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Influential Mechanisms and Potential Applications of Nano-Silicas in Cement Composites

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ABSTRACT: Nanosilicas have been known as super-pozzolanic materials and compared to silica fume, these materials have higher purity of silica and finer particles. However, in contrast to silica fume, nanosilicas are produced by various methods, leading to different morphologies and agglomeration statuses in their initial form. On the other hand, due to several mechanisms such as the bridging effect of calcium ions between particles, double layer compression at a high ionic concentration, and dehydration of silica surfaces, nanosilica particles are destabilized in the pore solution environment of cement mixtures. Thus, the behavior of these materials is different from that of silica fume. In this research, considering the recent studies, a comprehensive investigation has been carried out on the influence of nanosilicas on the mechanical, durability and microstructural characteristics of cement composites. This study investigates the mechanisms that influence the performance of nanosilica in cement-based materials. Based on these mechanisms, several applications have been suggested and discussed. Some of these applications include viscosity-modifying agent in self-compacting concrete, enhancing the cohesion of cement composites, increasing the adhesion capacity of repair mortars and shotcrete to the substrate surface, accelerating the cement hydration, developing low-alkali cements and fast early-strength cements.

Keywords: Application, Cement Composites, Mechanism, Microstructure, Nanosilica.

INTRODUCTION

Pozzolans have been utilized for many years as supplementary cementitious materials in concrete in order to provide technical or economic benefits (Askarinejad, 2017). Among the pozzolans, silica fume which is an ultrafine material with submicron particles, has found widespread applications in enhancing the mechanical and durability characteristics of cement mixtures.

Considering the developments in nanoscience, different types of nano-size amorphous silica have become available. The faster rate of the pozzolanic reactivity of nanosilica compared to silica fume, which is mainly a result of its high surface area and high purity of silica, is believed to be the main advantage of this material. In Figure 1, a comparison has been made between the size distribution of a nanosilica material and silica fume.

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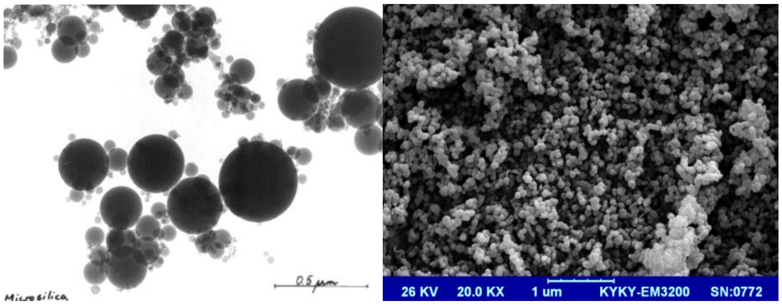


(a) (b)

Fig. 1. Dimensions of particles of: a) Silica fume (ACI 234) compared to, b) Nanosilica material

When ultra-fine particles are incorporated into cement composites, materials with improved characteristics may be obtained (Madani et al., 2016, 2014, 2012; Sanchez and Sobolev, 2010 ; Collepardi et al., 2004). However, contradictory results have been reported in several studies on the effect of nanosilicas on the characteristics of cement mixtures, especially mechanical properties. Some results indicated the significant influence of nanosilica materials on the enhancement of mechanical characteristics of cement composites (Shih et al., 2006; Chandra and Maiti, 1998), where some others reported negligible effect (Senff et al., 2012) and even lower compressive strengths (Ji, 2005; Ltifi et al., 2011) compared to plain mixtures. As a matter of fact, there are differences between the morphologies and dimensions of nanosilicas; moreover, the behavior of these materials in cement composites should be considered.

One of the challenges of using nanosilica in cement composites is its price and availability in certain countries. Despite the high price of nanosilica, it could have wide applications especially in dry and repair mortars. In utilization of nanosilicas, safety tips must be considered. However, in several researches it has been notified that synthetic amorphous silicas have not significant adverse health effects (Napierska et al., 2010; Merget et al., 2002; Lee and Kelly, 1992). It must be noted that high dosages of amorphous silica may cause some problems. The safety tips of the use of nanosilica should be considered: Inhalation of nanosilica should be avoided, because this material may cause lung problems. Moreover, nanosilicas should not contact with eyes or have long term exposure to skin.

This paper aims at investigating the properties of nanosilicas, their general classification, the effective mechanisms which influence their behavior in cement composites, and their potential applications in cement-based materials.

CLASSIFICATION OF NANO SILICAS

Nanosilica is a general term which includes a variety of types such as nanosilica sol, pyrogenic nanosilica, precipitated nanosilica, nanosilica gel, mesoporous silica, and hollow nanosilica. These materials are also produced with various specific surface areas (SSA) from about 50 m^2/g up to 1000 m^2/g. Unfortunately, the surface areas and types of nanosilica have not been considered appreciably in the investigations of cement-based materials. For instance, in many studies such as (Brinkmann et al., 2006; Korpa et al., 2008b; Jo et al., 2007b; Richard and Cheyrezy, 1994; Agarwal, 2006; Wang et al., 2008) the type of nanosilica or its surface area has not been reported.

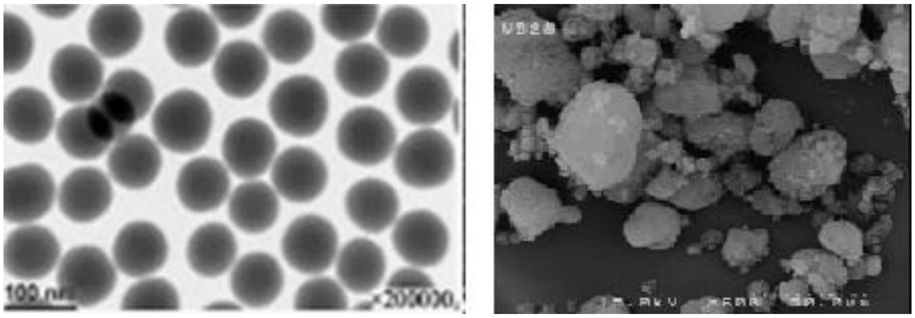
Nanosilica sols are commonly produced through the polymerization of silicic acid in the aqueous environment. They are mostly in the form of monodispersed particles. The influence of nanosilica sols on the properties of cement mixtures has been investigated in several studies (Bagheri et al., 2013a; Madani et al., 2012; Porro et al., 2005; Björnström et al., 2004; Gaitero et al., 2008; Dolado et al., 2007; Green, 2008). The monodispersed dispersion of particles of silica hydrosols is represented in Figure 2a.

Pyrogenic nanosilica is produced through a reaction between hydrogen, silicon tetrachloride, and oxygen in a high-temperature furnace (Brinkmann et al., 2006). In contrast to nanosilica sols, pyrogenic nanosilica is composed of large agglomerates with dimensions from one µm up to a few hundred µm (Bagheri et al., 2013a). Pyrogenic nanosilica aggregates also have a porous structure (Korpa et al., 2008b; Kurdowski and Wczelik, 1983; Korpa et al., 2008a). An agglomerate of this material is shown in Figure 2b.

Nanosilica gel is prepared by the sol-gel method. During preparation, first a stable sol is formed. Then, through the gelation process, the particles are coalesced to each other and create an interconnected network known as gel. According to the method of drying, two products can be obtained; if the entrapped water is released in such a way that the total volume of the gel would not decrease significantly, aerogel is produced; and if the gel sustains a significant contraction in the evaporation process, xerogel is formed. Furthermore, silica gel powder can be created with different aggregate sizes by milling (Schick and Hubbard, 2006; Bergna, 1994; Brinker and Scherer, 2013). The nanosilica gel has been investigated in several studies of cement composites such as (Kim et al., 2013; Sobolev et al., 2006). In Figure 3a, the interconnected structure of nanosilica gel is presented.

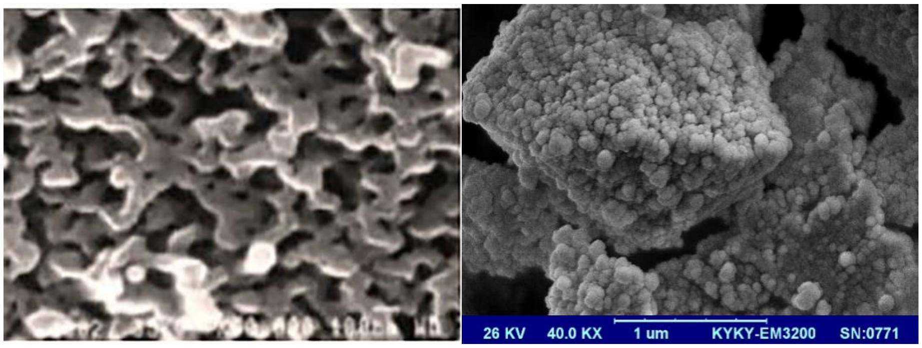
Precipitated nanosilica is produced through a reaction between mineral acids such as sulfuric acid and alkali silicates such as sodium silicate (Schick and Hubbard, 2006; Patterson, 1994) . In the process of production, the nanoparticles are formed in the aqueous medium, followed by destabilization and precipitation of silica particles in the form of agglomerates. Then, the products are dried by heating, and are eventually milled. In the production process of precipitated nanosilicas, large agglomerates with sizes from a few µm to a few hundred µmare formed (Bergna, 1994). As shown in Figure 3b, in contrast to the porous structure of pyrogenic nanosilica agglomerates, precipitated nanosilica agglomerates have a dense structure. Precipitated silica has been investigated in some studies of cement-based materials such as (Richard and Cheyrezy, 1994; Agarwal, 2006; Anderson et al., 2000; Rao, 2003; Bastien et al.,1997).

Hollow nanosilica could be produced by several methods. For instance, the following method can be presented (Gao et al., 2013): Monodisperse polystyrene (PS) nanosphere could be utilized as a template for the growth of silica coatings. Then, poly Vinyl Pyrrolidone (PVP) solution is added to the styrene solution and heated. Afterwards, potassium persulfate (KPS) solution is added to initiate the polymerization reaction. Dissolved NH_4OH in ethanol and tetraethyl orthosilicate (TEOS) is slowly added to them, reacting in the aqueous medium. Using the centrifugation technique, the solid material is separated from the mother solution. Afterwards, the sediment is washed with ethanol and is ultimately dried. The TEM image of the product has been shown in Figure 4. So far, experimental investigations have used hollow silica nanospheres (HSNS) to improve thermal insulation and energy efficiency in structures (Jelle et al., 2012; Gao et al., 2012; Sandberg et al., 2013; Grandcolas et al., 2013; Jelle et al., 2013, 2014; Gao et al., 2012). However, there are few studies on the use of these materials in concrete.



(a) (b)

Fig. 2. Agglomeration state; a) Sol of nanosilica (HyungMi et al., 2010), b) Pyrogenic nanosilica



(a) (b)

Fig. 3. Agglomeration state; a) Gel of nanosilica, b) Precipitated nanosilica

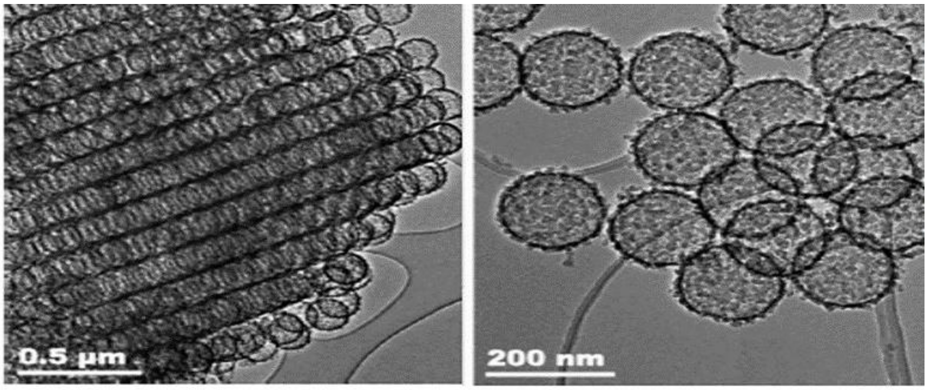


Fig. 4. TEM images of hollow nanosilica particles (Gao et al., 2013)

NANOSILICA BEHAVIOR AND ITS INFLUENTIAL MECHANISMS ON THE CHARACTERISTICS OF CEMENT MIXTURES

The Influence of Pore Solution Environment of Cement-Based Materials on the Stability of Nanosilica Particles

The pore solution ionic composition of cement-based materials is quite different from the ionic composition of nanosilica materials. In the first minutes of cement hydration, large amounts of different ions with different capacities are dissolved into the pore water. For example, in the initial minutes of cement hydration, due to the dissolution of alkali compounds, potassium and sodium ions are very quickly released in the pore space.

Calcium ions are liberated in the liquid phase due to the hydration of tri-calcium silicate, di-calcium silicate, and aluminate phases and the free lime dissolution. The ionic composition can strongly affect the primary size distribution of nanosilica particles. In the following section, the mechanisms which can lead to the instability of silica nanoparticles in the concrete pore solution are presented. Nanosilica has a hydrophilic structure and, therefore, a layer of water is strongly adsorbed on the surface of particles owing to the hydrogen connections between water molecules and surface silanols. This layer of water molecules acts as a steric coating, so the particles of nanosilica sols are kept apart from each other and do not form aggregates. It is interesting that despite the lack of electrostatic repulsion between the particles of nanosilica sols at their isoelectric point (PH = 2.5-3), the particles are mainly monodispersed due to the repulsive forces of the adsorbed water layers (Amiri et al., 2009; Allen and Matijević, 1969; Chen et al., 2007). This mechanism is true for the nanosilica sols. A schematic representation of water molecules' adsorption on the surface of silica particles is depicted in Figure 5.

Some researchers have tried to modify the theory of DLVO. The DLVO is taken from the first letter of names of four scientists, Derjaguin, Landau, Verwey, and Overbeek. DLVO is the explanation of the stability of colloidal suspension and describes the balance between two forces, electrostatic repulsion and van der Waals attraction by adding a term considering the effect of hydration forces. An increase of the alkalinity of the ambiance will promote the decomposition of surface silanol groups (Eq. (1)), as represented in Figure 6. The decomposition of silanol groups leads to the release of the water which has already been adsorbed on the surfaces of particles. In an environment like the pore solution of concrete with pH values higher than 12, all surface silanol groups are decomposed, and thus the surface hydrate layer disappears (Madani et al., 2012; Depasse, 1997) .

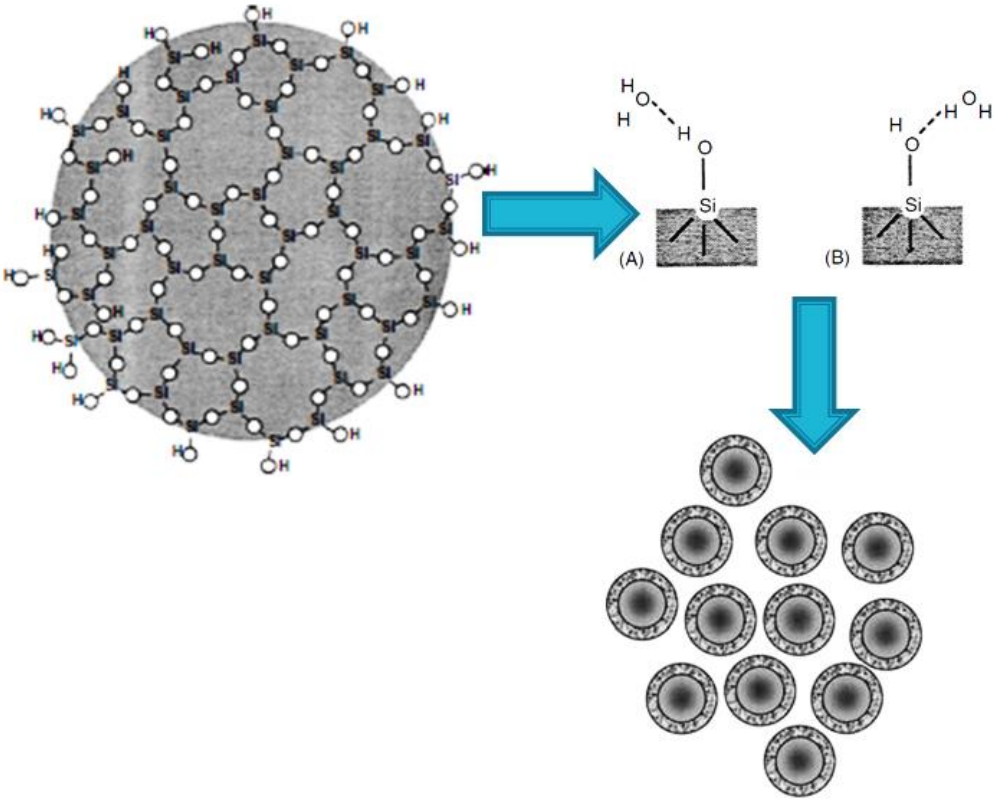


Fig. 5. Adsorption of water molecules on the surface of nanosilica

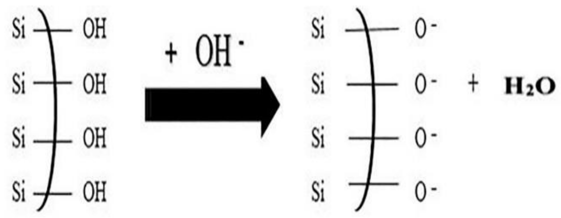


Fig. 6. The decomposition of surface silanol groups due to high alkalinity

By eliminating the surface hydrate layer, the repulsive hydration forces disappear due to the high alkaline environment, and the electrostatic forces will be the main reason of silica nanoparticles stability in the pore solution of concrete. However, the values of these forces depend on the thickness of the double layer. A schematic representation of the double layer is depicted in Figure 7. The thicker double layer leads to stronger and more effective electrostatic forces. Double layer thickness (1/k) is attributed to the concentration of ions in the environment (c) and their capacities (z) by the following relationship:

$$K = 0.329\times10^{10}\left(cz^{2}\right)^{0.5} \qquad (1)$$

The high concentration of ions in the concrete pore solution environment leads to a compacted double layer. Therefore, the influence of this layer in keeping the particles apart from each other is reduced (Chen et al., 2007; Depasse, 1997; Rahaman and Rahaman, 2006; Ravina and Moramarco, 1993). In other words, by reducing the thickness of the double layer, the van der Waals attractive forces are dominant and, thus, the particles are absorbed by one another. Figure 7 illustrates a double layer compaction and zeta potential reduction due to increasing the concentration of ions in the ambiance.

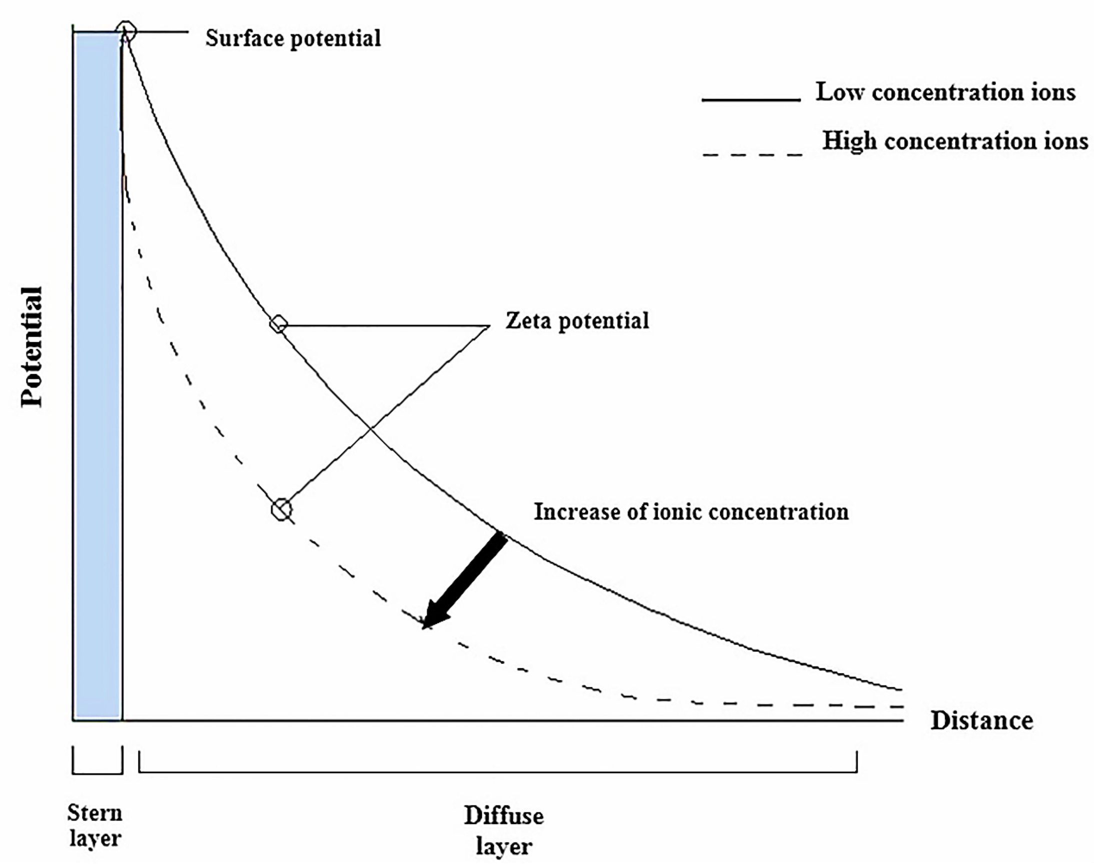


Fig. 7. Compression of double layer in environments with high ionic concentrations

Another mechanism which leads to silica nanoparticles' agglomeration in the pore space of concrete is the bridging effect of calcium ions (Madani et al., 2012). Calcium ions have two capacities, and can thus create bridges between nanosilica particles by sharing each positive charge with a nanosilica particle, as indicated in Eq. (2) (Iler, 1975; Zerrouk et al., 1990).

$$\begin{aligned} &SiO^{-} + Ca^{2+} + {}^{-}OSi \\ &\longrightarrow SiO^{-+}Ca^{+-}OSi \end{aligned} \tag{2}$$

The bridging effect of calcium ions appears to be the most important reason of the coagulation of silica particles in the Pore solution. On the other hand, absorption of calcium ions on the negative surface of nanosilica particles reduces the negative surface charge, which results in reduction of electrostatic force between particles and promotion of the agglomeration status. It is worth noting that before the beginning of the induction period, calcium ions reach to the saturation level , and this amount of calcium ions may be enough to create agglomerates (Iler, 1975).

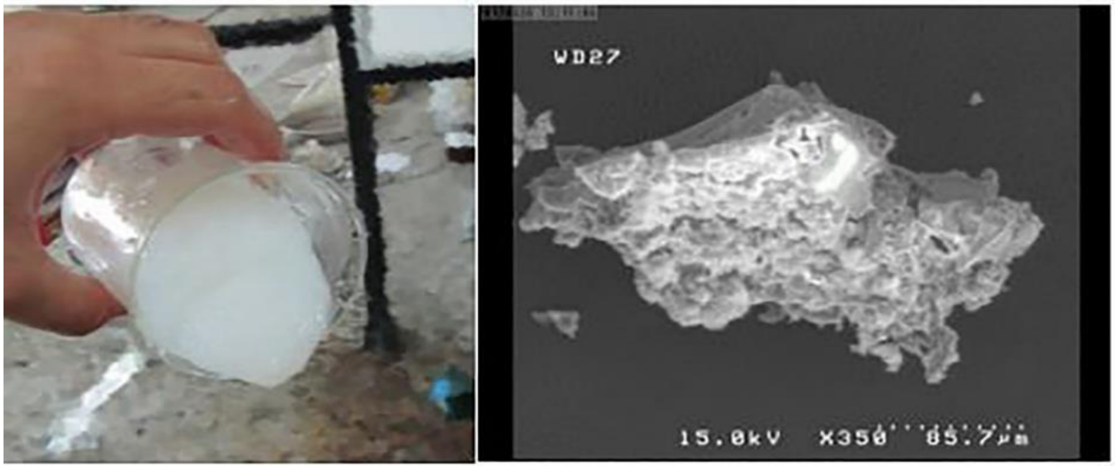
To illustrate the bridging effect, calcium ions were added to a silica sol with a specific surface area of 100 m^2/g by about 0.8% weight of nanosilica. In Figure 8, the agglomeration state of this material after addition of calcium ions is presented.

The Mechanisms by Which Nanosilica Influences the Properties of Cement Composites

Pozzolanic Reaction of Nanosilica

The studies (Madani et al., 2012; Madani and Bagheri, 2012) emphasize that the type and size of nanoparticles are significant factors on the rate of pozzolanic reactions. These results show that the pozzolanic reaction rate of nanosilica is enhanced at higher specific surface areas. For example, the pozzolanic reaction of a nanosilica sol with the SSA of 300 m^2/g in 3.5 h is equivalent to the pozzolanic reaction of a nanosilica sol with the SSA of 200 m^2/g in 24 h, a silica sol with the SSA of 100 m^2/g in 176 h, and a high-quality silica fume in 28 days.

The type of nanosilica is an important factor in its reactivity. For instance, regarding the monodispersed status of the nanosilicasol and the initial large agglomerates of the pyrogenic nanosilica, it may be anticipated that the pozzolanic reaction of the nanosilica sol should be higher than that of the pyrogenic nanosilica.



a) b)

Fig. 8. Coagulation of a nanosilica sol after the addition of calcium ions; a) nanosilica sol Coagulation, b) SEM image of Coagulation of nanosilica sol

However, it has been reported (Madani and Bagheri, 2012) that the rate of the pozzolanic reactivity of a nanosilicasol is significantly lower than that of the pyrogenic nanosilica with similar specific surface area.This result may have been due to the considerable coagulation of nanosilica sols in the cement paste environment.

Reduction of Dormant Period and the Initial Setting Time

The majority of studies emphasize that nanosilica could decrease the initial setting time in cement paste. This means that nanosilica has a shortening effect on the cement dormant (induction) period of cement paste (Bolhassani and Samani, 2015; Bagheri et al., 2013b; Pourjavadi et al., 2012; Ltifi et al., 2011; Qing et al., 2007; Lin et al., 2008; Singh et al., 2011, 2012a,b; Schwarz et al., 2007; Barnes and Bensted, 2002). In the following paragraph, the mechanisms which nanosilica influence the induction period in cement paste are expressed.

Minutes after the initiation of cement hydration, a layer of metastable CSH is formed on the surface of cement particles. This layer prevents the dissolution of cement particles in the pore space and delays hydration (Barnes and Bensted, 2002; Gartner and Jennings, 1987; Hewlett, 2003). When the metastable form of CSH is converted to the permeable CSH on the surface of cement, the induction period is terminated. Some researchers believe that the reason for the conversion of metastable CSH into the stable form of CSH at the end of the induction period is reduction in the amount of calcium and hydroxyl ions in the concrete pore space due to the creation of portlandite crystals (Barnes and Bensted, 2002).

As seen in previous sections, nanosilica, and especially those with high surface areas, have a high rate of pozzolanic reactivity at early ages. Due to the considerable pozzolanic activity, these substances can reduce calcium ion concentration, and thus accelerate the dormant period of cement hydration. Increasing the surface area and the percentage of these materials can lead to faster removal of calcium ions in the pore space, resulting in the shortening of induction periods of cement composites.

Enhancing the Rate of Cement Hydration

The results of several investigations indicate that nanosilica has an accelerating effect on the degree of cement hydration at early ages (Hou et al., 2013; Senff et al., 2009; Land and Stephan, 2012; Heikal et al., 2013; Jo et al., 2007a; Aleem et al., 2014), but this process is decreased at later ages. The reduction of the induction period due to the significant pozzolanic reaction of nanosilica and provision of a surface to precipitate cement hydration products cause the acceleration of the cement hydration at early ages (Land and Stephan, 2012) .

It is believed that the long-term reduction of cement hydration degree is due to the absorption of water in the structure of agglomerates (Madani et al., 2012). Amorphous silica particles have a significant influence on the process of C_3S hydration (Björnström et al., 2004).

The Mechanism by Which Nano Silica Influences the Workability Characteristics of Cement Composites

One of the most well-known effects of nanosilica materials on the characteristics of cement composites is the flow ability reduction (Ltifi et al., 2011; Khaloo et al., 2016; Bolhassani and Samani, 2015; Bahadori and Hosseini, 2012; Quercia et al., 2012; Liu et al., 2015; Stefanidou and Papayianni, 2012). Some studies claim that absorbing a significant amount of water on the high surface areas of nanosilica particles could lead to decreased fluidity. However, this assumption is confronted by serious problems. As mentioned earlier, nanosilica in the highly alkaline environments such as concrete not only does not adsorb water on the surface, but also releases a hydrate layer. Hence, this assumption may not be true.

The significant water-absorbtion in the agglomerated structure of nanosilica in the cement pore solution is the principal reason for decreasing flow ability. Nanoparticles are destabilized in the pore solution and create a gel-like structure in the cement matrix. The schematic representation of nanosilica coagulation in concrete pore solution is shown in Figure 9. This structure significantly increases the cohesion of cement matrix and reduces its fluidity. Nanosilica could reduce bleeding water and may improve the mixture cohesiveness in the fresh state (Collepardi et al., 2002). Adding nanosilica to the cement paste leads to an increase in cohesion, plastic viscosity, and yield stress (Ghafari et al., 2014; Pourjavadi et al., 2012).

Durability Characteristics of Cement-Based Materials

It is well established that the pozzolanic reactions result in improving the durability characteristics of cement composites (Taylor, 1997). Due to their high rate of pozzolanic reactivity, nanosilica materials can significantly enhance the microstructure and reduce the permeability of cement-based materials. For instance, the addition of nanosilica could reduce the pore connectivity (Belkowitz et al., 2015) and could increase the pore refining in cement mixtures (Hou et al., 2013).

In contrast to silica fume, a significant portion of nanosilica pozzolanic reactions occurs at very early ages. Therefore, these materials improve the microstructure at early ages. However, the microstructure is not well formed. The fast pozzolanic reaction cannot improve the microstructure compared to the pozzolanic reactions at the longer ages. The investigations (Bolhassani and Samani, 2015) also indicate that coarser nanosilicas have improved chloride permeability and electrical resistance compared to smaller ones in 28 and 90 days. It is interesting that silica fume may outperform nanosilica materials in enhancing the microstructure of concrete mixtures.

Although some studies suggest that the nanosilica is not as effective as silica fume in improving the long-term microstructure of concrete, the very fast pozzolanic reactivity of nanosilicas could provide a good opportunity for these materials because they can significantly improve the diffusivity of concrete when the mixture is subjected to a severe environment at early ages. For instance, in 7 days, a nanosilica hydrosol with the SSA of 100 m^2/g can enhance the chloride diffusivity of concrete; however, silica fume has no influence on durability (Madani et al., 2014).

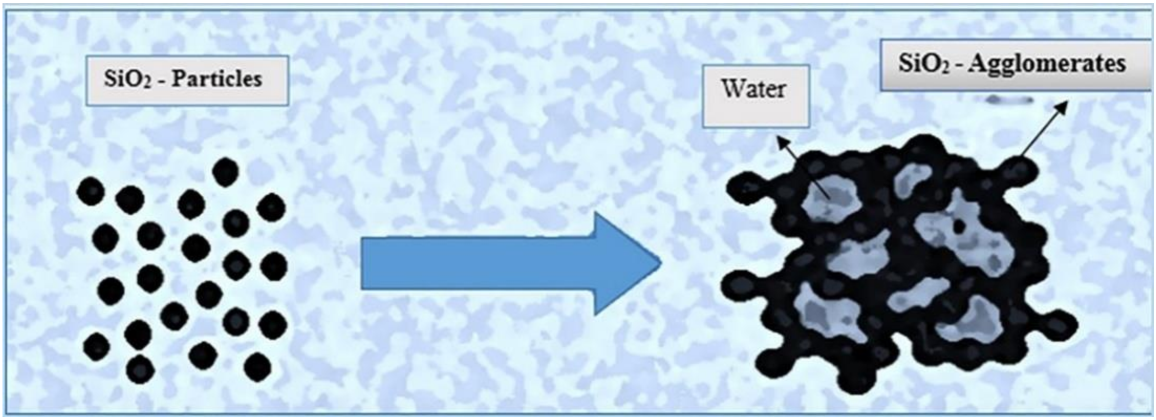


Fig. 9. Absorption of water in the nanosilica coagulates in the pore space of cement mixtures

The study (Schwarz et al., 2007) used electrical conductivities as a function of time to identify the different stages of the development of microstructure of the pastes. The results show densification of microstructure at early ages, which can also be observed from the compressive strength results.

Investigations show that the use of nanosilica in concrete mixtures leads to an improvement in water absorption, capillary absorption, and water permeability compared to the plain concrete (Belkowitz et al., 2015; Bahadori and Hosseini, 2012; Cardenas and Struble, 2006; Said et al., 2012; Givi et al., 2011; Li et al., 2004; Zhang and Li, 2011). Experiments revealed that use of nanosilica may modify cement paste microstructure when subjected to calcium leaching (Jain and Neithalath, 2009). In other words, adding nanosilica caused a reduction in mass loss and enhanced the microstructure tortuosity as compared with the plain paste. When specimens were exposed to leaching, the pastes containing nanosilica had a higher resistance against calcium leaching (Jain and Neithalath, 2009).

Evaluating the performance of nanosilica in the ultra-high performance concrete (UHPC) indicates that compared with silica fume, nanosilica could consume much more calcium hydroxide, particularly at early ages. MIP measurements also show that the inclusion of nanosilica material could lead to capillary pores' reduction and results in lower sorptivity and water absorption compared to the plain mixture. It is also suggested that the addition of nanosilica to UHPC can significantly enhance the microstructure of the interfacial transition zone (ITZ) between cement paste and aggregate (Ghafari et al., 2014).

The Effect of Nanosilica on the Mechanical Characteristics of Cement Mixtures

Investigations show that nanosilica materials have an accelerating influence on the mechanical characteristics of cement composites. Improving the mechanical properties at early ages is mainly attributed to the acceleration of cement hydration (Madani et al., 2012; Ghafari, et al., 2015b; Sanchez and Sobolev, 2010; Korpa et al., 2008b; Jo et al., 2007b; Khaloo et al., 2016; Heikal et al., 2013; Aleem et al. 2014), increase in the degree of polymerization of CSH gel, and rapid pozzolanic reactions (Madani et al., 2012; Korpa et al., 2008 ; Agarwal, 2006; Madani and Bagheri, 2012; Singh et al., 2013). However, as age increases, the effect of this material on improving the mechanical properties may be lower compared to the plain mixture.

Some references have reported that the mixtures with nanosilica may have higher flexural and compressive strengths at early ages compared to the plain mixes in cement pastes (Qing et al., 2007; Stefanidou and Papayianni, 2012), cement mortars (Li et al., 2004), and concrete (Givi et al., 2010) . It should be noted that flexural strengths have not been determined at early ages, and further studies are required on this subject. Adding nanosilica to the cement paste can also improve the modulus of elasticity to higher than 20% compared to the plain mixtures (Belkowitz et al., 2015; Mondal et al., 2010).

The highest mechanical properties are obtained at an optimum level of nanosilica. However, in studies, different optimum contents have been reported. It appears that the type and surface area of nanosilica are significant factors which influence their optimum level in cement composites (Bolhassani and Samani, 2015; Liu et al., 2015; Nazari and Riahi, 2011). It has also been shown that the concrete mixes with nano-SiO_2 have higher abrasion resistance compared to the plain mixtures (Li et al., 2006).

THE APPLICATIONS OF NANOSILICAS IN CEMENT COMPOSITES

Viscosity-Modifying Agents (VMA) in Self-Compacting Concrete, Grouts, and Slurries

Self-compacting concrete (SCC) is characterized by three main properties: stability, segregation resistance, and flow ability. The flow ability can be obtained by utilizing suitable super plasticizers; however, segregation resistance and stability should be provided by adjusting the paste volume and VMA compounds. The nanosilica can act as a VMA in SCC and similar highly flowable mixtures such as grouts and slurries. As mentioned previously, nanosilica materials lose their stability in cement environments and form a gel-like structure. Thus, these materials can enhance the viscosity of cement paste and, consequently, provide a higher resistance against aggregate segregation. The studies (Collepardi et al., 2002; Güneyisiet al., 2015) indicates that using nanosilica in SCC can provide a more cohesive and viscous mixture. Hence, these materials can improve the stability and segregation resistance of concrete. However, the use of nanosilica leads to a lower slump flow value in SCC (Singh et al. 2013; Güneyisiet al., 2015). The use of nanosilica also has a significant influence on enhancing the rheological parameters of grouts as indicated in the tests of mini-slump, plate cohesion meter, plastic viscosity, and yield stress (Belkowitzet al., 2015; Sonebi et al., 2015).

Use of Nanosilica in High Strength, UHPC and Highly Durable Concretes

UHPC is a revolutionary type of concrete developed in the past decade. This type of concrete commonly has compressive strengths higher than 150MPa. High-strength concrete also has compressive strengths higher than 60 MPa. As it has been previously mentioned, use of nanosilica in UHPC may lead to lower contents of capillary porosity and consequently lower sorptivity and water absorption compared to the plain concrete. The mechanical properties of UHPC mixtures may improve with increase in nanosilica content, especially at early ages.(Ghafari et al., 2014; Ghafari et al., 2015b; Norhasri et al., 2017).

The investigation (Mobini et al., 2015) demonstrated that using nanosilica can improve the mechanical and durability of fiber reinforced high-performance concrete (FRHPC). This study has also shown that the enhancement of mechanical properties due to using nanosilica may be attributed to the densification of cement matrix.

The studies (Yu et al., 2014; Norhasri et al., 2017) revealed that the retarding effect of some types of super plasticizers especially at high levels of utilization on the dormant period and setting time of UHPC mixtures could be compensated by the accelerating effect of nanosilica materials. It was also shown that the sustainable high-performance concretes containing nanosilica have high durability characteristics which may lead to lower repair and maintenance costs.

The results reported by (Ghafari et al., 2015a) indicate that the incorporation of nanosilica can significantly increase the polarization resistance of steel bars embedded in UHPC as a result of reduced rate of steel bars corrosion. The research (Bastami et al., 2014) has shown that high strength concrete mixtures with nanosilica have higher mechanical characteristics when subjected to high temperatures.

Use of Nanosilica in Lightweight Concrete Mixtures

A number of studies show that utilizing nanosilica can remarkably improve the segregation resistance of lightweight aggregate concretes (LWAC). Furthermore, nanosilica could improve compressive and tensile strengths, particularly at early ages, and may reduce the brittleness of LWAC (Gao and Zou, 2015). The results of research (Du et al., 2015) also indicate that using nanosilica, the water-resistant and chloride permeability characteristics of LWAC are improved. Such improvements are attributed to the influence of nanoparticles on creating a denser microstructure, especially in the interface between aggregates and paste, and refining the micropores.

Enhancing the Thermal Conductivity

Silica aerogel is a nanoporous material, with more than 90% of air voids in volume, extremely low density (3-100 kg/m^3), very low thermal conductivity (0.003-0.02 W/MK), and appropriate acoustic and fire resistances (Pierre and Rigacci, 2011; Pierre and Pajonk, 2002). In several cases, nanosilica aerogel has been used to produce high effective thermal insulation materials (Barbero et al., 2014; Buratti and Moretti, 2012a,b; Cotana et al., 2014; Gao et al., 2014b; Wei et al., 2011; Schultz et al., 2005; Stahl et al., 2012). In this regard, the level of density, thermal conductivity, and mechanical properties of aerogel-incorporated concrete (AIC) can be controlled by varying the aerogel content (Gao et al., 2014a).

It should be mentioned that replacing aggregates with aerogel reduces compressive strength and has no preferred mechanical properties. This can be attributed to the inappropriate ratio of the aggregates to matrix in the mortar system, and the decrease in the adhesion of the binder and aggregates (Ng et al., 2015). Hollow nanosilica were also utilized in concrete to improve thermal conductivity properties (Schlanbuschet al., 2014).

Use of Nanosilica in Low-Alkali and High-Volume Pozzolanic Cements

In recent years, considering the idea of sustainable development, significant efforts have been made on the concretes with high-volume pozzolan or slag materials. However, the concretes with a high volume of supplementary materials have long setting times and low compressive strengths, especially at early ages. In order to enhance the aforementioned characteristics, nanosilica has been used in several studies. For instance, the paper (Lothenbach et al., 2012) proposed that the use of nanosilica could significantly improve the early-age compressive strengths of low-alkali concretes with high-volume ground granulated blast furnace slag (GGBFS) and utilizing nanosilica could lead to a considerable reduction in the initial setting time of concrete. The results from studies (Hou et al., 2012; Zhu et al., 2015) confirm that the use of nanosilica can accelerate the setting time and cement hydration of high-volume fly ash concrete. Incorporating nanosilica in the concretes with high-volume fly ash may reduce chloride diffusivity and water sorptivity, could enhance pore structure, and provides higher corrosion resistance (Shaikh and Supit, 2015; Zhang and Islam, 2012). An experimental study by (Zhang et al., 2012) has been carried out on the influence of nanosilica on the setting time, cement hydration, and strength development of cement mixtures incorporating 50% GGBFS. The results reveal that the induction period was shortened and the rates of slag and cement hydration were enhanced by the inclusion of nanosilica in the cement pastes.

Geopolymer Mixtures

Geopolymer binders are generally synthesized by activating alumino-silicate materials and condensing them with sodium silicate in low-temperature and high-alkaline environments (Chen-Tan et al., 2009; Vickers et al., 2015; Olivia and Nikraz, 2012). Fly ash, GGBFS, metakaolin, and calcined clay are common source compounds for

Geopolymer (Pacheco-Torgalet al., 2014; Shi et al., 2006).

Reports indicate that microstructural and mechanical characteristics can be improved with the incorporation of nanosilica in geopolymer mixes due to the densification of mixtures. The study (Adak et al, 2014) has investigated the influence of nanosilica on the durability and mechanical properties of fly ash-based geopolymer mortar. Their results reveal that the addition of nano-SiO_2 to geopolymer mortar may improve flexural, tensile, and compressive strengths. Water absorption and rapid chloride permeability tests also show durability improvements. The analysis also demonstrates that nanosilica has a significant role in transforming the amorphous structure of primary compounds to the crystalline forms. It has also been found that nanosilica-based activators for alkali-activated fly ash binder improve the performance in terms of reduced porosity and densified microstructure (Rodríguez et al., 2013). Investigation (Gao et al., 2015) on the alkali-activated slag-fly ash blends suggested that the incorporation of nanosilica could significantly decrease the slump flow of paste mixture. Moreover, both initial and final setting times are slightly accelerated with the increase of the nanosilica content.

SUGGESTED APPLICATIONS FOR NANOSILICA

Based on the present discussion and the literature, the following applications are proposed for nanosilica materials:

1- Applications based on the instability of nanosilica particles in the pore solution environment of cement mixtures, leading to higher cohesiveness and adhesiveness characteristics:
  - Use of nanosilica as a VMA to improve the workability of high-flowable mixtures such as SCC and grouts.
  - Use of nanosilica in shotcrete mixtures due to high adhesion to the substrate surface.
  - Use of nanosilica in repair mortars to improve their adhesion to the substrate surface.

2- Applications based on the setting time reduction, cement hydration acceleration, and enhancement of early strengths:
  - Improving the hydration of cement (accelerating the time of setting and rate of strength developments) at early ages.
  - Use of nanosilica in high-volume pozzolan mixtures and low-alkali concretes to improve their early strengths.
  - Use of nanosilica in shotcrete concrete and repair mortars with reduced setting times and higher early strengths.
  - Use of nanosilica in UHPC to compensate for the retarding effect of high-volume superplasticizers on the setting time.

3- Applications based on the improved durability characteristics:
  - Use of nanosilica in order to improve the durability properties of cement composites, especially when the mixture is exposed to harsh environments at very early ages.
  - It is recommended that ultrafine nanosilica materials be used with other pozzolanic materials with a lower rate of pozzolanic reactivity such as silica fume in order to provide excellent durability improvements at both early and later ages.

4- Applications based on thermal insulating:
  - Hallow nanosilica and aerogel types could be the best candidates for the development of the future thermal superinsulation materials in construction.

CONCLUSIONS

In the current study, an overview on the influence of nanosilicas on the different characteristics of cement based materials has been presented. Furthermore, the types of nanosilica, their stability in the pore solution environment, and the influences and the potential applications of these materials in concrete have been investigated. In summary, the following results have been found:

1- In contrast to nanosilica sols which are monodispersed in media, pyrogenic nanosilica, precipitated nanosilica, and nanosilica gels are produced in the form of large micrometer aggregates.

2- Due to the presence of bivalent and polyvalent ions in the cement-based materials' pore solution and their high alkalinity, nanosilica agglomeration occurs. Therefore, the assumptions based on the monodispersed distribution of nanoparticles in cement environments such as the nucleation effect of nanoparticles or filler effect of nanosilica materials face serious problems.

3- Smaller nanosilica particles have faster pozzolanic reactions compared to the larger ones.

4- The use of nanosilica could lead to lower flow ability and higher adhesion of cement composites. The reason is a significant gelation of nanosilica particles in concrete pore solution environment.

5- Due to its fast pozzolanic reactions, nanosilica can reduce the number of calcium ions in the pore space, leading to lower dormant period and initial setting time of cementitious materials. Furthermore, use of nanosilica can accelerate the process of cement hydration.

6- Accelerating cement hydration, fast pozzolanic reactions at early ages, and increasing the degree of polymerization of CSH gel lead to accelerated mechanical properties at early ages.

7-Several applications of nanosilica have been suggested, including VMA in self-compacting concrete, high early-strength concrete, development of concretes with low alkalinity, increasing the adhesion of shotcrete mixture and repair mortars, enhancing the properties of UHPC and LWAC, and improving the thermal insulation properties and activator in geopolymer mixtures.

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