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# Physico-mechanical properties of composite cement () CrossMark pastes containing silica fume and fly ash

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# **KEYWORDS**

Composite cement; Hydration kinetics; DTA; XRD **Abstract** This works aims to study the effect of partial substitution of ordinary Portland cement (OPC) by silica fume (SF) and fly ash (FA) on the physico-mechanical properties of the hardened OPC–FA–SF composite cement pastes. The OPC was partially replaced by 20% and 30% fly ash along with 5% and 10% silica fume. The phase composition of the hydration products was investigated using XRD and DTA techniques. It was found that, the increase of FA content in OPC–FA–SF composite cement decreases the water consistency values and increases the setting times. On the other hand, the increase of SF content leads to increase the water of consistency and decrease the setting times. The partial substitution of OPC by FA and SF leads to higher porosity values with a consequent decrease in the compressive strength values especially during the early ages of hydration. At the later ages of hydration, however, the OPC–FA–SF cement pastes possess total porosity and compressive strength values close to those of the neat OPC paste. The lower of free lime contents were obtained for OPC–FA–SF composite cement pastes with the formation of further additional amounts of CSH as a result of the pozzolanic reaction. The results showed also that, the physico-mechanical properties of composite cement paste [OPC (65%)–FA (30%)–SF (5%)] were improved at later ages.

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# Introduction

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Manufacturing of Portland cement is a resource exhausting, energy intensive process that releases large amounts of the green house gas  $CO_2$  into the atmosphere. Production of 1 ton of Portland cement requires about 2.8 tons of raw materials, including fuel and other materials. As a result of decarbonation of limestone, manufacturing of 1 ton of cement generates about 1 ton of green house gas. Davidovits et al. [1] reported that the amount of carbon dioxide released during the

1687-4048 © 2014 Production and hosting by Elsevier B.V. on behalf of Housing and Building National Research Center. http://dx.doi.org/10.1016/j.hbrcj.2014.02.003 chemical reactions, the cement content of CO<sub>2</sub> emission based on the calcinations of limestone could reach up to 1800 million tons in the year 2000 BaU (Business as Usual). At present, efforts have been made to promote the use of pozzolans to partially replace Portland cement. Pozzolana is a natural or artificial material containing silica in a reactive form. ASTM C618 [2] describes Pozzolana as a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to exhibit hydrated cementitious properties [3,4]. The main hydration product of alite and belite in Portland cement is a calcium silicate hydrate (CSH) of colloidal dimensions, it is highly cementitious and represents about 60 to 65 wt.% of the total solids in a fully hydrated Portland cement. The other hydration product is about 20 wt.% portlandite, which usually occurs as large hexagonal crystals, and contributes little to the cementitious properties of the system. In addition, being relatively more alkaline than the other hydration products, it is easily subjected to attack by water or acidic solution, thus reducing the durability of Portland cement systems to such environments [5]. The reaction of pozzolanic materials with lime is called the "pozzolanic reaction" which is slow at ordinary temperature. Generally, amorphous silica reacts much more rapidly than the crystalline form. It is pointed out that calcium hydroxide is converted into cementitious material by the use of pozzolanic materials. The use of pozzolanic materials as a blended component of Portland Pozzolana cement production is generally associated with significant savings in energy and reducing the solid wastes [6]. Utilization of various types of by-products or waste materials such as fly ash, slag, silica fume, rice husk ash and limestone dust as additives in concrete results in better chemical resistance, higher strength or better durability.

Silica fume is a by-product of the silicon smelting process. It is used to produce silicon metal and ferrosilicon alloys by reducing quartz in an electric arc furnace. Silica fume is characterized by its small spherical particles, very high surface area and have a high content of glassy phase silicon dioxide (SiO<sub>2</sub>). The results of microstructure of the hydrated blended cement containing silica fume, indicated that it is a highly active Pozzolana and increases the resistance to sulfate attack for cement pastes [7]. Silica fume is known to produce a high strength concrete, and is used in two different ways: as a cement replacement, in order to reduce the cement content, and as an additive to improve concrete properties (in both fresh and hardened states) [8].

Fly ash is widely used in blended cements, and is a by-product of coal-fired electric power plants [9]. Two general classes of fly ash can be defined: low-calcium fly ash (LCFA: ASTM class F) produced by burning anthracite or bituminous coal; and high-calcium fly ash (HCFA: ASTM class C) produced by burning lignite or sub-bituminous coal. LCFA is categorized as a normal Pozzolanic material consisting of silicate glass, modified with aluminum and iron. LCFA requires Ca(OH)<sub>2</sub> to form strength developing products (pozzolanic reactivity), and therefore is used in combination with Portland cement, which produces Ca(OH)<sub>2</sub> during its hydration. It lowers the heat of hydration and improves the durability when used in concrete as a cement replacement. It also contributes to concrete strength by pozzolanic and filler effects [10–12]. Fly ash is characterized by its cheapness which reduces the unit cost of cement and concrete, and its positive effects, such as lower water demand [12], lower hydration heat [13,14], reduced bleeding [15], and satisfactory durability [8,16,17].

The combination of silica fume and fly ash in a ternary cement system (i.e., Portland cement being the third component) should result in a number of synergistic effects, some of which are obvious or intuitive, as follows:

- Silica fume compensates for low early strength of concrete with low CaO fly ash,
- Fly ash increases long-term strength development of silica fume concrete,
- Fly ash offsets increased water demand of silica fume,
- Low CaO fly ash compensates for higher heat release from silica fume concrete and
- The relatively low cost of fly ash offsets the increased cost of silica fume.

#### Experimental

The materials used in this study were ordinary Portland cement (OPC) supplied from Suez Portland Cement Company (Suez, Egypt), condensed silica fume (SF) provided from Ferro-Silicon Alloys Company (Edfo-Aswan, Egypt) and fly ash (FA) obtained from Geos Company (India). The chemical analysis of these materials is shown in Table 1.

The water of consistency and setting times (initial and final) for the fresh cement pastes, made of each cement blend, were determined using Vicat Apparatus according to ASTM: C191 [18].

To prepare fresh cement pastes made of OPC-FA-SF cement blends, some amount of each cement blend was placed on a smooth, non-absorbent surface, and a crater was formed in the center. The required amount of mixing water (water of consistency) was poured into the crater by the aid of a trowel. The dry cement was slightly troweled over the remaining to absorb the water for about one minute. Continuous and vigorous mixing was done for only three minutes. The fresh cement paste was placed into one inch cubic molds, manually pressed into the corners and along the surface of the mold until a homogeneous paste was obtained. After the top layer was compacted and pressed with hand, the surface of the paste was smoothed by the aid of a thin edged trowel. Immediately after molding, the specimens were first cured in a humidity chamber at 100% R.H. at room temperature  $23 \pm 1$  °C for 24 h then the cube specimens were demolded and curing was continued under tap water up to 3, 7, 28, 90 and 180 days, ASTM: C191 [18].

At each hydration time, all pastes were tested for their compressive strength, total porosity, free lime and phase composition of the formed hydration products.

A set of three cubic specimens of the same cement pastes and curing time were used for the determination of compressive strength according to ASTM C-150 [19].

The total porosity of the hardened cement pastes was determined according to Copeland and Hayes [20].

After the compressive strength determination, removal of free water was accomplished by using a stopping solution from 1:1 mixture by volume of methyl alcohol and acetone[21]. At any time a representative sample of the cement paste, about

Materials	Oxides										
	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	L.I.O		
OPC	20.89	4.68	3.43	63.33	2.18	2.95	0.44	0.25	2.20		
Silica fume	94.30	0.33	1.09	0.64	0.47	0.31	0.35	0.67	1.76		
Fly ash	60.27	27.99	4.54	1.16	0.37	0.35	0.15	0.98	0.91		

 Table 1
 Chemical oxide composition of starting materials, (wt.%).

10 g, was taken and ground in an alumina mortar under the surface of the stopping solution (100 ml), then filtered through sintered glass funnel (G4). Washing the content of the funnel was carried out using 50 ml of fresh diethyl ether and dried at 70 °C for 30 min. then kept in airtight bottles.

The free lime content, CaO (%), was determined by using the glycerol/ethanol extraction method and the mean value of the two independent determinations was recorded, Kondo et al. [22].

Differential thermal analysis (DTA) was carried out in the present study using DTA-50 thermal analyzer (Schimadzu Co. Tokyo, Japan). A sample of about 50 mg ( $-53 \mu m$ ) was used with a heating rate of 20 °C/min. under dynamic nitrogen atmosphere. X-ray diffraction technique was carried out on some selected hydrated cement pastes using a Philips diffractometer with a scanning speed of 20 °C/min. and Ni-filtered Cu-K $\alpha$  radiation. The identification of all samples was confirmed by computerized research of the PDF data obtained from the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD), 2001.

## **Results and discussion**

## Water of consistency and setting time

The water of consistency and setting times (initial and final) of the cement pastes containing different ratios of silica fume (SF) and fly ash (FA) are shown in Table 2. The results show that, the water of consistency of the blended cement pastes containing 20% and 30% fly ash admixed with 5% silica fume is lower than that of the neat OPC paste and decreases with fly ash content; this is mainly due to the spherical glass structure of fly ash with its low water absorption. The increase in silica fume content from 5% to 10% together with 20% and 30% fly ash contents leads to increase in the water of consistency; this is due to the high surface area of silica fume that is related to its fine particle size. The results indicate also that, the blended cement paste containing 5% silica fume together with 30% fly ash gives the lower water of consistency. The results indicate also that, the setting times (initial and final) increase with fly ash content from 20% to 30% together with 5% and 10% silica fume contents; this is due to the relatively low rate of hydration of fly ash as related to its mineralogical composition. The low hydraulic properties of fly ash are due to that it constitutes mainly of crystalline phases such as quartz, mullite and hematite [23]. The phases hinder the hydraulic characteristics which decrease the water demand. However, the setting times decrease with silica fume content from 5% to 10%; due to which, silica fume accelerates the hydration of OPC as well as its pozzolanic interaction with the free lime released from OPC hydration [24].

# Total porosity

The total porosity of the hardened composite cement pastes containing different ratios of silica fume and fly ash cured in tap water up to 180 days is shown in Fig. 1. The results show that, the total porosity of the hardened cement pastes decreases up to 180 days; this is mainly due to the formation and later accumulation of hydration products within the available pore spaces of the hardened OPC-FA-SF pastes which resulted in refinement of the total pore system with a consequent reduction of the total porosity. The results indicate also that, total porosity increases with Pozzolana (FA and SF) content of the hardened OPC-FA-SF cement pastes up to 90 days as compared to the hardened neat OPC especially during the early ages of hydration. The increase of Pozzolana content on the expense of OPC leads to the dilution of OPC in the blended cement pastes. This resulted in lower amounts of hydration products where the rate of pozzolanic reaction is relatively slower than the rate of OPC hydration especially during the early ages of hydration. At later ages of the hydration, however, the total porosity values of the composite cement pastes become closer to those of the neat OPC paste; this is attributed to the predominance of the pozzolanic reaction at the later hydration ages. This behavior is more pronounced for the hardened composite cement paste containing 5% silica fume and 30% fly ash where lower values of the total porosity at the later ages of the hydration are even lower than that of

 Table 2
 Mix proportion of OPC-FA-SF cement blends as well as the optimum water of consistency and setting times of their fresh pastes.

Mixes	OPC, (%)	Silica fume, (%)	Fly ash, (%)	Water of consistency, (%)	Setting time (min.)	
					Initial	Final
M.0	100	-	-	29.00	146	241
M.5SF-20FA	75	5	20	28.50	121	242
M.10FS-20FA	70	10	20	30.30	111	235
M.5SF-30FA	65	5	30	28.20	141	255
M.10SF-30FA	60	10	30	30.00	125	246



Fig. 1 Total porosity versus curing age of the hardened OPC-FA-SF blended cement pastes containing different ratios of silica fume and fly ash.

the neat OPC at 180 days of hydration. This effect is mainly due to the increase of the amount of hydrated cementitious materials produced by the pozzolanic reaction of FA and SF with the free lime with the formation of excessive amounts of calcium silicate hydrates which deposit in the open pores within the cement matrix and lead to a decrease of the total porosity. In addition, the total porosity values of the hardened OPC-FA-SF cement paste containing 10% silica fume together with 30% fly ash are relatively higher than those of the other pastes at all curing ages. This is mainly due to the increase of the W/C ratio (initial porosity) where the increase of SF content, with its higher specific surface area, leads to increase in the water demand (water of standard consistency) of 10% SF fresh blended cement paste.

## Compressive strength

The compressive strength of the hardened OPC–FA–SF composite cement pastes cured in tap water up to 180 days is graphically plotted in Fig. 2. The results reveal that, the compressive strength values of the hardened OPC–FA–SF cement pastes increase with curing time up to 180 days; this is due to the progress of hydration process and increase of the amount of hydrated products that lead to increase in the total contents of binding centers between the remaining unhydrated pastes of the grains of cement constituents. The results indicate also that, the compressive strength of the hardened blended cement pastes, containing different ratios of silica fume and fly ash, decreases with Pozzolansa (SF and FA) content at different curing ages up to 90 days as compared to the neat OPC paste; this is mainly due to the dilution of OPC in cement pastes. This results in less amounts of hydration products where the lower rate of pozzolanic reaction is lower as compared to that of OPC hydration and hence lower values of compressive strength are obtained especially at the early ages of hydration, [25]. When silica fume and fly ash are incorporated together in cement, the hydration is significantly retarded. The heat of hydration is decreased and the early reactivity of the silica fume is hampered. The accelerating effect of the silica fume is delayed. This reduces the contribution of silica fume to the early strength [26]. At later ages of hydration (180 days), the compressive strength values of the OPC-FA-SF cement pastes containing 5% or 10% silica fume together with 20% fly ash as well as the paste containing 5% silica fume together with 30% fly ash are higher than those of the hardened neat OPC paste. At later ages of the hydration, the blended cement paste containing 5% silica fume admixed with 30% fly ash gives the highest values of compressive strength than those of the other pastes at the later ages up to 180 days. This is due to the predominance of the pozzolanic reaction of FA and SF with the



Fig. 2 Compressive strength versus curing age of the hardened OPC-FA-SF blended cement pastes containing different ratios of silica fume and fly ash.

free lime liberated from OPC hydration. On the other hand, the compressive strength values of the blended cement paste with 10% silica fume admixed with 30% fly ash are lower than those of the other composite cement pastes at all curing ages; due to the dilution of OPC as well as the increase of the initial porosity of the hardened paste as controlled by the increase of the standard water of consistency (initial W/C ratio).

## Free lime content

The free lime contents of the hardened OPC–FA–SF blended cement pastes containing silica fume and fly ash cured in tap water up to 180 days are graphically plotted in Fig. 3. Evidently, the free lime content of the neat OPC paste increases with curing age up to 180 days; this is mainly due to the progressive hydration of calcium silicate phases (C<sub>3</sub>S and  $\beta$ -C<sub>2</sub>S) which are the main source of free lime liberated during OPC hydration. The results indicate also that, the free lime contents of the hardened OPC–FA–SF cement pastes decrease with the pozzolana content and curing ages; this is mainly due to the higher pozzolanic activity of silica fume and fly ash toward reaction with Ca(OH)<sub>2</sub>, as well as dilution of the OPC portion in the cement blends which liberates free lime [27]. In addition, there appeared a more noticeable decrease in the free lime contents of the blended cement pastes at the later hydration age

(180 days); this indicates that the amount of free lime consumed by the pozzolanic reaction with FA and SF exceeds the amount of free lime liberated by OPC hydration at the later curing ages. Also, the Pozzolana has a higher rate of pozzolanic reaction at later ages than at early ages of hydration [28,29]. Moreover, the free lime contents of blended cement pastes made of OPC–FA–SF blends richer in SF (10% SF) are lower than those of the pastes made of mixes with lower SF content (5% SF) at all ages; this indicates that the pozzolanic activity of SF is relatively higher than that of FA. In fact, the results of free lime contents given in Fig. 3 actually represent a net effect of the free lime liberated by OPC hydration and the free lime consumed by the pozzolanic reaction with SF and FA.

## Differential thermal analysis (DTA)

The DTA thermograms of the hardened cement pastes made of the neat OPC (M.0) and the OPC–FA–SF cement blend containing 5% silica fume and 30% fly ash (M.5SF-30FA) after 3, 28 and 180 days are shown in Figs. 4 and 5, respectively. There appeared four endothermic peaks in the DTA thermograms of Figs. 4 and 5; these are located at the temperature ranges of 60–100, 108–170, 470–500 and 710–750 °C. The endothermic peaks located below 100 °C, are attributed to the



Fig. 3 Free lime content versus curing age of the hardened OPC-FA-SF blended cement pastes containing different ratios of silica fume and fly ash.



Fig. 4 DTA thermograms of the hardened neat OPC paste after curing for 3, 28 and 180 days.



Fig. 5 DTA thermograms of the hardened OPC-FA-SF pastes of mix M.5SF-30FA after curing for 3, 28 and 180 days.

removal of free water. While the endothermic peaks observed at about 108–170 °C are attributed to the decomposition of CSH overlapped with calcium sulphoaluminate hydrates (ettringite and mono-sulfate hydrates) as well calcium alumino-silicate hydrates [30]. The endotherm located at about 470–500 °C is characteristic of the decomposition of portlandite. The last two overlapped endotherms located at 710–750 °C are related to the calcination of amorphous and crystalline calcite (CaCO<sub>3</sub>).

For thermograms of Fig. 4 obtained for the hardened neat OPC paste, the areas and intensities of the peaks characteristic of CSH and Ca(OH)<sub>2</sub>, which represent the main hydration products, increase with age of hydration. The endothermic peak characteristic of CSH becomes more distinguishable at the longer age of hydration up to 180 days.

The effect of partial replacement of OPC by 5% silica fume and 30% fly ash (M.5SF-30FA) can be observed from the thermograms shown in Fig. 5. The main features of these thermograms are the decrease in the peak area characteristic of the decomposition of  $Ca(OH)_2$  (portlandite phase) with curing time up to 180 days as compared to that the neat OPC paste. In fact, this decrease in the amount of free calcium hydroxide phase is due to the dilution of cement in the OPC–FA–SF blend as well as its consumption by the pozzolanic reaction with SF and FA. On the other site, the peak area of CSH observed in the thermograms of hydrated OPC-SF-FA blend of mix (M.5SF-30FA) increases with curing time up to 180 days; due to the pozzolanic reaction. The thermograms for the cement pastes made of mixes M.0 and M.5SF-30FA show an increase in the intensities of the endotherm characteristic of calcium carbonate with age of hydration; this is mainly due to the increase in the degree of carbonation of free calcium hydroxide to calcium carbonate with curing age.

Fig. 6 illustrates the DTA thermograms of the blended cement pastes made of mixes M.0, M.5SF-20FA, M.10SF-20FA, M.5SF-30FA and M.10SF030FA after curing for 180 days. Evidently, the endothermic peaks at temperatures lower than 100 °C are attributed to the removal of free water. The endotherm observed at about 100–170 °C is due to the decomposition of CSH overlapped with ettringite



Fig. 6 DTA thermograms of the hardened OPC-FA-SF pastes made of mixes M.0, M.5SF-20FA, M.10SF-20FA, M.5SF-30FA and M.10SF-30FA after curing for 180 days.

and monosulfate hydrates as well as alumino-silicate hydrate. The intensity of this endotherm increases with Pozzolana (SF and FA) content of the hardened OPC-FA-SF pastes. This is due to the high pozzolanic activity of fly ash and silica fume forming additional amounts of hydration products such as CSH and CAH. Also, the endotherm located at about 470-500 °C is characteristic of the decomposition of calcium hydroxide (portlandite). The intensity of this endotherm decreases with pozzolana content due to the dilution of cement as well as the consumption of free calcium hydroxide by the pozzolanic reaction. The endotherm appeared at about 710-750 °C is related to the decomposition of CaCO<sub>3</sub>. The peak area of calcium carbonate phase decreases as the Pozzolana (SF and FA) content increases due to the chance of carbonation of some residual Ca(OH)<sub>2</sub> to CaCO<sub>3</sub>. Therefore, Pozzolana addition increases the resistance of the hardened blended cement pastes toward carbon dioxide attack. The exothermic peaks located at 900-940 °C are due to the crystallization of the pseudo-wollastonite phase (mono calcium silicate, CS) [31]. This exothermic peak is characteristic of the decomposition of the hydrated calcium silicate produced as a result of pozzolanic reaction between silica fume and the free calcium hydroxide liberated during OPC hydration.

#### X-ray diffraction (XRD) analysis

The results of XRD in Fig. 7 for the hardened neat OPC paste, after 3, 28 and 180 days, show that the intensities of the peaks of the portlandite phase increase with the curing time, due to the continuous hydration of  $\beta$ -C<sub>2</sub>S and C<sub>3</sub>S. Also, the peaks characteristic of unhydrated calcium silicates are detected and their intensities decrease with curing time as a results of continuous hydration. Meanwhile, the intensity of the peak characterizing for the calcium silicate hydrate (CSH) overlapped with that of CaCO<sub>3</sub> increases with age of hydration; this is due to progress of hydration up to 180 days. The peaks characterizing for the calcite (CaCO<sub>3</sub>) could also be detected in the diffraction patterns and overlapped with those CSH at 3.03 Å.

The results of XRD shown in Fig. 8 for the hardened OPC– FA–SF blended cement paste made of (65% OPC + 5%SF + 30% FA) M.5SF-30FA blend at 3, 28 and 180 days indicate the formation of CSH and Ca(OH)<sub>2</sub> phases as the main hydration products. The peaks characterizing the anhydrous cement clunker (C<sub>3</sub>S and  $\beta$ -C<sub>2</sub>S), quartz (Q) and calcium carbonate appeared also in the XRD-diffractograms. The intensities of the peaks characterizing C<sub>3</sub>S and  $\beta$ -C<sub>2</sub>S decrease with curing time, the intensities of the peaks of the hydration



Fig. 7 XRD patterns of the hardened neat OPC paste hydrated for 3, 28 and 180 days.



Fig. 8 XRD patterns of the blended cement pastes containing M.5SF-30FA for 3, 28 and 180 days.



Fig. 9 XRD patterns of the hardened OPC-FA-SF pastes made of mixes M.0, M.5SF-20FA, M.10SF-20FA, M.5SF-30FA and M.10SF-30FA after 180 days of hydration.

products, mainly as calcium silicate hydrates (CSH), increase with increasing age of hydration. However, the intensities of the peaks characteristic free calcium hydroxide decrease with age of hydration; this is due to the enhanced rate of pozzolanic interaction of the released free lime from OPC hydration with FA and SF leading to a marked consumption in the free lime content with age of hydration.

Fig. 9 shows the XRD patterns of the hardened cement pastes made of mixes M.0, M.5SF-20FA, M.10SF-20FA, M.5SF-30FA and M.10SF-30FA at 180 days. The peak characteristic of calcium silicate hydrates (CSH), portlandite (Ca(OH)<sub>2</sub>) and unhydrated OPC constituents (C<sub>3</sub>S and β- $C_2S$ ) could be distinguished; the peaks characterizing quartz (Q) from fly ash and calcium carbonate are also detected. Evidently, the intensities of the peaks characteristic of portlandite decrease with the partial substitution of OPC by FA and SF; this is mainly due to the decrease of amount of OPC, which is the main source of portlandite, as well as the pozzolanic reaction of portlandite with FA and SF. Evidently, all of the peaks of the portlandite phase are almost disappeared with FA and/ or SF content of the blended cement pastes. The peak of calcite is almost overlapped with that of CSH at 3.03 Å. and increases with FA and SF contents in the blended cement pastes.

# Conclusions

The main conclusions derived from this study can be summarized as follows:

- 1. The partial replacements of OPC by SF and FA lead to an improvement of the physico-mechanical characteristic of the hardened cement pastes.
- 2. The water of consistency increases with silica fume content and decreases with fly ash content. While the setting times (initial and final) decrease with silica fume content and increases with fly ash content.
- 3. The compressive strength of the hardened OPC-FA-SF blended cement pastes, mixes M.5SF-20FA, M.10SF-20FA, M.5SF-30FA and M.10SF-30FA, is lower than that of OPC paste up to 90 days. At the later age of hydration, however, most of the blended cement pastes possess higher strength values than that of OPC paste.

- 4. The total porosity values of the hardened OPC-FA-SF blended cement pastes are higher than those of the neat cement paste at the early and intermediate ages of hydration (up to 90 days) and become closing, or even lower in some cement blends, to the neat OPC paste. In general, the total porosity of all of the blended cement pastes decreases with age of hydration.
- 5. The free lime content of the neat OPC increases with curing time; whereas, free lime contents of blended cement pastes decrease with the curing age.
- 6. XRD diffractograms show that the intensities of the peaks characteristic CH decreased markedly, or even completely disappeared, with the partial substitution of OPC by FA and SF. The reduced intensity of CH is actually attributed to the loss of OPC content and the pozzolanic interaction of FA and SF with the free CH liberated from OPC hydration.
- 7. DTA investigation confirmed the results of XRD where the areas of the endotherms characteristic of the decomposition of CH and CSH increase up to 180 days for the neat OPC paste. Meanwhile, for the hardened OPC-FA-SF pastes the endotherm of CH decreased, or even disappeared in some cases, with age of hydration; but the area of the endotherm characteristic of the decomposition of CSH increases continuously up to 180 days of hydration.

# Conflict of interest

None declared.

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