

Hydration of ternary cementitious system: Portland cement, fly ash and silica fume

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Abstract Hydration of ternary OPC–FA–SF cements has been studied using number of techniques. Heat of hydration studies were made with the help of TAM AIR calorimeter, and it was found that fly ash retarded the hydration of OPC and reduced the total heat evolution. However, fly ash and silica fume together improved the heat evolution, but the values were lower than that of OPC. Differential scanning calorimetric studies of cements hydrated for 28 days were made, and it was found that $\text{Ca}(\text{OH})_2$ produced during the hydration of OPC reacted with fly ash and silica fume. SEM pictures of hydrated cements were recorded. The results have shown that silica fume accelerates the hydration and minimizes the deficiencies of fly ash blended cement. Mechanism of hydration has been proposed.

Keywords Portland cement · Fly ash · Silica fume · Heat of hydration · Compressive strength

Introduction

Global warming and climate change have become one of the most important issues of present day research. CO_2 emission from industries is the main cause of global

warming. Cement industry is one of the major contributors to CO_2 emission, and therefore it should be reduced by some means. The most effective way is partial replacement of ordinary Portland cement (OPC) by pozzolanic or supplementary cementitious materials making blended cement. Presently, fly ash (FA) is being extensively used for partial replacement of Portland cement in mortars and concrete. FA plays two different roles: (i) filler effect and (ii) reacts chemically [1–5].

Fly ash fills the pores, increases the packing density and provides additional nucleation sites for hydration. FA due to filler effect promotes the hydration of OPC at early hydration times but does not react chemically up to 7 days [6, 7]. Due to low surface area, FA has lower pozzolanic activity up to certain period of time. However, after certain period of hydration, the pozzolanic reaction of FA with $\text{Ca}(\text{OH})_2$ starts and C–S–H is formed [8–10]. The major drawback of FA addition is that the early strength of mortars and concrete is decreased. Attempts are being made to remove this deficiency either by activating FA or by adding some suitable chemical admixtures [11, 12]. Different approaches have been used to accelerate the pozzolanic reaction of FA and, thereby, to increase the early strength of concrete containing FA. These include mechanical treatment (grinding), accelerated curing and autoclaving and chemical activation (alkali and sulphate activation) [13]. However, alkali activation used in concrete may lead to alkali–silica reaction, while the sulphate activation may impair the durability of concrete due to the formation of large quantities of ettringite. The main reason for the low early strength development of FA concrete is the unavailability of sufficient quantities of $\text{Ca}(\text{OH})_2$ to react with the FA particles [13]. Hence, there is a possibility of improving the pozzolanic reaction of FA by adding hydrated lime. Another reason for the poor early

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strength development of FA concrete is that the reactive silica in FA accumulates in the interior part of its particles, which is very slowly corroded in the hydrated cement paste environment [14]. Overcoming the deficiencies of FA on the early age properties of fly ash–cement mixtures is still a challenge. Silica fume (SF) appears to be a potential solution to this problem due to its highly reactive nature. Langan [15] reported that when SF and FA are incorporated together in cement, the hydration of the cement is significantly retarded. The heat of hydration is decreased and the early reactivity of the SF is hampered. The accelerating effect of the SF is delayed. However, SF, having a greater surface area and higher SiO₂ content, is expected to be more reactive than the FA [16] and, hence, it has been used in combination with FA in low levels of replacement of Portland cement with FA [13]. Silica fume may provide significant amounts of calcium silicate hydrates (C–S–H) at an early age which may be expected to increase the early strength. It is reported that FA compensates for deficiencies of SF and SF compensates for deficiencies of FA [17]. It is expected that the deficiencies of FA addition in OPC may be reduced by the addition of SF.

However, the exact role and mechanism of SF additions in removing the deficiencies of FA blended cement are not known. In the present investigation, effect of different amount of SF on the hydration of FA blended cement has been studied in detail and results have been discussed in order to understand the mechanism.

Experimental

Materials

Ordinary Portland cement obtained from Birla cement, India was used for hydration studies. FA was obtained from the Dadri Thermal Power Plant, India. A blended cement of

composition 80 mass % OPC + 20 mass % FA designated as OPC20FA was made. In this blended cement, 5, 10, 15 and 20 mass % SF was mixed and the mixtures are designated as OPC20FA5SF, OPC20FA10SF, OPC20FA15SF and OPC20FA20SF. Chemical compositions of OPC, FA and SF are given in Tables 1–3, respectively. Particle size distribution of OPC is shown in Fig. 1.

Preparation of the hydrated samples

Twenty grams each of OPC, OPC20FA, OPC20FA5SF, OPC20FA10SF, OPC20FA15SF and OPC20FA20SF were taken in different polythene bags and mixed thoroughly with 10 mL distilled water in order to have $w/s = 0.5$. The air of the polythene bags was removed and kept at room temperature for hydration. The hydrations were stopped at different intervals of time with isopropyl alcohol and ether and dried at 105 °C. The samples were stored in a desiccator.

Characterization methods

Determination of standard water consistency

Weighed quantities of cement and distilled water were mixed to make the pastes. The time of gauging was between 3 and 5 min. The gauging time was counted from the time of adding water to the dry cement until it was filled in the moulds resting upon a non-porous plate. After completely filling the mould, surface of the paste was smoothed. The mould was slightly shaken to expel the air. The rod bearing the plunger in the Vicat was gently allowed to touch the surface of the test block and quickly released. The pastes with varying percentages of water were made, and the tests as described above were made. This was done until the amount of water necessary for making up the standard consistency [IS: 4031 part 4, 1998

Table 1 Chemical composition of ordinary Portland cement mass%

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	L.O.I
Composition	20.50	5.05	2.99	62.0	2.07	0.48	0.09	2.40	3.10

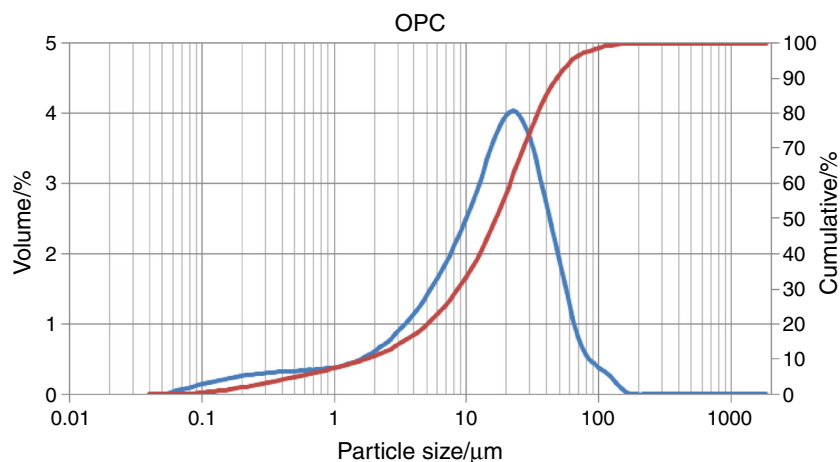
Table 2 Chemical composition of fly ash mass%

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	P ₂ O ₅	L.O.I
Composition	59.02	31.98	4.79	2.19	0.28	0.47	0.22	1.05

Table 3 Chemical composition of silica fume mass%

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	L.O.I
Composition	96.10	0.52	0.70	0.21	0.48	0.31	0.49	0.10	1.14

Fig. 1 Particle size distribution of OPC



reaffirmed 2005] was obtained. This permitted the vicat plunger to penetrate to a point 5–7 mm from the bottom of the vicat mould, which was read on the scale. Water required was expressed as percentage by mass of the dry cement.

Determination of setting times

The start of hardening of the cement paste after the addition of water to cement is called setting and it is divided into two parts called initial [IST] and final [FST] setting times. A neat cement paste was prepared by gauging the cement with water required for standard consistency. The paste was filled up in a Vicat mould placed on a glass plate. The mould was then placed under the Vicat apparatus fixed with a needle. The needle was gently lowered down allowing penetration into the paste. In the beginning, the needle completely pierced the test block. It was repeated until the needle failed to pierce the test block beyond 5 ± 0.5 mm. The period elapsing between the time when water was added to the cement and the time at which the needle failed to pierce the test block up to 5 ± 0.5 mm was the initial setting time (IST). Replaced the needle of the Vicat apparatus by another needle with an angular attachment. The period elapsing between the time when water was added to the cement and the time at which the needle failed to make an impression on the surface of the test block was the final setting time (FST).

Heat of hydration measurement

In order to determine the rate of heat evolution and the total heat evolved during the hydration, 2.0 g each of OPC, OPC20FA and OPC20FA5SF was weighed separately in different plastic vials and mixed with 1.0 mL water to have a water/solid ratio of 0.5 and vibrated for 30 s to have a homogeneous mixing. The vials were then immediately

placed in the TAM AIR calorimeter chamber. Blanc plastic vial was used as a reference. The experiments were performed at 20° C for 100 h.

Non-evaporable water contents

One gram of each cement sample hydrated for 28 days was measured in a ceramic crucible and heated at 105° C for 1 h to remove adsorbed water. After this, the samples were heated at 1,000° C for 1 h. From the mass losses, the non-evaporable water contents were determined.

Determination of water permeability (percolation) by permeability apparatus

The water percolations of the hydrated cements were determined by permeability apparatus. 140 g cement/blended cements was mixed with 700 g of sand to prepare premix. The premixes were mixed separately with 42 mL water to form mortars in order to have water/solid (w/s) ratio of 0.3. The mortars were thoroughly mixed in Hobart mixer. Each mortar was placed in a mould as per IS: 2645-2003. After 24 h, the mortars were demoulded and immersed in water tanks separately for 21 days. Each mould of height 4.5 cm and diameter 10.0 cm was then fixed in a permeability apparatus where pressure of 2.0 kg cm^{-2} was applied (pressure was slowly increased from 0.5 to 2.0 kg cm^{-2}). Water percolation was measured at every 1 h in terms of mass of percolated water for 8 h.

Determination of compressive strength

Compressive strengths of cement mortar [cement: sand-1:3] cubes of dimension $7.5 \times 7.5 \times 7.5 \text{ cm}^3$ made from OPC, OPC20FA, OPC20FA5SF, OPC20FA10SF, OPC20FA15SF and OPC20FA20SF were determined at different intervals of time with the help of compressive strength

testing machine at room temperature ($\approx 28^\circ\text{C}$) [IS: 4031-1988].

DSC studies

DSC studies of cement hydrated for 28 days were carried out at a heating rate of $10^\circ\text{C min}^{-1}$ between room temperature and 550°C in nitrogen atmosphere with NETZSCH STA 409 PC LUXX.

SEM studies

SEM pictures of OPC, OPC20FA, and OPC20FA5SF hydrated for 28 days were recorded with Quanta FEG 250 ESEM instrument. Gold coating was done on the samples.

Results and discussion

Changes in water consistency with the addition of SF in OPC20FA are shown in Fig. 2. It is observed that as the amount of SF is increased, the values increased. Since SF has high surface area, the overall surface areas of the cements are increased and as a result, water absorption is

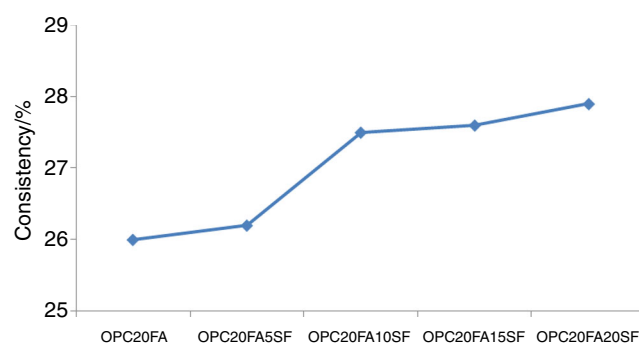
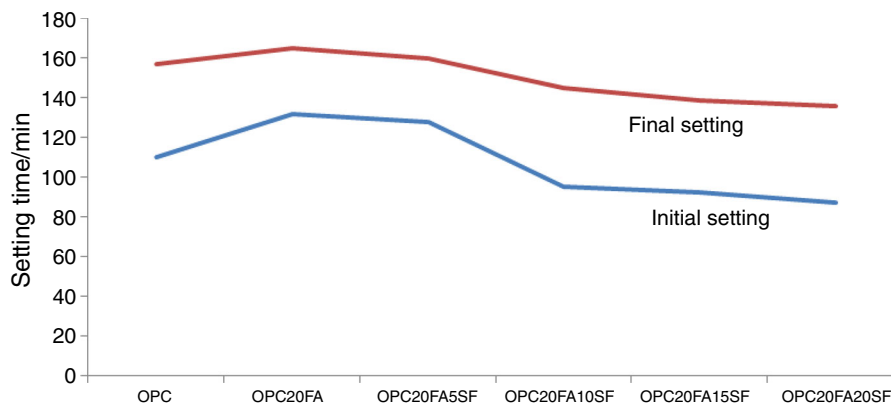


Fig. 2 Variation of water consistency

Fig. 3 Variation of setting time



increased. This leads to higher water consistency. Variations of initial and final setting times are shown in Fig. 3. In the presence of 20 mass % FA, the setting times are increased. However, as the concentration of SF in OPC20FA is increased, both initial and final setting times are decreased, indicating an acceleration of hydration. During the reaction of Portland cement with water, Ca(OH)_2 is produced as one of the hydration products and is known as free lime. In the presence of pozzolanic materials, this Ca(OH)_2 reacts to give C-S-H phase and as a result, the free lime is decreased.

Variation of free lime contents in the cements hydrated for 28 days is shown in Fig. 4. The results show that as the concentration of SF is increased, the free lime content is decreased. Variation of non-evaporable water contents (W_n) of the cements hydrated for 28 days is shown in Fig. 5. The values decreased with SF content. Non-evaporable water content is an indicator of the extent of hydration. However, in the present case, increased amount of SF decreased the free lime (Ca(OH)_2) contents and as a result, formation of CaCO_3 is decreased considerably. During hydration, CO_2 from the atmosphere gets dissolved in the solution of the paste and reacts with Ca(OH)_2 formed during hydration reaction. The carbonation is an acid–base

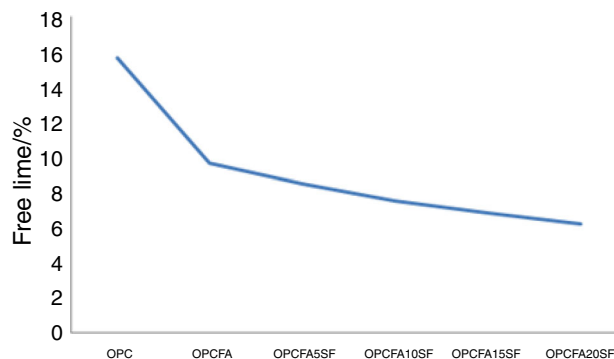
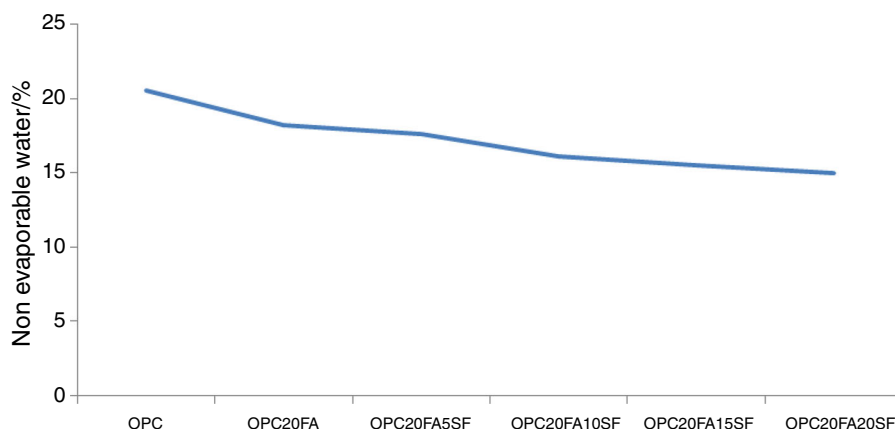
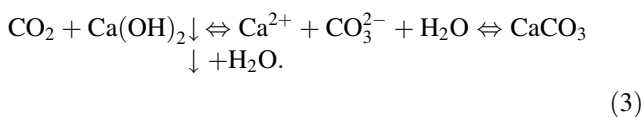
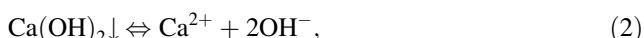
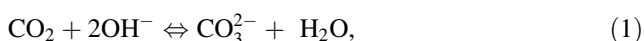


Fig. 4 Variation of Free lime in cements hydrated for 28 days

Fig. 5 Variation of non-evaporable contents in cements hydrated for 28 days

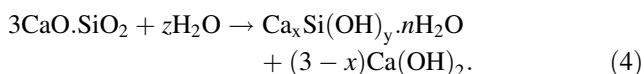


neutralization reaction due to an alkaline nature of cement. The CO₂ first dissolves in the pore solution and then reacts with the OH⁻, forming CO₃²⁻. As the solution becomes saturated in calcium ions due to the C₃S hydration, the precipitation of CaCO₃ starts. The overall reactions are given below [18]:

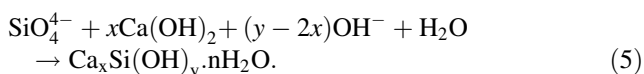


However, due to pozzolanic reaction, the OH⁻ ion concentration in the solution is decreased and as a result, lesser amount of CaCO₃ is formed. So when the hydrated samples were heated at 1,000° C, mass losses decreased resulting into decrease of W_n values.

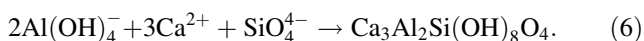
Further during the hydration of cement, interaction of C₃S with water gives C–S–H as given below:



The pozzolanic materials like SF react with portlandite in the following way:



The FA which contains alumina also reacts with calcium silicate to form calcium aluminosilicates:



The SF accelerates the early hydration of C₃S ensuring enough quantity of active centres as a basis for the formation of C–S–H. At this stage the intensity of the process is determined by the specific surface of the SF grains.

With inclusion of pozzolanic additives in cement, the quantity of portlandite cannot be used as a reliable criterion

for the degree of hydration due to the continuing pozzolanic reactions in the hydrating cement. From another side, the addition of SF and FA stimulates the polymerization of the hydrosilicates, which are formed during hydration of cement accompanied by evolution of water. Therefore, the quantity of chemically bound water is not a correct indicator for determining the degree of hydration of cements with pozzolanic additions [19]. Thus, in blended cements, increase in degree of hydration cannot be correlated with non-evaporable water contents.

The rate of heat evolution during hydration is shown in Fig. 6, and the curves consist of five parts: (i) rapid heat evolution, (ii) the induction period, (iii) the acceleration period, (iv) the deceleratory period and (v) retardation period. During the initial period, a rapid heat evolution occurs due to wetting of the cement, dissolution of different phases giving different ions and hydration of hemihydrate and aluminate phases. Rate of heat evolution decreases rapidly and becomes almost constant up to about 2 h. This period is known as the induction or the dormant period (period ii). During this period, the nuclei of hydration products acquire certain critical size. Once the critical size nuclei are formed, the hydration accelerates with time and the rate of heat evolution reaches to its maximum value at ≈ 20 h of hydration (period iii). This is mainly due to alite hydration of the cement. After this peak, deceleratory period starts and the hydration reaction becomes very slow (period iv & v). In the presence of 20 mass % FA, the rate of heat evolution is decreased. On the other hand, when 5 mass % SF is mixed with OPC20FA, the rate of heat evolution increased slightly but lower than that of OPC. The total heat evolved during the hydration as a function of time is shown in Fig. 7. The total heat evolved increases with time and follows the sequence given below:

$$\text{Total heat}_{\text{OPC}} > \text{Total heat}_{\text{OPC20FA5SF}} > \text{Total heat}_{\text{OPC20FA}}.$$

During the hydration, exothermic reactions occur as a result of dissolution of different phases giving different

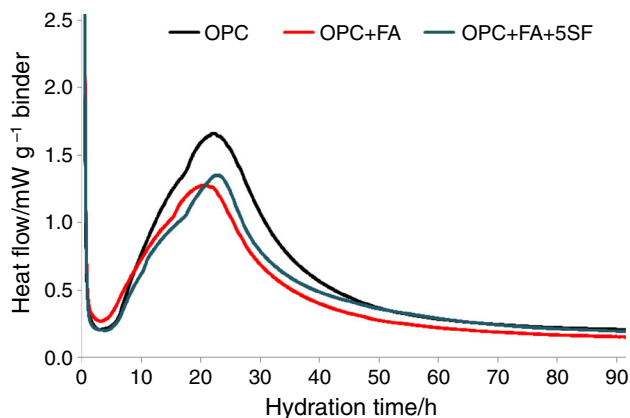


Fig. 6 Rate of heat evolution profile

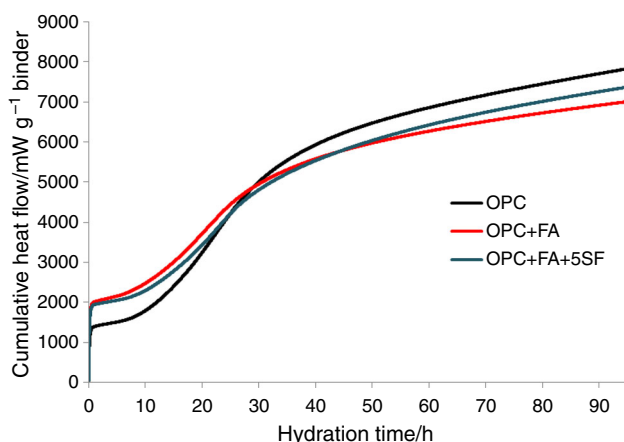


Fig. 7 Total heat evolved as function of time

ions in the solution. The ions move in a random fashion and try to unite. This depends on the surface area of the cement, temperature, pH and zeta potential [20]. When suitable number of ions of different nature assembles together and the size exceeds the critical size, nuclei formation and crystal growth starts and the reaction accelerate with time. However, in the presence of 20 mass % FA, there is a dilution effect and lesser number of ions goes into the solution. As a result, rate of heat evolution and total heat evolved decreases. SF which has much higher surface area as compared to FA when added (5 mass %) to OPC20FA, hydration is slightly increased. Addition of SF increases, the nucleation sites resulting into higher hydration with higher heat evolution. Even this addition of SF does not compensate the dilution effect, so the extent of hydration and heat evolution is lower than that of OPC.

Figure 8 shows DSC curves of anhydrous OPC and 28 days hydrated OPC, OPC20FA and OPCFA10SF. In the

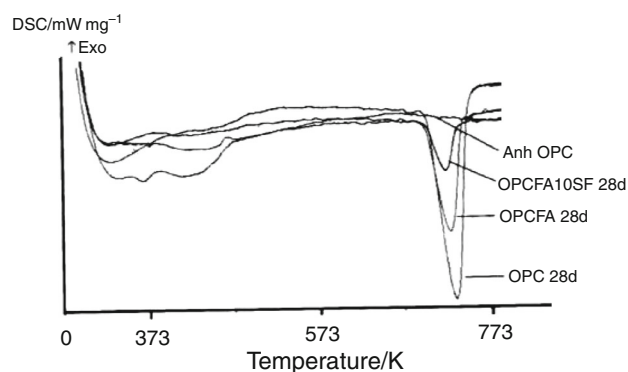


Fig. 8 DSC curves of cements hydrated for 28 days

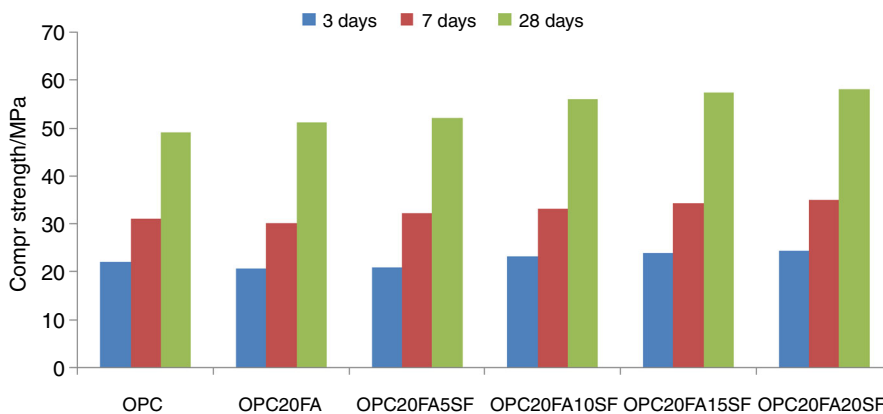
case of anhydrous OPC, there is an indication of some adsorbed water which is eliminated below 100° C. In the hydrated samples, there are broad endothermic peaks below 150° C. These may be due to desorption of adsorbed water molecules and removal of capillary water which is not chemically combined. No peak due to ettringite could be seen since the hydrated samples were dried at 105° C and as a result, ettringite might have been decomposed. It is reported that ettringite is unstable above 65° C [21]. The main and sharp peaks between 450° C and 475° C observed in DSC curves of the hydrated cements correspond to the dehydroxylation of $\text{Ca}(\text{OH})_2$. The intensity of the peaks decreased in the following way:

$$\text{OPC}_{\text{CH}} > \text{OPC20FA}_{\text{CH}} > \text{OPC20FA10SF}_{\text{CH}}$$

When OPC was allowed to hydrate, $\text{Ca}(\text{OH})_2$ liberated as one of the reaction products. In the presence of FA, pozzolanic reaction occurred and $\text{Ca}(\text{OH})_2$ was consumed to some extent, whereas when in addition to FA, 10 mass % SF was added to OPC, the pozzolanic reaction was increased and amount of $\text{Ca}(\text{OH})_2$ was decreased considerably. Due to decrease of the amount of $\text{Ca}(\text{OH})_2$, the intensity of the peak due to decomposition of $\text{Ca}(\text{OH})_2$ in DSC curves are decreased. This supports the results obtained from free lime determinations and confirms that SF accelerates the pozzolanic reaction. In effect, it is expected that addition of SF along with FA may increase the strength and durability of cement.

The strength of a porous material is governed largely by its pores. Strength is a function of porosity and pore size distribution. Unlike permeability, which is governed by the continuity of the pore system, strength is governed by the size of the largest pores, which act as local stress concentrations from which failure begins. Hydrated mortars have porous structure and therefore the compressive strength will also depend on pore size and pore size distribution. Compressive strengths of cement mortars

Fig. 9 Compressive strengths of cements hydrated for 3, 7 and 28 days



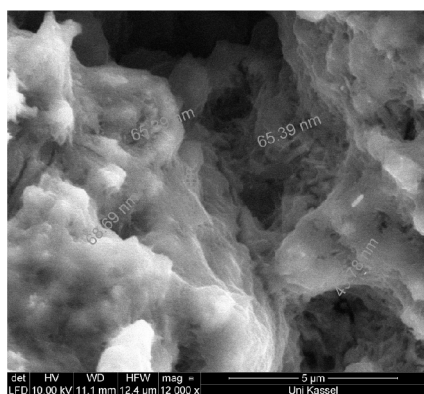
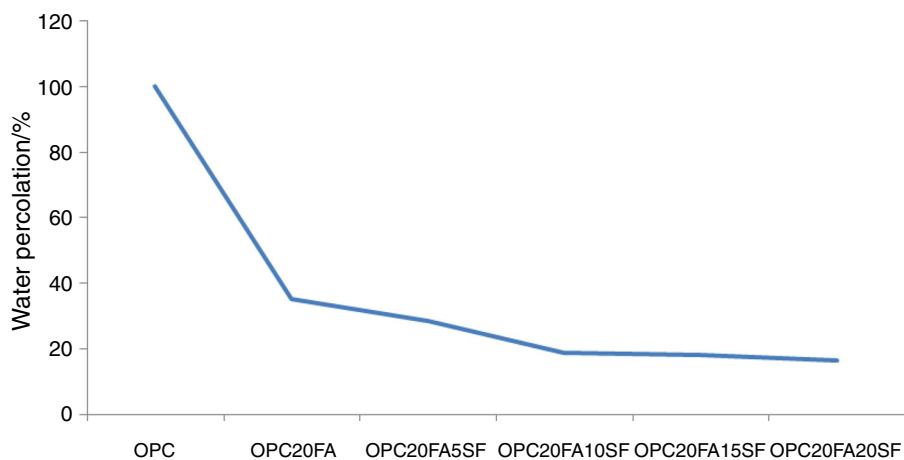
hydrated for 3, 7 and 28 days are shown in Fig. 9. During hydration, CH is formed. When 20 mass % FA was added to OPC, the strength at 3 days of hydration was slightly decreased because of dilution effect and lower pozzolanic activity of FA during this period. Compressive strength at 7 and 28 days of hydration was increased due to increased pozzolanic reaction and formation of C–S–H. The pozzolanic reaction minimizes the amount of a weak material (CH) by a stronger one (C–S–H). On addition of SF, the strength was increased even at 3 days of hydration. With the increase of SF concentration, the strength increased at all the days of hydration. In the presence of SF, there are both physical and chemical effects. Due to smaller size, SF fills the pores and also due to chemical reaction, larger amount of C–S–H are formed. Both filling of pores and formation of large amount of C–S–H, which is the main binding glue, increase the compressive strength even at early days of hydration (3 days). In addition there is a proper arrangement of small particles (packing effect) which fills the voids and contribute to the increment of compressive strength without any chemical reaction [22–25]. The smaller particle size of pozzolanic material tends to produce higher compressive strength than the coarser one [26, 27]. In addition to packing effect, both FA and SF act as centres for nucleation during hydration. When both FA and SF are present, large number of nuclei are available for hydration reactions. At the same time, these increase the pozzolanic reactivity and increase the amount of C–S–H. Since SF is of smaller size, its effectiveness in overall hydration process is more. Thus, in the presence of SF, the deficiencies of FA blended cement is minimised as a result of packing effect, increased nucleation centres and formation of increased amount of C–S–H.

Variation of percent water percolation in the cement mortars hydrated for 28 days is shown in Fig. 10. The water percolation decreased as the amount of SF is increased indicating that pores and pore sizes are

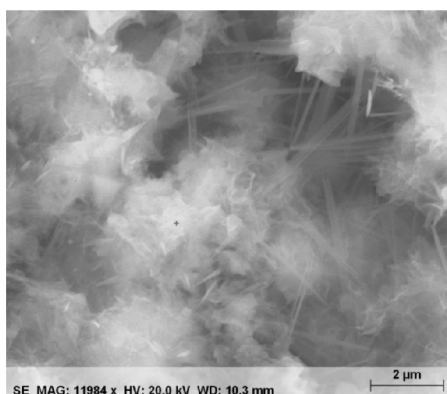
decreased. The results support the increase of compressive strengths in the presence of SF.

SEM pictures of OPC, OPC20FA and OPC20FA10SF hydrated for 28 days are shown in Fig. 11. SEM pictures show hydration products of nanodimensions. In the presence of SF, more compact morphology is seen. Also both in the presence of FA and FA + SF, needle shaped hydration products are seen. EDX spectra of OPC20FA10SF hydrated for 28 days are also given in Fig. 11 and the results do not give information about the presence of ettringite.

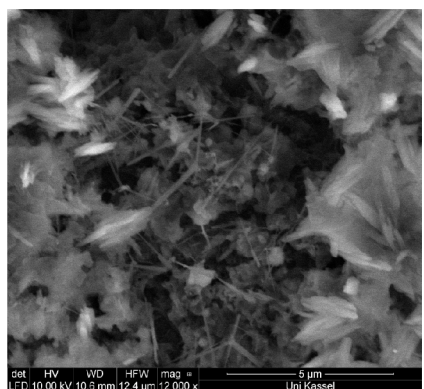
From the overall results, it can be inferred that when OPC comes in contact to water, exothermic dissolution and reaction occur. The solution becomes saturated or supersaturated with respect to different ions and the pH of the paste becomes very high. At such a high pH, when pozzolanic materials such as FA and SF are present, different ions present in the pozzolans are dissolved into the solution very quickly. Silicate network formers present in the pozzolans are also depolymerized and dissolved into the solution. When Ca^{2+} ions in solution came in contact to dissolved monosilicate species, calcium silicate hydrate C–S–H was formed. But after a certain period, the surface of pozzolans was covered by precipitated hydration products and the further reaction became diffusion controlled. The latter hydration was no longer a solution precipitation reaction but a topochemical reaction. However, if SF is also present, there is a possibility of competitive reaction and being smaller in size will have higher reactivity and packing effect. As a result in the presence of SF, the deficiencies of FA blended cement is minimised. Uchikawa et al. [28] have reported the hydration of ternary component blended cements composed of blast furnace slag, FA and Portland cement, where they have also proposed the concept of competitive reaction. Pane and Hansen [29] on the basis of their results have shown that ground-granulated slag (GGB) and FA in cement paste react more slowly compared to SF.

Fig. 10 Water percolation

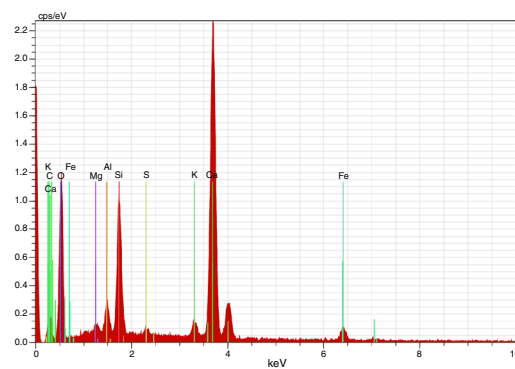
OPC-28d



OPC20FA-28d



OPC20FA-10SF-28d



OPC20FA-10SF-28d

Fig. 11 SEM pictures of cements hydrated for 28 days and EDX of OPC20FA10SF hydrated for 28 days

Conclusions

The results have shown that SF additions to OPC20FA accelerates the hydration reaction and increases the pozzolanic reactions even at 3 days of hydration and the compressive

strength of OPC20FA is comparable to that of OPC. At higher doses of SF, the strength even at 3 days is much higher than that of OPC. Thus, suitable combination of FA and SF minimizes the deficiencies of FA blended cement and FA can be used as a replacement material without its activation.

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