	0.588	0.176	3.47

C, W, P, A: kg of cement, water, SF, and aggregate, respectively, per m^3 of total mortar volume. W/C, P/C, A/C: the water to cement, SF to cement, and aggregate to cement ratio (by weight), respectively.

dration (third day). This is because of the higher content of calcium-silicate-hydrate (CSH; the main carrier of strength in hardened cement) in the SFA specimens, due to the reaction of the CH produced from cement hydration with the silica (S) of the SF. This increase rises as hydration time increases, but appears to be steady after 14 days. The strength gain for the SFA2 specimen relative to the control is about 20% after 1 year of hydration.

When cement is replaced by SF, there is a similar general behavior, but the strengths are lower, although higher than the control (Fig. 2b). This is because the content of active silica in the SF (90%) is much higher than that in the cement (20%), and such a replacement leads to higher CSH-content (provided enough CH is available). When the CH is completely consumed, additional replacement will lead to decrease of strength. The flexural strength results led to similar conclusions and will not be discussed further.

2.2. Heat development results

Typical heat development results are shown in Fig. 3 and refer to control and SFA2 specimens. A higher heat development can be observed in the SFA2 specimen from the first hours of hydration. This higher heat evolution is connected with the fast pozzolanic reaction of CH with the small particles of the SF. This result strengthens the previous conclusion for the initiation of the pozzolanic reaction of SF, i.e., that it is almost simultaneous with cement hydration.

2.3. H, CH, and porosity measurement results

The H-content (kg H_2O/m^3 mortar) of the control and SFA specimens is presented in Fig. 4a. As expected, an increase in H-content with time is observed, similar to that observed in strength evolution. Another significant observation is that the control specimen as well as all SFA specimens have the same H-content, at least for the first tests (3, 7, and 14 days). This means that the pozzolanic reaction of SF (practically the reaction of the S of SF with the CH of the hydrating cement) does not include any additional water. According to this observation and because water binding is the cause of the pore volume reduction, the porosity ϵ (m^3 of pores/m^3 mortar) should be expected to be constant, as was found (Fig. 4b).

However, after 14 days, the H-content of the SFA specimens decreases in relation to the control, and the porosity increases, proportionally to the SF content. This behavior can be explained by the selective reaction of CH with SF instead of its reaction with the C_3A and C_4AF phases of cement, which contribute significantly to water binding and porosity decrease. After 6 months, the H-content values and the porosity values coincide for all the specimens. It seems that, during this late period, the remaining amounts of the C_3A and C_4AF phases of cement have reacted, binding addi-
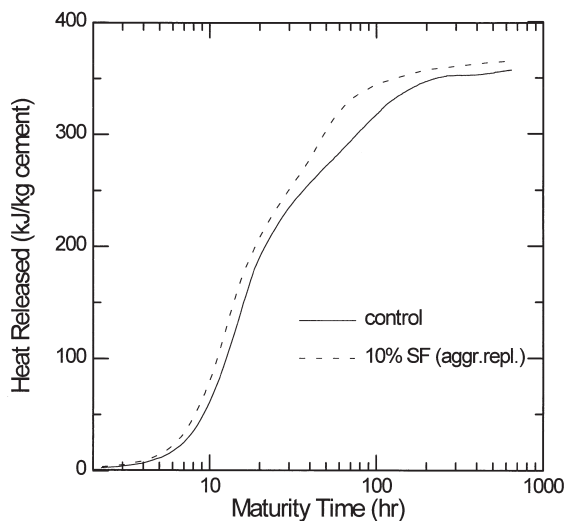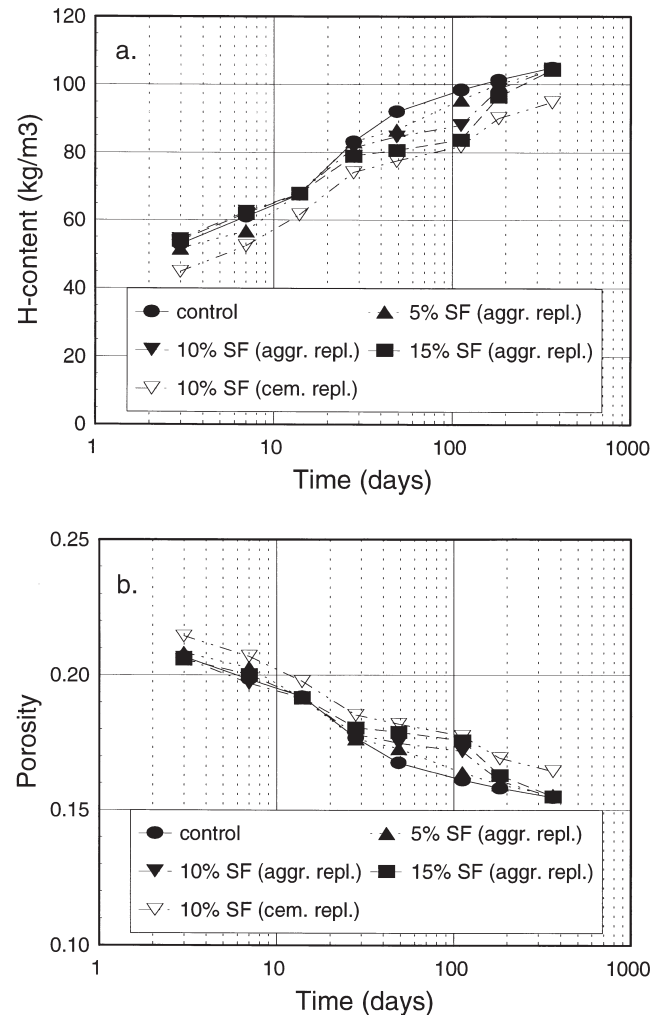
Fig. 4. Chemically bound water content (a) and porosity (b) of mortars with silica fume to replace aggregate (0, 5%, 10%, and 15% addition to the cement weight) and cement (10% cement replacement), as a function of time.

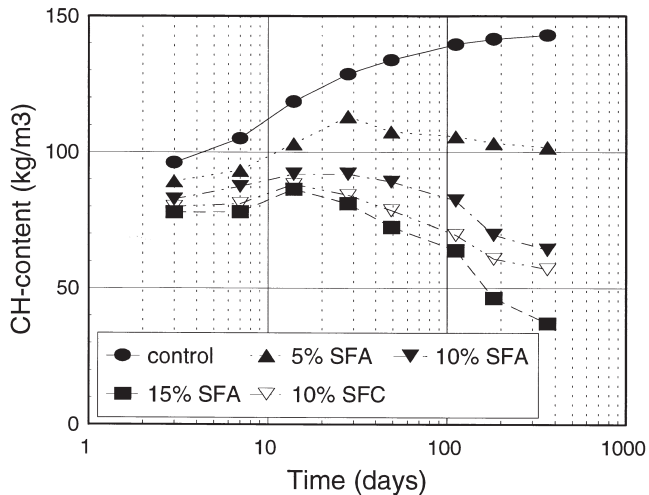Fig. 3. Comparative heat development results for control and SFA2 mixtures.

Fig. 5. Calcium hydroxide content in mortars with silica fume to replace aggregate (0, 5%, 10%, and 15% addition by cement weight) and cement (10% cement replacement), as a function of time.

tional water and reducing the total porosity as well. After this loop in H-content and porosity results, the "final" state is characterized by absolutely equal values of H-content and total porosity. This therefore strengthens the initial conclusion that the reaction of S with CH takes place without binding of additional water.

When SF replaces cement (Fig. 4), a decrease in the H-content and an increase in the total porosity are observed. This behavior is in agreement with the previous conclusions: SF reacts with CH without additional water binding; thus, the decreased content of C_3A and C_4AF phases of the total cementitious material leads to higher porosity values.

The CH-content (kg CH/m^3 mortar) for the control and SF specimens is shown in Fig. 5. It can be seen that the CH-content of the control specimen increases with time until a steady state is attained. For the SFA specimens, CH is consumed from the initiation of cement hydration. These CH-contents seem to pass through a maximum, due to higher CH production from cement hydration, but afterward decrease very rapidly, as the silica-CH reaction proceeds at higher rates.

2.4. Microscopic analysis and PVD results

Typical SEM images of the control and SFA2 specimens are presented in Fig. 6. At the beginning of hydration of the control specimen, long needles of ettringite are present, forming the early strength network. After 14 days, ettringite has disappeared; whereas the phases of CSH, CH and monosulphate are dominant. After 6 months, CH crystals have completely grown (hexagonal or leaf-type plates) and the remaining dense mass is mostly CSH and monosulfate (EDX). In the first days of hydration of the SFA2 specimen, ettringite presence is much less than in the control (selective
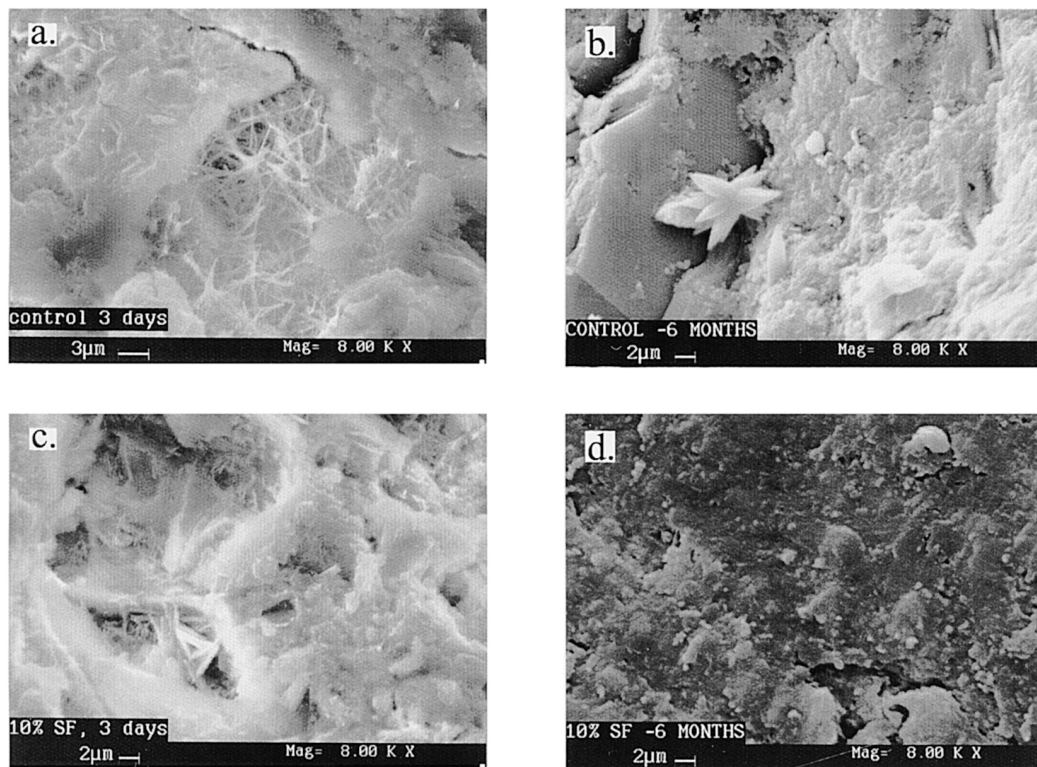

Fig. 6. SEM micrographs (8000×) of Portland cement paste (control) after 3 (a) and 182 (b) days of hydration, and of 10% SF–cement paste after 3 (c) and 182 (d) days of hydration.

reaction of CH with S). In contrast, the dense phase of CSH is present in higher amounts after 7 days. As time proceeds CH crystals disappear and a dense structure of CSH is formed.

The volume of micropores (pores with diameter less than 200 Å) of well-hydrated pastes (6 months) was measured using N_2 adsorption. This quantity (cm^3/g) was converted to content of micropores in the total pore volume. The micropore content of SFA2 specimen (12%) was found to be significantly higher than that of control (6%). Thus, although control and SFA2 specimens have the same total porosity, the latter presents significant pore refinement [2].

3. Theoretical approach of SF activity in concrete

3.1. Determination of products and reaction stoichiometry

As stated in the Materials section, SF is composed primarily of SiO_2 (S, 90.9%), which is almost completely vitreous (96%) and thus reactive. It also contains a small amount of carbon and very small amounts of other compounds. Because the carbon does not participate in hydration and the other constituents are present in very low concentration, it can be assumed that SF is practically active S (87.3%) and the rest is inert. Consequently, the SF activity can be described as shown in Eq. (1):

$$x\ S + y\ CH + z\ H \rightarrow C_yS_xH_{y+z} \qquad (1)$$

As the H-content and porosity results show, this reaction takes place without additional water binding more than that contained in the CH molecules. Thus, z = 0 and the reaction product has the stoichiometry of $C_yS_xH_y$. According to Sellevold [4], the amount of water bound in the CSH formed by the pozzolanic reaction of SF with CH was found to be the same as that contained in the CH, i.e., C/H = 1.0. Diamond [911], however, found the bound water per gram of cement to increase in SF–cement pastes. According to Li et al. [10], who also found that SF addition even reduces the amount of nonevaporable water, the SF due to the high surface energy could hold a thin layer of water, which is accountable for these deviations.

An equilibrium value of the totally consumed CH will define the y/x ratio. After 1 year of hydration, when the bulk of the SF should have reacted, the following values of CH consumed (difference between the CH-content in the control and that in the SF specimen) are observed: 41, 79, and 106 kg/m^3 for SFA1, SFA2, and SFA3 specimens, respectively (Fig. 5). The initial quantity of active S was as follows: SFA1: (87.3%) $\times$ 25.73 kg/m^3 = 22.46 kg/m^3, SFA2: 44.92 kg/m^3; and SFA3: 67.38 kg/m^3. The y/x ratios then can be determined from the reaction stoichiometry shown in Eq. (1) by the following equations (molecular weights of S and CH: 60.08 and 74.10, respectively):

$$74.10y/60.08x = 41/22.46 \Rightarrow y/x = 1.48$$

$$74.10y/60.08x = 79/44.92 \Rightarrow y/x = 1.43$$

$$74.10y/60.08x = 106/67.38 \Rightarrow y/x = 1.28$$

As can be seen from the above results, and given the slower rate of reaction with high SF contents, a y/x ratio value of 1.5 can be considered quite satisfactory. Eq. (1) then becomes Eq. (2):

$$2S + 3CH \rightarrow C_3S_2H_3 \qquad (2)$$

Thus, the SF-CH final product ($C_3S_2H_3$) seems to be exactly the same as the product of hydration of the C_3S and C_2S phases of Portland cement. Many researchers have reported this similarity in structure [1,2]. Sellevold [4], however, reports that the CSH gel produced from SF has a lower C/S ratio than that from the cement hydration. But it also was reported in the same paper that about 22% SF added to cement can eliminate the CH produced in 65 days (0.33 g per gram cement); these figures give y/x = 1.4, following the above calculation scheme.

3.2. Quantification of the final products

One common reference base is used: 1 m^3 of concrete, which contains C, W, A, and P kg of Portland cement, water, aggregate and pozzolan (SF), respectively. The Portland cement and the SF can be analyzed in terms of oxides: total CaO (C), SiO_2 (S), Al_2O_3 (A), Fe_2O_3 (F), SO_3 ($\bar{S}$), and other oxides or impurities denoted by R. Let us denote as $f_{i,c}$ and $f_{i,p}$ the weight fractions of the constituent i (i = C,S,A,F,,R) in the cement and pozzolan, respectively. In the case of SF, the weight fraction of S, $f_{S,p}$, and its active (glass) part, γ_S, are relevant for the quantitative calculations.

3.2.1. Portland cement concrete

The contents of the various phases (C_3S, C_2S, C_3A, C_4AF, $C\bar{S}H_2$) in Portland cement can be determined from the oxide analysis using Bogue's formulas [11]. Although the chemical reactions of hydration of these phases are complex and do not proceed to completion, a simplified view may be presented as shown in Eqs. (3–6) [12,13]:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad (3)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad (4)$$

$$C_3A + C\bar{S}H_2 + 10H \rightarrow C_4A\bar{S}H_{12} \qquad (5)$$

$$C_4AF + 2CH + 10H \rightarrow C_6AFH_{12} \qquad (6)$$

These reactions are valid in excess of gypsum, i.e., when $f_{\bar{S},c} > (0.786f_{A,c} - 0.501f_{F,c})$; as applies in Portland cement. Using this reaction stoichiometry and the molar weights of reactants and products, the amounts of the "finally" produced compounds can be determined. These amounts of CH, $C_3S_2H_3$ (CSH), $C_4A\bar{S}H_{12}$ (CA$\bar{S}$H), C_6AFH_{12} (CAFH), rest constituents (R), and bound water (H) are given as shown in Eqs. (7–12), in kg/m^3 of concrete:

$$CH = \{1.321(f_{C,c} - 0.7f_{\bar{S},c})$$
$$\qquad - (1.851f_{S,c} + 2.182f_{A,c} + 1.392f_{F,c})\}C \qquad (7)$$

$$CSH = 2.85f_{S,c}C \qquad (8)$$

$$CA\overline{S}H = (6.106f_{A,c} - 3.898f_{F,c})C \qquad (9)$$

$$CAFH = 5.099f_{F,c}C \qquad (10)$$

$$R = (f_{R,c} + 1.7f_{\overline{S},c} - 1.689f_{A,c} + 1.078f_{F,c})C \qquad (11)$$

$$H = \{0.321(f_{C,c} - 0.7f_{\overline{S},c}) + 1.236f_{A,c} - 0.113f_{F,c}\}C \qquad (12)$$

3.2.2. SF–Portland cement concrete

When SF is present in concrete, in addition to the hydration reactions, the pozzolanic reaction shown in Eq. (2) takes place. In this case, the CAFH, CA$\overline{S}$H, and H-contents will be exactly the same as previously. The CH, CSH, and R contents can be determined easily by Eqs. (13–15), taking into account the stoichiometry of the reaction shown in Eq. (2):

$$CH = \{1.321(f_{C,c} - 0.7f_{\overline{S},c}) \\ - (1.851f_{S,c} + 2.182f_{A,c} + 1.392f_{F,c})\}C \\ - 1.851\,\gamma_S f_{S,p}P \qquad (13)$$

$$CSH = 2.85(f_{S,c}C + \gamma_S f_{S,p}P) \qquad (14)$$

$$R = (f_{R,c} + 1.7f_{\overline{S},c} - 1.689f_{A,c} + 1.078f_{F,c})C \\ + (1 - \gamma_S f_{S,p})P \qquad (15)$$

The CSH-content increases with SF addition, regardless of whether SF replaces aggregates or cement, because $\gamma_S f_{S,p}$ is always higher than $f_{S,c}$. The H-content remains constant when SF replaces aggregates (C constant), as well as the H/C ratio (chemically minimum required W/C). For the completion of pozzolanic activity, the left-hand side of Eq. (13) must be positive. If CH = 0 in Eq. (13), the maximum pozzolan content that can react with all lime produced during cement hydration, P_{max}, can be obtained as shown in Eq. (16):

$$P_{max} = \{1.321(f_{C,c} - 0.7f_{\overline{S},c}) \\ - (1.851f_{S,c} + 2.182f_{A,c} + 1.392f_{F,c})\} \\ C/(1.851\gamma_S f_{S,p}) \qquad (16)$$

3.3. Estimation of final pore volume

The concrete porosity ϵ is given by Eq. (17):

$$\epsilon = \epsilon_{air} + W/\rho_w - \Delta\epsilon_h - \Delta\epsilon_p - \Delta\epsilon_c \qquad (17)$$

where ϵ_{air} is the volume fraction of entrapped or entrained air in concrete, ρ_w is the water density (1000 kg/m³), and $\Delta\epsilon_h$, $\Delta\epsilon_p$, $\Delta\epsilon_c$ are the porosity reductions due to hydration of Portland cement, pozzolanic activity, and carbonation, respectively. The term $\Delta\epsilon_h$ is given by Eq. (18):

$$\Delta\epsilon_h = (C_3S)\Delta\overline{V}_{C_3S} + (C_2S)\Delta\overline{V}_{C_2S} \\ + (C_3A)\Delta\overline{V}_{C_3A} + (C_4AF)\Delta\overline{V}_{C_4AF} \qquad (18)$$

where $\Delta\overline{V}_j$ (j = C$_3$S, C$_2$S, C$_3$A, C$_4$AF) are the differences in molar volumes between solid products and solid reactants in the reactions shown in Eqs. (3–6) (in m³/kg). They can be calculated knowing the stoichiometry of the reactions and the molar volumes of the solid reactants and products [13]: $\Delta\overline{V}_{C3S} = 0.2334 \times 10^{-3}$ m³/kg C$_3$S, $\Delta\overline{V}_{C2S} = 0.2285 \times 10^{-3}$ m³/kg C$_2$S, $\Delta\overline{V}_{C3A} = 0.5769 \times 10^{-3}$ m³/kg C$_3$A, and $\Delta\overline{V}_{C4AF} = 0.2321 \times 10^{-3}$ m³/kg C$_4$AF. By substituting these values in Eq. (17), the final value of the porosity of a noncarbonated Portland cement concrete is given by Eq. (19):

$$\epsilon = \epsilon_{air} + W/\rho_w - \{0.249(f_{C,c} - 0.7f_{\overline{S},c}) \\ + 0.191f_{S,c} + 1.118f_{A,c} - 0.357f_{F,c}\}(C/1000) \qquad (19)$$

The porosity reduction, if any, due to the pozzolanic reaction of SF [Eq. (2)] should be correlated with $\Delta\overline{V}_S$, the difference in molar volumes between solid products and reactants. However, $\Delta\overline{V}_S = (1/2 \times 150 \times 10^{-6} - 3/2 \times 33.08 \times 10^{-6} - 27.28 \times 10^{-6})/(60.08 \times 10^{-3}) = -3.2 \times 10^{-6}$, almost zero [14]. Thus, $\Delta\epsilon_p \cong 0$, and the final value of the porosity of the SF-concrete is given by the same expression as for Portland cement concrete. According to this equation, the porosity remains constant when SF replaces aggregates (C: constant). On the other hand, when SF replaces cement, the porosity increases proportionally with the amount replaced. These conclusions are supported not only by the experimental results of this work (see Fig. 4b), but also of other researchers. Goldman and Bentur [15] observed that SF concretes with the same W/C and different SF-content have the same total porosity, although they have different strengths. However, despite the almost same porosity, SF mortars presented different PVD, with an increase in micropore volume as compared to the control. This can be due to pore refinement (transformation of a system containing larger pores into one with smaller pores) and grain refinement (transformation of larger crystals, such as calcium hydroxide, into smaller crystals [2]).

Table 3
Final chemical and volume compositions of SF specimens

	Control 0% SF	SFA1 (5% aggr)	SFA2 (10% aggr)	SFA3 (15% aggr)	SFC1 (5% cem)	SFC2 (10% cem)	SFC3 (15% cem)
CH	151.73	110.17	68.62	27.06	102.59	53.44	4.30
CSH	294.77	358.76	422.74	486.74	344.03	393.28	442.53
CA$\overline{S}$H	63.53	63.53	63.53	63.53	60.35	57.18	54.00
CAFH	91.57	91.57	91.57	91.57	86.99	82.41	77.84
R	38.90	42.18	45.45	48.73	40.23	41.57	42.90
H	126.06	126.06	126.06	126.06	119.76	113.46	107.15
ϵ	0.1412	0.1412	0.1412	0.1412	0.1470	0.1528	0.1586

aggr: aggregate; cem: cement.

3.4. Application

For the specimens of the present work (C, P, and W contents are given in Table 2), for cement: $f_{C,c} = 0.632$, $f_{S,c} = 0.201$, $f_{A,c} = 0.0425$, $f_{F,c} = 0.0349$, $f_{\bar{S},c} = 0.0288$, and $f_{R,c} = 0.0608$. For SF: $f_{S,p} = 0.909$ and $\gamma_S = 0.96$. By applying Eqs. (7–16) and (19), the "final" composition of the specimens is given in Table 3. The calculated values of CH, H, and ϵ are in good agreement with the corresponding experimental values, when the time approaches infinity.

P_{max}/C is calculated as 0.183 kg SF/ kg cement, i.e., SF addition exceeding 18.3% of the cement weight is inert and thus unnecessary. When SF replaces aggregate by 5%, 10%, and 15% (by weight of cement), CSH increase is 21.7%, 43.4%, and 65.1%, respectively. When SF replaces cement by 5%, 10%, and 15%, then CSH increase is 16.7%, 33.4%, and 50.1%, respectively. These increases present proportional similarities with the strength results. Porosity remains the same for all SFA specimens. It increases by 4.1%, 8.2%, and 12.3%, when SF replaces cement by 5%, 10%, and 15% respectively.

4. Conclusions

A series of experimental techniques were used to elucidate and determine SF activity in concrete (strength, heat development, CH, H, and porosity measurements, SEM, EDX, and PVD determination). When aggregates or cement are replaced by SF (up to a certain level, P_{max}) higher strengths are observed. The final strength gain is roughly proportional to the content of active silica in the concrete volume.

The reaction of SF with the CH of the hydrating cement takes place without an additional binding of water, presenting finally the same total porosity as the control specimen. However, due to the selective reaction of CH with the silica particles, a lower bound water content and a higher porosity are observed at intermediate ages. Using the experimental results, an accurate description of the reaction and product of SF in concrete is possible.

A quantitative model predicting the behavior of concrete containing SF was developed. This model comprises quantitative expressions for estimation of the final chemical and volumetric composition of SF-concrete. Excellent agreement was found between model predictions and experimental results. Knowing these characteristics (CSH, CH, H-content, and porosity), the concrete strength and durability can be determined indirectly [13,14]. Intermediate values can be obtained using the presented experimental results. Finally, the model enables mixture proportions to be specified accurately and the performance and durability of the concrete predicted reliably.

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