Effects of Nano-silica on Concrete Properties—Literature Review

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Abstract This paper is a reviewing study about the use of Nano silica as an additive or a cement partial replacing material to enhance most of concrete properties. Due to their ability to fill even in extremely small voids and their pozzolanic reactivity, silica nanoparticles were found to effectively modify concrete microstructure into refined denser system. They considerably improve the cement-aggregate Interfacial transitional zone by filling the voids, consuming CH crystalline particle and producing more CSH gel. These modifications are presented as SEM images, XRD and thermogravimetric TG graphs as reported by the researchers. Through the microstructure improvement, NS was found to enhance most of concrete mechanical and durability properties. The effects of incorporating NS on concrete compressive, flexural and tensile strengths, water permeability, sulfate resistance and resistance to chloride permeability were reviewed and discussed. Effect of NS on fresh concrete workability and setting time were also studied.

Keywords Nano technology · Nano-silica · Fly ash · Concrete microstructure · Durability

1 Introduction

The use of fine mineral materials in concrete as mineral admixtures or as partial cement replacements has attracted a great attention in the last few decades. It looks an ideal way when an expensive, energy intensive material like cement which also causes high levels of CO_2 emission, is partially replaced with by-product materials that are regarded as sustainable environment-friendly materials. At the same time, they relieve pressure on natural resources and secure great savings with energy

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F. Mohamed Nazri (ed.), *Proceedings of AICCE'19*, Lecture Notes in Civil Engineering 53, https://doi.org/10.1007/978-3-030-32816-0_35

consumption, these mineral admixture are found to achieve considerable enhancement in mechanical and durability properties of concrete.

One of the most significant developments during the last decade is the use of different types of powdered material with a granular size that lies in the Nano scale, called Nano materials or nanoparticles. Nano-silica (or also called silica nanoparticles) is a nano material mainly composed of silica SiO_2 ground to nano levels. This material has been progressively researched due its unique features that come mainly from its particle size and chemical reactivity.

As a result of refining effects on the pore structure of concrete and improvements to the interfacial transitional zone, Nano Silica has been reported to enhance mechanical and durability properties of concrete. Incorporating this pozzalanic material was found to produce denser concrete microstructure and, therefore improve mechanical strength. It effectively reduces water and ions permeability, and thereby enhances concrete durability properties.

The most common supplementary cementitious materials used in concrete industry nowadays are fly ash (FA) and granulated blast furnace slag (GBFS). Both of these two pozzalan are by-product materials. FA is collected during the manufacture of coal, while GBFS is obtained during the manufacture of steel from its ores. Researchers have found that after 90 days, FA increases the strength and durability of concrete, and that product is more environment-friendly and cheaper than cement [1]. However, when the more widely used class F fly ash partially replaces cement, it tends to slow down early strength development and also retard concrete setting to impractical levels. The use of nanoparticles with FA concrete was found to be efficient in compensating some of the delay in setting time and strength development [2].

The object of this paper is to review some of the research efforts that concern the effects of Nano-Silica on concrete properties. It involves studying how the use of silica nanoparticles affects fresh concrete properties including workability and setting time. The study also reviews the effects of NS on the microstructure, mechanical properties as well as durability properties of hardened concrete. A special emphasis is placed on the enhancing role that incorporating these nanoparticles in fly ash and slag concretes can play as a compensation for the reduced early strength and retarded setting time.

2 Nano Silica

2.1 Description

Nano silica is a pozzolanic material that exhibit extremely high effectiveness. It generally consists of very finely ground vitreous particles typically less than 1/1000 of the average size of cement particles, usually available in the forms of powdered or colloidal particles [3]. It has been proven as a very useful cement admixture to

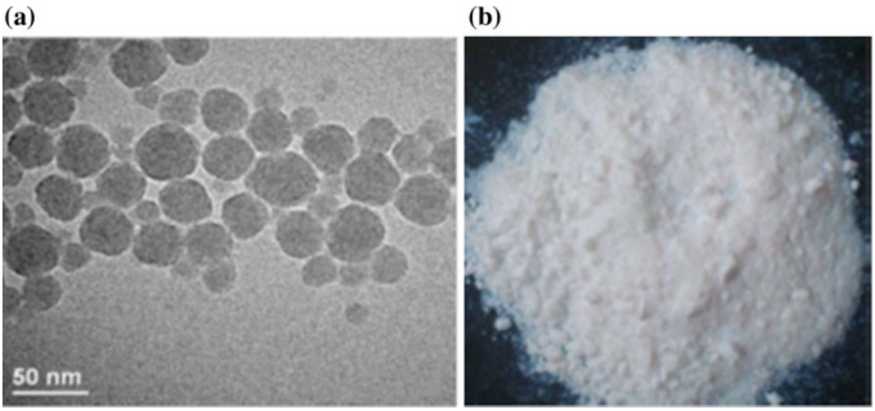

Fig. 1 Morphology of nano silica, **a** NS TEM image, **b** NS powder [2]

improve the overall strength properties and durability aspects of concrete. Nano-silica is generally produced by direct synthesis of silica solution or by crystallization of nano-sized crystals of quartz [4]. Images in Fig. 1 shows the morphology of Nano silica in powder size and under microscopic level [2].

The size of NS may vary widely from 10 to 150 nm. Jittabut [5] reported that Nano silica with 12 nm particle size with its high surface area has given the highest reactivity and can enhance mechanical strength with as low as 1% by cement weight.

2.2 Dispersion

The process of dispersion of nanoparticles effectively influences their reactivity within the fresh and hardened concrete. Improper dispersion may lead to cause nanoparticle agglomerate, where part of the particle's surface area becomes covered, and therefore, not available to react. For that reason, it has been suggested that nanoparticles should be adequately dispersed prior to mixing with cement or other mix ingredients. In most of the cases, nanoparticles are added to cement products as nano-powders, where they are simply mixed into the products. In some cases, they are pre-dispersed in water with ultra-sonication process, sometimes with a chemical dispersing agent. For example, nano-silica may be pre-suspended in a saline solution, while using deionized water in the concrete mix [6].

Sonication of powder-form nanoparticles prior to mixing is reported to improve mechanical properties including compressive strength. Organic ligands such as polycarboxylate-based HR water reducer were used as dispersing agents, which consisted of the HRWR and probe sonication [7]. Using such agents has proven to facilitate dispersion process both in deionized water and weak ionic solutions.

Adding Nano Silica material in excess of 6 percent is not usually recommended as it may lead to chemical incompatibility issues as a result of dispersion problems [8].

3 The Effect of Nano-silica on Fresh Concrete Properties

3.1 Workability

It has been agreed that concrete workability is reduced with the inclusion of Nano-Silica in concrete. Higher surface area and aggregation of the powdered SiO_2 nanoparticles are expected to reduce the fresh concrete slump.

Supit and Shaikh [9] reported drops of OPC concrete slump in the range of 40–57% with the addition of 2–4% of Nano-Silica, however the reduction was considerably lower (12–25%) for high volume fly ash mixes, Fig. 2.

Bahadori and Hosseini [10] conducted slump test for concrete incorporating Nano-Silica in the range 1–3% of cement associated with the reduction of cement in the range 10–30%. While enhancing many concrete properties, nano-silica caused intensive slump loss when the ratio of superplasticizer to cementitious materials was kept fixed.

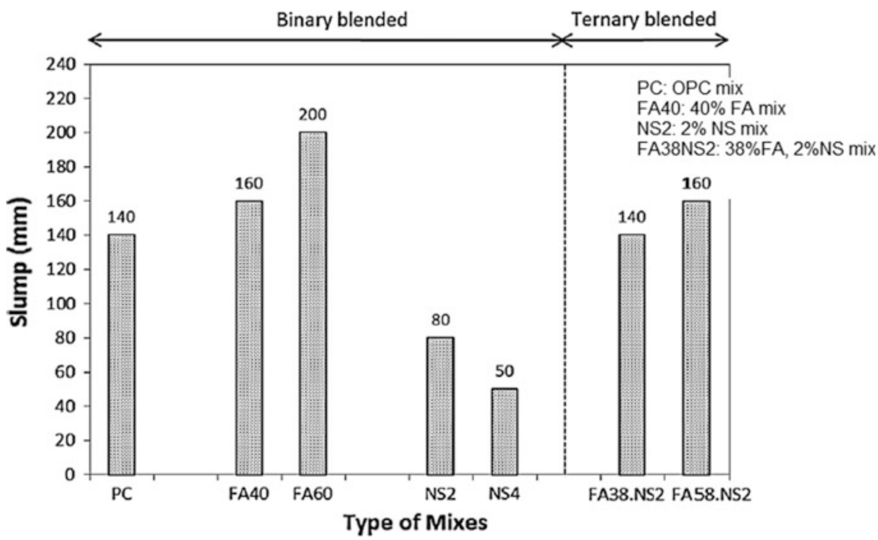

Fig. 2 Workability levels for various mixes [9]

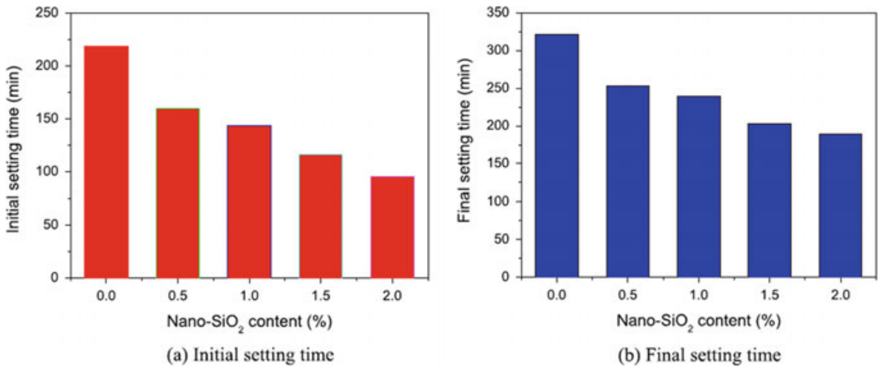

Fig. 3 Initial and final setting time as influenced by NS content [12]

3.2 Setting Time

Due to the higher surface area of its particles and the consequent faster hydration rate, Nano-Silica is generally expected to reduce initial and final setting times. The influence of Nano Silica particles on initial setting and final setting times of concrete is demonstrated in Fig. 3a, b respectively. It can be noted that the addition of NS particles generally reduces the initial and final setting time. The higher the dosage of NS the higher is the reduction in setting time compared to the reference no nanoparticles concrete [11, 12].

In some situations it is beneficial to reduce the setting time, namely in the cases where fly ash and blast furnace slag are used as high volume replacement of cement in concrete. Zhang and Islam [13] investigated the possibility of using Nano Silica to reduce the extended setting time and improve the strength development of concrete containing 50% cement replacement of fly ash or slag. They stated that the application of 2% silica nanoparticles per cementitious materials mass reduced the initial setting and final setting times by 90 and 100 min, compared to the reference concrete which contained 50% fly ash and no NS. Similar degree of reduction was observed with high-volume blast furnace slag concrete when Nano-Silica is added.

4 Effect of Nano-silica on Properties of Hardened Concrete

The majority of literature have reported improvements in most of the mechanical properties as a result of incorporating Nano-Silica in concrete. The significance of these improvements depends to a high extent on types and proportions of mixture ingredients. The improvements are more evident and of higher importance when the NS particles are used with concrete where the cement is partially replaced with pozzolanic materials such as fly ash and blast furnace slag. Concretes incorporated with one of these two materials are generally slow in their rate of hydration and consequently suffer a low rate of mechanical strengths gain. The use of Silica nanoparticles was found to enhance these properties, and that may be particularly true when high volume of fly ash and high-volume blast furnace slag are included.

Nano silica is reported to improve the mechanical properties through modifying the microstructure of concrete (resulting in denser and finer pore structure). This may occur due to four main mechanisms:

1. The pozzolanic reaction between the NS and $Ca(OH)_2$ which results in the formation of more amounts of C–S–H gel.
2. By the very fine nanoparticles of NS acting as a filler which refines and disconnects the pores with larger radii.
3. Improving the Interfacial transition zone which is the weakest more porous zone that is responsible for limiting the mechanical strengths of concrete.
4. With their ultra-high surface area, nano-silica particles may provide nucleation sites where the products of cement hydration can precipitate of producing more amounts of gel.

4.1 Microstructure, Porosity and Compressive Strength

The effect of adding Nano silica to OPC paste on mechanical strength, porosity and microstructure was studied by Tsampali et al. [14]. Nanoparticles were used in 0, 1.5 and 3% of cement weight. The samples were tested for compressive strength at different ages ranging from 7 to 120 days. The microstructure was scanned using SEM technology and porosity was tested according to EN 1015-11 and RILEM CPC 11.3 under vacuum. A porosity decrease of 41% for 1.5% NS and 59% for 3% NS addition were achieved, showing a considerable improvement in the density. Results of compressive strength tests showed a slight improvement when a percentage of 1.5% NS was used, whereas the compressive strength generally decreased with the use of 3% NS by weight of cement. The drop of strength was attributed to the agglomerate formation of products as well as the non-homogeneous dispersion of nanoparticles.

The results of SEM analysis are shown in Figs. 4 and 5. At an age of 7 days, the voids and cracks appearing with OPC samples are observed to improve into denser and homogeneous microstructure when Nano Silica is used both at 1.5 and 3% additions. The agglomeration produced at an age of 120 days with 1.5% NS and as early as 7 days for 3% NS were thought to be mostly responsible for the drop in later age strength when the Nano silica was used with 3% by the mass of cementitious material. A poor particle packing is obtained When the grains having concave shape are included in the mixture, which makes it hard to fulfill the filling of intergranular space between the grains, diminishing of particle packing is the result of such case.

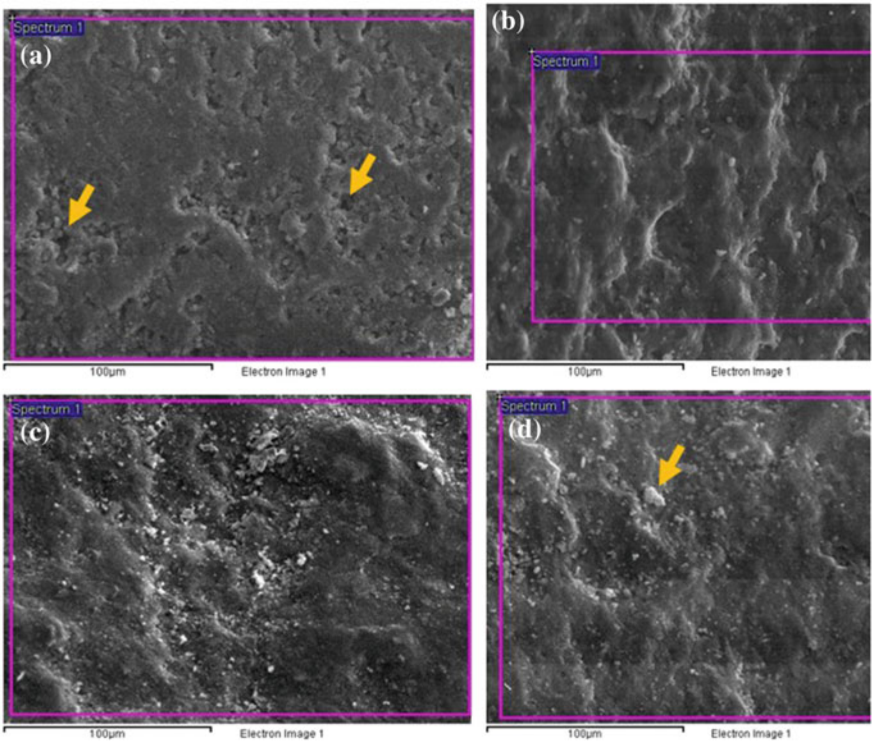

Fig. 4 Effect of NS content on microstructure (SEM), **a** OPC at 7 days, **b** 1.5% NS at 7 days, **c** OPC at 120 days, **d** 1.5% NS at 120 days [14]

Senff et al. [15] investigated the combination and individual effects of silica fume and Nano silica on the microstructure and strength properties. SEM results of the mortars tested in this research showed poor dispersion of solid particles within the microstructure when OPC mortar samples with no addition of silica fume or nano silica, Fig. 6a. The best particle distribution with the lowest pore size obtained was with the samples of 10.2% silica fume replacement plus 2% of Nano silica, Fig. 6b. However, with the addition of 3.5% pure Nano silica to OPC mortar, a discrete particle size distribution is noticed as shown in Fig. 6c. This kind of particle distribution was thought to enhance cement reactions in the fresh state and increase early age strength, however, the agglomeration effect of discrete particles is expected to have adverse influence on the strength in later ages. This was attributed to van der Waals forces and electrostatics that are expected to happen between the agglomerated Nano silica particles. The SEM was in agreement with the mechanical compressive strength results as shown in Fig. 7. Mortars with 10% Silica fume and 2% nano silica have given higher 90 day strengths than those of the individual Nano silica or Silica fume additions. Nano silica mortars showed better results for the early age strength (up to 7 days). Gupta [4] also stated that adding NS together with silica fume greatly improves the strength and durability of concrete.

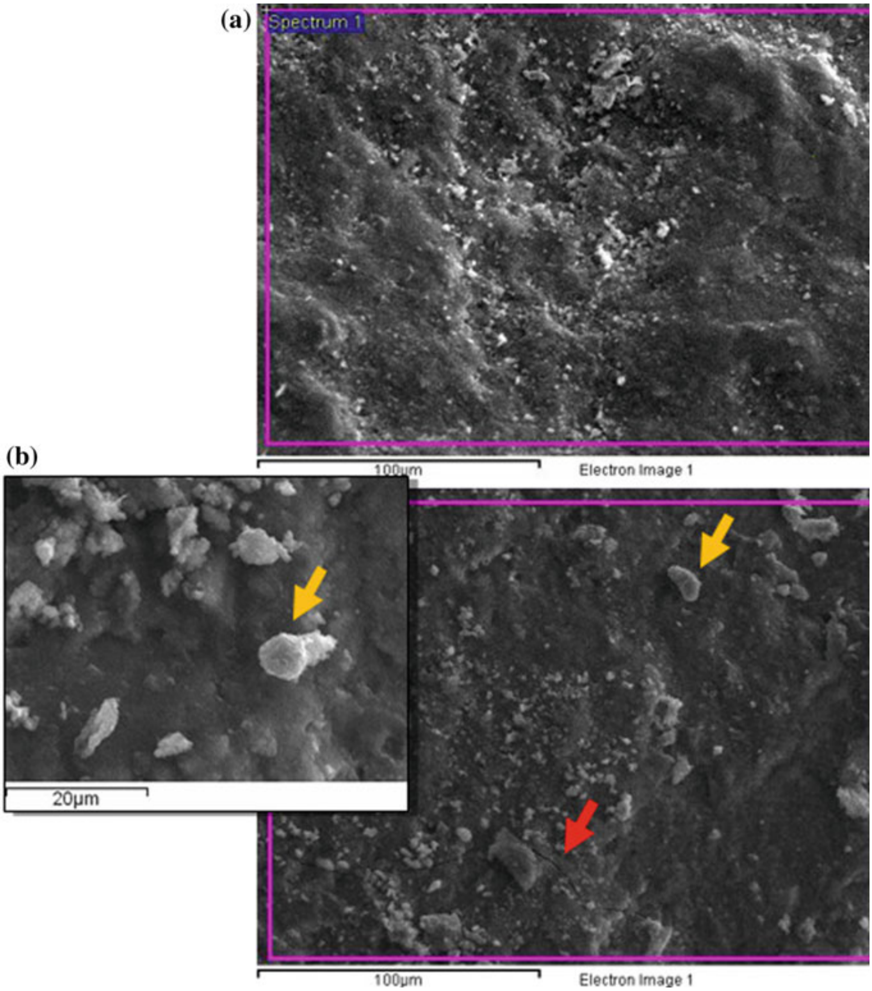

Fig. 5 Effect of NS content on microstructure (SEM), NS = 3%, **a** after 7 days, **b** after 120 days [14]

Li et al. [2] reported results of density enhancing behavior when 1% silica Nanoparticles were added to UHPC with 10% of fly ash and 20% of silica fume as shown in the SEM images of Fig. 8. Image in Fig. 8b with 1% NS shows that the main hydration product is the CSH gel. No calcium hydroxide crystal can be easily found in the 1% NS incorporated specimen, compared to image in Fig. 8a with no NS added which shows a high portion of CH crystalline phase.

El-Baky et al. [16] reported significant increase of as high as 55% of 28-day compressive strength caused by the addition of 7% Nano silicate to concrete. The strength improvement was attributed to the additional formation of C–S–H gel that

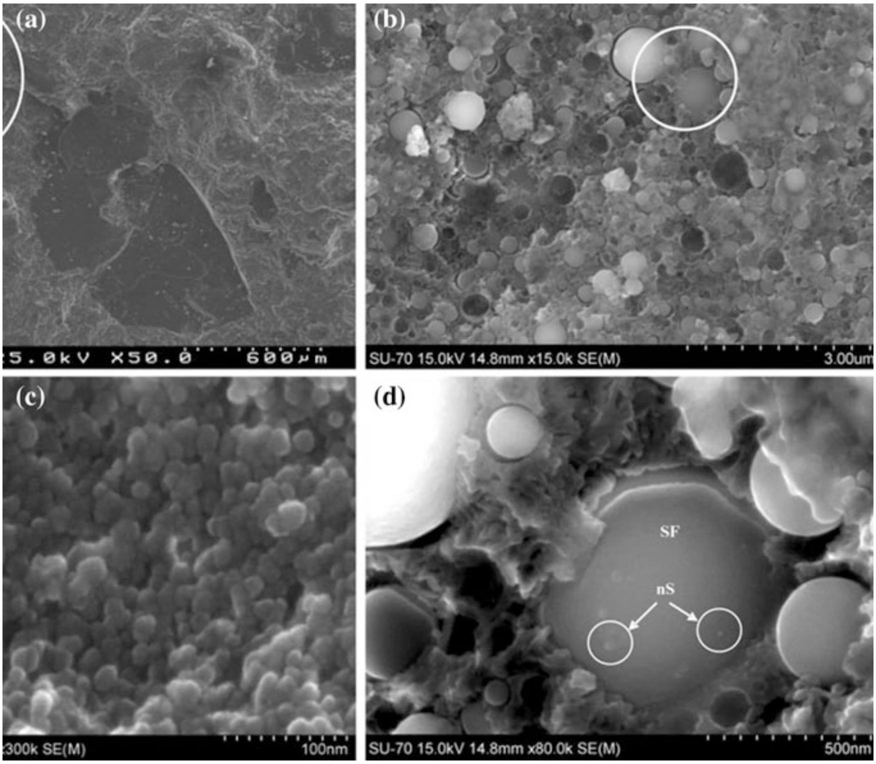

Fig. 6 Effect of NS, SF on microstructure of mortar (SEM), **a** OPC, **b** NS = 2%, SF = 10.2%, **c** NS = 3.5%, **d** magnified from (**a**) [15]

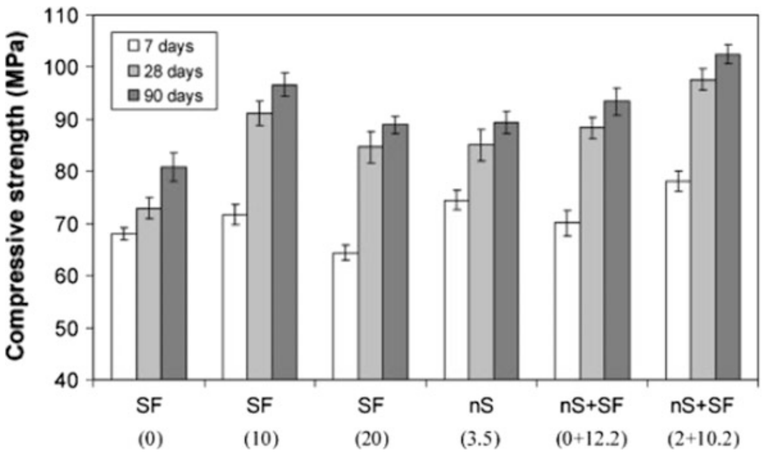

Fig. 7 Effect of NS and SF contents on compressive strength of a mortar [15]

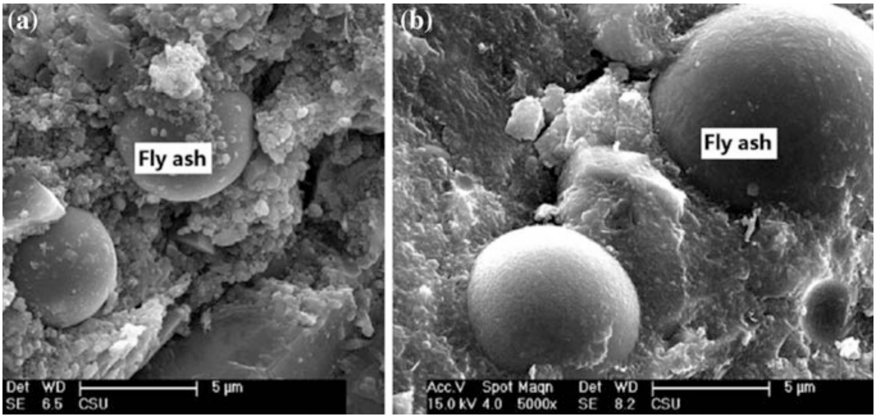

Fig. 8 Microstructure modification, **a** without NS, **b** with 1% NS to FA concrete [2]

fill the pores within the microstructure and the improvement to the Interfacial transition zone between the phases of aggregate and cement paste, as shown in the SEM images, Fig. 9.

Nano silica was found to be an effective measure to compensate for drop on strength development caused by the addition of fly ash to OPC in partial replacement [1].

Said et al. [17] investigated the effect of adding 1.5, 3 and 6% of Nano-Silica to OPC concrete both with and without the cement replacement of 30% with fly ash on the strength development for ages extending up to a year. Results which are shown in Fig. 10 indicated a considerable increase of up to 36% with both mix series when NS was added. The results strongly indicated the efficiency of adding these nanoparticles to improve the slow strength gain of fly ash concrete. The trend was attributed to the refinement in pore structure of the concrete caused by the pozzalanic reaction and filling behavior of these fine particles. Pore structure refinement was investigated using a Mercury intrusion technique. Figure 11 shows the results of MIP for the FA concrete, and similar trend was also reported for OPC concrete. A significant decrease of the pores in the range 0.01–0.1 µm can be noted. This range contains all the suggested threshold pore sizes that control the mechanical behavior as well as major durability effects of concrete.

The partial mass of $Ca(OH)_2$ was measured using a thermogravimetric technique. Results as shown in Fig. 12 revealed a significant drop of CH as a result of using 3% of Nano Silica while the increase of NS from 3 to 6% has resulted in almost similar CH percentages.

Similar promising results have been reported by Sankaranarayannan and Jagadesan [18] for compressive strength of concrete with high volume fly ash containing 50% FA as partial replacement of cement, when 1% of Nano-Silica was added. Strength improvements of as much as 44–46% at ages of 3 and 7 days and

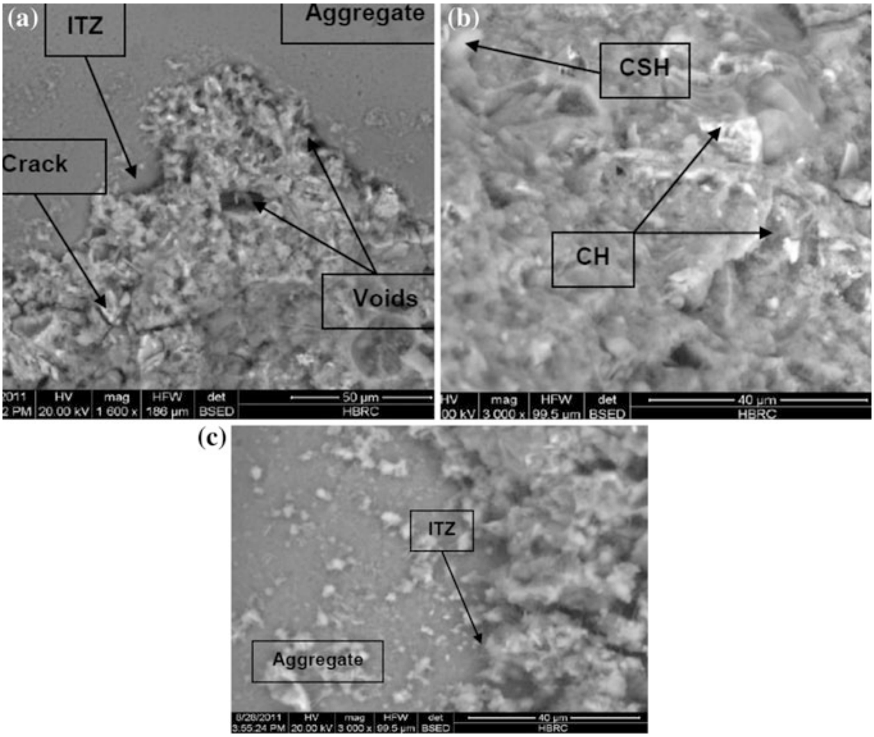

Fig. 9 Improvement of ITZ due the addition of 7% NS to mortar specimens, **a** conventional mortar for ITZ, **b** mortar with 7% NS, **c** mortar with 7% NS for ITZ [16]

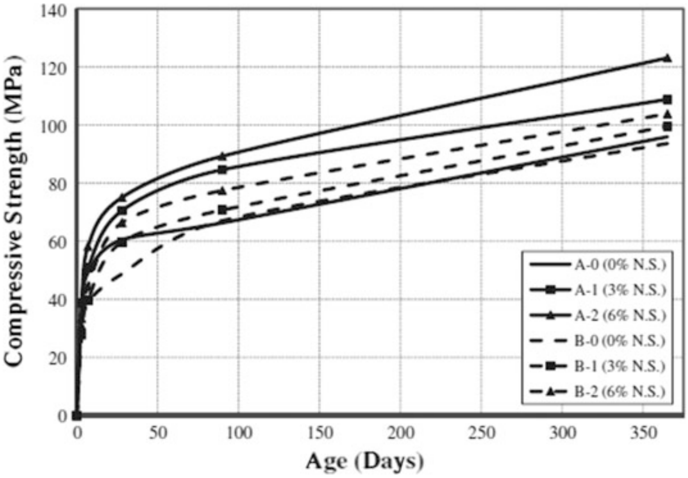

Fig. 10 Influence of nano-silica and fly ash on compressive strength [17]

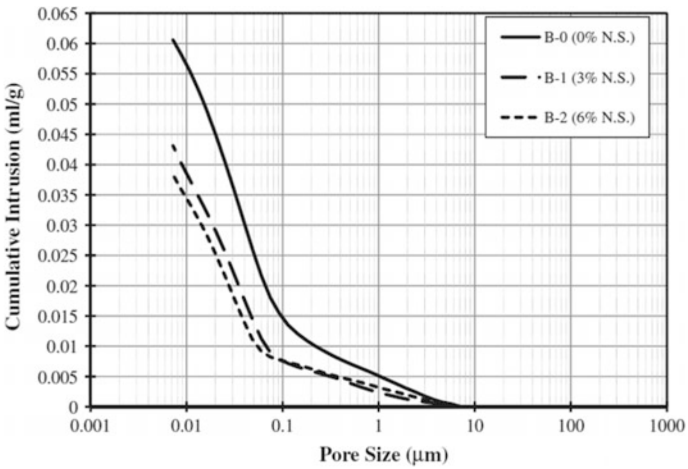

Fig. 11 Pore size distribution as affected by NS content for fly ash concrete [17]

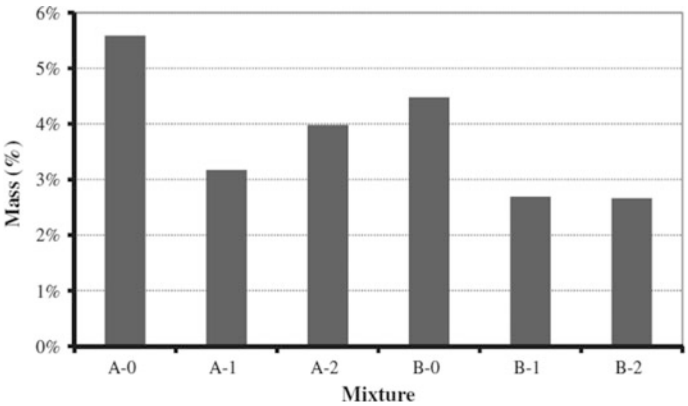

Fig. 12 TG analysis showing $Ca(OH)_2$ peaks for various OPC and FA mixes [17]

53% at an age of 28 days were obtained. Such results are of great significance in terms of sustainability as concrete with half quantity of cement can be produced maintaining adequate levels of strength.

The beneficial influences of using Nano silicate in HV fly ash pastes to reduce the amount of $Ca(OH)_2$ is well demonstrated in XRD results reported by Supit and Shaikh [9] as shown in Fig. 13b (with NS) when compared to Fig. 13a (without NS). The intensity count of the highest CH peaks of paste with (58% FA, 2% NS) went down below 6500 compared to about 5500 for paste with (40% FA, 0% NS). The same degree of reduction was also reported when NS was added to the paste with 40% FA. These results indicate that silica nanoparticles in HV fly ash system

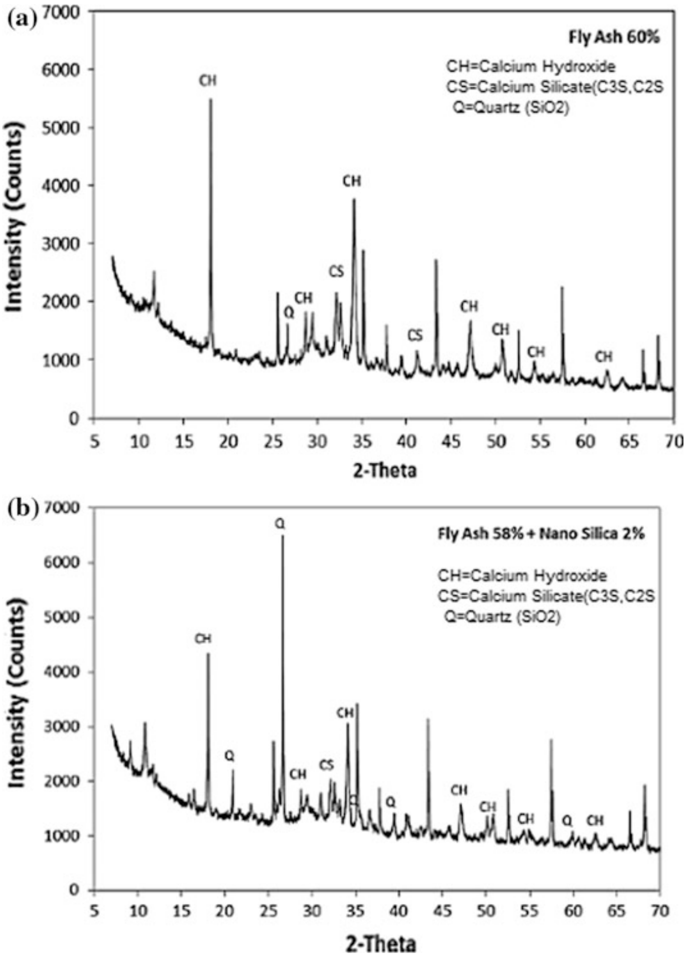

Fig. 13 XRD results for OPC and FA (40 and 60%) at 28 days [9]

contribute more to the pozzolanic reaction in early ages than FA due to their extremely small particle size distribution which produces high particles surface area.

4.2 Flexural Strength

El-Baky et al. [16] investigated the effect of Nano-Silica on the flexural strength of concrete. The bar chart shown in Fig. 14 compared flexural strength at ages of 3, 7 and 28 days as influenced by the addition of NS ranging from 1 to 10% of the

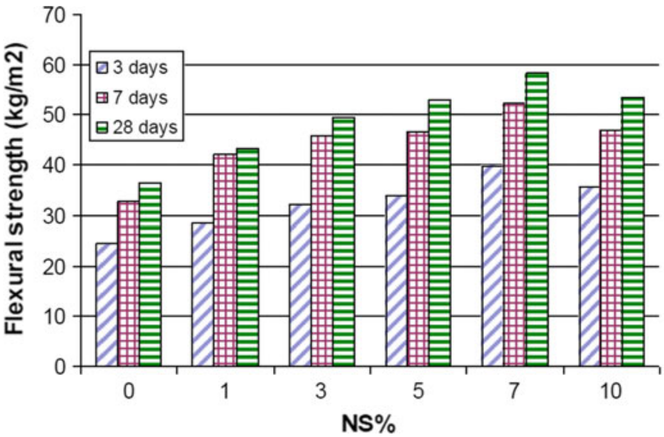

Fig. 14 Influence of nano-silica on concrete flexural strength [16]

cementitious material. The flexural strength increased considerably with the increased NS, with a percentage of 7% NS representing the optimum content that has given the maximum flexural strength. The behavior was attributed to increasing the improvement silica nanoparticles have caused to bond strength of cement paste aggregate interfacial zone.

A similar trend but with significantly lower range and optimum value has been reported for UHPC with the addition of silica fume and fly ash at 0.16 w/binder ratio and with superplasticizer. The flexural strength kept increasing with the increase of NS up to an optimum ratio of 1% beyond that it decreased slightly [12].

4.3 Tensile Strength

Kumar and Singh [19] reported a slight increase of splitting tensile strength as a result of 5% NS in OPC mortar. The tensile strength increased from 4.97 MPa at no NS mortar to 5.26 MPa with the 5% NS specimens.

In a local study carried out by Saleh et al. [20], Nano-silica was produced from silica sand taken from Al-Anbar area. Different contents of various sizes of NS were incorporated. Results of tensile strength showed slight increases, which were inconsistently dependent on NS content. The best tensile strength improvement was attained by mixture containing NS of 6% with particle size of 30–100 nm which has given a tensile strength of 2.65 MPa after 28 days of curing, compared to 2.2 of the reference no NS specimens.

5 Effect of Nano Silica on Durability Properties

5.1 Water Permeability

Concrete water permeability is expected to be lowered when silica nanoparticles are used. The pozzolanic reaction along with the filling role of these nanoparticles result in denser microstructure with relatively discontinuous pore structure that may limit the movement of water through concrete pore system.

Supit and Shaikh [9] reported more than 27% reduction of water absorption after 28 days and 90 days when 2% of Nano silica was added to OPC, 40 and 60% high volume fly ash replacement. Givi et al. [11] concluded that the application of NS resulted in denser concrete compared to normal no NS concrete, with greatly lower levels of permeability as measured by percentage, speed and coefficient of water absorption.

5.2 Sulfate Attack

Saloma et al. [21] reported considerable improvement of resistance to sulfate attack for concrete samples immersed in Na_2SO_4 solution for exposure period extending up to 180 days, when 10% of Nano silica was incorporated. The improvement was expressed as reductions in weight and strength loss upon the exposure, Fig. 15. The behavior was attributed to the reduction of permeability and the comparatively denser microstructure of concrete due to the filling action and pozzolanic activity that increased CSH gel phase when NS was used.

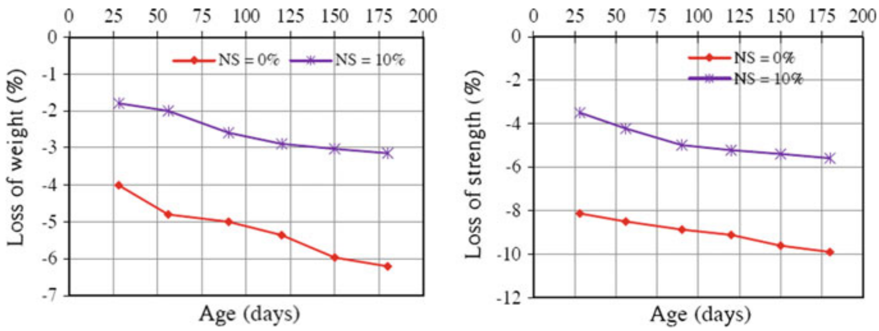

Fig. 15 Loss of weight, strength due to sulfate exposure as affected by NS addition [21]

5.3 Chloride Penetration Resistance

Resistance of concrete to the ingress of chloride ions is an essential durability requirement to reduce the possibility of reinforcement corrosion. The presence of chloride ions with sufficient content in the vicinity of steel bars is the main reason of steel corrosion in concrete. Due to the improvement they achieve to concrete microstructure, and specifically because the continuity of the pore system can effectively be disconnected, nanoparticles are expected to improve chloride penetration resistance.

Kong et al. [22] reported reductions in rapid chloride penetration depths of 31.3% and 20.3% after 28 days and 180 days respectively when adding 1% of NS to OPC mortars, compared to the reference 0% NS specimens. Said et al. [17] obtained remarkable improvement of chloride impermeability using a small dosage of silica nanoparticles 3% added to both OPC and OPC with 30% fly ash concretes.

6 Conclusions

1. Fresh concrete workability and setting time are reduced as the ratio of NS is increased in concrete. Though these are generally regarded as negative influences with OPC concrete, accelerating the setting is found beneficial for HV fly ash and HV slag concretes.
2. The incorporation of NS results in the refinement of the pore structure of concrete and improving the ITZ. These are thought to be the most significant two factors responsible of enhancing concrete properties by NS addition.
3. Concrete compressive strength is generally improved with the inclusion of NS in dosages up to 6% of cementitious material. Strength improvement is the most significant when NS is used with high volume fly ash or slag concretes.
4. Denser and more homogeneous microstructure with more strength enhancement can be obtained when using a mixture of SF with NS than using any of the two materials individually.
5. Flexural strength increases with the increased dosage of NS. There exists an optimum level of NS that may achieve the maximum flexural strength. The value of this optimum content might vary widely from 1 to 7% depending on mixture ingredients and proportions.
6. Tensile strength is slightly enhanced by the use of NS. This improvement increases inconsistently with the increase of NS content.
7. NS reduces both water and chloride permeability of concrete due to its filling action and pozzolanic reactivity that result in the formation of more amount of gel which refines concrete pore structure.
8. NS enhances the protection against corrosion of reinforcement by significantly limiting chloride ion ingress with small levels of NS content that does not exceed 3% of cementitious material.

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