Int. J.Nano Dimens. 3(4): 321-328, Spring 2013
ISSN: 2008-8868

Contents list available at **IJND**

International Journal of Nano Dimension

Journal homepage: ***www.IJND.ir***

Investigation of the effects of nano-silica on the properties of concrete in comparison with micro-silica

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Received 29 May 2012
Accepted 31 August 2012

ABSTRACT

The effects of adding Nano-Silica particles on the compressive strength and water permeability of concrete and its comparison with that of Micro-Silica were investigated in this work. The effect of combination of Nano- silica and Micro-silica were also studied in this work, which resulted in an increase in compressive strength of concrete in comparison with other concrete specimens tested in this study. In addition, it has been well shown that the concrete specimens made of Nano-Silica particles were more impermeable in comparison with other concrete mixes tested in this work. To study the microstructure of the concrete mixes some images were also taken by the scanning electron microscope (SEM), which has shown the ever more uniformity of the samples containing the Nano-particles compared with the control samples. The XRD analysis showed that the $Ca(OH)_2$ amount of such samples is considerably less than that of the control sample.

Keywords: *Nano-silica; Concrete; Cement paste; Compressive strength.*

INTRODUCTION

Nano materials possess unique physical and chemical characteristics, which would improve the structure and would also cause some variations in the compositions of the currently existed materials. According to the scale variations of the Nano particles applications, and considering the distinctive characteristics of such materials, it is possible to have some developments in the construction industry, applying them in cement production or concrete mixtures, which can be raised due to the mechanical resistance and lifetime of the concrete [1]. The pozzolanic activity of the Nano-Silica particles is distinctively more than that of the micro-Silica ones due to the considerably high surface to volume ratio of them.

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Therefore, more likely, these nano particles can chemically well react with $Ca(OH)_2$ in the interfacial transition zone (ITZ) resulting in an stable Calcium Silicate Hydrate (CSH) product which can decrease the amount of the $Ca(OH)_2$ and increase the compressive strength of the concrete, especially in few first days. In addition, replacing cement with Nano-Silica in concrete mixture can behave as a nucleus to provide tightly bond with cement hydrates, which can be considered as one of the factors of binding past matrix and permeability reduction in Nano-Silica equipped concrete mixtures.

A general review on concrete mixtures containing nano-particles

- **Adding Nano-Colloidal Silica in the Cement Paste**

The experiment accomplished by Shih, et al [2], can be considered as one of the most important researches conducted on the colloid Nano-Silica addition in cement paste, in which adding different Nano-Silica ratios were examined and the maximum compressive strength increase was obtained as 60% in 0.6% ratio of the Nano-Silica to cement in the 14^{th} day. In addition, the studies carried out by Khanzadi, et al [3] on the effect of the colloid Nano-Silica on concrete properties showed the maximum increase in compressive strength of the concrete in 10% Nano-Silica by the weight of cement content added up to the concrete mixtures. Sadr Momtazi, et al [4] complemented this experiment by adding 50nm colloid Nano-Silica's in average where the optimum application percentage was obtained as 7%. Ramazanianpour, et al [5] obtained the best result of the same experiments in 7.5% Nano-Silica to cement ratio by 38% increase in concrete strength at the age of 3^{rd} day.

- **Adding up Nano-Silica to Cement Paste in Powder Form**

The studies accomplished by Lin, et al [6] can be mentioned as one of the other experiments investigated the affects of adding powder Nano-Silica on cement paste properties. The Nano-silica powder with an average 10nm pieces size and with $670m^2/g$ special surface was applied. The effects of different ratios of Nano-Silica to cement content were well investigated, and the optimum ratio of 3% was reported. Jo, et al [7] has also accomplished this experiment with average 40nm size in which the best nano powder percentage was obtained as 12%. In 2004, Li, et al [8] have investigated the effects of the nano materials on the mechanical characteristics of the cement paste and have reported the optimum nano powder percentage as 10%. In addition, Quing, et al [9] have conducted such researches on adding Nano-silica powder with an average 15nm particle size, have reported 0.22 water to cement ratio, and the maximum compressive strength is in 5% nanomaterials to cement ratio.

EXPERIMENTAL

The Type II Portland cement of Sufian Cement Factory conforming to ASTM C150-4 standard was used as received. The chemical and physical properties of the cement are shown in Tables 1 and 2.

Table 1. Characteristics of cement

Characteristics	Cement
Density (g/cm^3)	3.15
Blain fineness (cm^2/g)	2860
Average compressive strength (kg/cm^2)	370

Table 2. Chemical properties of cement

Material	Cement
SiO2	21.29
Al2O3	4.85
Fe2O3	3.46
CaO	64.56
MgO	2.38
SO3	1.71
K2O	0.97
Na2O	0.34
Lo.I	0.75

Crushed coarse aggregates, with a maximum size of 12.5mm and a specific gravity of 2.68g/cm^3, were used in this work. The fine aggregates were river sand with a fineness modulus of 3.00 and specific gravity of 2.67g/cm^3. Different sizes of the aggregates were separated to provide single sized aggregates and specific amounts of each size were applied to mix designs. This was accomplished to have a more accurate comparison between the samples and to guaranty the coarse and fine aggregates to meet the ASTMC33-03 standard. In addition, it was conducted to have the maximum destiny to have as more dense materials as possible to feature the nano particles application and to stabilize the sand fineness module in all samples as well as being able to obviate all variables during the concrete production. It is important to note that the aggregates were washed before the sampling process and are completely dried in oven under 105 $^{\circ}$C. The maximum size of the coarse aggregates is considered as 12.5 mm to decrease the effect of aggregates breaking in high compressions as much as possible.

Due to completely dried aggregate used during this study, the water amount was the same in all mixtures.

Powder Nano-Silica was used in this work. The chemical and physical properties of the Micro-silica and nano- silica are shown in Tables 3 and 4 Transmission electron microscope (TEM) and size distribution diagrams of SiO_2 nano particles are shown in Figures 1

Table 3. Properties of nano_SiO_2 and micro _ SiO_2

Characteristics	Micro_ SiO_2	Nano_SiO_2
Diameter(nm)	1000±100	20±5
Surface to volume ratio(m²/g)	20±5	220±20
Density (g/cm³)	2.25	<0.20

Table 4. Chemical properties of nano_SiO_2 and micro_SiO_2

Material	m_SiO2	n_SiO2
SiO_2	93.6	98.31
CaO	0.49	0.392
Al_2O_3	1.32	0.076
Na_2O	0.81	0.328
Fe_2O_3	0.37	0.293
SO_3	0.1	0.185
Cl	0.04	0.044
TiO_2	0	0.64
K_2O	1.21	0.08
MgO	0.97	0.05
P_2O_5	0.16	0.129
ZnO	0	0.021
CuO	0	0.02
Total	99.07	99.7

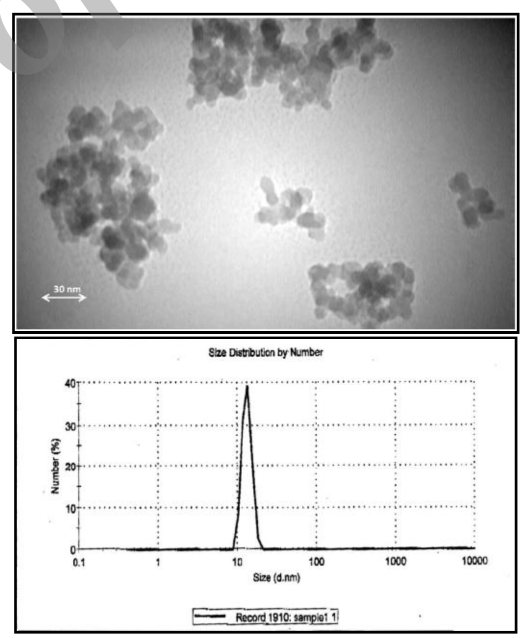

Fig. 1. TEM of nano- SiO2 and size distribution diagrams of SiO2 nano particles

Nine different concrete mixes were tested.NS3, NS6, NS9, MS6, MS9, MS15, MN15-3, M18, and OC as control specimen. Mix proportions tested in this work, are presented in Table 5.

Table 5. Mix Proportion

Mixture no.	W/C	Nano_SiO_2 (kg/m^3)	Micro_SiO_2 (kg/m^3)	Cement (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Super plasticizer (kg/m^3)
OC	0.45	0	0	445	200	859	872	1.35
NS3	0.45	13.35	0	431.65	200	859	872	7.164
NS6	0.45	26.7	0	418.3	200	859	872	11.125
NS9	0.45	40.05	0	404.95	200	859	872	24.475
MS6	0.45	0	26.7	418.3	200	859	872	4.005
MS9	0.45	0	40.05	404.95	200	859	872	5.785
MS15	0.45	0	66.75	378.25	200	859	872	5.34
MS18	0.45	0	80.1	364.9	200	859	872	5.785
MN15_13	0.45	13.35	66.75	364.9	200	859	872	8.01

In MN15-3, Nano-Silica and Micro-silica were used simultaneously, in which 15% of the cement weight was replaced by Micro-Silica, and 3% by Nano-Silica. It is important to note that the Nano-silica particles initially tend to mix with the concrete mixture water. Therefore, the mixtures were initially placed in bath ultrasonic set for one hour to control the uniformity of the concrete mixtures.

In all mixes, the polycarboxylate ether based super plasticizer, which is the product of the Abadgaran Corporation under Type 1 super plasticizer trade name, was used with different ratios by the weight of cement content order to have approximately the same slump in all mixes. All concrete mixtures are mixed for 5 minutes using ELE rotary vertical mixer. The samplings were accomplished for 10×20 cylindrical and 10×10×10 cubic molds in 3 layers. Each layer was vibrated on the vibration table with constant frequency for 15 seconds. All specimens were remolded after 24 hours of maintenance in curing cabinet with 90%-100% humidity ratio and 22-23°C temperature and then cured in water for the remaining days before testing.

Testing method

- **Compressive Strength Test**

The cubic samples with 10×10×10cm size were tested at the ages of 7 and 28 days to measure the compressive strength of the concrete mixes and also the trends of their strength gaining over the time. The results of different tests carried out in this work are presented in Table 6.

- **Water permeability tests**

These tests carried out to assess the permeability of the concrete specimens, based on water permeation depth. In permeability test method used in this work, the permeability criterion is based on the permeation depth according to DIN1048Part1 standard. The 10×20 centimeter cylindrical samples were initially brought out of the water after 28 days of curing and were dried for 24 hours in 100-110°C in an oven before permeability tests. The water pressure imposed to the end of the samples was five bars. The samples were subjected under such pressure for 24 hours in permeability device and then were immediately broken using the Brazilian method to record the water permeation depth. In order to determine the permeability depth ratio, this depth is measured in three different points and the average of them was noted as the water permeability depth in the samples.

The permeability factor is calculated for concrete by using the following relation and in respect with Darsi law [10]:

$$K=Q/AI \qquad (1.a)$$

In this relation, the parameter I is the hydraulic gradient, Q is the discharge, and A is the cross section area of the sample, where I=H/d and H is the hydraulic load difference imposed to the sample and d is the permeation depth.

Table 9. Test result

Mixture no.	Slump (mm)	Compressive strength of 7 days (Mpa)	Compressive strength of 28 days (Mpa)	The average penetration depth (mm)	The permeability 10^{-10} index (cm/sec)	Compressive strength increase in 7days percentage	Compressive strength increase in 28 days percentage
OC	30_50	42.27	48.86	30	17.3	0.00%	0.00%
NS3	30_50	51.12	56.65	25	14.45	20.91%	15.93%
NS6	30_50	58.77	67.47	18	9.8	36.89%	38.07%
NS9	30_50	64.53	76.82	14	7.67	52.65%	57.21%
MS6	30_50	55.15	63.40	25	14.41	30.44%	29.75%
MS9	30_50	57.29	65.30	24	13.14	35.52%	33.64%
MS15	30_50	57.84	68.22	23	12.6	36.81%	39.61%
MS18	30_50	57.63	67.19	23	13.09	36.32%	37.50%
MS15_3	30_50	64.16	81.83	17	9.804	51.76%	67.47%

RESULTS AND DISCUSSION

The Compressive Strength of the Samples

According to the test results shown in graphs of Figure 2(a) and the Table 6, the specimens containing both Nano-Silica and Micro-Silica shows the highest increase in the compressive strength at the age of 28 days compared with that of the control specimen. According to existing reports, the optimum Micro-Silica consumption is claimed to be 15% [11], which can also be confirmed by the results of this study. However, it is specified that using nano-silica beside micro-silica leads to more increase in compressive strength of the concrete. As can be seen in the table 6, the specimens containing 15% micro-silica and 3% nano–silica have an increase of 67.5 % in their compressive strength in comparison with that of control specimens whereas it was 39.6% for the specimens containing 15% micro-silica only.

The water Permeation in Concrete

As it can be seen in the Table 6 and Figure 2(b), the results of permeability test on different concrete specimen's shows that replacing a specific amount of the cement with Nano-Silica or Micro-Silica would decrease the permeation of water in concrete. According to test results, for the specimens containing different percentages of nano-silica and micro-silica, a minimum water permeation depth of 14mm is related to the specimens of 9% nano-silica and a minimum water permeation depth of 17mm is related to the specimens of 15% nano-silica. It has been shown in the table 6 that using 3% nano-silica beside 15% micro-silica led to more decrease in permeability of the concrete in comparison with that of the specimens containing 15% micro-silica only.

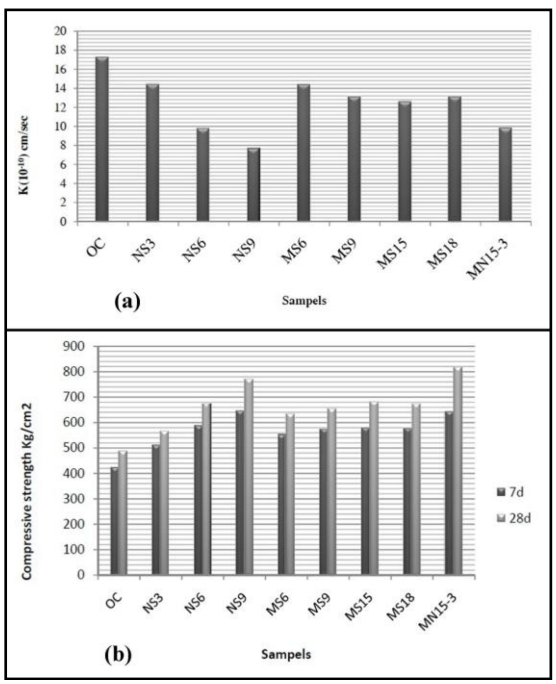

Fig. 2. Test results graphs (a) The permeability index (b) Compressive strength of 7,28 days

SEM Test

Some samples from all experimental specimens were sliced for the electrographic at a specific age. On the other hand, the samples were kept in Iso propanol alcohol to stop the hydration process. Some photos were taken by SEM from the 28-day-old cured samples. It is important to note that the surface of the samples should be completely smooth.

It can be seen from Figures 3 and 4 that the Nano-Silica samples have more uniformed and filled structure in compare with the control sample. In these samples the large $Ca(OH)_2$ structures are less visible and are changed in to more stable and smaller C-S-H structure.

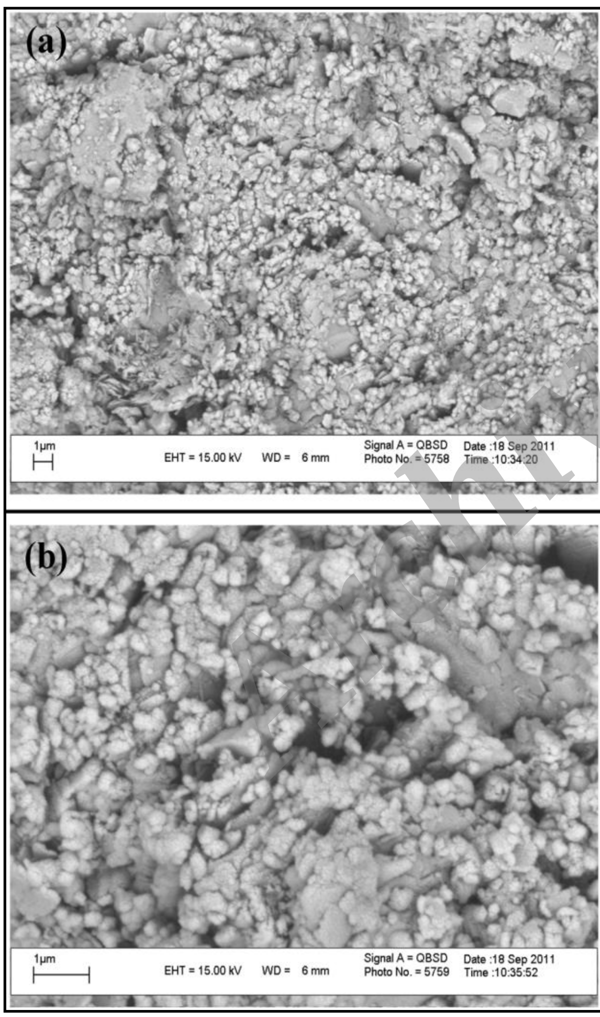

Fig. 3. Microstructure of normal concrete at different scale

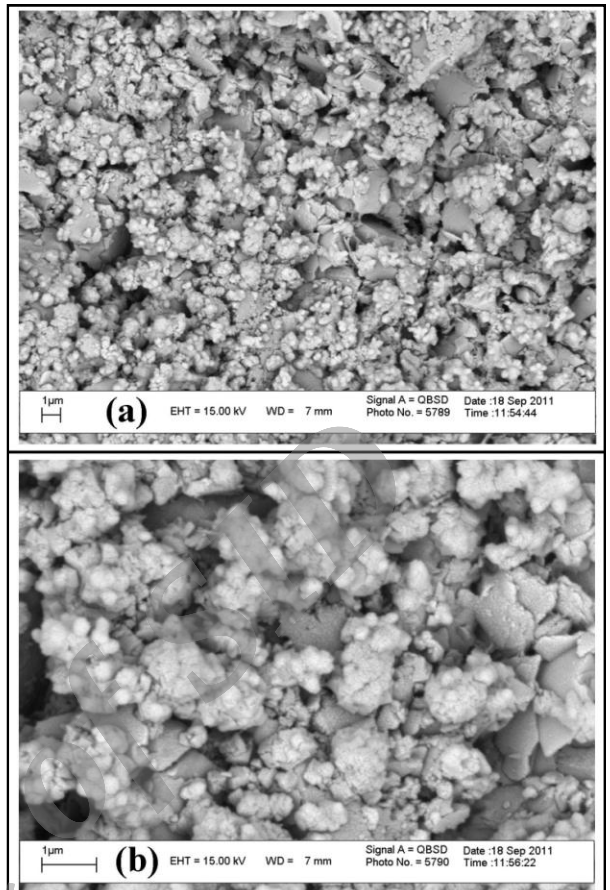

Fig. 4. Microstructure of Nano-Silica concrete at different scale

The X-Ray Diffraction Spectroscopy Test

It is possible to reveal the amount of different crystals existing in concrete specimens using the XRD test. As it is obvious from the Figure 5, the amount of the $Ca(OH)_2$ crystals existing in the normal concrete, is more than that of the concrete containing the Nano-Silica particles. On the other hand there is an increase in the amount of the calcium silicate hydrate (C-S-H) crystal in the concrete containing Nano-Silica compared with that of the normal concrete. It should be noted that the sampling was conducted at the age of 28^{th} day of the concrete specimens.

Nano-Silica is prone to have an extreme activity due to its high special surface and can chemically react with the $Ca(OH)_2$ crystals existing within the concrete and consequently produces the C-S-H material and decreases the amount the $Ca(OH)_2$ crystals. About 50%-60% of the completely hydrated cement paste is formed by C-S-H. Therefore, C-S-H is the most important factor that affecting to cement paste properties determination and due to possessing strong inter-layer van der Waals forces shows more compression strength in comparison with that of the calcium hydroxide crystals, which forms 20%-25% of the hydrated cement paste.

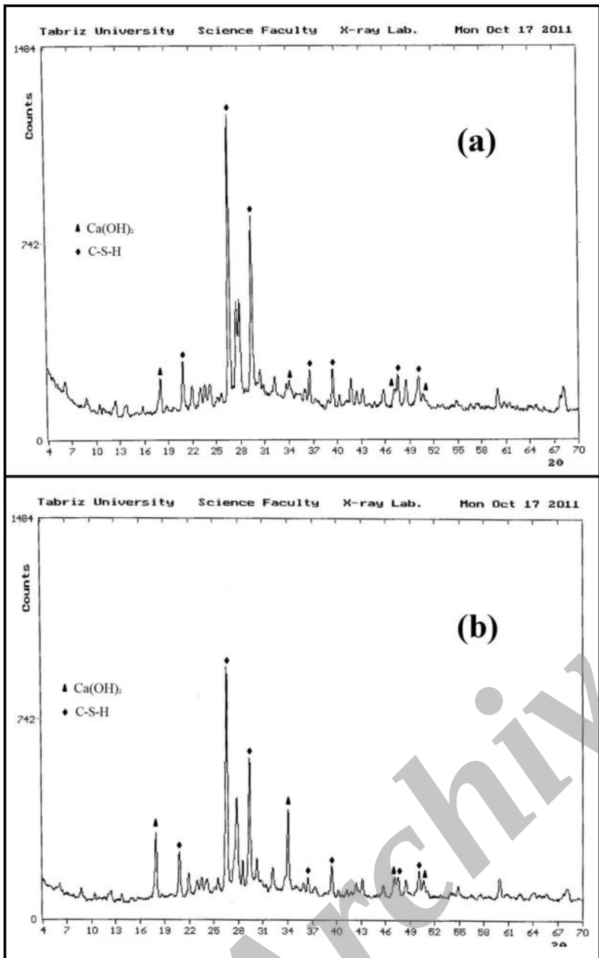

Fig. 5. XRD results of concrete at the curing age of 28 days (A) concrete with nano-silica (B) normal concrete

The calcium hydroxide is washed out over the time and is derived out of the concrete in sediment form and results in more voids in the hardened concrete. On the other hand, the C-S-H particles sizes are in nanometer and since the nano particles are in seed form, adding nano particles to the concrete would fulfill the voids of the material and then accumulate the whole mixture. Therefore, applying Nano-Silica particles in concrete structure would increase the stability and uniformity of the hydration products and improve the mechanical properties and durability of the concrete.

CONCLUSIONS

- Applying Nano-silica particles in concrete mixtures can result in an increase in compressive strength of the concrete in comparison with that of normal concrete.

- Applying Nano-silica particles in concrete mixes can result in a decrease in water permeability of the concrete.

-according SEM test results, the structure of the concrete containing nano particles seems to be more uniform than that of the normal concrete.

- According to the test results, it is specified that the combined application of Micro-Silica and Nano-Silica would lead to a higher compressive strength among all samples. This can be related to different part playing of them in concrete mixes. These particles well operate as filler leading to fewer pores in cement paste to be occupied by calcium silicate production.

- The maximum effects of Nano-Silica occur in the first few days after mixing due to the intensive activity of this Nano-Pozzolanic, which is well depicted in the accomplished experiments and existing literatures.

- There exists significant problem in using low water to cement ratio (w/c). According to the intensive reactivity of Nano-Silica and its high special surface, using lower w/c ratio can lead to inconsistency in dispersion of the Nano particles in overall sample body and more likely to formation of the flocs by clumping the nano particles in a specific parts of the concrete.

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Cite this article as: J. Esmaeili *et al.*: Investigation of the effects of nano-silica on the properties of concrete in comparison with micro-silica.
Int. J.Nano Dimens. 3(4): 321-328, Spring 2013