



Hydration Behavior of Composite Cement Containing Fly Ash and Nanosized-SiO₂

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Abstract: In recent years, there is a great interest in replacing a long time used materials in concrete structure by nanomaterials (NMs) to produce a concrete with novel functions. NMs are used either to replace a part of cement, producing ecological profile concrete or as admixtures in cement pastes. The great reactivity of NMs is attributed to their high purities and specific surface areas. A number of NMs been explored and among of them nanosilica (NS) has been used most extensively. This work aims to study, the hydration behavior of composite cements containing fly ash (FA) and nanosilica. Different cement blends were made from OPC, FA and NS. OPC was substituted with FA up to 30.0 mass, %, then the FA portion was replaced by equal amounts of NS (2.0, 4.0 and 6.0 mass, %). The hydration behavior was followed by determination of free lime (FL) and combined water (Wn) contents at different curing ages. The required water for standard consistency (W/C), setting times (IST & FST), bulk density (BD) and compressive strength were also estimated. Some selected hydration products were analyzed using XRD and DTA techniques. The results showed that, both of FA and NS improve the hydration behavior and mechanical properties of the investigated cements. But, NS possesses higher improvement level than FA, due to that, both of them behaves not only as filler, but also as activator to promote pozzolanic reaction, which enhances the formation of excessive dense products. The higher beneficial role of NS is mainly due to its higher surface area, seeding effect and pozzolanic activity in comparison with FA. The composite cement containing 70.0% OPC, 26.0% FA and 4.0% NS gave the desirable mechanical properties at all curing ages.

Keywords: Hydration, Mechanical Properties, Composite Cement, Fly Ash, Nanosilica, Curing Time

1. Introduction

Concrete is the second most consumed material after water and it shapes the built environment around the world. Preparation of concrete involves use of natural resources like sand, stone, aggregates, water etc. According to U. S. Geological Survey, mineral commodity summaries January 2015 and the cement production in the world in 2014 is 4.18 billion metric tons [1]. Estimated concrete production in the world in 2009 was more than 25 billion metric tons according to CSI (Cement Sustainability Initiative) report [2]. Since the 2nd half of the 20th century, the addition of supplementary cementitious materials (SCMs) to Portland cement (PC) has received renewed attention. The most commonly used SCMs in cement and concrete are, fly

ash (FA), silica fume (SF), blast furnace slag (BFS), metakaolin (MK) and rice husk ash (RHA). SCMs are widely used in concrete either in blended cements or when the concrete is made, due to sustainability action, environmental issues and the technical advantages [3-10].

Thomas et al. [11] concluded that, the superior performance of composite cements over those of PC is mainly due to the following characteristics: i) The pozzolanic reaction of SCMs with Portlandite (CH) produced during cement hydration; ii) The C₃A reduction, i.e. dilution effect; iii) The pH reduction therefore, the ettringite becomes less expansive; iv) The formation of additional CSH, which produces a coating layer on the alumina-rich and other reactive phases, thereby hindering the secondary and lastly

ettringite formation; and v) The secondary CSH formation also results in pore size refinement, which reduces the permeability as well as the ingress of aggressive ions. Among of the most reactive commonly used SCMs deserve a special place; FA has a beneficial effect.

Fly ash is known as pulverized fly ash (PFA). It is finely divided byproduct that electro-statically precipitated from the combustion of pulverized coal in boilers of power plants. The PFA particles are spherical and have the same fineness as cement so that, the silica is readily available for pozzolanic reaction with lime [12].

The major mineral components of PFA are silicates and aluminates. The silicates are usually present as spherical particles. They are believed to be the melted products of clays, feldspars, quartz, mullite (3Al₂O₃.2SiO₂) and the other common minerals in coal [13].

Approximately 33% of FA is used in Europe as a constituent of blended cements and as mineral addition for the concrete production [14]. Previous studies [15–17] have shown that, the replacement of PC by FA improves the workability and durability of concrete, reduces hydration heat and helps in the development of long term compressive strength.

Recently, there is a great interest in replacing a long time used materials in concrete structure by new materials to produce cheaper, harder and durable concrete. There are many applications of nanotechnology in construction engineering field [18–21]. It is being accepted that, by adding a portion of nanoparticles (NPs), even at a very small content, the properties of cement-based material can be enhanced to a great extent in respects of workability, strength gain and durability [22].

The great reactivities of nanomaterials (NMs) are attributed to their high purities and specific surface areas in relation to their volume [23, 24]. Due to their sizes; some researchers have recorded an increased water demand for mixtures containing NMs of the same workability [25–26].

The behavior of NPs in cement can be summarized as follow: i) NPs act as fillers in the empty spaces; ii) NPs act as crystallization and seeding centers of hydrated products, promoting cement hydration; iii) NPs assist the formation of small sized CH crystals as well as homogeneous C-S-H clusters; and iv) NPs improve the ITZ structure [27, 28].

Zhang et al [29], studied the effect of NS on the properties of cement concrete containing high volume of FA. They reported that, NS particles reduce setting times and increase

the early age strength of concrete. Both FA and NS are pozzolanic materials, and both adsorb, react with CH that is generated from cement hydration. To get a considerable strength improvement, the NS content shall not be less than 5 mass, % of binder. It is estimated that, the addition of 5g NS can consume almost 50% of the CH produced by 100g of cement when assuming that, NS has been fully hydrated and a total of 20 g of CH can be generated, giving CSH with Ca/Si ratio of 1.7. Since NS and FA compete in consuming CH, but NS is far more reactive than FA.

In a previous work [30], the effect of colloidal nano-SiO₂ (CNS) on FA hydration was studied and it was concluded that, i) the early age strength gain of CNS-FA-cement pastes is mainly due to the NS acceleration effect on both cement and FA hydration; ii) Although CNS can enhance the pozzolanic reaction of FA by increasing the alkalinity of solution in the early age, its later age hydration may be adversely affected and iii) There is a dense coating around FA particles in the CNS modified pastes, which, with a low Ca/Si ratio may result from the reactive CNS hydration at the early age and acts as a barrier that hinders ion penetration and consequently the FA hydration at later ages.

Few researches were done on the use of FA and NS in cement paste, mortar and concrete. This work aims to study the hydration behavior of composite cement containing FA and NS. PC type (I) was partially substituted with FA up to 30.0 mass, %, then the FA portion was replaced by equal amounts of NS (2.0, 4.0 and 6.0 mass, %). The hydration kinetics of cement blends with and without NS was studied and the hydration products were identified using XRD, DTA and SEM techniques.

2. Materials and Experimental Details

The materials used in this investigation were OPC, FA and NS. OPC with Blain surface area of 3000±50.0 cm²/g was provided from Lafarge Cement Company, Egypt. FA with specific surface area of about 10.672 ± 2 m²/g, was supplied from Sika Chemical Company, Egypt. NS with average particle size, Blain surface area and purity percentage of about 15.0 nm, 50.0 m²/g and 99.9%, respectively was supplied from Nanotechnology Lab, Faculty of Science, Beni-Suief University, Beni-Suief, Egypt. The oxide analyses of OPC and FA obtained by X-ray fluorescence (XRF) spectrometry are given in Table 1. The mineralogical composition of OPC is listed in Table 2.

Table 1. Chemical oxide analysis of OPC and FA (mass, %).

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	L.O.I	Total
OPC	19.30	3.94	3.80	62.67	1.90	3.22	0.44	0.39	3.04	99.70
FA	63.1	26.54	5.4	2.33	0	0.09	0.85	0.52	0.8	99.63

Table 2. Mineralogical composition of OPC.

Compound	Abbreviation	Chemical formula	Content, %
Tri-calcium silicate	C ₃ S	3CaO.SiO ₂	66.08
Di-calcium silicate	C ₂ S	2CaO.SiO ₂	5.50
Tri-calcium aluminate	C ₃ A	3CaO.Al ₂ O ₃	4.02
Tetra-calcium aluminoferrite	C ₄ AF	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	11.55

The NS used in this study was prepared as described in our previous work [26]. The amorphous glassy nature of FA and NS was verified by different techniques (Figs.1-5). The starting materials were completely dried at 110°C for 2h. Each dry mix was blended in a steel ball mill using some balls for 1h to achieve complete homogeneity.

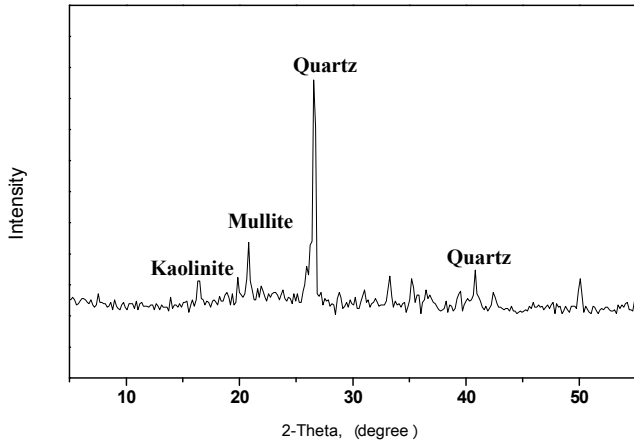


Fig. 1. XRD pattern of FA.

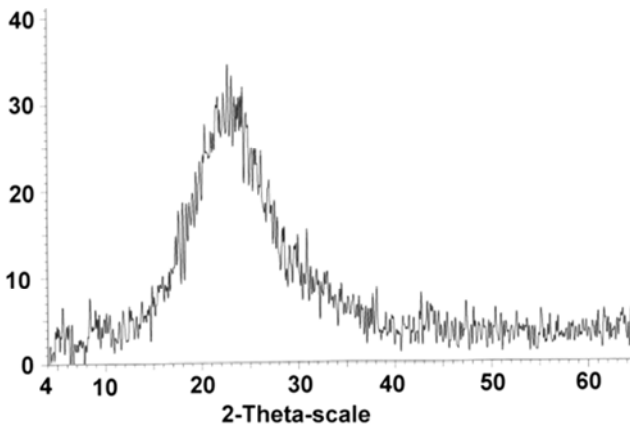


Fig. 2. XRD pattern of NS.

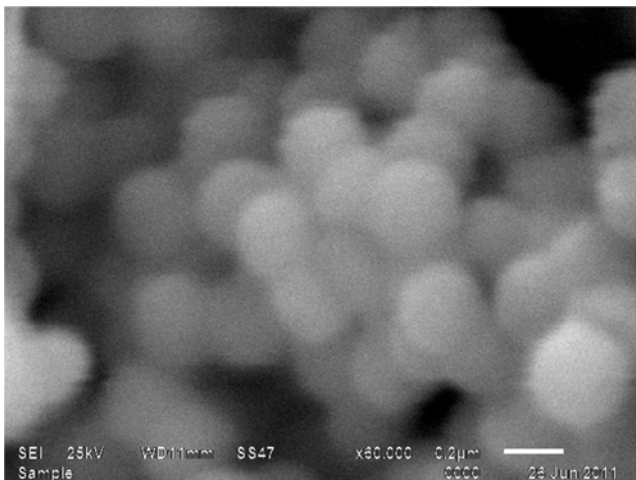


Fig. 3. SEM photograph of NS.

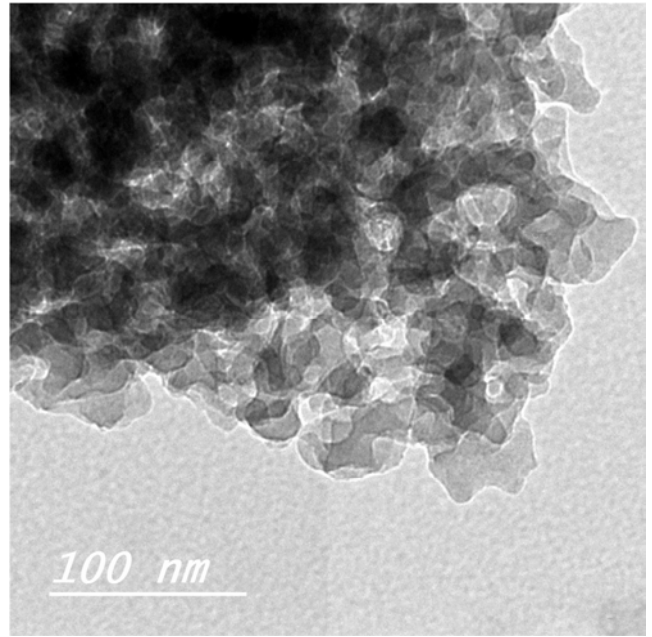


Fig. 4. TEM photograph of NS.

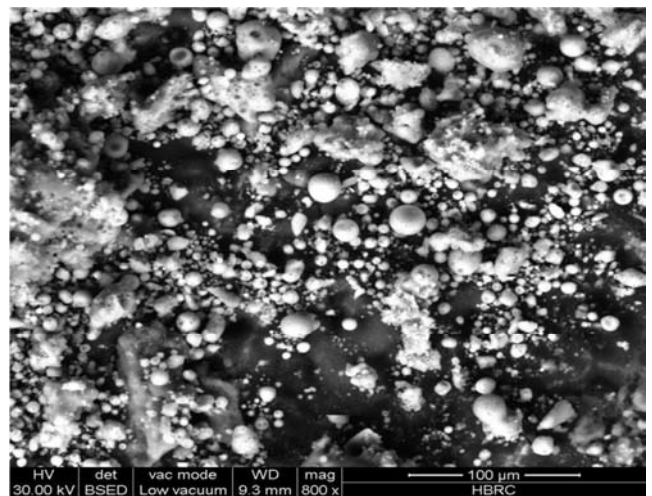
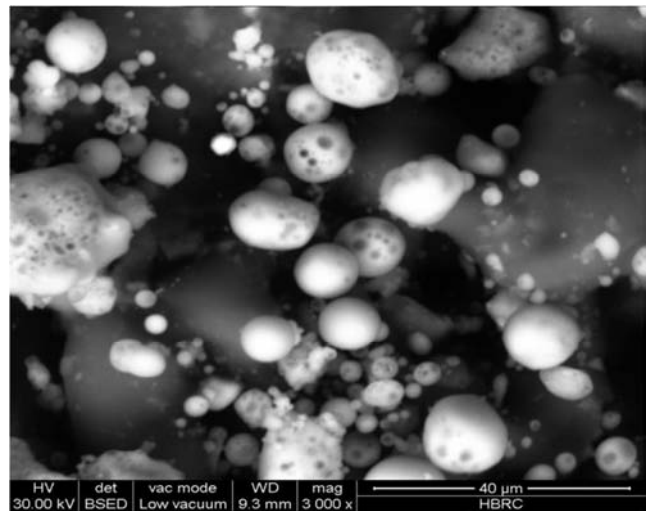


Fig. 5. SEM photographs of FA.

The cement blends were mixed in a rotary mixer. NS-particles are not easy to disperse uniformly in water. Accordingly, the NS mixing was performed as follows: (i) NS was stirred with 25% of the required water for standard consistency at speed of 120 rpm for 2min; (ii) The cement containing FA and the residual amount of mixing water were added to the mixture and homogenized at speed of 80rpm for another 2min; (iii) The blend was allowed to rest for 90s, and then mixed for 1 min at speed of 120rpm and (iv) The paste was manually placed, pressed and homogenized in stainless steel molds. After the top layer was compacted, the top surface of the mould was smoothened by the aid of thin edged trowel. For preparation of mortars, the sand was added gradually and mixed at a medium speed for 30s after step (ii). The mortars were prepared according to ASTM (C109-93) by mixing 1 part of cement and 2.75 parts of Lafarge standard sand proportion by weighing with water content that sufficient to obtain a flow of 110 ± 5 with 25 drops of the flowing table [31, 32]. All specimens were cast in stainless steel molds ($50 \times 50 \times 50$ mm cubes), demoulded after 24h, and then cured in fresh tap water at $23.0 \pm 2^\circ\text{C}$ until the testing time. The mix compositions of the prepared cements are given in Table 3. The mixing water was measured to get all specimens having the same workability. The water of consistency and setting times for each mix were determined according to ASTM specification [33]. After the predetermined time, the hydration of cement pastes was stopped as described in a previous work [34]. The chemically combined water (W_n), free lime (FL) and bulk density (BD) were determined as mentioned elsewhere [35-37]. The compressive strength was measured according to the ASTM specifications (C-150) [38]. A compressive test was carried out in a hydraulic universal testing machine (3R), Germany, of 150.0 MPa capacity. To verify the mechanism predicted by the chemical and mechanical tests, some selected hydrated samples were examined using XRD, DSC, TG and SEM techniques.

Table 3. Mix composition of OPC and blended cements, mass%.

Mix No.	OPC	FA	NS
M1	100	0	0
M2	90	10	0
M3	80	20	0
M4	70	30	0
M5	70	28	2
M6	70	26	4
M7	70	24	6

For XRD, a Philips diffractometer PW 1730 with X-ray source of Cu K α radiation ($k = 1.5418 \text{ \AA}$) was used. The scan step size was 2θ , the collection time 1s, and in the range of 2θ from 10° to 55° . The X-ray tube voltage and current were fixed at 40.0 KV and 40.0 mA, respectively. An on-line search of a standard database (JCPDS database) for X-ray powder diffraction pattern enables phase identification for a large variety of crystalline phases in a sample. The DTA was carried out in air using a DT-30 Thermal Analyzer Shimadzu Co., Kyoto, Japan. Calcined alumina was used as inert material, about 50 mg ($\sim 76\mu\text{m}$) of each. The finely ground

hydrated cement paste was housed in a small platinum-rhodium crucible. A uniform heating rate was adopted in all of the experiments at $20^\circ\text{C}/\text{min}$ [39]. The microstructure was investigated by SEM, model quanta 250 FEG (Field Emission Gun), with accelerating voltage 30K.V., magnification power $14 \times$ up to 1000000 and resolution for Gun.1n). FEI Company, Netherlands.

3. Results and Discussion

3.1. Characteristics of Composite Cements Containing Fly Ash

The variations of mixing water (W/C, %) as well as initial and final setting times (IST& FST) of the prepared cement pastes are graphically represented in Fig. 6 (A& B). The results show that, the FA-cements require higher water demands and longer setting times (STs) comparing with the OPC. Also, W/C, % and STs increase with FA content. This is mainly due to the higher surface area of FA than OPC. The retardation of setting process may be due to the decrease of cement portion (dilution effect) [40], forming CSH, which has higher setting characteristics [41] in comparison with fly ash pozzolanic cement pastes.

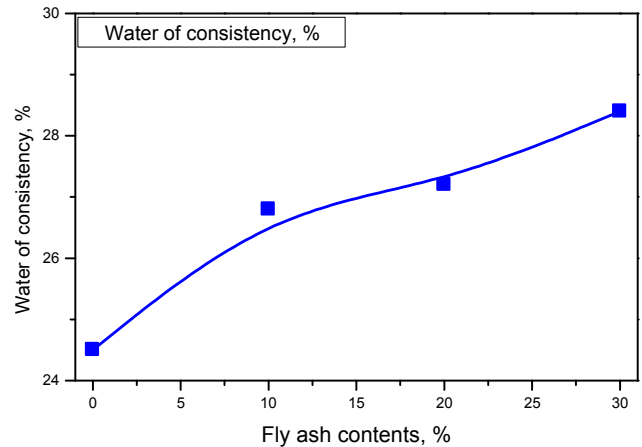


Fig. 6(A). Water of consistency of OPC-FA pastes.

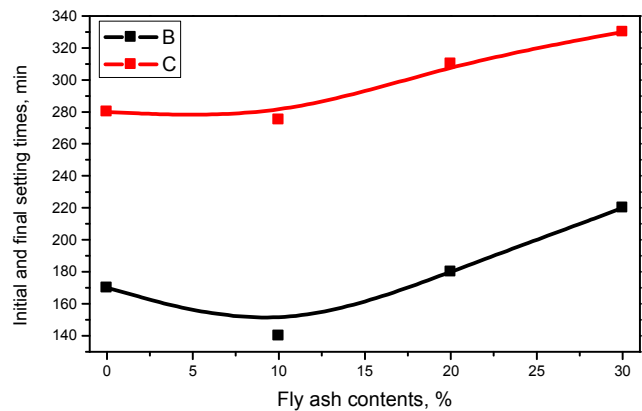


Fig. 6(B). Initial and final setting times of OPC-FA pastes.

Also, the slight pozzolanic activity of FA may be adversely affect setting process of FA-blended cement pastes. So

cement pastes containing 10 wt. %, of FA tends to shorten the initial setting time than the plain cement paste. This is principally due to the nucleating effect, which accelerates the rate of cement hydration. As the amount of FA increases up to 30 wt. %, the initial setting time is accordingly elongated. This is mainly due to the dilution effect of the cement and the low rate of hydration of FA in comparison with OPC.

The final setting time of FA-blended cement pastes elongates with the amount of FA. This is essentially due to the decrease of the formed CSH gel at early ages and the dilution of the cement content. The hydration of cement is faster than the pozzolanic reaction of FA with Portlandite.

The variation of Wn. % of the hydrated FA-blended cements as well as OPC with curing time up to 90-days and FA content is graphically plotted in Fig. (7). Generally, the values of combined water increase with curing time for all cement pastes, due to the continuous hydration of cement phases and pozzolanic reaction, leading to the formation of hydrated aluminates, silicates and aluminosilicates with high water contents [42]. On the other hand, FA-cement blended cements have lower Wn values comparing to the control (OPC). Also, the amount of Wn decreases with FA content. This is mainly attributed to that; the fly ash sample used in this work is mainly composed of crystalline phases such as quartz and mullite in addition to small amount of amorphous material. Therefore, it has slight pozzolanic activity, which decreases the hydration characteristics. Hence, the combined water content (Wn. %) decreases in accordance with Hanehara et al. [43], but in contrast with other workers [44, 45]. The combined water content of FA cement paste decreases, with FA content, due to that, the CSH formed has low C/S with low water content [46].

The free lime contents of OPC and blended cement pastes cured up to 90d is given graphically illustrated as a function of curing time in Fig. (8): The free lime content of OPC pastes increases with curing time up to 90 days, due to the continuous hydration of alite and belite phases in OPC, liberating portlandite $\text{Ca}(\text{OH})_2$ during the hydration period. On the other side, the free lime contents of all pozzolanic cement pastes increase up to 3 days then decrease up to 90 days. This is in a good agreement with earlier work [47, 48]. The initial increase of free lime in pozzolanic cement is mainly due to the fast hydration of the clinker. As fly ash content increases, the liberated portlandite increases, due to the nucleating agent as well as the very low pozzolanicity of FA at one day. The increase of FA content tends to separate the hydrated CSH-gel, which enhances the liberation of portlandite. The decrease after 3d is due to its consumption by the FA. There are two different processes; one tending to increase the portlandite and the other tends to decrease its value due to the pozzolanic reaction [49]. This determination of free lime content is more significant for the demonstration the pozzolanic properties of FA. It provides an indication on the progress of the pozzolanic reaction. These are consistent with those found that; the fly ash commences reaction with $\text{Ca}(\text{OH})_2$ between 3 and 7 days, but considerable amounts of $\text{Ca}(\text{OH})_2$ and fly ash still remain un-reacted up to 90 days of

hydration. Therefore, it can be concluded that, this fly ash is poorly pozzolanic material. Both of free lime and combined water contents of FA-blended cement pastes are lower than those of OPC pastes. This may be attributed to the low pozzolanic activity of FA, especially at early hydration ages.

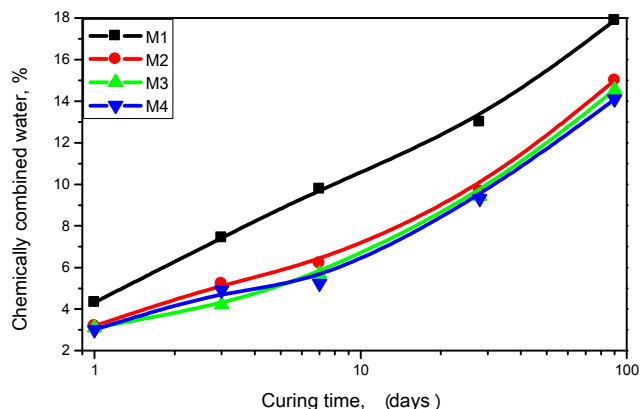


Fig. 7. Combined water contents of OPC-FA pastes with curing time.

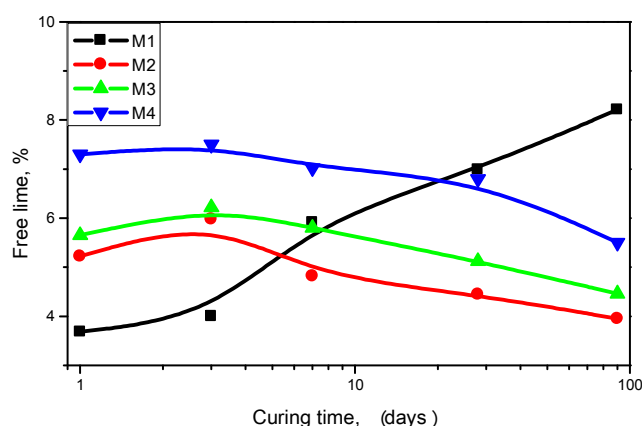


Fig. 8. Free lime contents of OPC-FA pastes with curing time.

The bulk density of OPC as well as Pozzolanic cement pastes cured up to 90 days is given graphically illustrated in Fig. (9). It is clear that, as the curing time proceeds, the bulk density for all hardened pastes increases. This is due to the gradual filling of large pores by the hydration products of cementitious materials. Substitution of OPC with fly ash produces a significant decrease of bulk density [50]. The increase of water of consistency with the fly ash content decreases the bulk density. This is mainly due to the slight pozzolanicity of fly ash. Generally the density of CSH from pozzolanic reaction is lower, than that formed from the hydration of OPC. OPC pastes show high value of portlandite, which gives CSH rich in calcium and water, which increases the bulk density of OPC cement in comparison with pozzolanic cement paste.

The compressive strength data of OPC as well as pozzolanic cement mortars cured up to 90-days is shown the graphically represented as a function of curing time in Fig. (10). The results show that, the compressive strength increases with curing time for all hardened cement mortars. As the hydration proceeds more hydration products and more

cementing materials are formed. This leads to an increase of compressive strength of hardened cement mortars. This mainly attributed to that the hydration products possess a large specific volume than un-hydrated cement. Therefore, the accumulation of these hydration products will fill a part of available pore spaces, then giving higher strength. On the other side, as the fly ash content increases, the compressive strength decreases, as observed elsewhere [51]. This is due to the lower pozzolanic activity of the FA-particles. In addition, the decomposing reactions of the glassy phase network of the fly ash would be slowed down. Therefore, these factors affect the structure of the hardened pastes, so that its strength is reduced. The compressive strength was also in harmony with the bulk density. Also, the compressive strength values are in a good harmony with those of combined water contents. The increase of the hydration products is the main factor of compressive strength.

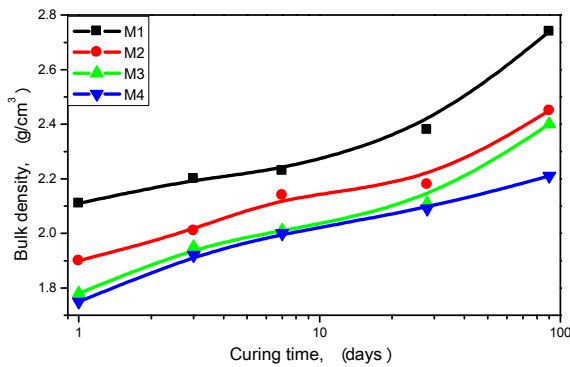


Fig. 9. Bulk density of hardened FA-cements with time.

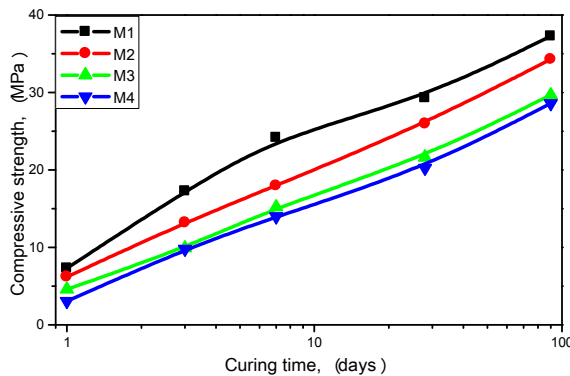


Fig. 10. Compressive strength of hardened FA-cements with time.

The effect of curing time up to 90-days on the hydration characteristics of blended Portland cement containing 30 mass, % of FA can be seen from XRD patterns in Fig. (11). It is obvious that, the characteristic peak of CSH increases, whereas the peaks of Portlandite (CH) decrease markedly with curing time. This is mainly due to the reaction of FA portion with the liberated lime, forming additional amounts of CSH. The rate of FA pozzolanic reaction with lime increases with the time, therefore, the rate of lime consumption exceeds the rate of its production. The behavior of CH peaks is in accordance with the results of chemically determined free lime. Also, the XRD patterns show CaCO₃

peak that increases with curing age, due to the increase of Portlandite, which is available for carbonation with atmospheric CO₂.

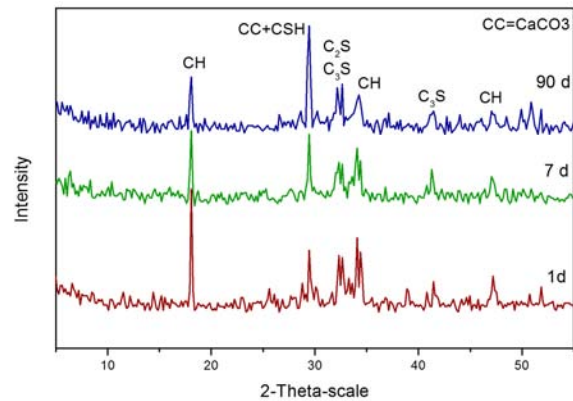


Fig. 11. XRD patterns of M4 with curing time.

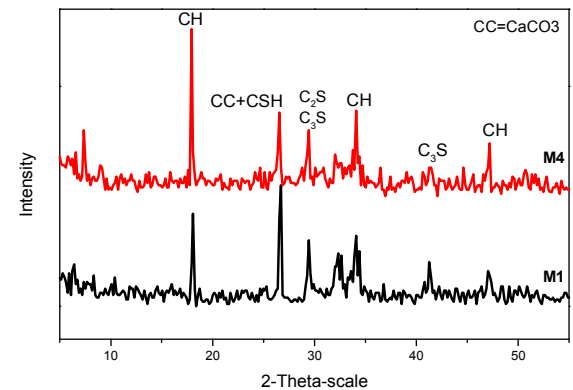


Fig. 12. XRD patterns of different mixes at 7-days.

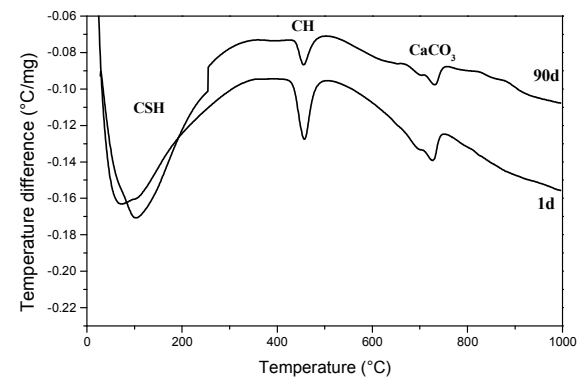


Fig. 13. DTA thermograms of M4 hydrated as a function of time.

The XRD patterns of hardened OPC (M1) and 30 mass% FA (M4) cement pastes, at 7 days of hydration are shown in Fig. (12). The results show the presence of un-hydrated silicates (β -C₂S and C₃S), calcium hydroxide (CH), calcite (CC) and calcium silicate hydrate (CSH). The presence of 30% of crystalline FA with Portland cement decreases the amount of OPC. Also, the used FA has low pozzolanic activity, especially at early hydration ages. Therefore, the intensity of CSH and CC peak in OPC pastes is higher than the corresponding peak in A blended cement pastes. Calcium hydroxide behaves in an

opposite manner of CSH. The peak of unhydrous silicates decrease with the presence of FA, due to the dilution of clinker phases with 30 mass, % FA. The intensity of Portlandite peak is in accordance with that of chemical analysis.

Figure (13) shows the DTA thermograms of hydrated M4 (30% FA) at 1 and 90-days. There are three main endothermic peaks. The first peak appears at 100°C, which refers to dehydration of CSH. The second peak, in the temperature range 450-500°C, is attributed to Ca(OH)_2 decomposition [52]. The intensity of CSH peak increases with curing time. But, the characteristic CH peaks decrease with time, due to the hydration progress and formation of successive amounts of hydrated products (CSH, CAH and CASH). The results of DTA are in a good harmony with each other and with those of XRD, free lime, bulk density and Strength. The endothermic peak of cement paste at one day located round 50 -100°C is due to the removal of moisture of the cement paste. As the hydration precedes the endothermic peak of CSH increases with curing time. The dissociation of Portlandite at 1d occurs at lower temperature than that cured at 90-days. This is mainly due to its amorphous state at one day but, at 90-days, the dehydroxylation of Portlandite occurs at higher temperature due to its crystallinity. This is mainly due to the two process of the formed Portlandite, one is amorphous, which decomposes at lower temperature and crystalline type, which decomposes at relatively higher temperature.

Figure (14) illustrates the TG of FA-cement paste (M4) at 1 and 90-days of hydration. It is clear that, the CSH loss of sample at 90-days is higher than that at 1 day. On the other side, the Portlandite increases with curing time. The loss occurs at 600–700°C is mainly due to the CaCO_3 decomposition. These results are in an agreement with those of free lime contents determined by the chemical method and those of XRD analysis.

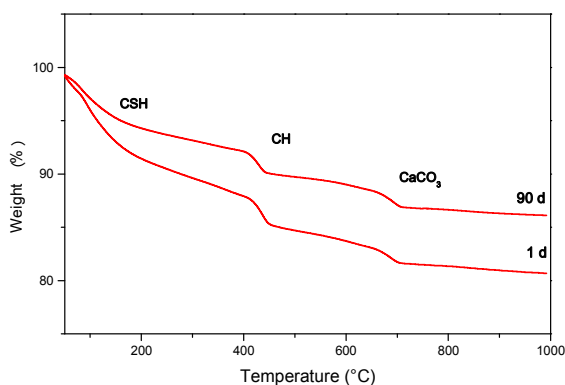


Fig. 14. TG analysis of M4 hydrated at different ages.

3.2. Characteristics of Composite Cements Containing FA&NS

The variations of water of consistency as well as setting times of the investigated cement pastes are graphically plotted in Fig. 15(A&B). The results show that, the water demand and setting times increase with NS, content. The increase in water demand is mainly attributed to the increase

of surface area of NS in comparison with FA [53-55]. Thus, the specimens containing NS require more water to rapid forming of hydrated products [56]. The setting process is elongated due to the increase of water of consistency. As the water of consistency increases, the free water increases, which delays the setting of cement paste [57].

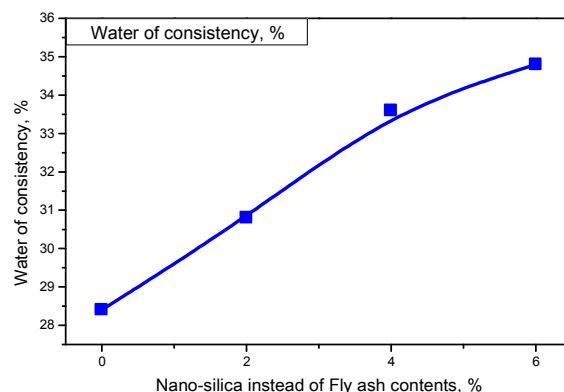


Fig. 15(A). Water of consistency of cement pastes with NS, %.

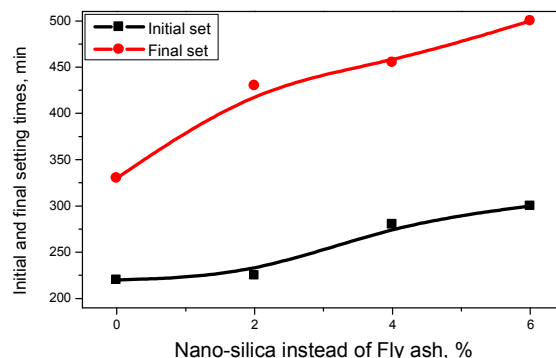


Fig. 15(B). Setting times of cement pastes with NS, %.

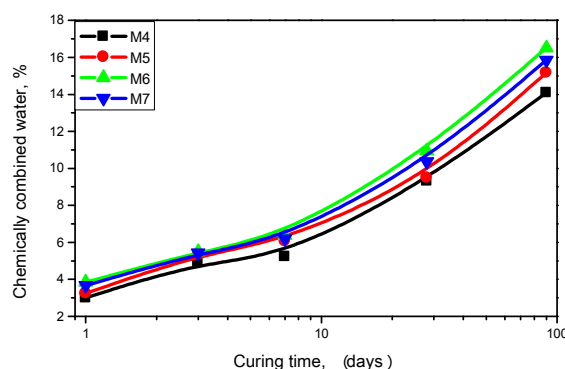


Fig. 16. Combined water of hydrated M4, M5, M6 and M7 with time.

The combined water contents of FA-pozzolanic cement replaced with 2, 4 and 6 wt. %, NS is graphically represented in Fig. (16). It is clear that, the replacement of equal amount of FA with NS is accompanied with gradual increase of combined water content up to 4 wt. % NS, then decrease at 6 wt. %, NS. Generally, the FA-pozzolanic cement pastes give lower values of combined water (W_n , %) than FA-NS cement pastes up to 90-days. This is principally attributed to the high pozzolanic activity of NS portion to react with the liberated CH, leading to

the formation of additional amounts of hydrated silicates and aluminosilicates with high water contents. From the chemical point of view, NS is highly reactive pozzolana which reacts with formed calcium hydroxide (CH) from the hydration of cement clinker phases producing calcium silicate hydrates (CSH) [58]. This is also due to the high surface area and glass content of NS in comparison with FA.

The effect of substituted amounts of FA with NS on the free lime is graphically represented in Fig. (17). It can be seen that, the free lime contents decrease with curing time for all hydrated cement pastes. This mainly attributed to the pozzolanic activity of FA and NS. The pozzolanic reaction of FA and/or NS with the liberated Portlandite through the hydration of cement phases increase with curing time. The substitution of FA with 2 and 4 wt. % NS is accompanied with gradual decrease of free lime, i. e. the cement pastes containing 4 wt. % NS show lower values of F. L., than the plain and FA-cement pastes. At 6 wt. % NS the free lime is increased as previously decreased [56, 57].

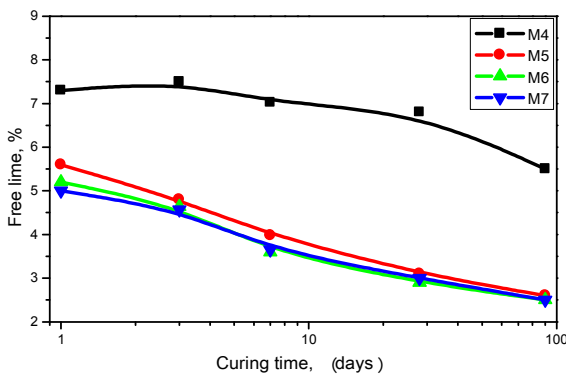


Fig. 17. Free lime of hydrated M4, M5, M6 and M7 with time.

The bulk density (dp) values of FA-NS cement pastes cured up to 90-days is graphically depicted in Fig. (18). The results indicate that, the bulk density (dp) increases with curing time for all hydrated cement pastes, due to the continuous hydration of cement clinker and pozzolanic reaction, leading to the formation and accumulation of excess amounts of hydrated silicates and aluminosilicates which tends to increase the gel/space ratio as well as the bulk density [42]. This leads to the formation of homogeneous and compact microstructure. The bulk density (dp) increases with the nano-silica content up to 4 wt. % and then decreases at 6 wt. %, but still higher than that of the control mix (30 wt. % FA). This can be interpreted as follows [59]. Suppose that, NS particles are uniformly dispersed in cement paste and each particle is contained in a cubic pattern, therefore the distance between nano-particles can be determined. After the hydration begins, hydrated products diffuse and envelop NS particles as kernel [56]. If the NS content and the distance between them are appropriate, the crystallization will be controlled to be a suitable state through restricting the growth of Ca(OH)₂ crystals. Moreover, the nano-particles located in cement paste as kernel can further promote cement hydration due to their high activity. This makes the size of Ca(OH)₂ crystals smaller, the cement matrix is more homogeneous and compact, then the pore structure is

improved. With increasing the NS content more than 4 wt. %, the improvement of the pore structure of cement paste is weakened. This can be attributed to that, the distance between nano-particles decreases with NS content, and Ca(OH)₂ crystals cannot grow up enough, due to limited space, then the crystal quantity is decreased, which leads to the decrease of crystal to gel space ratio [57].

The data of compressive strength of OPC-FA-NS cement pastes cured up to 90-days are shown graphically depicted in Fig. (19). The compressive strengths of the fly ash mortars were increased with the incorporation of the NS in comparison to the corresponding reference mortars containing 30 wt. % FA at all curing ages. The strength generally increased with the substitution of nano-silica up to 4 wt. %. In particular, the compressive strength was considerably improved for the cement with 26 wt. % fly ash and 4 wt. % NS. This indicates that, the inherently slower rate of strength development of mortars containing fly ash, can be improved by the substitution of small dosages of nano-silica up to 4 mass, %. The overall performance of mortar with and without fly ash was significantly improved with the addition of variable dosages of nano-silica. More refinement of the pore structure was achieved with increasing the nano-silica dosage up to 6 mass, % [60].

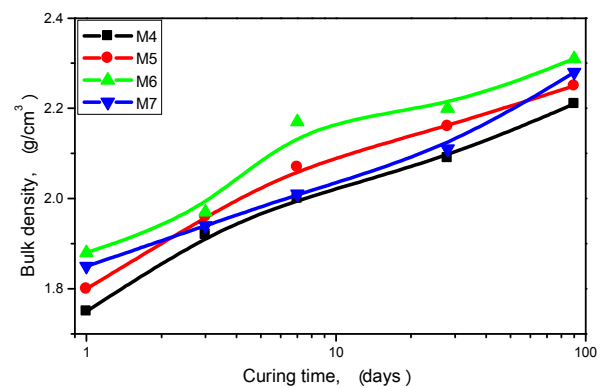


Fig. 18. Bulk density of hardened M4, M5, M6 and M7 with time.

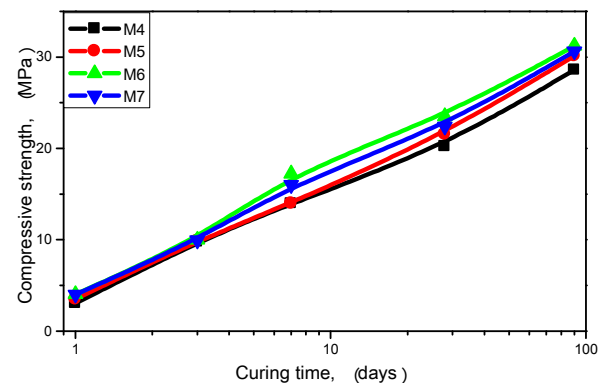


Fig. 19. Strength of hardened M4, M5, M6 and M7 with time.

The effect of 6 mass, % of NS on the hydration of FA-blended cement paste can be seen from the XRD patterns of hydrated M13 (70% OPC + 24 % FA + 6% NS) with curing time in Fig. (20). the results show that, the peaks of CH

decrease with curing age whereas with that of CSH and calcite (CC) increases. This mainly due to the continuous hydration of clinker phases as well as the pozzolanic reaction of both FA and NS with the liberated $\text{Ca}(\text{OH})_2$. It can be concluded that, NS compensate the poorly pozzolanic action of FA, especially at early ages of hydration. The effect of mix composition on the hydration characteristics of OPC-FA blended cements with and without NS can be shown from XRD patterns of M4 and M7 in Fig. (21). The results indicate that, NS has positively effect on the hydration of FA-cement blends, because nano-sized SiO_2 particles behave not only as nano filler to promote the hydration of clinker silicate phases but also as a good pozzolanic additive. Indeed, NS has very higher pozzolanic reactivity comparing to FA, which has lower amorphous silica content and higher amounts of quartz as well as mullite, which are crystalline phase. These crystalline phases show no or very weak pozzolanic activity. Therefore, the peak of CSH and CC phases increases with the presence of NS.

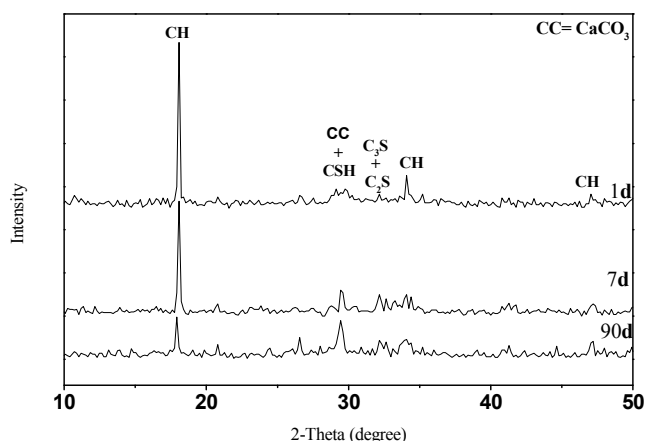


Fig. 20. XRD patterns of M7 as a function of curing time.

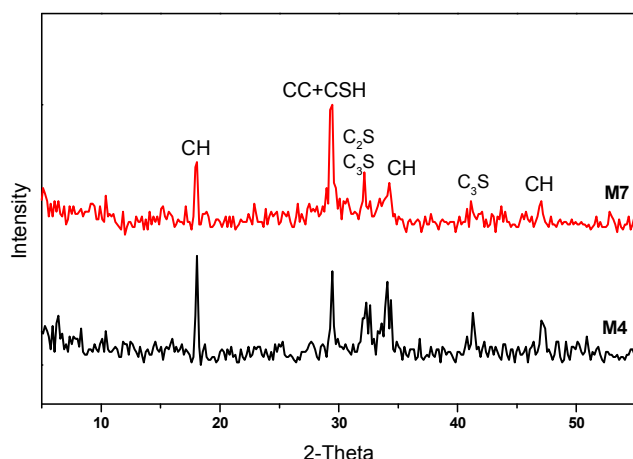


Fig. 21. XRD patterns of hydrated M4 and M7 at 7-days.

4. Conclusions

The results obtained in this study indicate that, the substitution of 10 wt. % OPC by FA accelerates the initial

setting time, due to the nucleating effect without any detectable effect on the final setting time. On the other side, the increase of FA up to 30 wt. % elongates the initial and final setting time. The FA increases the water of consistency from 24.5 up to 28.4 % for 0 and 30 wt % FA substitutions. The substitution of OPC with FA up to 30 wt. % has no detectable effect on the values of chemically combined water of cement pastes up to 90-days of hydration. But, these values are lower than those of OPC pastes, due to the low pozzolanic activity of FA. The increase of FA content up to 20 wt. % increases the liberated Portlandite, especially at early ages of hydration up to 3-days. At 30 wt. % FA, the free lime contents of blended-cement pastes are higher than those of only OPC pastes up to 7-days then decreases due to its consumption by FA at later hydration ages.

The replacement of OPC with FA decreases the bulk density as well as the compressive of cement mortars up to 90-days. As the amount of FA increases, the bulk density and compressive strength decrease gradually. It can be said that, 10 wt. % FA is the optimum substitution level.

In OPC-FA blended cement, the replacement of FA with 2, 4 and 6 wt. % NS, increases the amount of water of consistency and elongates the setting times with higher level than FA. This is due to its higher surface area in comparison with FA of micro-particles, whereas the NS has nano-particle size of about 15 nm. The NS is completely amorphous. In the preparation of nano-modified blended cements containing 2, 4 and 6 wt. % NS instead of FA it was found that, 4 wt. % NS enhances the chemical and physico-mechanical properties of blended cement.

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