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Superior-mechanical, Microstructure Properties of Composite Cement Incorporating SiO_2-nano-particles

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THE impact of silica-nano-particles (SNP) on the hydration characteristics of composite cement containing fly ash (FA) and/or fine granulated slag (FGS) was investigated. The physico-chemical characteristics of different composite-pastes are studied in the presence of 4mass% SNP and 40% FA and/or FGS with the existence of 1mass% polycarboxylate superplasticizer (SP). The physicomechanical characteristics are studied by determination of the water of consistency, setting times (STs), compressive strength (CS), total porosity, (TP), bulk density (BD), chemically combined water (Wn), free lime (FL) contents and gel/space ratio (*X*). The phase composition of the formed hydrates is investigated using XRD, DTA/TGA, and SEM techniques. The represented data shown that 4% SNP improved the hydration process of the composite cement pastes and exhibited superior-compressive strength than neat-cement without SNP, this is due to nano-sized-particles and higher-efficiency of good pozzolanic-action of SNP in the comparison with FA and FGS. The composite cement containing OPC–40%FGS–4%NS in presence of 1%SP possess the highest improvement of mechanical-properties, hydration-kinetics, and microstructure of hardened cement pastes.

Keywords: Silica-nano-particles, Physicochemical characteristics of composite- cement pastes, Gel/space ratio, and compressive strength.

Introduction

Concrete is the backbone of the building industry and construction material. The main binding component of the concrete is the cement. The hydration of cement includes a series of reactions, that are affected the cement composition, particle size distribution, surface area, temperature, and chemical admixtures. Mineral admixtures such as fly ash (FA), fine granulated slag (FGS), silica fume (SF) are inorganic materials that have pozzolanic and/or latent hydraulic properties. These are very finely ground materials added to improve the properties of concrete [1]. The technological and economic benefit for the use of these materials, that uses as a partial replacement for cement in concrete include improvement of impermeability and chemical durability, they enhanced the resistance of thermal behavior and enhance the strength [2].

FGS used as a partial replacement of ordinary Portland cement (OPC) which, develops strength and durability of concrete. The use of FGS as cementitious components saves the amount of energy compared with the production of Portland cement. The partial replacement may reduce the early strength but enhanced the later strength, microstructure and durability of hardened OPC concrete considerably [3]. The use of FA in cement-composites not only leads to reduces CO_2 emission but also utilizes as by-products of industrial manufacturing processes. Fly ash is produced by the burning of coal in power plants. The residue from the burning of coal hardens in spherical glassy particles. FA particles are

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round in shape, containing amorphous and crystalline phases (quartz, mullite, hematite, and melilite). When adding FA particles to cement-based materials their workability increased as well as the heat of hydration and water demand decreased [4,5].

Nowadays, nanotechnology is one of the most important topics in construction materials and civil engineering. A small number of nanoparticles can improve the performance of nano-composites building materials. Cement composites having nano-materials (NMs) have high strength concrete (HSC) and high-performance concrete (HPC) and self-compacting concrete (SCC) [6,7]. Today's many researchers are looking for the ultra-high performance of concrete with enhanced mechanical properties. NMs used as partial replacement of cement pastes, leading to produced ecological profile concrete with superior performance [8-11]. There are many advantages on using the nano-composites including, low environmental impact, high strength, lightweight structure with low CO_2 emission as well as enhanced the durability properties. The impact of nano-particles on the performance and microstructure of cement based materials can be explained by the filler effect, nucleation or seeding effect, which prompt the hydration of the cement to form of calcium silicate hydrate (CSH) during the pozzolanic reaction [12]. Nano-particles are used in polymer, ceramic and construction materials to produce cement nano-composites that display superior mechanical and physical characteristics. Several types of nano-materials used in concretes or cement based materials namely silica nano-particles (SNP), Al_2O_3-nano-particles (ANP), clay-nano-particles (CNP), nano-Fe_2O_3, nano-ZnO_2, nano-MgO, nano-TiO_2, carbon nanotubes [13-15]. Silica nano-particles (SNP) characterizes by a narrow particle size distribution, small particle size, a large number of hydroxyl groups and large surface area as well as unsaturated residual bonds on its surface indicting high reflectivity to long wave, ultraviolet ray and visible light. SNP is the most common nano-additive to concrete enhances concrete strength and improves resistance to water permeability [16,17]. Wang, et al., [18] showed the early strength was improved by incorporation of 3 mass % SNP, the compressive strength increases with 33.2%, and 18.5% at 3 and 28 days. El-Didamony, et al., [19] showed that both FA and NS improve the hydration behavior and mechanical properties of composite pastes. Ehsani, et al., [20] concluded that the addition of SNP activated the early-age FA-based concrete and improved the strength development of cement paste and concrete than those specimens without SNP. The compressive strengths and flexural strengths improved in cement pastes including SNP as well as those of the cement pastes containing SF and FA, this is due to the nano-sized particles and extensive surface area of SNP [21,22]. Zhang et al. [23] investigated the impact of SNP on the properties of concrete and mortar including a high content of FGS. It was found that the strength of concrete with SNP improved by 22% and 18%, at 3- and 7-day respectively, as compared to the corresponding strength of concrete containing FGS only.

The object of this study is to investigate the effect of SNP on the hydration characteristics and mechanical properties of hardened composite pastes. The chemically combined water, free lime contents, the compressive strength and the bulk density at different ages of hydration were tested. The phase composition has been examined using XRD, DTA/TGA, and SEM.

Materials and experimental procedures

The materials used in this study were OPC, FGS, FA, and SNP. OPC was obtained from Suze Portland cement Company, Egypt. The Blaine surface area of OPC was 3050 cm^2/g. FA was provided from Sika Chemical Company for building materials, Egypt, it's specific Blaine surface area ∽3570 cm^2/g. FGS was supplied from the smelting (the process of reduction of iron from its ores) of Iron Steel Company, Helwan, Egypt, with Blaine surface area 3950 cm^2/g. SNP used in this work was obtained from Nanotechnology Lab, Faculty of Science, Beni-Suief University, Beni-Suief, Egypt, with blain surface area 49.99 m^2/g and purity percentage ≈99.9%. Superplasticizer based on polycarboxylate (SP) was supplied from Sika construction chemicals Company. The oxide analysis of OPC, FGS, FA, and SNP determined by X-ray fluorescence (XRF) as shown in Table 1. The TEM of SNP was shown in Figure 1.

TABLE 1. Oxide analysis of SNP, FGS, FA, and OPC (mass, %).

	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	K_2O	MgO	SO_3	Loss at 1000°C	Total
SNP	0.01	0.03	98.59	0.01	0.3	0.04	0.01	0.3	0.01	99.9
FA	5.4	26.54	63.10	2.33	0.85	0.52	0.00	0.09	0.8	99.63
FGS	0.59	9.97	43.21	35.96	0.79	0.67	5.43	1.37	1.98	99.97
OPC	3.80	3.94	21.30	62.67	0.44	0.39	1.90	2.05	3.04	99.53

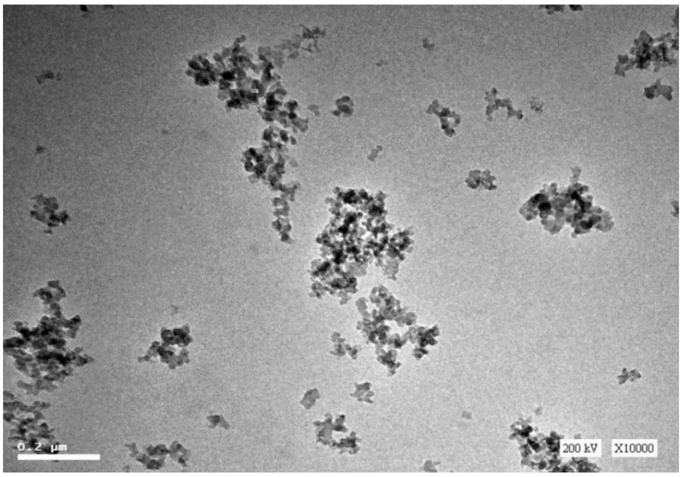

Fig. 1. TEM of SNP.

The starting materials FA, FGS, OPC were intermixed in a ball mill mixer as shown in Table 2. SNP are difficult to disperse uniformly so that SNP mixing was performed as follows; SNP was stirred with the suitable amount of water of consistency at speed of 120 rpm for two min; then the cement containing FA, and or FGS was added to the mixture and stirred at speed of 90rpm for two min to full homogenization; the superplasticizer was inserted to homogenized rotary mixer at 120rpm upto the 30s. After that the mixing blends were allowed to rest for 90s, and then mixed for one min at speed of 120rpm and then the paste was cast into 2.5*2.5*2.5cm^3 moulds, then compressed into layers manually, and then stored in a humidity cabinet (100%RH) at 20°C for one day. After decasting, the moldings were immersed under tap-water until 360 days. The consistency and setting times (STs) of composite cement were determined according to ASTM specification [24]. The hydrated cement pastes were stopped as described in previous work [25]. The chemically combined water content (Wn), free lime (FL), bulk density (BD) and total porosity (TP) were determined as shown elsewhere [26,27]. The compressive strength was determined after the determination of BD, TB according to the ASTM specifications (C-150) [28]. A compressive test was performed in a hydraulic universal testing machine (3R), Germany, of 150.0 MPa capacity. Some selected hydrated samples were examined using XRD, DTG/TGA and SEM techniques to verify the mechanism predicted by the chemical and mechanical tests.

XRD technique was carried out on some specifically hardened cement pastes to indicate the phase hydrated composition of products. For XRD technique, PW 1730 with X-ray source a Philips diffractometer of Cu Kα radiation (λ = 1.5418 Å) was used. The speed of the scan is 2θ/min between 5°-65°. The X-ray tube voltage is 40 kV and the current was 25mA. The analysis of XRD was performed with computer software search of the PDF diffraction data (JCPDA-ICDD), 2001.

The microstructure of some selected cement pastes was investigated by scanning electron microscope (SEM), model quanta 250 FEG (Field Emission Gun) attached with EDX unit (Energy Dispersive X-ray Analyses).

TABLE 2. Composition of different mixes, mass%.

Mix	OPC,%	FGS,%	FA,%	SNP,%	SP,%	Water of consistency,%	Setting times	
							Initial	Final
A0	100	0	0	0	1	19.5	70	260
A1	96	0	0	4	1	27.7	68	215
A2	60	0	40	0	1	20	190	300
A3	56	0	40	4	1	29	96	250
A4	60	40	0	0	1	17	98	264
A5	56	40	0	4	1	23	70	200
A6	56	20	20	4	1	24.8	85	220
A7	36	40	20	4	1	24	80	205

Results and Discussion

Consistency, and setting times

Consistency (W/C), and STs of the composite-pastes containing FA and/or FGS in existence of 4mass% SNP and 1 mass% SP is determined in Table 2. The results show that OPC-composite-pastes containing 4mass% SNP required a higher water/cement ratio to give standard consistency. SNP reacts with the liberated lime to form extra additional calcium silicate, calcium aluminate, and calcium aluminosilicate (C-S-H, C-A-H and C-A-S-H hydrated gel products. The STs were accelerated in the presence of SNP in the composite cement pastes (CCP). The setting times were elongated in the presence of 40% FA in the case of 0% or 4% SNP, this is due to the high surface area of SNP [7]. when SNP is added to cement grains, H_2SiO_4 forms and reacts with available Ca^{+2}, to form an additional amount of CSH which spread on the water-filled spaces between the cement grains and serve as seeds for the formation of more close and compact CSH gel so the STs are shorted. The data also showed that the consistency and STs of the cement-pastes prepared from OPC–FGS mixes lower than neat OPC and OPC-FA mixes with and without of SNP, wherever the FA-composite-cement pastes require more W/C ratio and longer STs; this is attributed to lower activity of FA than FGS [29]. By increasing FGS contents the consistency decreases, whereas the STs elongated as shown in the mixes A6, A7 this is mainly attributed to the reduction of the OPC-content as shown in Table 2.

Hydration kinetics

Chemically combined water contents (W_n)

The W_n content of OPC–FA and/or FGS composite-pastes with and without 4mass%SNP in the entity of SP cured upto 360-days were illustrated in Figure 2. The data show that the W_n increases with the increase the age; this is attributed to the formation of more hydrates products during the progress of hydration process of cement phases which speed up filling of the pores-system in cement-pastes. The results show also that the presence of SNP gives higher W_n than neat-OPC pastes and other composite pastes, due to the nucleating effect, and the filler effect of SNP. SNP enhances the production of C–S–H, CAH and CASH structure to fill with the voids between the cement grains to obtain a denser and stronger cementitious matrix [30,31]. So the rate of hydration, as well as the W_n content, increased. The data also show that the pozzolanicty action of FA is lower than of FGS, due to its composition, which contains crystalline quartz and mullite phases, hence FA-composite-cement-pastes have lower Wn values than FGS-composite-cement-pastes in the presence of SNP. The values of Wn decrease with the decreases FGS and OPC fraction as shown in mixes A6 and A7, where mixA7 has higher-values of Wn than mix A6 especially at early ages of hydration.

Free lime contents (FL)

The FL content of OPC and SNP-composite cement pastes including FA and/or FGS cured upto 360-days were illustrated in Figure 3. Data show that the addition of SNP tends to reduce the residual portlandite, this effect is attributed to the pozzolonic interaction of SNP with $Ca(OH)_2$ CH leading to the formation of calcium silicate hydrates CSH, CAH and CASH hydrated gel products. FL content of the OPC pastes increases with ages upto 360 days, this is mainly due to the continuous hydration of alite (C_3S) and belite (β-C_2S) phases giving $Ca(OH)_2$. In the presence of SNP, the FL content rises to 3-days due to the increase of lime production, then decreases up to 360 days. SNP enhances the hydration rate of OPC and CCP pastes between 1 and 3 days and acts as nucleating agents to increases the seeding of $Ca(OH)_2$ [32,33]. After 3 – 7 days up to 360 days the FL sharply decreases where the rate of consumption of $Ca(OH)_2$ is higher than the rate of liberation due to higher pozzolanic activity of SNP. The result also represented that the values of lime consuming decrease, with the increase of the FGS and FA contents, so the free lime content decreases as shown in mixes A5, A6, and A7, where mix A7 have a lower value than mixes A6 and A5. The presence of SP tends to approach the SNP particles from the liberated lime to form extra C-S-H in the open pore system, hence the porosity decreases as shown letter.

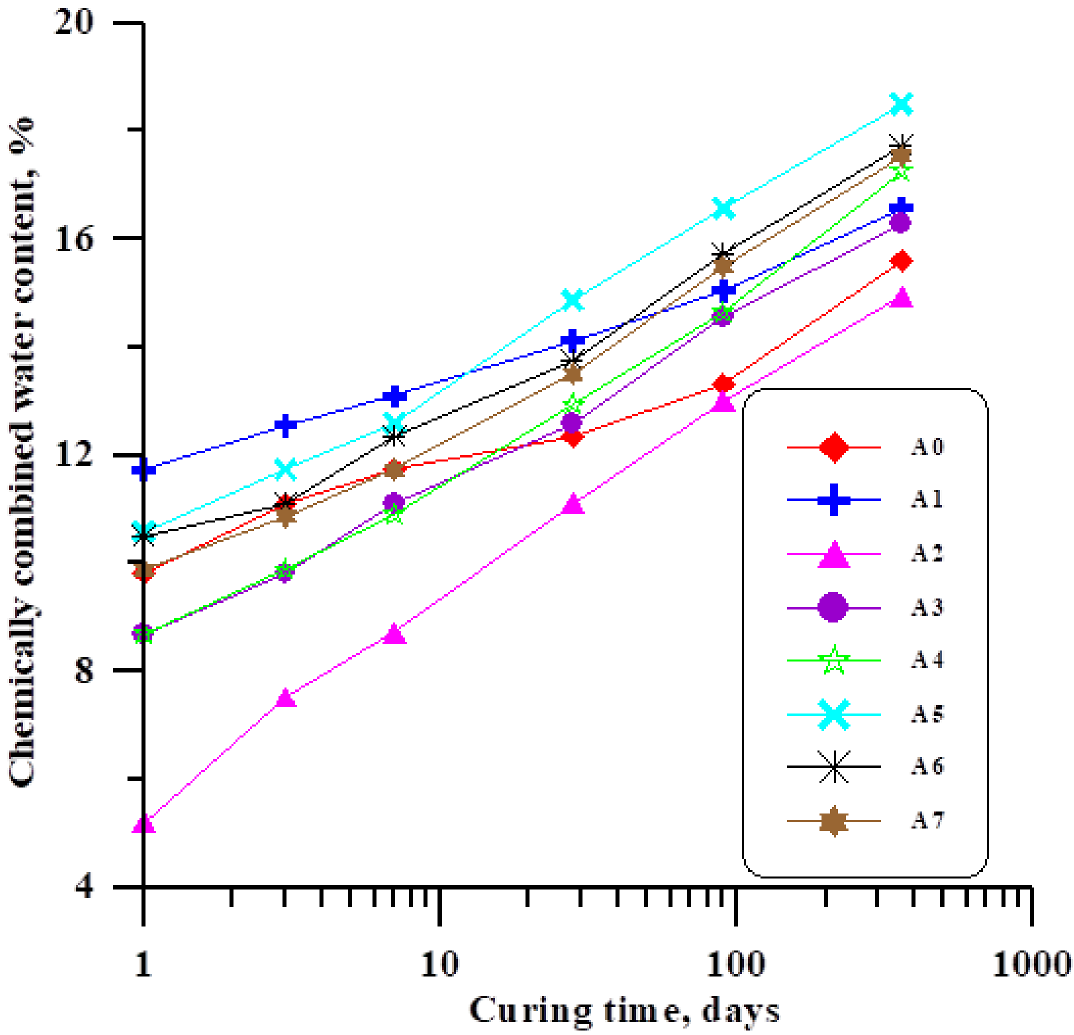

Fig. 2. W_n of composite pastes with and without 4%SNP.

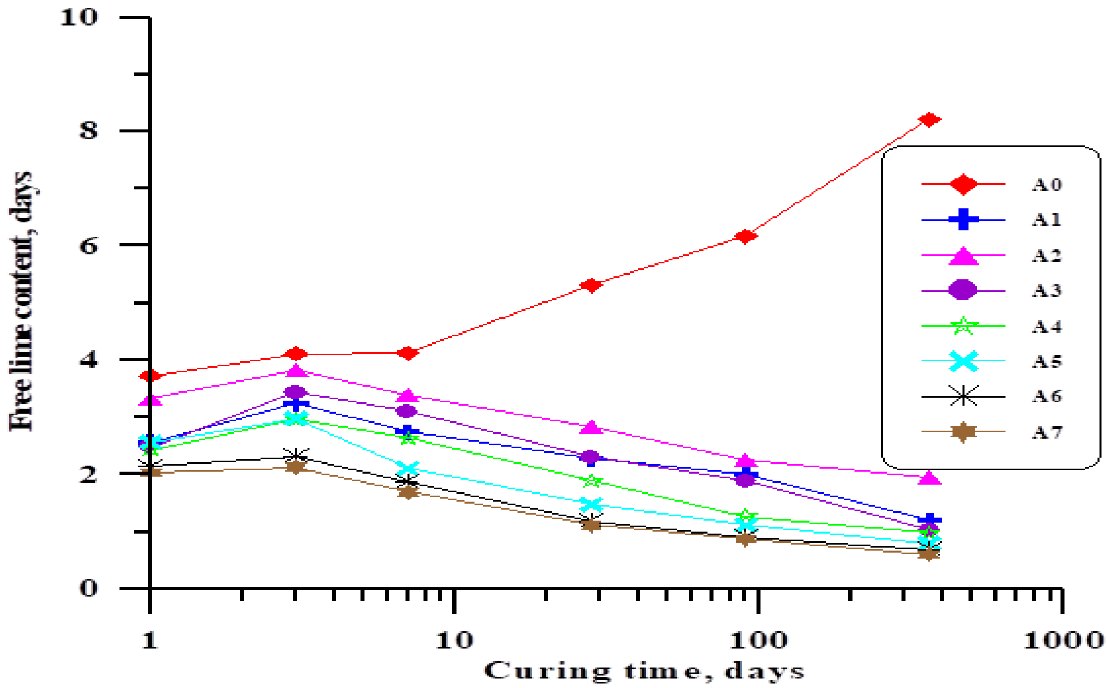

Fig. 3. FL of composite pastes in the presence of 4%SNP.

Physico-mechanical properties

Compressive strength (CS)

The effect of 4% SNP content on the CS of the composite-pastes (CCP) up to 360-days was represented in Figure 4. The data show the CS increases with ages-period for all composite-pastes, this is due to the formation of a large amount of calcium silicate (CSH), calcium aluminates (CAH) and alumino-silicates (CASH) hydrates (main source of strength) which formed during hydration process, these hydrates leading to form dense cementitious structure [7]. The addition of 4mass% SNP gives higher CS than other composite-pastes without SNP as shown in Figure 4, because of the formation of nano-sized hydrates which constitutes the compact structure. The data also shows the mechanical properties of the composite cement pastes improves in the hybrid of SNP and SP, this is due to the coating layer which formed on the surfaces of cement particle in existence superplasticizer, leading to mutual repulsion, causing break up flocks, high degree of dispersion, so that the workability increases at lower values consistency. This effect decreases the initial porosity of pastes and leads to a decrease in the distance between the active silica from SNP and active silica and alumina from FA and FGS to produce CSH, CAH and CASH hydrates. Figure 4 shows that the CS of the composite pastes containing OPC+FGS+SNP (mix A5) higher than FA-blended cement pastes (mix A3). Mixes containing SNP give higher CS values at all curing ages especially at later ages as given by mixes A5, A6, and A7. This effect is represented by the formation and accumulation of hydration products from the pozzolanicity reaction to form nano-and/or micro rigid structure in the hybrid of SNP, FA, and FGS. SNP enhances the FA and FGS to form CSH, CAH, and CASH products [34-36].

Gel/space ratio (X)

The *X* ratio of the cement pastes containing FA and/or FGS with and without SNP in the existence of SP was represented in Figure 5. The *X*-ratio is influenced by W/C ratio and hydration degree. Figure 5, the increases in the *X* ratio is due to the formation of large amounts of CSH, CAH and CASH products [37]. In the presence of SP, W/C, and TP decrease so that *X* values increase [38]. Data show that mixes A5 shows a higher value of gel/space ratio in comparison with neat-OPC and FA-blended cement (mix A3) as shown in Figure 5. The FGS improves the hydration process of CCP, especially at later hydration times. The gel/space ratio increases in all mixes containing SNP. SNP acts as a promoter effect to activate the pozzolanic reaction with liberated lime from the OPC cement phases, mix A5 gives the higher values of gel/space ratio at all ages, due to the presence of 4%SNP, which activate the reaction of FGS to give higher CS.

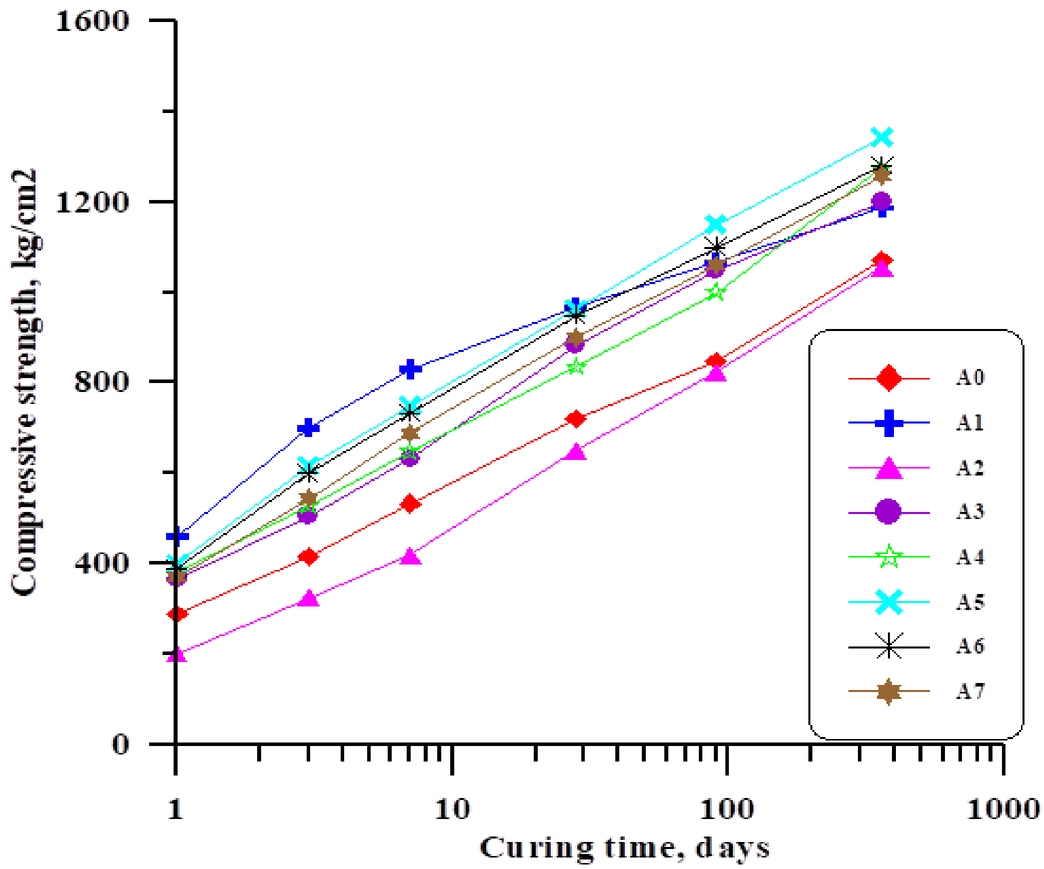

Fig. 4. Compressive strength of cement pastes containing 4%SNP.

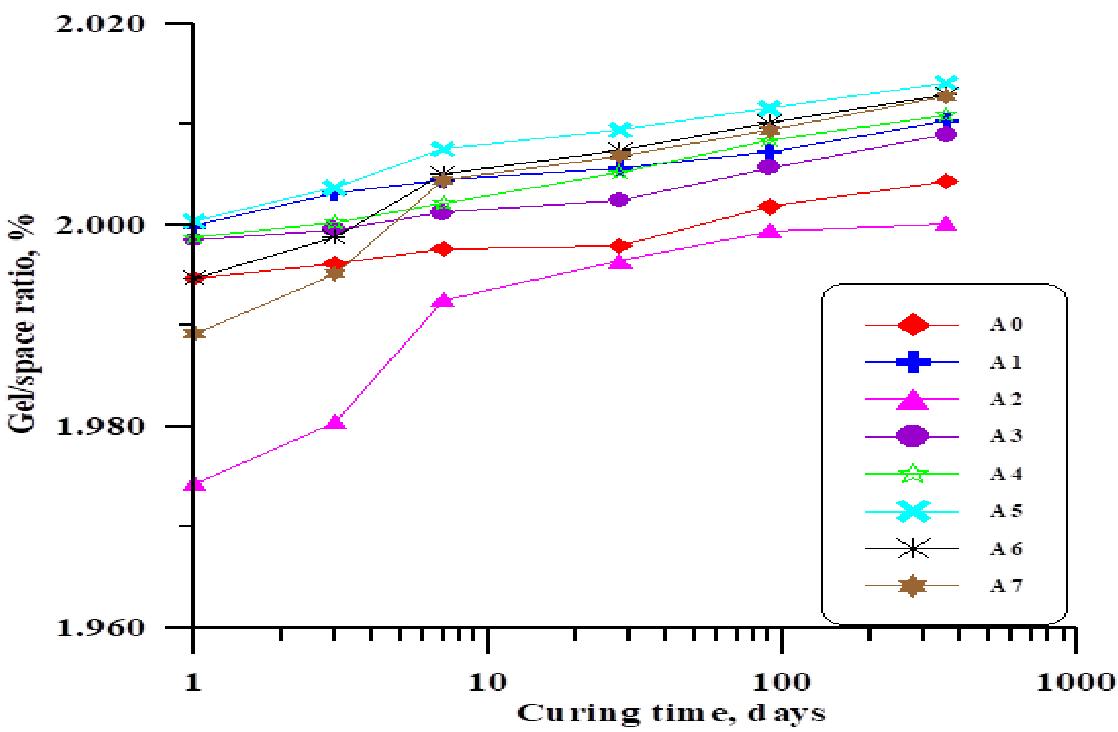

Fig. 5. Gel/space ratio of cement pastes incorporating 4%SNP.

Bulk density (BD) and Total porosity (TP)

The variation of BD and TP of composite-pastes in the presence and absence of 4%SNPand SP cured-up to 360-days as represented in Figure. 6. The BD increases where the TP decreases with time increasing, this is attributed to the continued of the hydration reaction of cement phases, which produces excessive amounts of the ore-dense structure of hydrates [36]. The BD of the cement-pastes containing SNP is higher than neat OPC and other-mixes without SNP [7]. The mechanical-properties improved in the cement pastes containing SP, where the BD shows a higher value in the conjugated of SP so that the TP decreases. BD of mix A5 higher than the values of those of neat-OPC and mix A3 especially at later-ages of hydration as shown in Figure. 6. By increasing the FBFS-content, the BD increases and TP decreases [39]. The results concluded that physicomechanical properties, namely CS, gel/space ratio, TP, and BD are in good agreement with each other. Where the physico-mechanical properties show an increase in the values of CS, gel/space ratio, and BD from 1-days upto 360-days.

Phase composition

XRD patterns

Figure. 7 represented X-ray diffraction patterns of the hardened mixes A0, A3, A5, A6 and A7 composite-pastes hydrated at 1, 90 days. Figure7 shows the presence of different diffraction lines of hydrated and un-hydrated phases of CH, β-C_2S, C_3S, C, calcium silicate hydrates (CSH), and quartz. OPC-cement paste exhibits the highest intensity of portlandite (CH) as shown in Figure 7. As the hydration-proceeds, the intensity of the peak characterizing for the CSH increases, whereas the peaks corresponding to CH decreases at one-day upto 90-days for composite pastes containing SNP (mixes A3 and A5). This is due to the pozzolanic reaction of SNP with liberated CH during the hydration of OPC leading to the consumption of some portlandite and formation of additional C-S-H so that the peak intensity of C-S-H increases, whereas the diffraction-lines corresponding to CH decreases for specimens containing FA, FGS, and SNP. These lines nearly -disappeared for mixes A5 and A7 hydrated at 90-days. By increasing FGS-content, the peak intensity corresponding to CH, and C decreases; as shown in Figure 7.

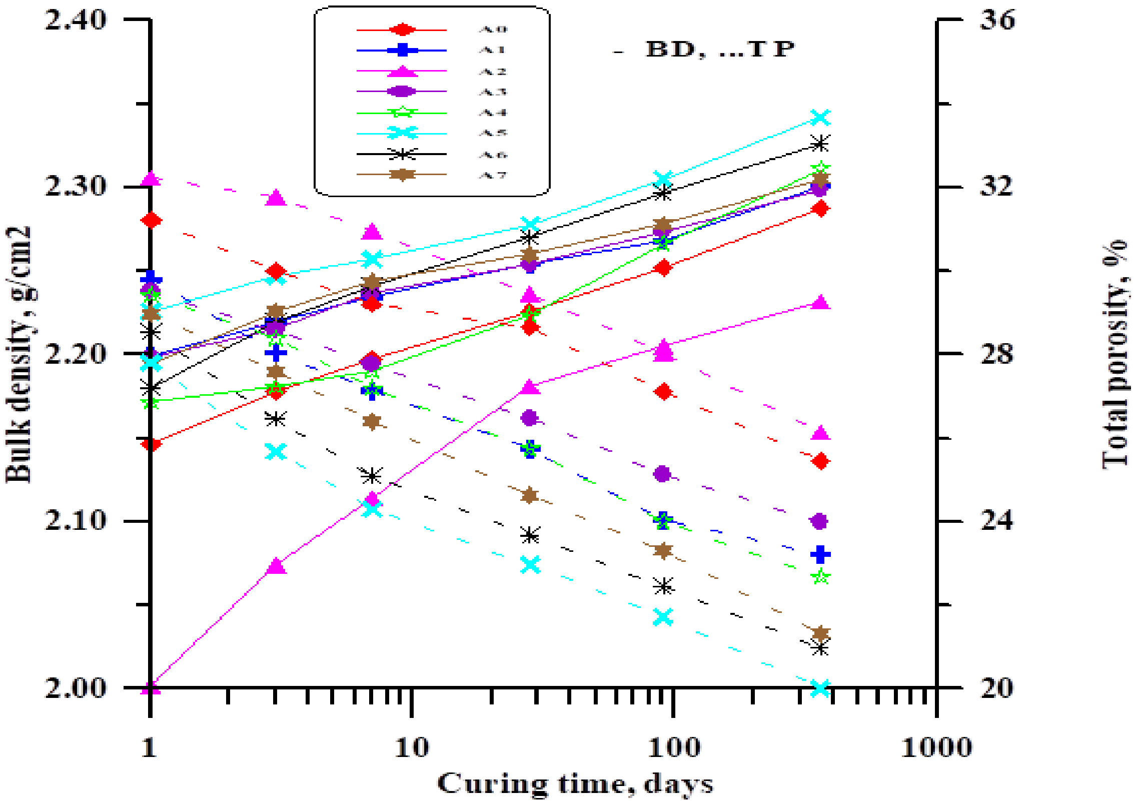

Fig. 6. Bulk density and total porosity of composite pastes in the presence of 4%SNP .

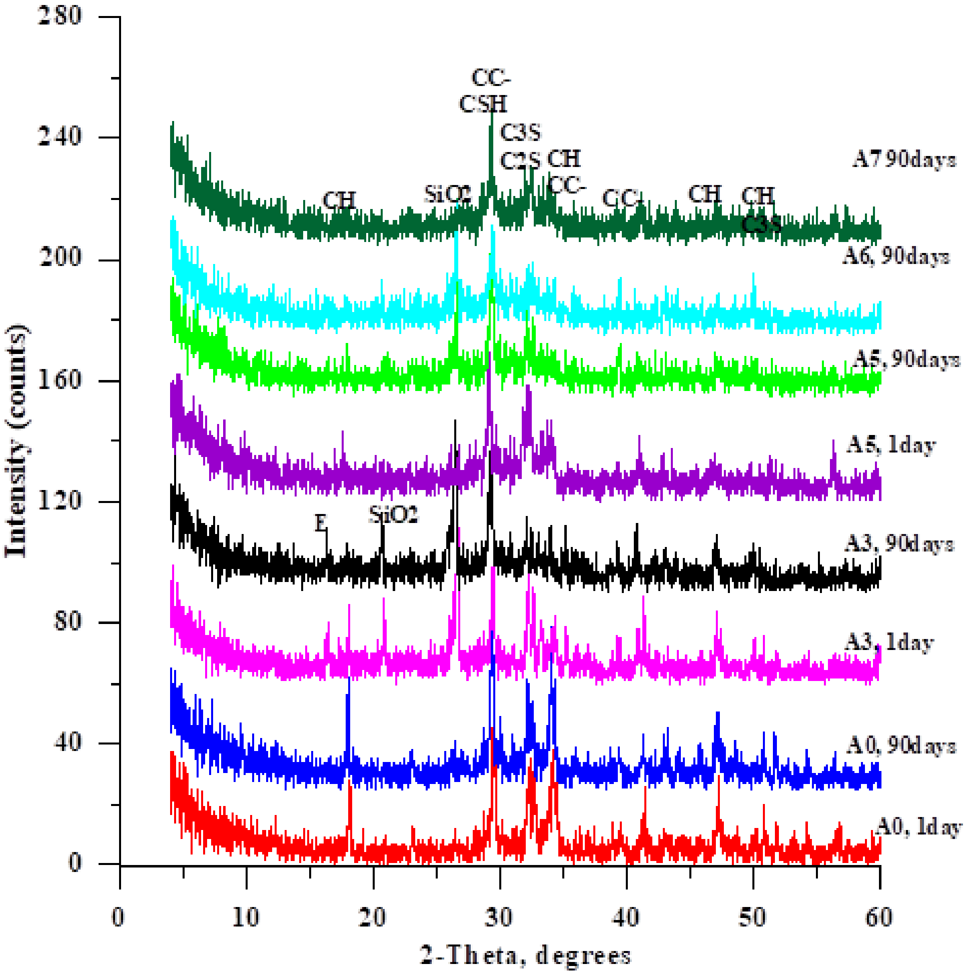

Fig.7. XRD patterns of composite cement pastes containing 4mass%SNP curing at 1, 90 days.

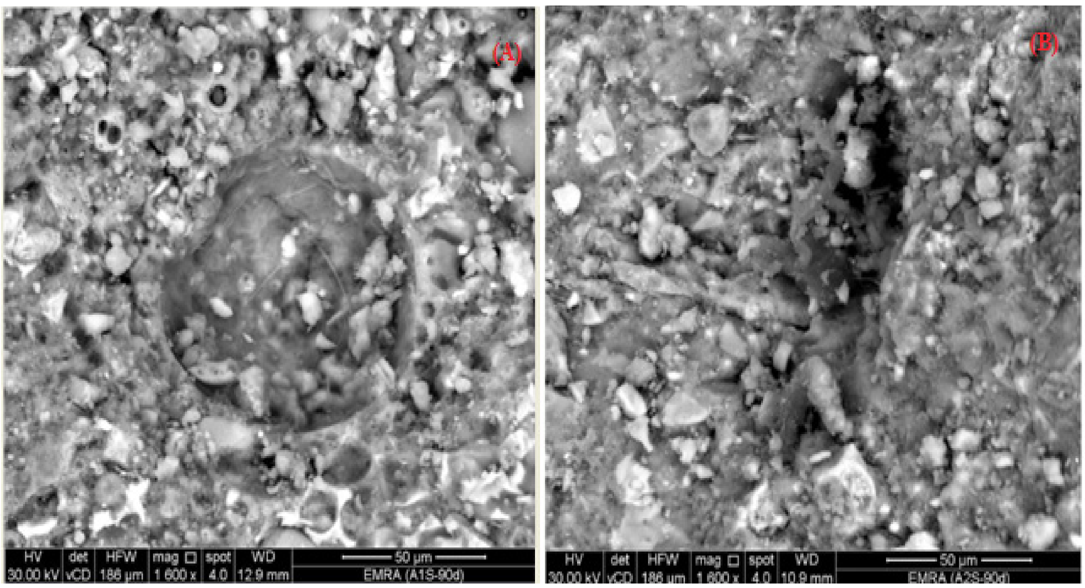

Fig. 8. SEM micrograph of composite cement pastes; A) A3-90 days; B) A5-90 days.

Microstructure and morphology of composite cement pastes

Microstructure and morphology of the OPC-composite-cement-pastes containing FA, FGS and 4%SNP (mixes A3 and A5) cured at 90 days are shown in Figure. 8. Figure 8A shows the effect of SNP on the hydration characteristics and morphology of the formed hydrated products of composite-pastes. SEM micrograph of mix A3 (OPC+40%FA+4%SNP) hydrated at 90-days shows the existence of prolonged CSH as a rod-like particle of having a porous and wider pore structure. Figure. 8 shows the SEM micrograph of mix A5 (OPC+40%FGS+4%SNP) depocites the denser structure. This paste has a higher degree of hydration and compact-morphology with marked-reduction in the porosity of the hardened cement paste, where the presence of SNP fills these pores and decreases CH crystal then growing the CS as shown in Figure (8,B and 4) [40].

Conclusions

From his study we can conclude the following

1. The CS of composite cement pastes (CCP) containing FGS is greater than OPC and other composite-cements containing FA pastes.
2. The values of TP of the composite-pastes with a hybrid of 4%SNP are lower than that those of the CCP.
3. CCP containing SNP gives higher W_n than neat-OPC pastes and other composite pastes, due to the nucleating effect, and the filler effect of SNP, where SNP enhances the production of C–S–H-structure to fill with the voids between the cement grains to obtain a denser and stronger matrix.
4. Mix A5 shows a higher value of gel/space ratio in comparison with neat-OPC and higher than FA-blended cement where FGS improved the hydration process, especially at later hydration times.
5. In the presence of SNP free lime contents decrease with the increase of the FGS, FA contents, so the free lime content decreases as shown in mixes A5,A6,A7 where the mix A7 has a lower value of free time than mixes A5 and A6.
6. SEM represents the close, denser structure with nano-matrix as represented of mix A5.

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