Characteristics of Portland Cement Pastes Blended with Silica Nanoparticles

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Abstract

The effect of silica nanoparticles (SNP) addtion on the specific characteristics of Portland cement pastes was investigated. The results revealed that the addition of SNP to the fresh Portland cement pastes reduced both w/c ratio and setting times, but increased significantly the early age strength development. The presence of the water-reducing admixture (Na-lignosulphonate) further improved the wokability and performance of cement pastes.The replacing of SNP up to 1.5 wt. % at the expense of cemen improved and enhanced the combined water content, bulk density, total porosity and compressive strength at all curing ages of hydration. The cement mix incorporated 1.5 wt. % (Sn3) is considered to be the optimum cement patch, where it exhibited the best results and were becoming better and higher than those of the pure cement (Sn0) at all curing stages of hydration. With the addition of more than 1.5 wt. % SNP to the cement (Sn4 and Sn5), all cement properties were adversely affected. Therefore, the higher additions of NSP must be avoided.

Keywords: Cement, Nano-Sio$_2$, Consistency, Setting, Density, Porosity, Strength.

Abbreviations: C : CaO, S : SiO$_2$, A : Al$_2$O$_3$, F : Fe$_2$O$_3$, H : H$_2$O, CH : Ca(OH)$_2$, CSH: calcium silicate hydrate, SNP: silica nanoparticles.

1. Introduction

In recent years, researchers investigated on cement-based composite materials. Cement can be described as a crystalline compound of calcium silicates and other calcium compounds having hydraulic properties, i.e. they can react with water to produce other important components. The four major compounds that constitute cement are Tricalcium silicate, 3CaO. SiO$_2$ abbreviated as C$_3$S, Dicalcium silicate, 2CaO.SiO$_2$ abbreviated as C$_2$S, Tricalcium aluminate, 3CaO. Al$_2$O$_3$ abbreviated as C$_3$A, and Tetracalcium aluminoferrite, 4CaO. Al$_2$O$_3$. Fe$_2$O$_3$ abbreviated as C$_4$AF. C, S, A and F are pointing to CaO, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$, respectively. Both calcium silicate phases represent the major constituents to the strength development of cement, together are constituting 69-71 % of cement. Dry cement does not have adhesive properties. Hence, it cannot bind the raw materials together to form cement pastes or even concrete. When cement is being in contact with water, chemical and hydraulic reactions will occur. This is referred to as hydration process. The products of this exothermic reaction are CSH gel and Ca (OH)$_2$. Calcium hydroxide has a lower surface area, and hence it does not resposible for the strength of cement pastes, mortars or concretes. On hydration of C$_3$A, a product of needle-like crystals is formed known as ettringite, which contributes for an early few strength, while cacium silicate hydrates (CSH) are making up > 60 % of the strength development of the hardened cement pastes or concretes. It has a structure of short fibres which vary from crystalline to amorphous form. Owing to its gelatinous structure [1-3], it can cement the various inert materials by virtue of Van der Waal forces, where it is the primary strength phase in cement pastes or concrete. Various additives can't fill in the micro level pores. Thus, they have adverse effects on the properties of materials [1,2]. In order to reduce these effects, nanoparticles can be added into cement mortar. The addition of nano-sized particles improves the performance of cement.

Concrete is the material of the far and near past, present and future, and moreover, it is the most plentiful resource on Earth. It is considered as the second most consumed material on Earth and may be after water. The wide use of concrete from buildings to factories, bridges and airports, makes it as one of the most

investigated materials of the 21st century. On account of the rapid population explosion, and the technology boom to cater these needs, there is an urgent need to improve both mechanical properties and durability of concrete. Inbetween of the various materials used in the production of concrete, cement plays a major and vital role due to its very fine size as well as adhesive and binding properties. So, to produce concrete with improved properties, the mechanism of cement hydration has to be studied properly and better substitutes to it have to be suggested.

Different materials known as supplementary cementitious materials are added to cement or concrete to improve its properties. Some of these are fly ash [3-9], blast furnace slag [5-11], silica fume [5,7-10], rice husk ash [12-17], sugarcane bagasse ash [18-24], metakaolin [25-28], limestone [29-31], perlite [32-36], bentonite [37] and many more as fibers and volcanic tufs. From the various used technologies, nano-technology looks to be a promising approach to improve the concrete properties.

Nanomaterials are very small grain-sized materials with a particle size in nanometres. In general, a nanoparticle has an ultrafine size in the range of 1 - 100 nm, where 1 billionth of a meter (10^{-9} m) is equal to 1 nm). These materials are very effective in changing the properties of concrete at the ultrafine level by the virtue of their very small size. The small sized particles also mean a greater surface area [38-40], where the rate of pozzolanic reactions is proportional to the surface area available and faster reactions can be achieved. Only a small percentage of cement can be replaced to achieve the desired results. These nanomaterials improve the strength and permeability of concrete by filling up the minute voids and pores in the microstructure. The use of nanosilica in concrete mix increases the compressive, tensile and flexural strengths of concrete. It sets early and hence generally requires admixtures during mix design. Nano-silica mixed cement can generate nano-crystals of CSH gel after hydration. These nano-crystals accommodate in the micro pores of the cement concrete, hence improving the permeability and strength of concrete. Well-dispersed nanoparticles are acting as nuclei for cement phases. Hence, it can promot the rate of hydration due to their high reactivity. Nanosized particles lead to crushed size of crystals as Ca (OH)$_2$, and the formation of small-sized uniform clusters of CSH. Also, nanoparticles accelerate the pozzolanic reactions, resulting in the consumption of Ca (OH)$_2$ to form an additional CSH gel. The contact zone structure of aggregates can be improved by use of nanoparticles, resulting in a better bond between cement paste and aggregates. Nanograin size particles provide crack detention and interlocking effects. This in turn improves toughness, shear, tensile and flexural strength of cement-based materials. Moreover, nanograin size particles can act as nano reinforcement, and therefore the tensile strength of concrete could be strengthened. The previously mentioned beneficial effects of nanoparticles can limit the rate of hydration, strength development and performance of cementitious materials [40-44].

The main objective of the current investigation is to study the influence of silica nanoparticles (SNP) on the specific properties of the hardened cement pastes specially focussing on the physical, chemical and mechanical properties in the presence of Na-lignosulphonate admixture, which is a water-reducing admixture.

2. Experimental

2.1. Raw materials

The raw materials used in the present research article are Ordinary Portland cement (OPC Type I- CEM I 42,5R) with the blaine surface area 3450 cm^2/g, and nanosilica which is abbreviated as Nano-SiO$_2$ or NS (its particle size was about 12 nm). The OPC sample was supplied from Sakkara cement factory, Giza, Egypt, and its commercial name is known as "Asmant El-Momtaz", while silica nanoparticles (SNP) were obtained from Sigma Aldrich Company. During casting, a small ratio of sodium lignosulphonate as an admixture (Fig. 1) was added to the prepared cement mixes so as to avoid the agglomeration of the nanoparticles of the used SNP or OPC. Sodium lignosulfonate superplastecize (SL) was applied due to its higher activity than other conventional ones. Its molecular weight is 534.51, while its molecular formula is C$_{20}$H$_{24}$Na$_2$O$_{10}$S$_2$. It helps greatly to improve cement dispersion and to facilitate blending process [1,2,24].
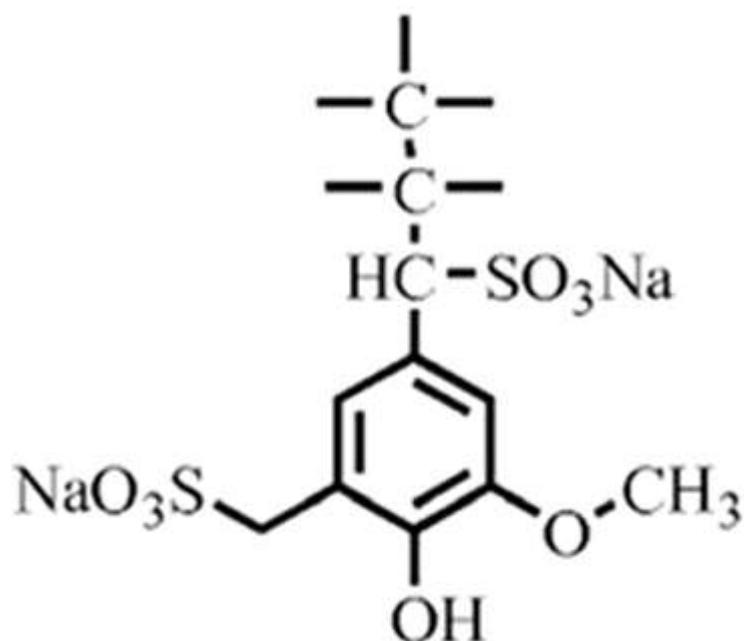
Figure 1-The chemical structure of sodium lignosulphonate.

The chemical analysis of the OPC and Nano-SiO$_2$ samples is shown in Table 1. The mineralogical composition of the OPC sample was C$_3$S, 61.88 %, β-C$_2$S, 11.69 %, C$_3$A, 6.43 % and C$_4$AF, 12.07 % as supplied by the cement company. The mix composition is givwn in Table 2. The physical properties of OPC and NS are recorded in Table 3.

Table 1-Chemical compositions of raw materials, wt. %

Material Oxide	Portland cement (OPC)	Silica nanoparticles (SNP)
L.O.I	0.85	-----
SiO$_2$	20.33	98.82
Al$_2$O$_3$	4.96	-----
Fe$_2$O$_3$	3.97	-----
CaO	62.75	-----
MgO	2.23	-----
TiO$_2$	-----	-----
SO$_3$	2.40	-----
Na$_2$O	0.35	-----
K$_2$O	0.21	-----
Blaine area ,cm^2/g	3300	2430

Table 2-Composisition of the defferent OPC/SNP blended cement batches, wt. %

Cement batches	OPC	Nano-SiO$_2$
M0	100	----
M1	93	0.5
M2	86	1.0
M3	79	1.5
M4	72	2.0
M5	65	2.5

Table 3- Physical properties of OPC and SNP raw materials.

Physical characteristics	OPC	SNP
Specific gravity	3.18	2.36
Specific surface area, cm^2/g	3450	2530
Particle size, nm	26.4 μm	10 nm

2.2. Preparation and methods

The OPC sample was replaced by 0, 0.5, 1.0, 1.5, 2.0 and 2.5 wt. % SNP having the symbols Sn0, Sn1, Sn2, Mn3, Sn4 and Sn5, respectively. The blending process was mechanically made in a porcelain ball mill (Lab.monomill, Puluerisette 6- FRITSCH, Germany) for one hour using four porcelain balls to assure the complete homogeneity of all mixes. The standard water of consistency and setting times of the freshly prepared cement pastes were directly determined by Vicat Apparatus [45,46], where, water of consistency could be determined from the following relation:

WC, % = A / C x 100   (1)

Where, A is the amount of water taken to produce a suitable paste, C is the amount of cement mix (300 g). The cement pastes were mixed using the predetermined water of consistency, moulded into one inch cubic stainless steel moulds (2.5 x 2.5 x 2.5 cm^3), then vibrated manually for 2-3 minutes, and on a mechanical vibrator for another two minutes. The surface of the moulds was smoothed by using a suitable spatula. The moulds were kept inside a humidity chamber for 24 hours at 23 ± 1 °C and 100 % relative humidity. It demoulded in the following day and soon cured under water till the time of testing for combined water and free lime contents, sbulk density, total porosity and compressive strength at 1, 3 , 7, 28 and 90 days. The bulk density (BD) of each specimen at any hydration age was determined [1,5,36,47] from the following equation:

$$BD, g/cm^3 = W_1 / W_1 - W_2 \tag{2}$$

Where, W_1 is the saturated surface dry weight in air (g) and W_2 is the submerged weight in water (g). The total porosity (ε) [48,49], was calculated from the following equation:

$$\varepsilon = (0.99 \text{ x We x BD}) / (1+Wt) \tag{3}$$

Where, 0.99 is the specific volume of free water, We is the free or evaporable water content, BD is the bulk density, g/cm^3 and Wt is the total water content which is equal to the sum of We and Wn contents, where Wn is the combined water. The compressive strength [50] was measured using the following equation:

$$CS, MPa = L (KN)/Sa (cm^2) KN/m2 \text{ x } 102 (Kg/cm^2)/10.2 \tag{4}$$

The loading was applied perpendicular to the direction of the upper surface of the cubes. Three samples were tested for each mix at every hydration age and the mean value was considered. The broken specimens from the determination of compressive strength were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration [49,50]. The kinetics of hydration in terms of chemically combined water and free lime contents were also measured [36,51]. The combined water content (CWn) of the hydrated samples predried at 105 °C for 24 hours, was determined on the basis of ignition loss at 900 °C for 30 minutes from the following relation:-

$$CWn, \% = W1-W2/W2 \text{ x } 100 \tag{5}$$

Where, CWn, W1 and W2 are combined water content, weight of sample before and after ignition, respectively. The free lime content (FLn) was measured by the modified extraction Franke method [52-54]. About 0.5g sample + 40 ml ethylene glycol → heating to about 20 minutes without boiling. About 1−2 drops of pH indicator were added to the filtrate and then titrated against freshly prepared 0.1N HCl until the pink colour disappeared. The 0.1 N HCl was prepared using the following equation: Where, Wn, W1 and W2 are combined water content, weight of sample before and after ignition, respectively. The free lime content of the hydrated samples pre-dried at 105°C for 24h was also determined. About 0.5 g sample + 40 ml ethylene glycol → heating to about 20 minutes without boiling. About 1−2 drops of pH indicator were added to the filtrate and then titrated against freshly prepared 0.1 N HCl until the pink colour disappeared. The 0.1 N HCl was prepared using the following equation:

$$V1 = N \times V2 \times W (7) \times 100/D \times P \times 1000 \tag{6}$$

Where, V1 is the volume of HCl concentration, V2 is the volume required, N is the normality required, W is the equivalent weight, D is the density of HCl concentration and P is the purity (%). The heating and titration were repeated several times until the pink colour did not appear on heating. The free lime content [3,55-57] was calculated from the following relation:

$$FLn, \% = (V \times 0.0033/1) \times 100 \tag{7}$$

Where, FLn and V are the free lime content and the volume of 0.1 N HCl taken on titration, respectively.

3. Results and Discussion

3.2. Water of consistency

The water of consistency of cement pastes containing SNP is shown in Fig. 2. Water of consistency of the pure OPC pastes (Sn0) was 28.65 %. This ratio tends to decrease with the various blended cement pastes (Sn1-Sn5) gradually as SNP content increased, i.e. the higher SNP content is the lower water absorption. This is

essentially attributed to the fact that the used SNP could not absorb water in addition to the effect of the superplasticizer action [1,2,58-64]. Hence, as the SNP addition increased, the water of consistency decreased.
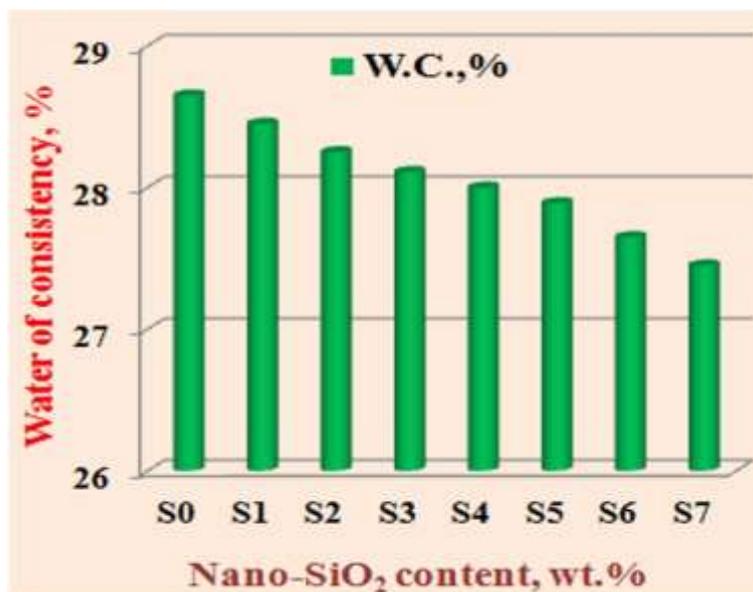

Figure 2-Water of consistency of cement pastes containing SNP.

3.2. Setting times

On the other side, the setting times (Initial and final) of cement pastes containing SNP are represented in Fig. 3. The initial and final setting times also slightly diminished and decreased with the increase opf SNP content. This is mainly contributed to the solid nature of SNP particles which tends to absorb no water during mixing process besides the action of the used admixture [59-63]. Therefore, it can be concluded that the SNP acts as an accelerator for cement pastes. Also, the diminishing of the cement portion due to the incorporation of SNP is another reason for the set acceleration [60-64].
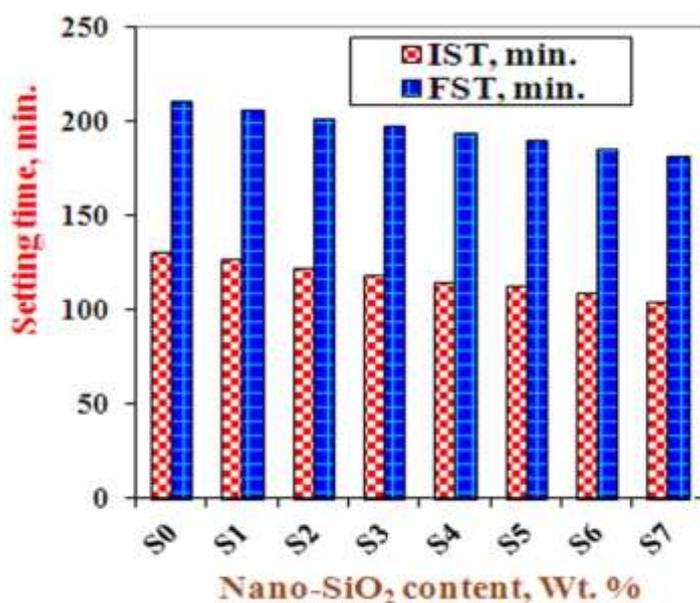

Figure 3- Setting times of cement pastes according to SNP contents.

3.3. Chemically-combined water contents

The chemically combined water contents (CWn) of the different cement pastes containing various proportions of SNP are shown in Fig. 4. The combined water content increased as the curing times gradually proceeded up to 90 days of hydration. This is principally attributed to the hydration of the main cement phases, especiallyC_3S, C_3A and C_4AF at early ages of hydration up to 28 days, whereas β-C_2S often hydrates at later ages from 28 days onward [1,2,51,66].
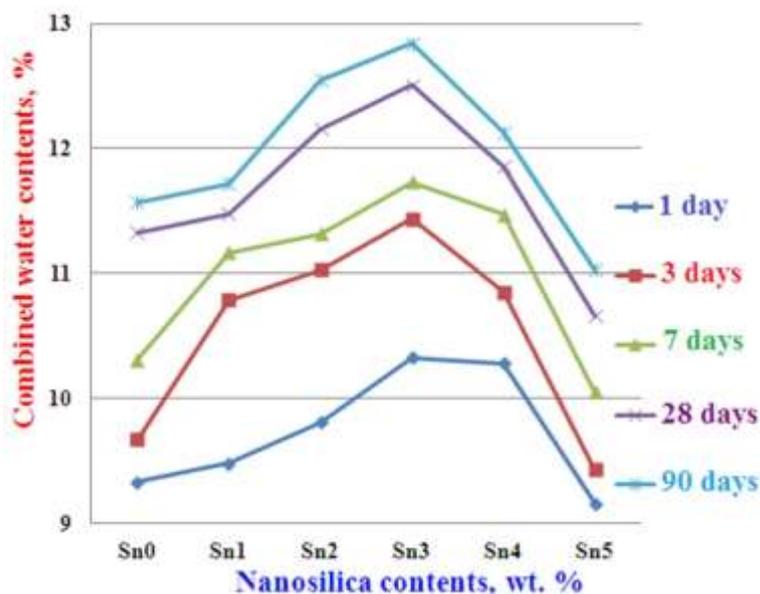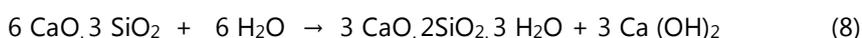

Figure 4- Combined water contents of cement pastes according to SNP content.

The combined water contents slightly increased as the SNP content increased up to 1.5 wt. % at all curing ages of hydration and then decreased. This trend was displayed by all cement mixes. With further increase of SNP, the combined water contents decreased at all curing ages as obtained by Sn4 and Sn5 blends, i.e. the cement blends Sn1, Sn2 and Sn3 are slightly higher than those of the pure OPC (Sn0). This is primarily due to the filler effect of SNP, whereas, the combined water contents of Sn4 and Sn5 blends were becoming lower than those of the control mix (Sn0) at all curing stages of hydration. This is prinsipally due to the large deffiency of the main cement phases responsible for the hydration process [1,2,5,58-64]. Accordingly, it can be concluded that the optimum addition of SNP does not exceed 1.5 wt, % because the higher amount of SNP is undesirable due to its adverse effect, i.e. the higher quantity of SNP must be avoided because it may be hindered the hydration of cement phases.

3.4. Free lime contents

Figure 5 indicates the free lime contents of cement mixes containing various ratios of SNP hydrated up to 90 days. The free lime contents of the pure OPC (Sn0) gradually increased with the hydration ages indicating an evidence of hydration [1,2,65]. As the SNP content increased in the cement, the free lime content was slightly decreased up to 90 days, and became lower than those of the control (Sn0). The increase of free lime content is due to the normal hydration process of cement with water as shown in the following relations:
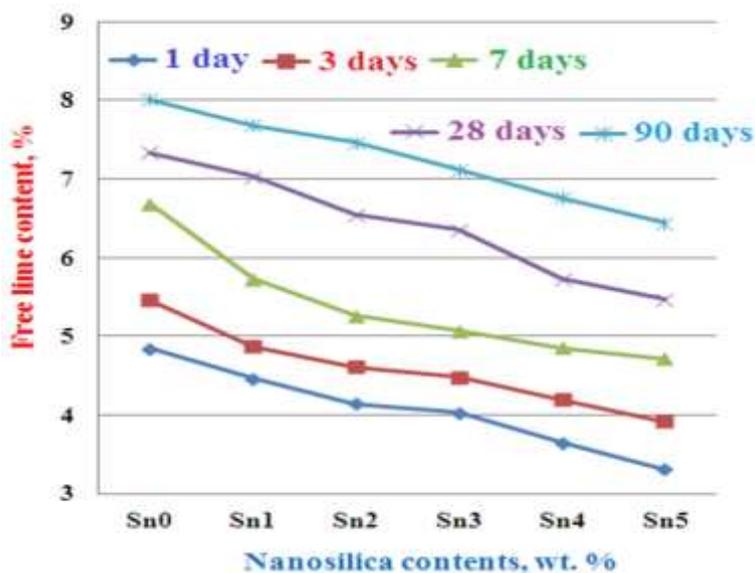
6 CaO. 3 SiO$_2$ +   6 H$_2$O → 3 CaO. 2SiO$_2$. 3 H$_2$O + 3 Ca (OH)$_2$ (8)

4 β-CaO.SiO$_2$ +   4 H$_2$O → 3CaO. 2SiO$_2$. 3 H$_2$O +   Ca (OH)$_2$ (9)

Figure 5-Free lime contents of the cement pastes according to SNP content.

The decrease of free lime contents is mainly due to the deffiency of cement phases which are responsible for the hydration process. The obtained results proved that the SNP acts as a filling material, and therefore the higher the amount of SNP, the higher is the filling activity [60-64].

3.5. Bulk density and total porosity

Figures 6 and 7 demonstrate the graphs of the bulk density and total porosity of the cement pastes containing different ratios of SNP versus the hydration ages up to 90 days. Generally, the bulk density of the various cement mixes increased as the hydration periode progressed up to 90 days, while the total porosity decreased. This is mainly contributed to the fact that: as the hydration ages proceed, the hydration process starts to produce CSH which soon deposites in the pore system leading to a decrease in the total porosity. This reflected positively on the bulk density, i.e. the bulk density increased as the total porosity decreased [1,2,61].
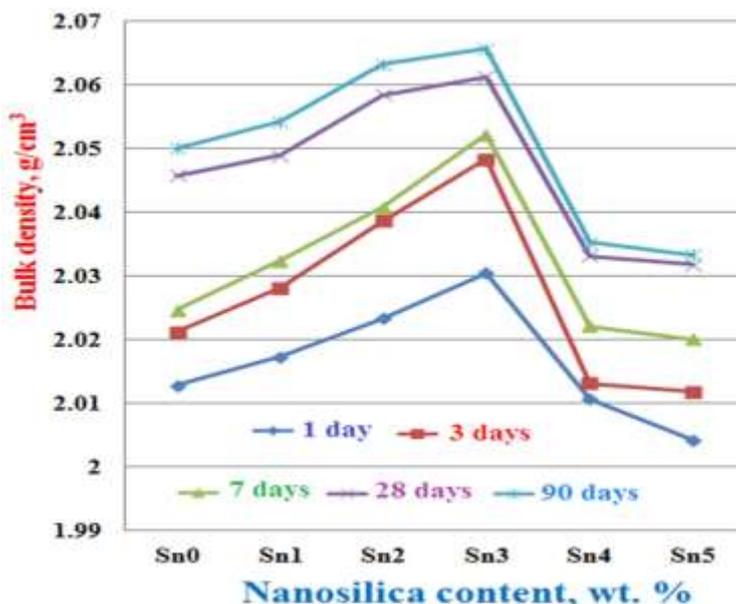

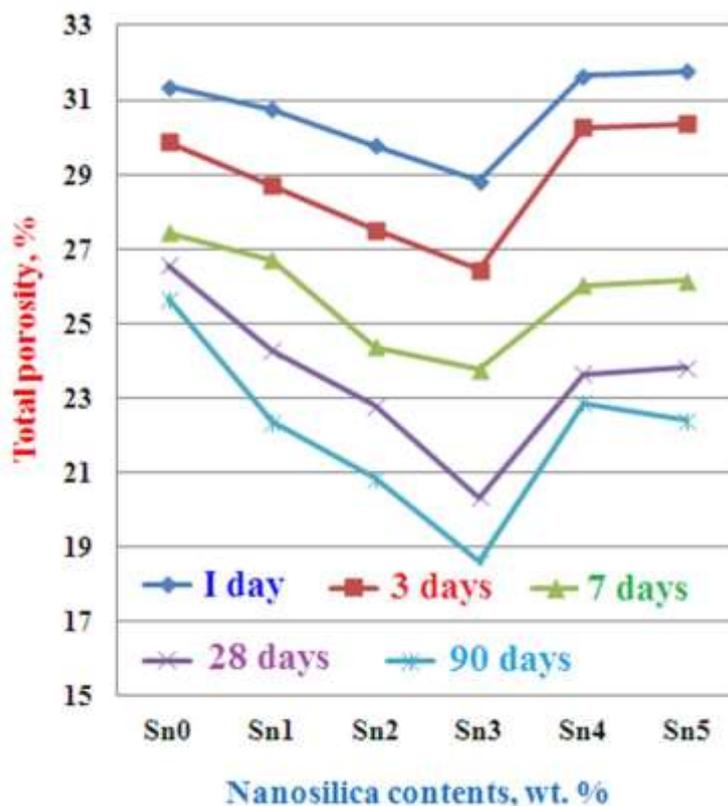**Figure 6– Bulk density of cement pastes according to SNP content.**

Figure 7-Total porosity of cement pastes according to SNP content.

The bulk density of the cement mixes containing SNP (Sn1-Sn3) gradually increased as the SNP content increased only up to 1.5 wt. % (Sn3), whereas the total porosity decreased, i.e. the cement blends Sn1, Sn2 and Sn3 are slightly higher than those of the pure OPC (Sn0). This is evidently due to the filling action of the SNP besides the positive action of the admixture [61-64]. The addition of more than 1.5 wt. % SNP, the BD suddenly was decreased, while the total porosity increased at all hydration ages. This is principally due to the decrease in the main binding material of the OPC, and also the higher quantity of SNP may obstruct and hinder the hydration process, i.e. it affects negatively and decrease the rate of hydration accompanied by a decrease of BD [2,8,36,51,65-67]. Hence, the increase of total porosity and the decrease of BD resulted by the incorporation of large amounts of SNP at the expense of the used OPC. As a result, the higher amount of SNP was undesired due to its adverse effects.

3.6. Compressive strength

It is well known that the w/c ratio influences the workability and durability of cement pastes and concrete, which in turn influences its strength, i.e. the decrease of w/c-ratio results in an increase of workability accompanied by an increase in the strength, and the opposite is correct. Fig. 8 represents the compressive strength of cement pastes incorporating different ratios of SNP versus the hydration ages up to 90 days. Generally, the compressive strength improved and enhanced as the hydration time proceeded till reach 90 days. This is mainly attributed to the well dispersion by the used admixture, the well compaction during moulding [24,68] and the formation of CSH due to hydration of cement phases [1,2,5,8] These CSH are always precipitated into the pore structure. This leads to a decrease in the total porosity and an increase in the bulk density. This in turn was reflected positively on the compressive strength. As a result, the compressive strength improved and increased [5,36,61,66]. The compressive strength also increased as the content of SNP increased up to 1.5 wt. % at all hydration ages, and then decreased. This is essentially due to the filling action of SNP in addition the good compaction during moulding, where the SNP also increase the compaction of the hardened cement pastes.
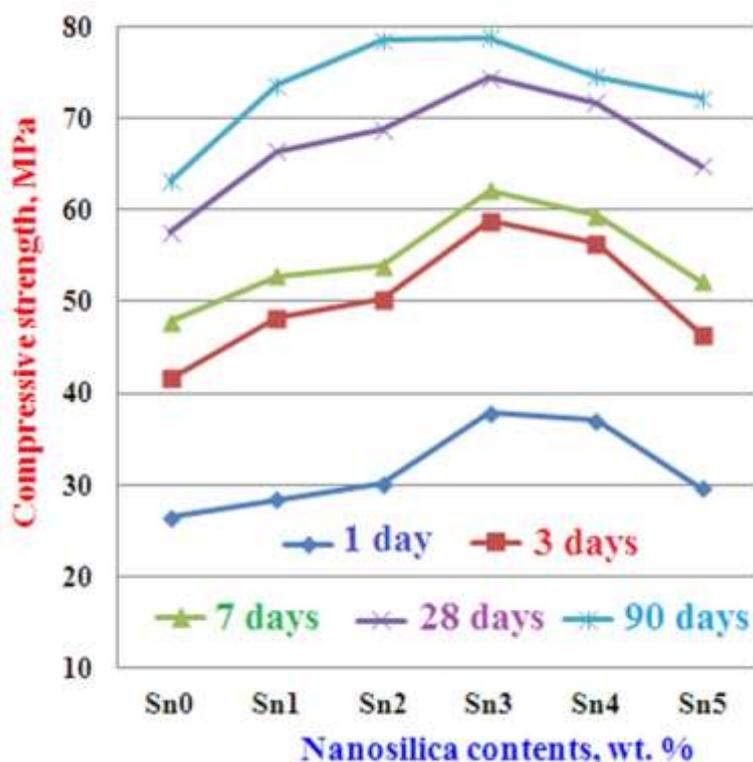
Figure 8- Compressive strength of the cement pastes containing SNP.

The decrease of free lime improved the physicochemical and mechanical properties of the hardened cement pastes, and therefore the compressive strength increased [24,17,61-63,66]. Moreover, the decrease of w/c ratio due to the presence of Na-lignosulphonate (Fig. 1) results in an improvement in the physical and mechanical strength of the hardened cement samples. The compressive strength also increased as the SNP content increased only up to 1.5 wt. %, and then suddenly decreased. The increase of compressive strength is related to the physical and chemical reaction of SNP with the constituents of the cement. This would be led to the segmentation of large capillary pores and nucleation sites due to the continuous deposition of hydration products (CSH) from the normal hydration of cement phases and additional CSH from the various reactions of SNP with the cement [59,61-64]. The decrease is due to the large deffeciency of the essential cementitious material of cement. On the other side, the higher amount of SNP stands as an obstacle against the normal hydration of cement phases. So, the rate of hydration declined. Accordingly, this should be reflected negatively on the compressive strength [3,37,38,68]. The cement mix of Sn3 recorded the highest values of compressive strength, whilst that of Sn5 exhibited the lowest. On this basis, the cement batch containing 1.5 wt. % SNP is the optimum mix. Hence, the SNP does not only improve the various characteristics of the OPC, but from an economical point of view, it also reduces the cost of the very expensive OPC production.

4. Conclusions

The following overall conclusions could be obtained:-

1- Both water of consistency (w/c ratio) and setting times are gradually decreased as the SNP content increased.

3-The chemically combined water contents increased as the hydration ages proceeded up to 90 days. It increased only up to 1.5 wt. % SNP, and then decreased with further increase of SNP.

3-The free lime content increased up to 90 days with Sn0 containing no SNP, whilst it decreased with cement blends containing SNP, i.e. the free lime contents are lower than those of the pure cement (Sn0).

4-The bulk density improved and enhanced as the SNP content increased up to 1.5 wt. %, and then decreased with further increase of SNP, whilst the total porosity declined with replacing of SNP up to 1.5 wt. % (Sn3), and then increased onward.

5-The compressive strength significantly improved and enhanced with increasing the SNP content only up to 1.5 wt. %, and then diminished sudenly at all curing ages of hydration. The increase could be done by increasing the good filling action by SNP and the good compaction of the hardened cement pastes, whereas the decrease is due to the deffeciancy of the main binding material of the cement.

6-The optimum cement/SNP batch is Sn3 which is incorporating 1.5 wt. % SNP. It could be applied without any adverse effects on its physical, chemical and mechanical properties, i.e. the specific characteristics of cement pastes were improved and enhanced at lower dosages of SNP in the range between 0.5-1.5 wt. %.

7-Na-lignosulphonate admixture is responsible for the modification and improving most of the physical, chemical and mechanical of the hardened cement pastes particularly the workability of the fresh cement pastes.

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Compliance with ethical standards

Conflict of interest: There is no conflict of interest anywhere.

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