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Pozzolanic activity of silica fume with lime

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Abstract

This article aims to study the pozzolanic activity of silica fume by the reaction with $Ca(OH)_2$ (CH) at room temperature. The pozzolana includes the natural or artificial type containing amorphous alumina or silica structure. It can be added or substituted with OPC in concrete that can react with CH liberated during the hydration of cement forming calcium silicate hydrate (C-S-H) gel, the main binding agent in the matrix. This hydrated gel is deposited in some of the open pores of concrete then the pores are diminished and improved its durability in sulphate, chloride and seawaters. The pozzolanic activity of silica fume (SF) was investigated by the determination of free lime, free silica, and combined water contents as well as the hydration products were investigated by the aid of DTA, XRD, FT-IR and SEM, techniques. The results of chemical reaction are in good agreement with those determined by the different equipment. It was also concluded that the reaction is complete for all mixes in the first 28 days.

1. Introduction

Silica fume (SF) is by-product of the reduction of high purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. After environmental concerns necessitated the collection and land-filling of SF, it became economically justified to use SF in various applications. The properties of SF depend very much upon the type of the product produced and the process of manufacture. SF generally contains more than 90% SiO_2. However, the contents of SiO_2 and the degree of the amorphous nature may vary considerably depending upon the method of production [1].

The particle-size distribution of SF shows most particles to be smaller than one micrometer (1 μm) with an average of ≈ 0.1 μm, which is approximately 100 times smaller than the average of cement particle. The chemical composition of SF from the ferrosilicon corresponds, generally, to 82-92% SiO_2 ≈ 0.5-3%, Fe_2O_3 ≈ 1-3%, alkalis ≈ 1-2% carbon; and minor amount of Al_2O_3, CaO as well as MgO. SF consists of very fine vitreous particles with a surface area ≈ 15-20 m²/g when measured by nitrogen absorption techniques (BET). Silica fume is highly effective pozzolanic material [2]. The percentage of $Ca(OH)_2$ consumed by SF has been used as an index of its pozzolanic activity, but the reported shows large variation.

Pozzolanic materials are generally able to combine with the hydrated calcium hydroxide $Ca(OH)_2$ at room temperature forming the hydrated calcium silicate (C─S─H), which is responsible for the strength of hydrated cement pastes. In addition, an increase in bulk density of concrete results as the mixture avoid is filled with very small admixture particles (mirco filler effect). The (C-S-H) produced has a lower C/S ratio than that of fly ash (FA). The lower C/S ratio tends to confirm in reports of [3]. [4] concluded that much of SF remains unreacted after 7 days of hydration.

The SF particles surround each cement grains to densify the matrix and filling the voids with strong hydration products. [5] has reported that Ca^{+2} ions are actively dissolved from alite, its adsorption on the silica surface layers, the Ca^{+2} ions concentrations in the liquid phase and the hydration of alite at early ages is accelerated. Research aims to study the pozzolanic activity of silica fume, with hydrated lime up to 90 days of hydration.

SF can produce both chemical and physical effect, which cause meaningful changes in the microstructure, diminishing its permeability and improving its strength [6]. A scanning electron microscope (SEM) analysis

shows that the microstructure of this material is more homogenous and denser than concrete without SF [7].

2. Experimental

The chemical analysis of SF is mainly composed of $SiO_2 \approx 95.6$, $Fe_2O_3 \approx 2.29$, $Al_2O_3 \approx 0.05$ and $MgO \approx 0.87$ mass %. SF is spherical particles having an average diameter of about 0.1- 0.5 µm. It consists of amorphous silica as shown in Fig. 1 having Blaine specific surface area of ≈ 20 m^2/g. The microstructure and the morphology (SEM) and (TEM) of SF is seen in Figs 2 and 3.
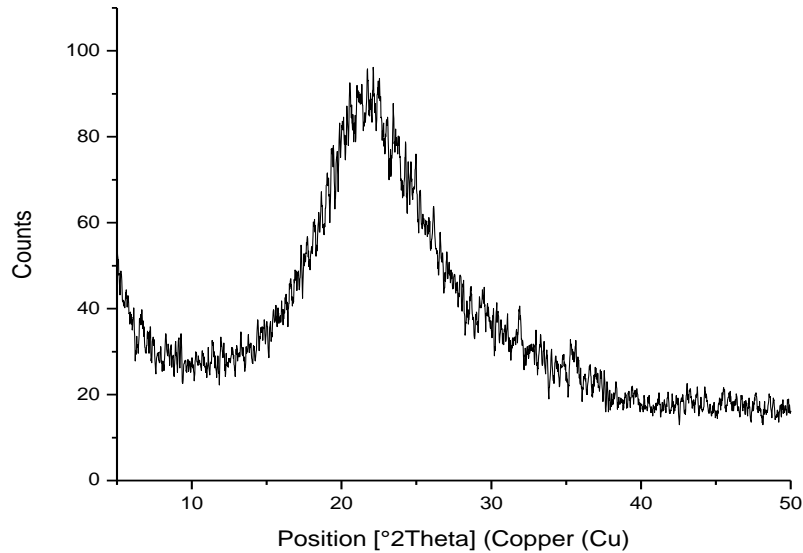

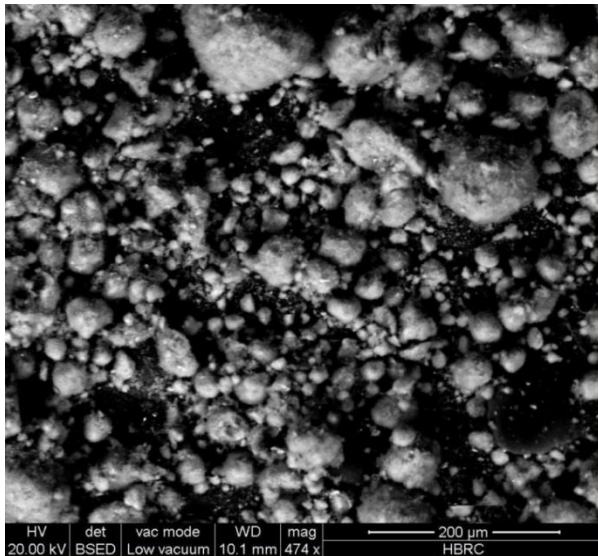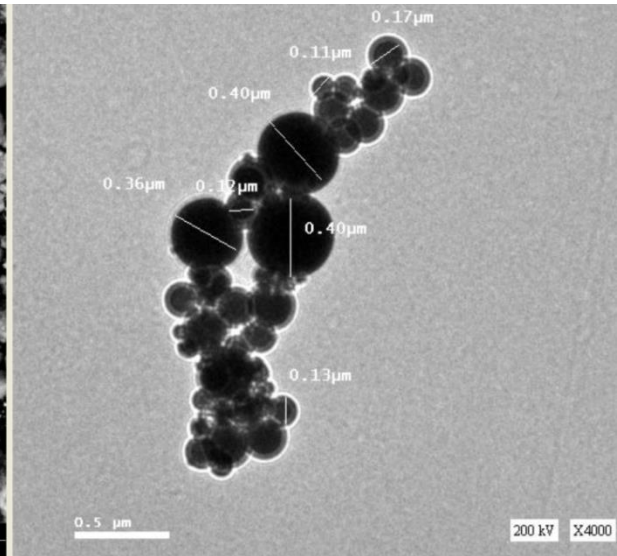Fig. 1: X-ray diffraction patterns of SF

Fig. 2: SEM of SF

Fig. 3: TEM of SF

The pozzolanic activity of SF is the rate of the hydration with $Ca(OH)_2$ (CH) with lime at room temperature. The mixes are denoted as A.1, A.2, A.3, A.4 and A.5 respectively. SF was substituted by 5, 10, 15, 20 and 25 mass %, CaO as seen in Table 1. The pozzolanic activity was studied as suspension in bottles at water/solid ratio of 10. The hydration of each mix was investigated after 1, 3, 7, 28, and 90 days of hydration. Suspensions of SF were mixed with different ratios of lime (5%, 10%, 15%, 20% and 25%) as shown in Table 1. Each suspension is introduced into air-tightened bottles containing 100 ml of distilled water (about 10 gm of the mixture). The bottles were tightly stoppered and mixed with paraffin wax to

avoid any carbonation from atmospheric air. The bottles were mechanically stirred from time to time, daily, with mechanical shaker, in order to attain complete homogeneity with water. After each time of hydration, the hydration was stopped by chemically method [8]. In this method the suspension was filtered with G_4 sintered glass and washed four times with acetone/methanol 1:1 for stopping of the hydration [8]. The precipitate was then dried at 6 ºC for 4h to evaporate the alcohol.

The chemically combined water content (W_n) is the percent of the ignition loss of the pre-dried sample at 1000 ºC for 1hr. W_n was calculated using the following equation:

$$W_n\% = \frac{W_1 - W_2}{W_2} \times 100 \qquad (1)$$

where W_1, mass of the dried sample before ignition; W_2, mass of sample after ignition **[9,10]**. Free lime contents of the hydrated cement pastes can be determined by the extraction of CaO with ethylene glycol at 60-70 ºC on a

water bath for 1 hour and then titrated with standardized aqueous solution of HCl **[11].**

Some selected samples were examined by the aid of DTA, XRD, SEM and IR techniques.

Table 1: Mix composition of SF and CH, mass%.

Sample No.	SF	CH
A.1	95	5
A.2	90	10
A.3	85	15
A.4	80	20
A.5	75	25

Results and Discussion

Free lime contents

The variations of free lime contents in relation with curing time up to 90 days for the various mixes made of SF in the presence of CH are graphically represented as a function of curing time as shown in Fig. 4.
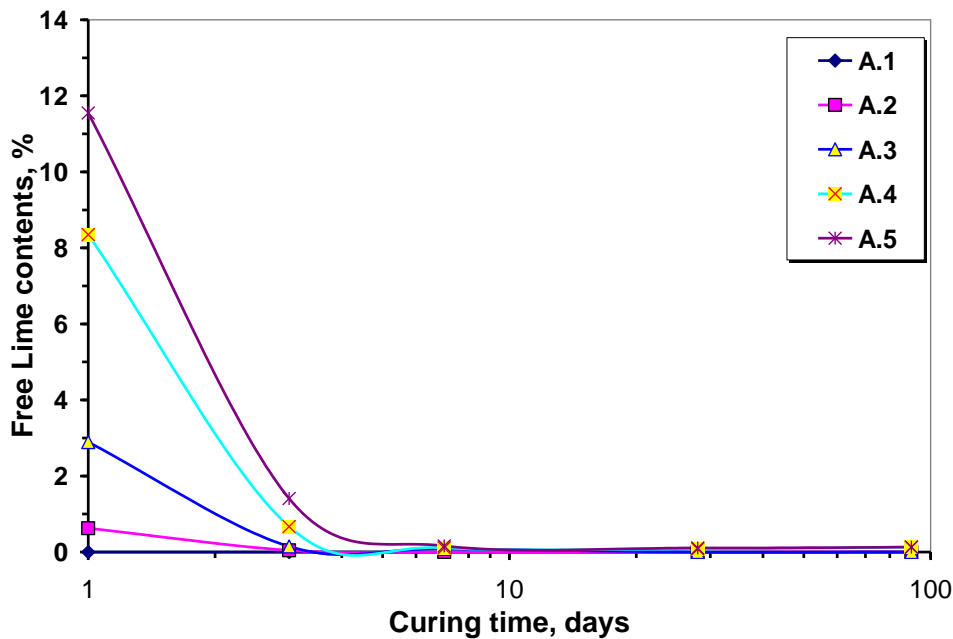

Fig. 4: Free lime contents of SF/CH mixes in the suspension form up to 90 days

Fig. 4 shows a gradual decrease in the free lime contents in the suspensions until the 1 day, this is due to the higher pozzolanic activity of SF. The free lime contents of all mixes decrease sharply during the early hydration ages. Evidently, the suspensions of SF/CH mixes A.1 and A.2 possess lower values of lime (CH) content than those of A.3, A.4 and A.5. This is mainly due to the increase of CH content on the expense of SF content as shown in Table 1, which is linearly increases the lime content and decreases in SF content [12]. There are appeared as a sharp decrease in the residual free lime contents from one day to 3 days and almost consumed (zero %). After 1 day, the residual free lime content for mix A.1 is completely consumed. SF acts as nucleating

agent, which accelerates the rate of hydration, which reacts with CH forming (C-S-H). SF has higher lime fixation ability especially at the early ages of hydration. The rate of lime consumption depends on the remaining unreacted lime contents in the mixes, indicating the relatively higher pozzolanic activity of SF.

Free silica contents

The free silica contents of mixes A1, A3 and A5 containing 95:5, 85:15 and 75:25 SF-CH in suspension cured up to 90 days are represented in Fig. 5. The results show that the free silica contents, decrease continuously with curing time for all SF/CH suspension.
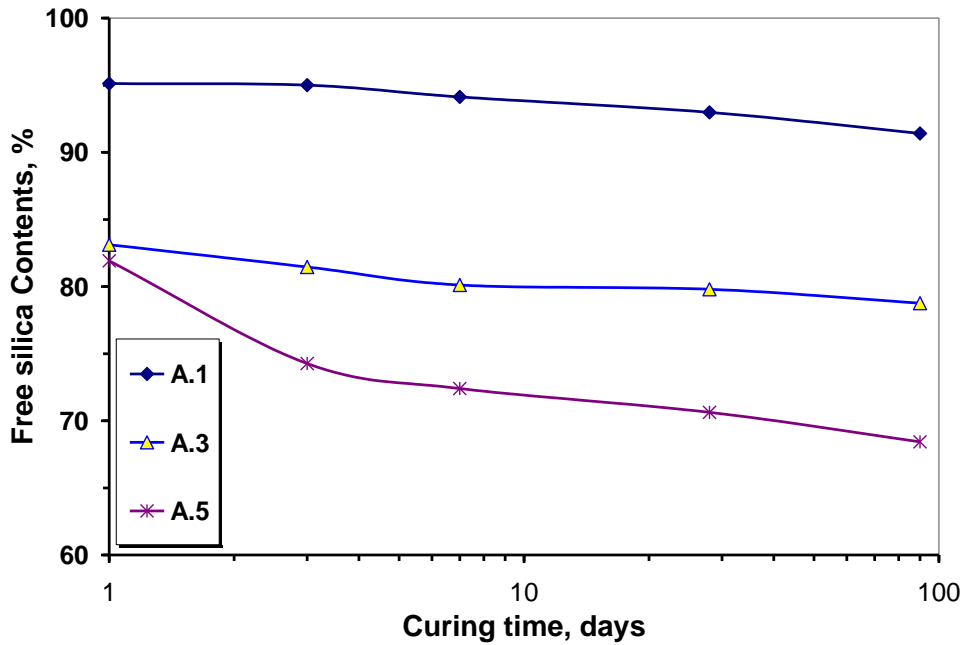
Fig. 5: Free silica contents of SF/CH mixes in the suspension form up to 90 days

As the hydration time increases, the rate of hydration accordingly, increases with the formation of more C-S-H hydrated products [13]. Evidently, the amount of free silica contents decreases, since the amount of CH disappears, equal to the reacted with SF to form C-S-H, due to pozzolanic reaction. Mix A.5 has a lower value of free silica contents up to 90 days.

Chemically combined water contents

The chemically combined water contents (Wn,%) for all investigated suspensions, are graphically represented in Fig. 6. Evidently, the chemically combined water contents increase gradually with curing time for all mixes, which is due to the progress of hydration process with curing time and the formation of C-S-H. It is clear that after 28 days up to 90 days of curing time, there is a gradual decrease in the combined water content. This is assumed to be due to a release of water during polymerization of silicates, and the combined water content appears to be reduced with time [14]. It appears that in the first 28 days of hydration, the pozzolanic reaction takes place later than the reaction of hydration, because a certain period of time is needed for the dissolution of silica [15].
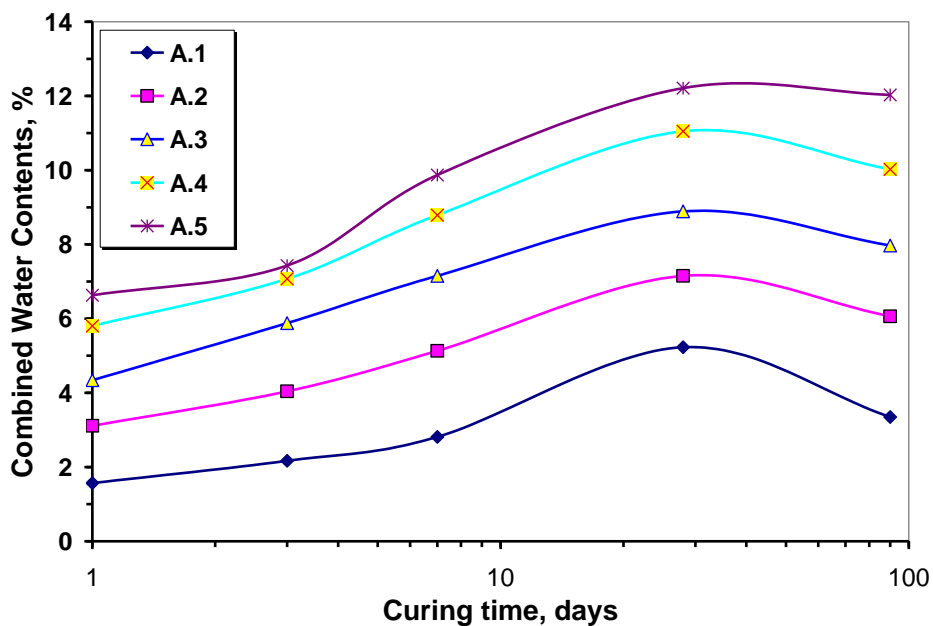

Fig. 6: Chemically combined water of SF/CH mixes in the suspension form up to 90 days

Phase composition and microstructures

Differential thermal analysis

Thermal analysis is one of the best methods for studying the characterization of pozzolanic activity, which allow predicting the properties of hardened cement materials.
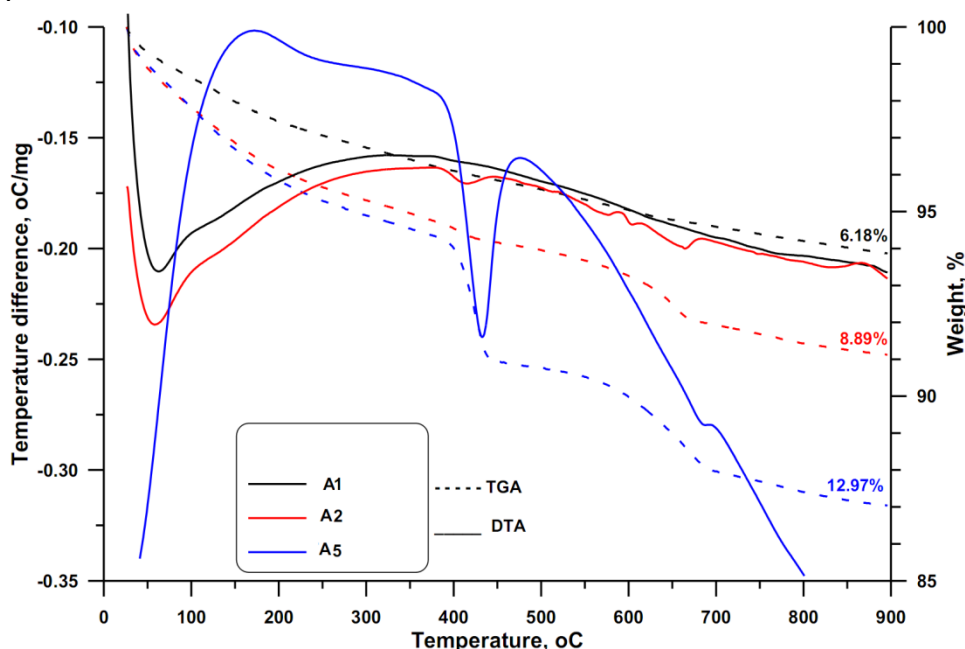

Fig. 7: DTA/TGA thermograms of A.1, A.2, and A.5 in suspension up to 1 day

Fig. 7 represented DTA/TGA thermograms of the investigated mixes of A.1, A.2, and A.5 samples cured for 1 day. DTA/TGA thermograms show four endothermic peaks. Two endothermic peaks located at 90-200°C are attributed to the decomposition of C-S-H (I,II) hydrated products. The third endothermic peak located at 420-550°C is attributed to the dehydroxylation of CH. The fourth peak observed at 705 °C and 752 °C, is due to the decomposition of amorphous and crystalline $C\bar{C}$ [16]. The weight loss at 900 °C was found to be 6.18, 8.29 and 12.97% corresponding to mixes A1, A2 and A5 respectively cured for 1 day. The thermograms are characterized by an increase in the peak area of C-S-H due to continuous increase of the hydrated products of A1, A2 and A5 mixes hydrated in suspension form. The mass loss of endothermic peak of mixes A.1, A.2 and A.5 corresponding to the decomposition of C-S-H hydrated products below 200 °C increases with the increase of the contents of CH in the corresponding mixes.

The main features of the thermograms are characterized by an increase in the peak area of C-S-H due to continuous hydration of the cement pastes. The mass loss of endothermic peak of mixes A1, A3 and A5 corresponding to the decomposition of C-S-H, hydrated products below 200 °C were 2.55, 3.88 and 4.16% respectively. The mass loss of endothermic peak located at 420-500 °C attributed to the dehydroxylation of CH. The consumption of $Ca(OH)_2$ in the formation of calcium silicate hydrates during the pozzolanic reaction as more consumption of CH is occurred in the pozzolanic reaction and less amount of CH converted during carbonation with atmospheric CO_2 to form $CaCO_3$ as shown in the peaks observed at

705 and 752 °C. Mixes A1 and A3 show a zero CH value at 1 day.

Only one exothermic peak located at about 850°C is obtained which is attributed to the crystallization of the pseudo-wollastonite phase (mono-calcium silicate, CS) this exothermic peak is characteristic for the decomposition of C-S-H (tobermorite-like phase). One of the ideas presented to explain the exothermic peak at the end of the DTA-profile (at about 850°C) was the degree of crystallization between Ca and Si. It is evident that this peak is growing with curing time. [17] ,supported the idea that the different types of C-S-H can coexist in cement-based systems. In his work, is proposed that the type of C-S-H may be differentiated by the C/S ratio. Accordingly, a higher C/S shall be preferably found in a cement-based reaction and a low C/S ratio in the secondary reactions, viz. pozzolan-based reaction [8]. The assumption of crystallization occurring upon decomposition of the C-S-H (I) at the DTA peak at 850°C is due to the characteristic of calcium monosilicate, which is developed during the crystallization of monocalcium silicate (wollastonite) [18].

Fig. 8 shows the DTA thermograms of mix A.5, suspensions cured for 1, 7 and 90 days hydrated in suspension form. The weight loss at 900 °C was found to be 12.97%, 14.45 and 18.45 for 1, 3 and 90 days respectively. The mass loss of endothermic peak of mix A5 for 1, 3 and 90 days corresponding to the decomposition of C-S-H, hydrated products below 200 °C were 4.16, 8.38 and 10.17% respectively. The thermograms are characterized by an increase in the peak area of C-S-H due to continuous hydration of mix A5. The main features of the thermograms are characterized by an

increase in the peak area of C-S-H up to 90 days. The mass loss of endothermic peak located at 420-500 °C attributed to the dehydration of CH was 4.11, 0.10, 0.00% for 1, 7 and 90 days respectively. The crystallinty of C-S-

H increases with the increase of lime content as indicated by the sharpness of the exotherm in the range of 800-850°C [18].
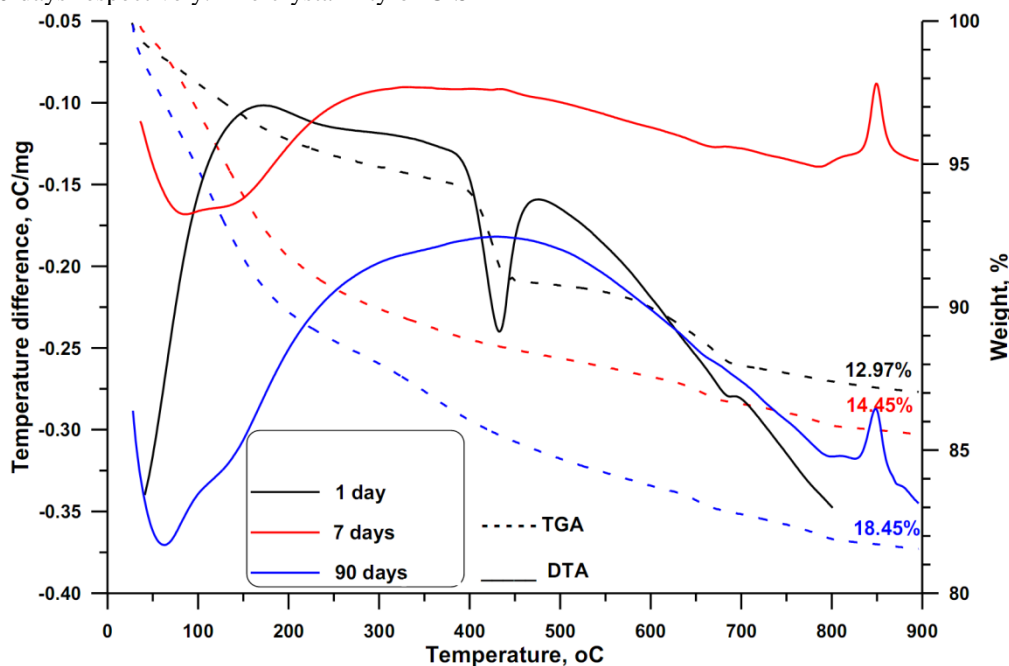

Fig. 8: DTA/TGA thermograms of mix containing A.5 cured up to 90 days

Infrared spectroscopy

FT-IR is very important tool to identify the hydrated and unhydrated cementitious products. The fundamental modes of vibration are stretching and bending modes in the region 4000–400 cm^{-1}. The vibration frequencies of theses modes for the species under study depend on the molecular structure, chemical bending, crystal structure, impurities in solid solution [19].

Fig. 9 shows FT-IR spectra of mix A.5 cured for 1, 3, 7, and 90 days. The broadening and the asymmetric shape of the band at about 1439 cm^{-1}, are presumably due to the presence of portlandite, [20,21]. The changes of shape and intensity of absorption bands located in the range characteristic for the H–O–H valence vibrations 3700–3200 cm^{-1}, including sharp peak characteristic for the OH group vibrations in $Ca(OH)_2$, located at about 3642 cm^{-1} [22,23], which is only detected for A.5 cured for 1 day. The band at 3460 cm^{-1} is attributed to stretching of hydroxyl groups associated with water in (C-S-H), which is increased with the curing time. The intensive bands appearing at about 1094 cm^{-1}, is characteristic for silicate phases [24]. The deterioration with hydration time of the sharp absorption band of vibration of OH⁻ group in

$Ca(OH)_2$, confirms pozzolanic properties Absorption band related to the vibrations of Si–O bonds indicate the progress in formation of binding compounds for A.5 for all curing times. After 3 days, there is a clearly visible absorption band formed at about 970 cm^{-1}. It evidences that silicate phases fade away, and C-S-H phase is formed because of pozzolanic reaction [25]. There is an inflection from the side of lower wave- numbers (below 1000 cm^{-1}). This fact gives a reason to ascertain that a pozzolanic reaction takes place and the C–S–H hydrates are formed; the band located below 1000 cm^{-1} is much more distinct and indicates the increase of the C-S-H phases. The bands located at 1420, 1430 and 870 cm^{-1}, are due to the presence of carbonate. C-S-H hydrated show bending band at 972 cm^{-1} as $v_2SiO_4^{-4}$ [24], attacks the form of tetrahedron, while it reported Raman spectra of C-S-H(I) a bending vibration frequency around 670 cm^{-1}, increasing with $Ca(OH)_2$ mass %. The bands at 785 and 771 cm^{-1} are due to amorphousness of SF. Si–O bond gives characteristic bonds due to bending vibration at 464 cm^{-1}, decreasing with curing time.
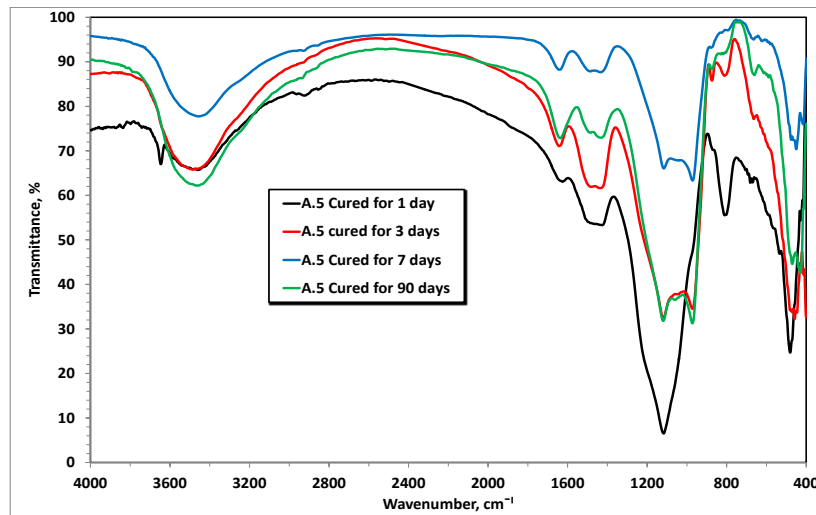
Fig. 9: FT-IR of mix A.5 cured for 1, 3, 7 and 90 days

Fig. 10 shows FT-IR spectra of the hydrated samples of mixes A1, A2, A3, A4 and A5, cured for 1 day. The intense and sharp band at $\cong 3648$ cm^{-1} represents the free lime, which is only detected for A5, cured for 1 day, [22, 23]. The band in the region 900-1000 cm^{-1} is due to silicate group [24], while that at 3460 cm^{-1} is attributed to stretching of hydroxyl groups associated with water in calcium-silicate-hydrates [24]. The bands located at 1430 and 870 cm^{-1} are due to carbonate. It is clear that the bands at 3449 cm^{-1}, 1642 cm^{-1}, and 975 cm^{-1}, which represent to H_2O, and C-S-H respectively have high intensity for A2, A3, and A5, curing time per days [22]. The band at 785 and 771 cm^{-1} are due to amorphousness of quartz. Si–O bond gives characteristic bonds due to bending vibration at 464 cm^{-1}, decreasing with curing time.
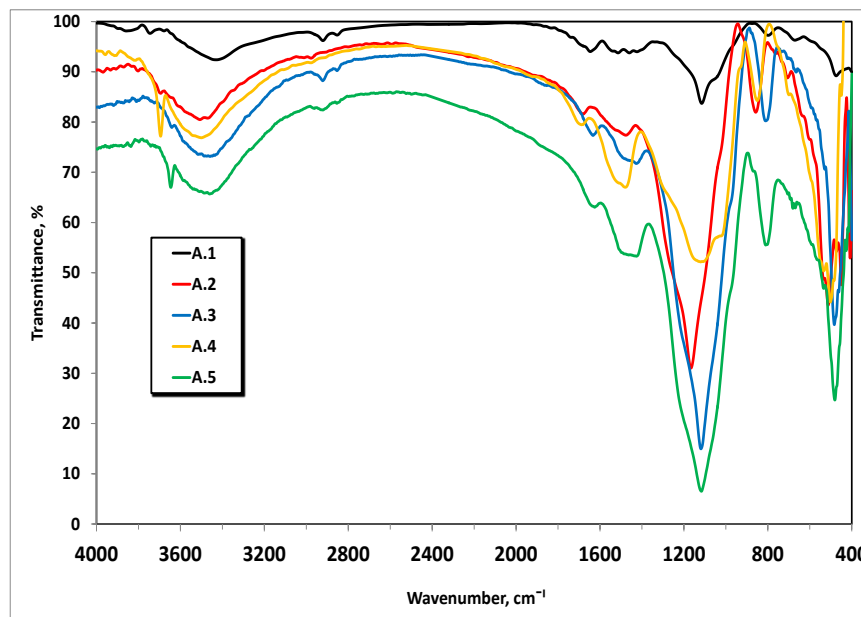

Fig. 10: FT-IR of mixes A.1, A.2, A.3, A.4 and A.5, cured for one day

X-ray diffraction analysis

The XRD patterns of mixes A1, A2 and A5 hydrated at 1, 7 and 90 days are shown in Figs. 11, 12 and 13 respectively. The XRD patterns of Figure 11 indicate the presence of calcium carbonate (CaCO₃), calcium silicate hydrates (C-S-H), calcium hydroxide (CH) and small peaks characteristic for quartz (Q).

The XRD patterns of mixes A.5 hydrated at 1 day and A.3 and A.4 cured for 90 days are shown in figures 12, 13 respectively. The XRD patterns of Figure 12 indicate the presence of amorphous (C-S-H), calcium hydroxide (CH) and small peaks characteristic for quartz (Q) and calcium carbonate (CaCO₃), which overlaps with (C-S-H).
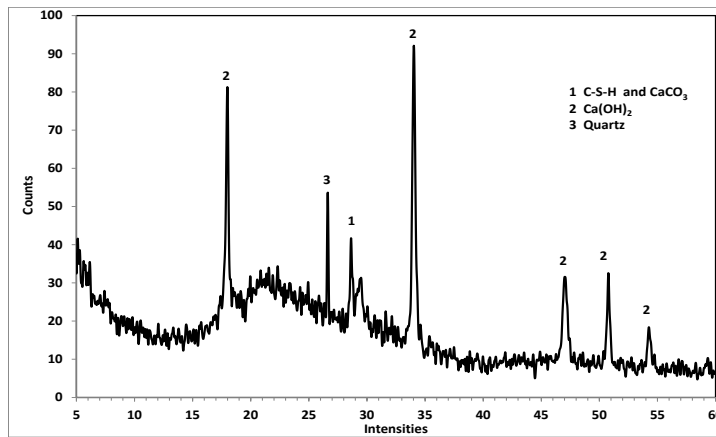
Fig. 11: XRD patterns of mix A.5 cured for 1 day in suspension

Obviously, the results of Figs. 12 and 13 show that the intensities of the peaks characterizing CH decrease with increasing age of hydration; however, the peaks characteristic for free CH are completely disappeared after 7-90 days of curing in suspension form, this is due to the consumption of CH by the pozzolanic reaction leading to the formation of larger amounts of C-S-H hydrated products.

The features of X-ray diffractograms as shown in Figures 12 and 13 are the complete disappearance of the intensities of the peaks characterizing the portlandite (CH) phase with age of hydration and (ii) the increase in the intensities of the peaks characteristic for calcium silicate hydrates (C-S-H). These two findings are mainly due to the enhanced rate of pozzolanic reaction between CH and the active silica with increasing age of hydration [26].
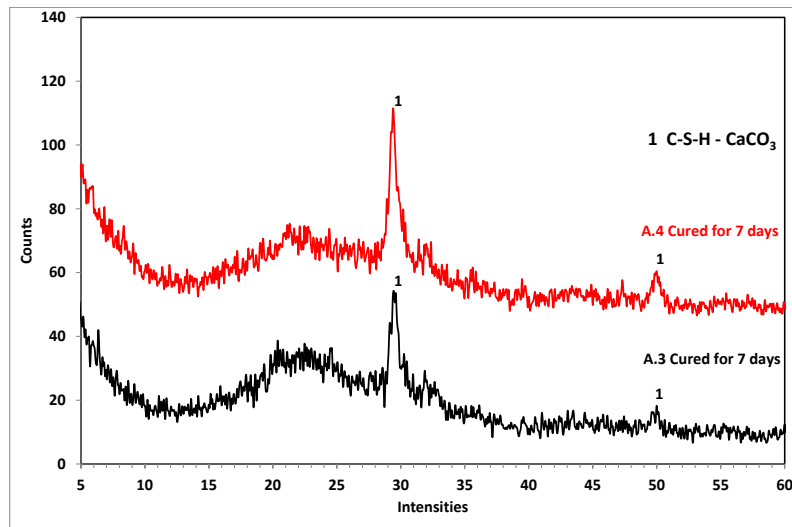

Fig. 12: XRD patterns of A.3 and A.4, cured for 7 days in suspension
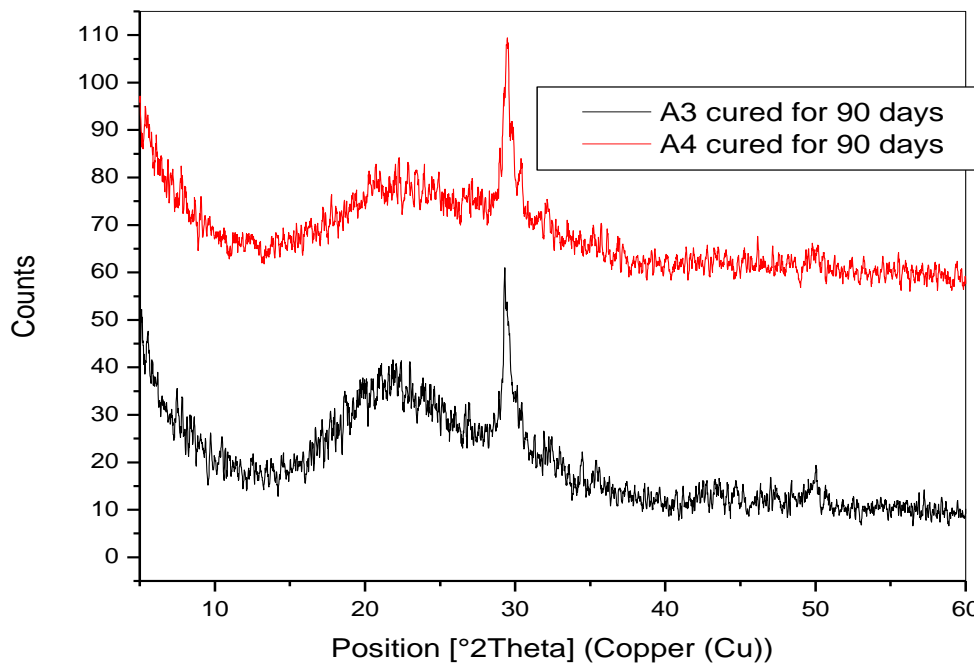
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Fig. 13: XRD patterns of A.3 and A.4, cured for 90 days in suspension

Microstructure

The microstructure of mix A.5 containing SF/CH: 75/25 in suspension hydrated for 7 and 90 days is seen in Figs. 14 and 15. The micrograph displayed the formation of various nearly amorphous and microcrystalline (C-S-H) hydration products around the SF-CH grains constituents after 7 days of hydration (Fig. 14).
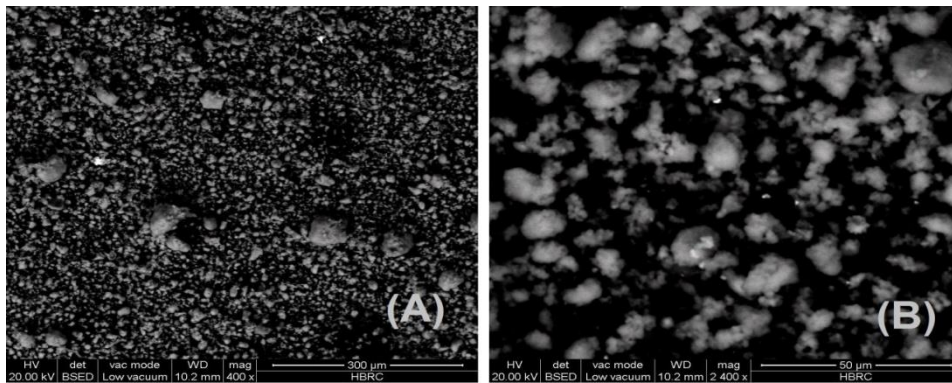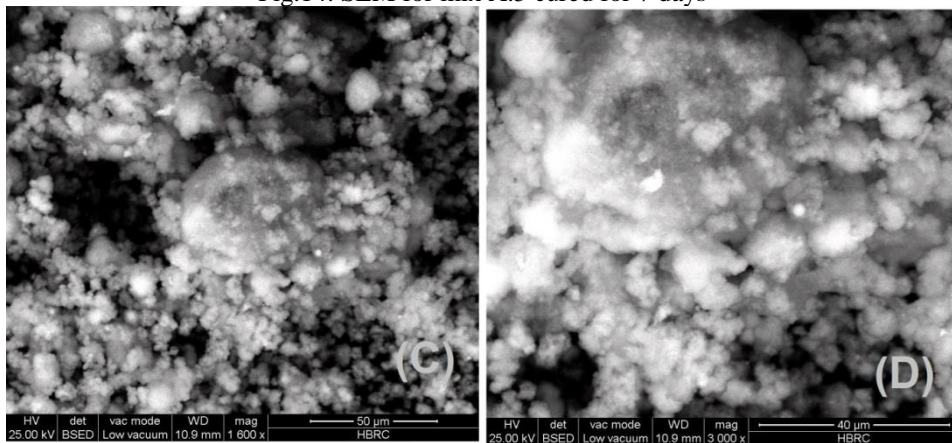

Fig.14: SEM for mix A.5 cured for 7 days

Fig.15: SEM for mix A.5 cured for 90 days

SEM micrographs display excessive amounts of (C-S-H) gel are produced because of pozzolanic interaction of active SF with the CH on prolonged of hydration, after 90 days (Fig. 15). A closely packed structure was appeared which composed mainly of amorphous microcrystalline hydration products, fibroid and lumpy products. Pozzolanic activity of materials depends generally on the active silica content. In pozzolanic cement paste, this active silica dissolves and precipitates in the form of (C-S-H) phase [27].

Conclusions

From the previous investigations, it can be concluded that:

1. Silica fume is an amorphous nature and has diameter range in between 0.1- 0.5 µm therefore it is high active pozzolanic material.
2. The free lime contents at high concentration of CaO from 20-25% mixes are disappeared after 3 days, whereat low concentrations the free lime is disappeared after one day.
3. Combined water contents increases for all pastes up to 28 days and then decreases from 28-90 days. This is due to the release of some combined water during the polymerization of C-S-H.
4. The free silica content decreases with time up to 90 days, then there is free unreacted silica for all pastes due to the increase of silica for pozzolanic reaction.
5. The results of DTA thermograms are on good agreement with those of XRD and SEM.

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