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Improvement of Concrete Characterization Using Nanosilica

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ABSTRACT

In recent years, different research works have been conducted to evaluate the addition of nanometer materials to concrete materials. In this paper, the influence of Nanosilica on compressive strength, abrasive strength, durability, and improvements in the micro-structure of concrete are discussed. The results showed that the compressive strength of concrete samples with Nanosilica and silica fume were higher than the compressive strength of other samples without nanometer materials in all ages, as well as increasing the dosage percentage of Nanosilica led to higher levels of compressive strength. In the mix designs with an equal dosage percentage, samples containing Nanosilica have shown a higher level of strength in comparison to samples containing silica fume. The application of Nanosilica in self-compacting concrete resulted in higher level of compressive strength, flexural strength, abrasive strength, elasticity module, ultrasonic waves permeability velocity (UPV), and lower water absorption compared to samples without Nanoparticles. Despite the evidences which show the improvement in mechanical characteristics of concretes with Nanosilica-particles, further developments for the applicability of Nanoparticles for improving the characteristics of concrete require the right knowledge and higher control over the effective mechanisms of Nanoparticles on concrete's structure.

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1. Introduction

Nano technology is defined as the applicability of materials engineering practices at the atomic-molecular scale and thus creating new materials with different characteristics in the Nano scale. While using the properties of materials in the Nano scale, benefits such as reduction in the energy consumption, economic savings, time savings, supply of larger product volumes with lower costs, improvements in the quality of product, and consequently the reduction of economical dependency of foreign advanced technologies with higher levels of domestic revenues can be realized [1]. The concrete is a material with multiple phases, Nano structures, and different constituents. Such structure consists of irregular crystal phases in micrometer to nanometer dimensions [2]. In addition, the non-crystal phase and the Nano structure of hydrated calcium silicate (C-S-H) lead to the formation of the adhesive substance that sticks the aggregates of concrete together [3]. The conventional admixtures of concrete do not always lead to improving all of the characteristics of concrete; instead, nanotechnology proved the performance of concrete from all perspectives. Some of the most well-known Nano-admixture of concrete are cement Nanoparticles, Nano-clays, Nano- fibers, Nano-coatings, Nano iron-oxides, Titanium dioxide, Aluminum oxide and Nanosilica. With the great advances in nanotechnology, the researchers of various sciences, especially civil engineers, focused on the application of Nanosilica as one of the most useful nanotechnology products since it can act as a very active synthetic Pozzolanic material in the concrete [4–6]. The studies on Nanosilica in concrete use this material for enhancing the characteristics of concrete mixes as much as possible. According to various studies [7–9], it is proved that the addition of Nanosilica to a concrete mix lead to increase in compressive, tensile, and flexural strengths, while the setting times and water penetrability inside the concrete are reduced while the resistance against chemical attacks increases. The experiments performed on Nanosilica particles show that these particles are not only harmless for the environment, but also lead to better results in comparison to concretes containing Microsilica [10–12]. Researches showed that the addition of Nanosilica lead to larger improvements in the strength of concrete in comparison to addition of Microsilica [10]. Also, concrete mixed with Nanosilica leads to maintaining the safety and health of workers and the environment in the long term [11]. In addition, Nanosilica can lead to lower consumption of concrete, production of high quality concrete and higher operational efficiency [13].

Jo et al. [14] investigated that Nanosilica-particles have a good effect on increasing the strength of mortar, because Nanosilica can act as an activator to promote Pozzolan reaction. Singh et al. [15] compared the influence of Nanosilica-particles on the mechanical properties of concrete, and found that Nanosilica-particles can enhance the amount of C-S-H in mortar and improve the mechanical properties of concrete. Li et al. [16] used a three-point bending test for testing the bending strength of a composite containing Nanosilica. They resulted in the flexural strength and the brittleness of the composite increased. Ma et al. [17] showed that with the increase of Nanosilica content, the mass of C-S-H gradually increased and the pore structure of recycled aggregate concrete was optimized. Mohammed et al. [18] indicated that the pore volume of cement slurry containing Nanosilica can be reduced by 13.4 percent, and Nanosilica cannot adversely have an effect on the porosity and permeability of cement slurry. Zhang et al. [19] found that Nanosilica and silica fume modified cement mortar protected the concrete surface

while enhancing impermeability. The addition of Nanosilica to the cement materials can accelerate the early hydration of concrete, which is very useful for increasing the early strength of concrete [20]. Liu et al. [21] showed that the addition of an appropriate dosage of Nanosilica to the concrete can effectively reduce the water permeability of concrete because of enhancing the interface strength and refining the pores. Zhuang et al. [22] investigated the axial compression behavior of Nanosilica-reinforced concrete filled stainless steel circular tube short columns. They found that the impact of Nanosilica dosage on the axial compressive capacity of Nanosilica-reinforced concrete filled-round, stainless-steel short columns was discrete. Vahedi et al investigate the amount of energy dissipated in the steel circular tube [23]. When the Nanosilica dosage was one percent, the axial compressive capacity was highest. He et al. [24] found that the load bearing capacity and initial stiffness increased as the compressive strength of the concrete specimens modified with Nanosilica was improved.

Nanosilica improvements in concrete materials is also gaining increased attention in the accelerated bridge construction industry when utilizing ultra-high-performance concrete (UHPC). A large applicability of UHPC mixes is limited to proprietary products using silica fume, micro-silica, and other mineral additives, and although it has shown proven strength and corrosion-resistance performance in structural components and overlays [25–27], it could drive up costs of implementation with great variations depending on the market due to fiber and silica fume availability [28–31]. Therefore, Nanosilica represents a cost-effective mineral additive solution when developing non-proprietary UHPC mixes for structural applications, while enhancing corrosion resistance [32].

In the current study, the main focus is placed on the impact of nanotechnology on concrete production technology as well as the influence of adding Nanosilica to conventional mixture of concrete with some specific additives. In other words, the effect of Nanosilica on compressive strength, abrasive strength, durability, and improvements in the micro-structure of concrete is discussed.

2. The impact of nanosilica on the compressive strength of concrete

One of the most significant impacts of adding Nanosilica particles is the improvement in the strength of concrete. Ghiasian et al provided a test-driven approach to evaluate material component such as silica in design of corrosion resistance concrete structure [33]. It was shown in the study of Li et al. that adding a small amount of Nanosilica particles to concrete mixtures leads to higher levels of compressive, flexural, and abrasive strengths [34]. In order to investigate the impact of Nanosilica on compressive strength, it can be referred to the results of compressive and flexural strength tests according to JTJ 053-94 standard [35], elasticity module, and UPV measurement (ultrasonic wave permeability velocity). When comparing the results of compressive and flexural strength tests in different samples, it was observed that the addition of the lowest dosage of Nanosilica led to increase in these strengths. If the concrete does not have any crack or crevice, the two strengths parameters increase simultaneously, but in practice, the growth in the compressive strength is larger than the flexural strength. The reason behind this difference is due to the presence of micro-cracks with different sizes in the concrete, while their

impact on flexural strength is more than compressive strength. When the volume of Nanoparticles of the concrete increases, the number of micro-cracks increases which leads to the lower efficiency of produced concrete. Such circumstances translated to deterioration of compressive strength, meanwhile it should be mentioned that the homogenous and balanced distribution of Nanoparticles inside the mortar is difficult to achieve, leading to formation of weak and unstable areas inside the concrete which reduce the flexural strength of concrete [34]. The relation between flexural strength of concrete and particle size also studied by Sarajpoor et al. [36]. Another experimental study was performed in the Amirkabir University; samples with different percentages of Nanosilica and a blank sample without Nanosilica were generated in the first step and then broken at ages of 7, 28 and 90 days. The results of compressive strength tests for the required ages are shown in Figure 1.

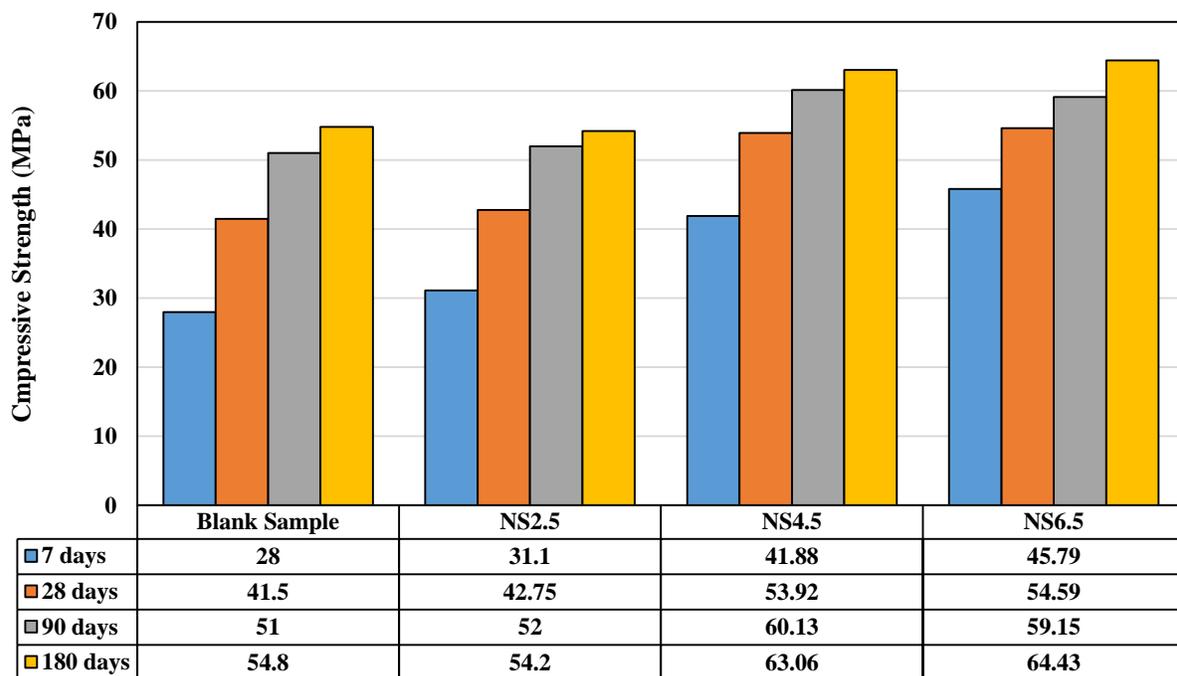


Fig. 1. Compressive strength of samples at various ages: 7, 28, 90, and 180 days [34].

According to the results, it can be seen that Nanosilica led to the creation of more core surfaces for hydration product and after the formation of stable gel, the increase in the volume of Nanosilica improved the mechanical properties of hardened cement paste [36,37]. In Figure 1, it is clear that the compressive strength of samples containing Nanosilica in all ages is higher than the compressive strength of the Blank Sample, meanwhile any increase in the percentage of Nanosilica substitution lead to higher compressive strength. The increase of strength in comparison to the Blank Sample even for the early ages is clearly seen in samples with 4.5 and 6.5 percent of Nanosilica substitution. The trend of strength increase is shown in Figure 2. Nanosilica had a high level of surface energy because the activity of atoms was relatively high, which results in high levels of reactivity of Nanosilica-particles with external atoms and the Pozzolanic activity of Nanosilica even at very early ages [13,38]. The increase rate in the strength of samples containing Nanosilica was at the maximum level until the 7th day and

reduced after the age growth of samples. In fact, in the samples with 6.5 percent of Nanosilica, more than 70 percent of the ultimate strength of the samples was reached until the age of seven days [39–41]. Therefore, Nanosilica can effectively accelerate the setting and hydration processes and consequently increase the tensile strength of hardened cement paste, bonding strength of aggregate with paste, and structural strength of transition zone [13]. Another study [42,43] proved that the addition of Nanosilica led to significant improvement in compressive strength of self -compact concrete, a dramatically increase in the level of compressive strength, and reduction of ductility which was mostly observed in concretes with high strengths. Generally, one of the main weaknesses of such concrete mixes was their higher brittleness and fragile behavior in comparison to normal mixes. It seems that reinforcement with fiber can solve such a problem and thus better the ductility of concrete mixes containing Nanosilica. In the elasticity module experiments, the addition of seven percent weight Nanosilica cement led to 70 percent increase in the elasticity module [44]. According to this characteristic, it can be concluded that for higher concrete compressive strengths, its failure happens at lower levels of strains and vice versa. In the UPV passing experiment, increase in the speed of waves passing through samples containing Nanosilica led to improvement in their mechanical strength [37].

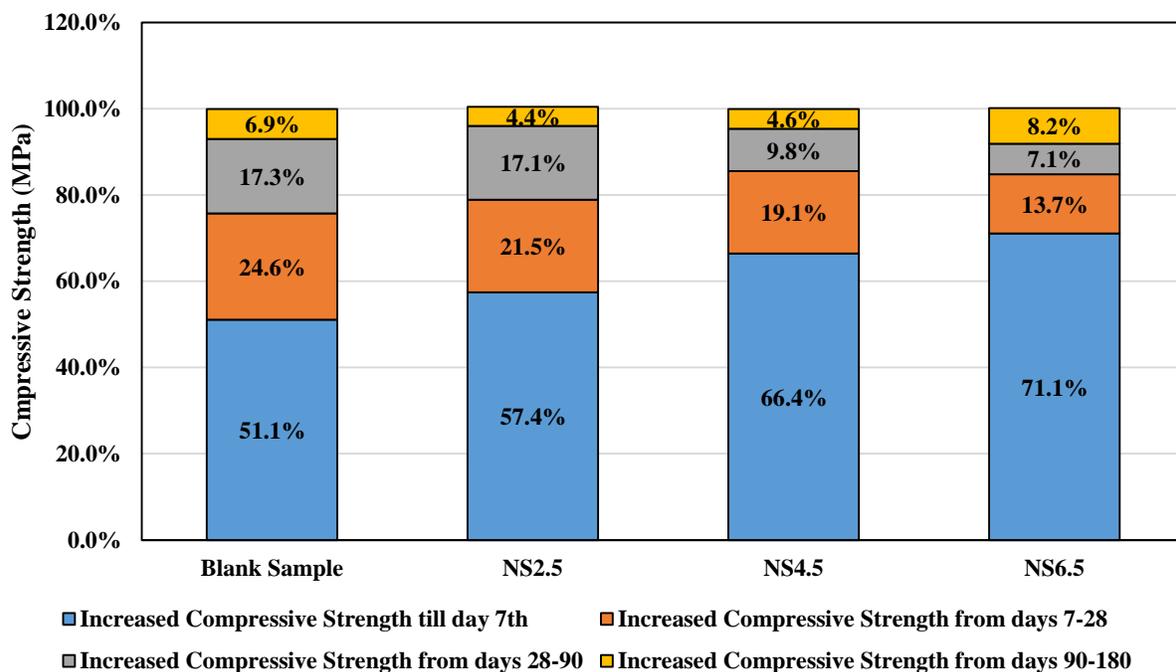


Fig. 2. Acquired compressive strength at 7, 28, and 90 days in comparison to strength at 180 days.

3. The impact of nanosilica on the abrasive strength of concrete

The most important impact of increase in abrasive strength is reflected in concrete pavements. Concrete pavements are used for covering the surface of roads, bridges, airport runways, and bearing of dynamic loads. Studies show that the concrete's abrasive strength is influenced by compressive strength, curing technique for concrete surface, setting and curing types, and characteristics of aggregates [45]. There are two viewpoints about the relationship between

compressive and abrasive strengths. In one perspective, it is assumed that compressive strength is the factor which has an impact on abrasive strength and whenever the compressive strength increase, the abrasive strength will also increase [45,46]. Nike et al. and Guro et al. [45] showed that the relationship between these two strengths is a linear relationship. The second viewpoint assumes that the abrasive strength is independent of compressive strength. In the study of Lee et al. [34], the significant improvement in the abrasive strength of concrete containing Nanoparticles was considered. In addition, it was proved that if Nanoparticles are used in the concrete mixture, the effective operational lifetime of pavement will also increase. In Table 1, the significant increase in the abrasive strength of samples containing Nanosilica-particles is represented, meanwhile the lateral abrasive strength has higher values in comparison to surface compressive strength [34].

Table 1

Experimental results for abrasive and compressive strengths of 28-day samples.

Type of Mixture	Surface Abrasive Strength Index		Surface Compressive Strength Index	
	Experimental Results	Increase in abrasive strength in comparison to normal concrete (%)	Experimental Results	Increase in compressive strength in comparison to normal concrete (%)
Normal Concrete	1.19	0	1.55	0
Concrete with 1% Nanosilica	3.06	157	3.71	139.4
Concrete with 3% Nanosilica	2.39	100.8	2.93	89

In order to better understand the influence of Nanoparticles in increasing the abrasive strength of concrete, it is recommended to assume that Nanoparticles are distributed homogeneously and each particle has a cubic form. Thus, this configuration gives the ability to visualize the distance between the Nanoparticles. After the beginning of hydration, the hydrated products are distributed and cover the Nanoparticles like a nucleus. If the amount of Nanoparticles and the distance between them are appropriate, the crystallization process would be controlled in an efficient manner and therefore the growth of Ca(OH)_2 crystals with Nanoparticles is limited. This type of process makes the cement mortar more homogeneous and denser. According to Table 1, it is clear that the abrasive and compressive strengths of concrete mixtures with one percent of Nanosilica experience a higher level of improvement in comparison to the others. When the amount of Nanoparticles increases, the distance between them decreases and Ca(OH)_2 crystals cannot grow appropriately, so that the ratio of crystal to C-S-H gel reduces. Therefore, the microstructure of cement mortar becomes looser, and consequently the abrasive and compressive strengths of concrete decrease [13]. Some studies [47,48] showed that the number of Nanoparticles have a great impact on water demand of cement paste: with an increase in the number of Nanoparticles, the consumed water also increases. If the mixing ratios of concrete are equal, the efficiency of concrete reduces with the increase of Nano-particle dosages, and consequently the compressive and abrasive strengths of concrete decrease. On the other hand, higher amounts of Nanoparticles make it more difficult to distribute the Nanoparticles

appropriately in the concrete mixture and such circumstances also lead to reduction of compressive and abrasive strengths [49].

As previously mentioned, the usage of Nanoparticles for filling the micro-pores of cement paste is achievable since the micro-structure of cement paste has Nano-pores in its structure and such an addition translates into an increase in the compressive strength and durability of concrete. In the study performed by Jey et al. in 2009 [50], the impact of Nanosilica properties on the seepage and penetrability of concrete was discussed, and the lowest amount of seepage was seen in the sample with the highest amount of cement, the lowest ratio of water to cement and the highest amount of Nanosilica. In fact, the usage of Nanosilica had some effects such as an improvement in the micro-structure of cement paste, a reduction in the sizes of empty pores inside the concrete and a penetrability inside it which led to higher strength of the concrete sample. The Rapid Chloride-ion Permeability Test (RCPT), water permeability test, capillary water absorption test, and electrical resistance test of concrete are performed to analyze the impact of Nanosilica on improving the durability of concrete. Nanosilica leads to a significant decrease in the amount of electric charge passing through the sample and consequently increasing its resistance for permeability of chloride ion. Results showed that a small amount of Nanosilica in comparison to the same amount of silica fume led to higher impact for the reduction of passing flux, but after the increase in the substituted percentage of Nanosilica, the difference in their impacts would be much lower [37]. In addition, the Nanosilica has a higher level of Pozzolanic activity in comparison to silica fume and generates C-S-H gel which gives it an ability to fill the pores of concrete and eliminate micro-pores in its silicate gel. These conditions lead to reduction of effective pores for permeability of water inside the concrete but it might be gradually faded over time when the Pozzolanic reactions of silica fume are completed [37]. The usage of silica fume and Nanosilica has an impact on reducing the amount of water absorption in concrete samples and by increasing the amount of these components in the sample concrete mixture, water absorption reduces. The amount of water absorption in the samples containing silica fume is less than the samples containing Nanosilica. A probable reason for such observation is the higher amount of super plasticizer used in Nanosilica samples in comparison to silica fume samples and consequently the number of confined pores is increased in the compacting phase. Also, the reactions of Nanosilica inside the concrete structure consume a higher amount of water, so the water absorption potential in samples containing Nanosilica is larger than samples containing silica fume [37]. The addition of Nanosilica and silica fume to concrete leads to increase in the electrical resistance, although with the increase in the age of samples, the difference in the electrical resistance of Nanosilica and silica fume is decreased.

4. The impact of nanosilica on the concrete's micro-structure

The mechanical and physical properties of cement materials such as strength and permeability are greatly dependent on the micro-structure of hardened cement paste. Nanosilica has the ability to react quickly with crystalized $\text{Ca}(\text{OH})_2$ and generates C-S-H gel which leads to significant improvement in concrete's micro-structure, which the new structure is more homogeneous and the strength and durability of concrete also increase. For determination of Pozzolanic activity of silica fume and Nanosilica, X-ray diffraction spectroscopy test is performed. Results showed that

in samples containing Nanosilica, with increase in the age of sample, there would be a small increase in the amount of $\text{Ca}(\text{OH})_2$, which show the reduction of Pozzolanic activity of this sample and the production of more $\text{Ca}(\text{OH})_2$ due to continuous hydration of cement paste [39]. The next test is conducted through the Scanning Electron Microscope (SEM), in which the collected images show the Nanosilica had a much higher impact on increasing the density of paste structure and elimination of its pores. These conditions are regarding the higher reactivity of Nanosilica in comparison to silica fume and it has a higher level of Pozzolanic activity in its early ages. After comparing the performance of Nanosilica and silica fume for reducing the amount and size of $\text{Ca}(\text{OH})_2$, it is clear that Nanosilica has better performance for the reduction of this material in the modeled transition zone. By filling the pores of gel, Nanosilica leads to reduction in the size and number of pores in the micro-structure and higher consistency and uniformity for the samples.

5. Effective mechanism of nanosilica-particles for improving the mechanical properties of concrete

In previous studies about improving the mechanical properties of concrete by Nanosilica-particles, different mechanisms were introduced. Qing et al. (2007) showed that Nanosilica has higher Pozzolanic properties in comparison to Microsilica and leads to higher improvement in strength of concrete [13]. Li (2004) reported that Nanosilica-particles can even increase the reaction velocity of fly ash in concrete, which usually has a very slow Pozzolanic reaction [51]. The experiments of Jo et al. (2007) showed that the percent of strength improvement is 3-12 percent in mortars containing Nanosilica [52]. Li et al. (2007) proved that Nanosilica-particles increase the fatigue strength of concrete. They also reported that by increasing the amount of Nanosilica, the micro-structure of concrete also improves and a structure with less pores and higher density is created [53]. Ji (2005) showed that the permeability of concrete containing Nanosilica is reduced [50]. Li et al. (2006) reported an increase in the abrasive strength of concrete containing Nanosilica [53]. Bjeornstream (2005) reported the better performance of concrete containing Nanosilica against freezing and thawing [50]. One of the most well-known mechanisms for improving the mechanical properties of concrete is related to filling effect of Nanosilica-particles. Ji (2005) and Li et al. (2004) believed that the filling effect of Nanosilica-particles in the pores of cement paste is the main reason for increase in compressive strength of concrete. They showed that the addition of Nanoparticles prevented concrete from the development of $\text{Ca}(\text{OH})_2$ crystals, and therefore the volume of the crystals decreases and the volume of C-S-H gel in cement matrix increases [50]. Jo (2007) also emphasized on filling capability of Nanosilica-particles and proved that fine granularity of these particles leads to increase in temperature of hydration reaction as well as the velocity of strength improvement [52]. Li et al. (2004) believed that the main reason for improvement in mechanical properties of concrete containing Nanosilica is the nucleation mechanism, and Nanoparticles act like bone against cement gel just like aggregates. Li argued that the nucleation mechanism of Nanoparticles leads to faster hydration of cement because of having a bigger specific surface area [49]. Qing (2007) believed that the Pozzolanic activity of Nanosilica is a significant reason for improving the compressive strength of concrete. In fact, the Nanosilica-particles with SiO_2

purity of more than 99 percent and high specific-surface area make reactions with $\text{Ca}(\text{OH})_2$ crystals produced from hydration, which the result of this reaction is C-S-H gel. Such a reaction improves the bonding probability of aggregate paste [13]. Jo (2007) showed that the Pozzolanic characteristic of Nanosilica-particles is much higher than microsilica and consequently the velocity of its reaction increases [52]. Jo (2008) believed that the effect of Nanosilica due to the Pozzolanic activity is more than the effect provided by filling capability (first mechanism) [52]. Despite most of studies in the field of Nanoparticles related to the increase in the strength of concrete due to the Pozzolanic activity mechanism of Nanosilica, the study of Li et al. (2004) showed that Fe_2O_3 Nanoparticles which do not have Pozzolanic feature, lead to higher increase in compressive and abrasive strengths in similar conditions compared to the Nanosilica-particles [54]. Although Nanosilica has higher Pozzolanic activity due to the higher purity and larger specific surface area, the studies about the strength increase in samples containing Nanosilica showed that these mechanisms cannot separately justify the increase of strength in concrete mixtures. Generally, in the Pozzolanic activity, the trend of strength improvement passes a very slow trend since the amorphous SiO_2 s in Pozzolanic materials do not react directly with the water, while they should react with the products of hydration to generate the C-S-H gel. In the samples containing Nanosilica, the rate of strength improvement is high in early ages, but the rate of strength improvement reduces in the later ages and the strength of samples containing microsilica reach a higher level than samples containing Nanosilica. In the micro-structure of samples containing Nanosilica, there are clear evidence of controlled crystal growth and a more amorphous structure is detected but there are still quite large pores in this structure which show the heterogeneous distribution of hydration products inside the concrete structure [55]. Li (2004) showed that the nucleation of Nanosilica-particles leads to enhancement in the size of pores and reduction in the porosity of concrete, even in the short period of curing [50]. Azad et al. showed that reduction in the porosity decrease crack aperture [56]. On the other hand, the high Pozzolanic activity of Nanosilica causes the lower porosity of concrete which leads to more and faster reactivity of fly ash [57]. Li noted that Nanosilica-particles make higher and faster activity of other Pozzolanic compounds [58]. The filling mechanism can explain this phenomenon in a better way. The ideal granularity theory and fuller curve acquired better results in term of demonstration and measuring the effect of filling mechanism in samples containing Nanosilica [59]. The filling effect of particles leads to lower porosity of cement paste and smaller volumes of pores, but on the other hand, the nucleation effect of Nanoparticles leads to larger pores and generation of a more amorphous matrix in paste's structure which results in reduction of strength in the samples. In general, the Pozzolanic reaction of Nanosilica-particles which still maintained their reactivity and are not confined with hydration products can further improve the strength of samples in the long term [55].

6. Discussion and conclusion

The effects of Nanosilica on the compressive strength, abrasive strength, and durability were described in detail in this review, and the strengthening mechanism of Nanosilica was explained by micro-structure. By reviewing the previous studies on concrete mixtures with Nanosilica, the following conclusions can be drawn:

- 1- When the size of particles reaches the Nano scale, like Nanosilica-particles, the specific surface area and the number of atoms in the surface of material increase significantly. The availability of atoms in such a surface with these dimensions leads to the creation of free and unsaturated bonds with a large amount of residual valance force that is essentially unstable. On the other hand, with the reduction in the size of particles, a great level of atomic roughness is generated which increases the number of chemical reactions. Because of these circumstances, Nanoparticles such as Nanosilica have a high level of surface energy and the surface activity of their atoms is much higher than normal atoms which leads to the easier reactions with other external atoms. Therefore, the Pozzolanic activity of Nanosilica is much higher than silica fume that is quite reasonable since the specific surface area of Nanosilica is bigger than silica fume. In normal concrete, there are $\text{Ca}(\text{OH})_2$ crystals with larger dimensions and smoother edges, in which the crystals are also smooth edged but smaller in silica fume.
- 2- In the samples containing Nanosilica, the reduction in size of sample is much bigger and the availability of corroded and rough edges proves the continuity of reactions. Therefore, the higher reactivity of Nanosilica in comparison to silica fume is confirmed.
- 3- The most significant impact of Nanosilica for increasing the compressive strength is because of very high speed of Pozzolanic reactions in the early ages and in the later ages the impact of these materials reduces. In the case of silica fume, the most of activities are done in the age of 7-28 days.
- 4- By further focusing on the trend of durability increase in concrete samples, it can be seen that samples containing Nanosilica have a higher rate of increase in the durability in comparison to samples containing silica fume. On the other hand, the higher level of super plasticizer in Nanosilica samples, the higher number of confined pores in the compacting phase, the filling of larger pores because of filling effect of silica fume particles, the water consumption of Nanosilicas for initiation of reactions in concrete structure and the higher fragility of these Nanosilica samples which lead to more surface cracks in core phase in samples containing Nanosilica.
- 5- The addition of Nanosilica does not change the trend of increase in the strength or quality of concrete. If cements with higher quality are used, the strength of concrete is increased since the Nanosilica-particles have a desired agglomeration because of their high specific surface area. Therefore, it is possible to generate a weak zone area which leads to the reduction of strength. The compressive strength of samples containing Nanosilica and silica fume is higher than blank samples in all ages, and by increasing the substitution percentage of Nanosilica, the compressive strength increases.
- 6- In the mixture with equal substitution rates, samples containing Nanosilica have a compressive strength higher than the samples containing silica fume.
- 7- The benefits of using Nanosilica in self-compacted concrete are higher compressive strength, higher flexural strength, higher elasticity module, higher UPV, and lower water absorption.
- 8- The nucleation mechanism accelerates the cement hydration in samples containing Nanosilica and leads to heterogeneous distribution of solved components and generation of structures with big pores. Such circumstances can be the main reason for reduction in the

ultimate strength of these samples in comparison to samples containing microsilica. This phenomenon is specially worrying with respect to durability properties of concretes containing Nanosilica and limits their usability.

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