

## **Influence of Colloidal Nano-SiO<sub>2</sub> Addition as Silica Fume Replacement Material in Properties of Concrete**

**A.M. Raïss Ghasemi, T. Parhizkar, and A.A. Ramezani-pour**

*Building and Housing Research Center, P.O. Box 13145-1696, Tehran, Iran,  
<raïssghasemi@bhrc.ac.ir>, <parhizkar@bhrc.ac.ir>, <ramezani-pour@bhrc.ac.ir>*

### **ABSTRACT**

The influence of nano SiO<sub>2</sub> (NS) addition as silica fume (SF) replacement on mechanical and durability properties of concrete has been studied through measurement of compressive strength, rapid chloride permeability (RCPT), depth of water penetration (DWPT) and chloride profile tests. Nano SiO<sub>2</sub> was used as colloidal sol with 50% wt of solid content. Results indicated that the use of 0.75% wt NS and 3% wt SF better performance in compressive strength and DWPT. In the RCPT, the use of 0.75% wt NS and 6% wt SF showed lower chloride permeability. The influence of NS alone didn't have significant effect on the reduction of water penetration and chloride permeability tests.

### **INTRODUCTION**

In recent years much research has been done on the application of SiO<sub>2</sub> nano-particles in cement based materials (such as paste, mortar and concrete). However, little research has been done on the effect on the durability of concrete using nano SiO<sub>2</sub> particles.

The amorphous or glassy silica, the major component of pozzolan, reacts with calcium hydroxide formed from the hydration of calcium silicates. The rate of the pozzolanic reaction is proportional to the amount of surface area available for reaction. Super fine inorganic materials including active composite (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO) such as slag, zeolite and coal ash were proved to be indispensable ingredient of some high-strength cement. According to some research results, silica fume is valuable for improving mechanical properties, and enhancing freeze-thaw durability, vibration damping capacity, abrasion resistance, bond strength with steel rebars, chemical attack resistance and corrosion resistance of steel rebars. Furthermore, silica fume decreases the alkali-silica reactivity, the drying shrinkage, permeability, creep rate and thermal expansion [D.D. Chung 2004, 2002; M. Tang et al. 2003].

The pozzolanic activity of nano-SiO<sub>2</sub> is more obvious than that of silica fume. Nano-SiO<sub>2</sub> can react with calcium hydroxide (Ca (OH)<sub>2</sub>) crystals, which are arrayed in the interfacial transition zone (ITZ) between hardened cement paste and aggregates, and produce C-S-H gel [Q. Ye 2001, R.S. Chen 2002, Q. Ye et al. 2003]. However, it has not yet been established whether the more rapid hydration of cement in the presence of nano-silica is due to its chemical reactivity upon dissolution (pozzolanic activity) or to a considerable surface activity. One main objective of the present work is to clarify of this ambiguity [J. Bjornstrom et al. 2004]. Nano-SiO<sub>2</sub> can improve the pressure-sensitive properties of cement mortar [H. Li

et al. 2004, H. Li et al. 2004]. Byung-Wan et al. demonstrated that the nano-particle were more valuable in enhancing strength than silica fume. Their results of the examinations indicate that the SiO<sub>2</sub> in nano scale behave not only as a filler to improve the microstructure, but also as an activator to promote pozzolanic reactions [Byung-Wan Jo et al. 2007]. Q. Ye et al. [Q. Ye et al. 2003] indicated that high-strength concrete with nano-SiO<sub>2</sub> has higher flexural strength. Penetrability in cement mortars and some concrete were studied extensively [P. Halamickova 1995, K.S. Chia 2002, R.P. Khatri 1997, A. Boddy 2001, C.C. Yang 2003, C.J. Shi 2004].

Colloidal silica (CS) denotes small particles consisting of an amorphous SiO<sub>2</sub> core with a hydroxylated surface, which are insoluble in water. The size of the particles can be varied between 1 and 500 nm, hence they are small enough to remain suspended in a fluid medium without settling. Parameters such as specific surface area, size and size distribution can be controlled by the synthesis technique. Due to the high specific surface area for the nano-meter sized CS particles they constitute a highly reactive siliceous material [J. Bjornstrom et al. 2003].

However, up to now, there is little report on the durability of concrete. In this paper an effort was made to investigate the effect of nano-SiO<sub>2</sub> on the durability of concrete. A water permeability test and rapid chloride permeability test were performed to investigate the durability of concrete with nano-SiO<sub>2</sub>. A comparison was also made among silica fume incorporating nano-SiO<sub>2</sub>, silica fume and nano-SiO<sub>2</sub> alone in two rate of silica fume replacement (low volume, 4.5% wt and medium volume, 7.5% wt). Results indicated that the use of 0.75% wt NS and 3% wt SF better performance in compressive strength and DWPT. In the RCPT, the use of 0.75% wt NS and 6% wt SF showed lower chloride permeability. The influence of NS alone didn't have significant effect on the reduction of water penetration and chloride permeability tests.

## EXPERIMENTAL INVESTIGATION

### Material properties

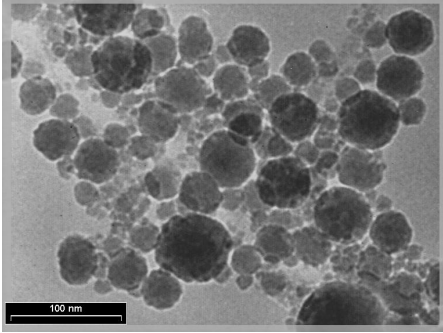
The cement used is Portland cement (32.5 grade, Type II accordance ASTM C150). The chemical analysis of cement and silica fume used in this study is shown in Table 1.

**Table 1. Chemical analysis of Portland cement and silica fume**

| Chemical analysis              | Portland cement, % | Silica fume, % |
|--------------------------------|--------------------|----------------|
| SiO <sub>2</sub>               | 20.96              | 91.1           |
| Al <sub>2</sub> O <sub>3</sub> | 4.2                | 1.55           |
| Fe <sub>2</sub> O <sub>3</sub> | 4.6                | 2.00           |
| CaO                            | 61.88              | 2.24           |
| MgO                            | 3.4                | 0.60           |
| NaO <sub>2</sub>               | 0.5                | -              |
| K <sub>2</sub> O               | 0.4                | -              |
| Ignition Loss                  | 1.74               | 2.10           |
| Free lime                      | 0.84               | -              |
| SO <sub>3</sub>                | 1.79               | 0.45           |

Fine and coarse aggregates are natural river sand. Fineness modulus of sand is 3.5. Maximum size of the coarse aggregate is 19 mm. The specific gravity and saturated surface dry (SSD) water absorption of sand and aggregates were 2.56 kg/m<sup>3</sup>, and 3.2% and 2.57 kg/m<sup>3</sup>, and

1.9%, respectively. High range water-reducing agent used was one kind of carboxylic ether base (Glenium 110). The colloidal silica sol used (Cembinder 8™) contained 50% wt of solid material. The density was 1.4 g/cm<sup>3</sup> with an 80 m<sup>2</sup>/g specific surface area, supplied by EKA Chemicals AB, Bohus, Sweden. Transmission electron microscopy (TEM) of colloidal silica is shown in fig. 1.



**Fig. 1. TEM picture of nano colloidal silica**

### Mix proportions

Details of the mixture proportions for the concrete containing different amounts of silica fume (SF) and nano-SiO<sub>2</sub> (NS) are given in Table 2.

**Table 2. Mixture proportion**

| Sample      | Cement,<br>Kg/m <sup>3</sup> | Silica<br>fume,<br>Kg/m <sup>3</sup> | Nano-<br>SiO <sub>2</sub> <sup>1</sup> ,<br>Kg/m <sup>3</sup> | Water,<br>Kg/m <sup>3</sup> | w/cem. | Aggregates,<br>Kg/m <sup>3</sup> | HRWRA,<br>% |
|-------------|------------------------------|--------------------------------------|---|-----------------------------|--------|----------------------------------|-------------|
| CON         | 400                          | 0                                    | 0   | 180                         | 0.45   | 1750                             | 0.17        |
| NS2.25/SF0  | 382                          | 0                                    | 18  | 180                         | 0.45   | 1730                             | 0.24        |
| NS0.75/SF3  | 382                          | 12                                   | 6   | 180                         | 0.45   | 1740                             | 0.27        |
| NS0/SF4.5   | 382                          | 18                                   | 0   | 180                         | 0.45   | 1743                             | 0.12        |
| NS1.5/SF4.5 | 370                          | 18                                   | 12  | 180                         | 0.45   | 1730                             | 0.40        |
| NS0.75/SF6  | 370                          | 24                                   | 6   | 180                         | 0.45   | 1735                             | 0.30        |
| NS0/SF7.5   | 370                          | 30                                   | 0   | 180                         | 0.45   | 1740                             | 0.31        |

1- Amount of nano-SiO<sub>2</sub> is colloidal form (with 50% solid content).

2- Total water content adjusts according to water content of colloidal nano-SiO<sub>2</sub> and aggregates.

Water to cementitious material ratios (w/cm) for all mixes was 0.45. Four different content of SF of 3, 4.5, 6 and 7.5% and three different amounts of NS (0.75, 1.5 and 2.25%) by weight of cement were used. The dosage of super-plasticizer was shown as percentage of the weight of the cementitious materials and adjusted according to the effect of the different levels of silica fume and nano-SiO<sub>2</sub>. The amount of super-plasticizer used was sufficient such that workable concrete and no segregation were reported.

### Testing procedure

The concrete mixtures were mixed in pan mixer. Silica fume (SF) was mixed with water to slurry form. All materials except NS and super-plasticizer for 2 min stirred, a 2 min stop and

1 min mixing, and then colloidal nona-SiO<sub>2</sub> (CS) added. After 1 min mixing, super-plasticizer was also added and mixing for 1 min was continued.

- Compressive strength tests were carried out on 100 mm cube specimens, according to the European norm EN 12390-3:2000.
- Depth of Water Penetration under pressure (DWPT), was carried out on 10 mm cube specimens, according to the European norm EN 12390-8:2000.
- Rapid Chloride Permeability Tests (RCPT), according to the American standard, ASTM C1202, on  $\phi$ 100\*50 mm specimens were carried out.

Compressive strength, Depth of Water Penetration and RCPT were carried out in 7, 28, 91 and 180; 28 and 91; 28 and 91 days respectively.

## RESULT AND DISCUSSION

### Compressive Strength

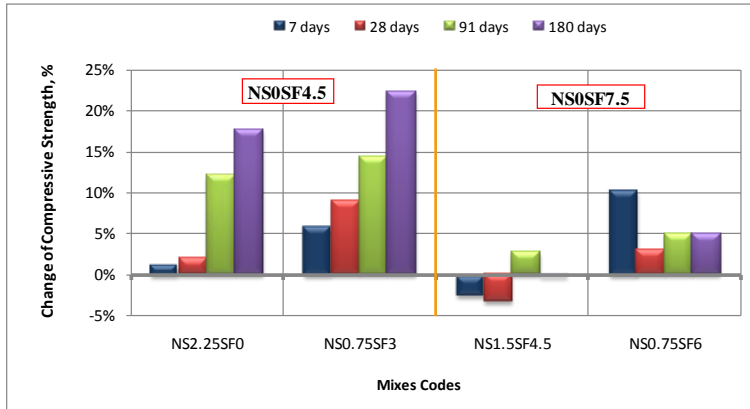
The compressive strength and its development of the mixtures are shown in Table 3. The CON is control mixture; in early age (7 and 28 days) samples had a lower compressive strength in comparison with other mixtures.

**Table 3. Compressive strength of all concrete mixtures**

| Sample      | SF,<br>Kg/m <sup>3</sup> | CS,<br>Kg/m <sup>3</sup> | Compressive strength (N/mm <sup>2</sup> ) |         |         |          |
|-------------|--------------------------|--------------------------|---|---------|---------|----------|
|             |                          |                          | 7 days                                    | 28 days | 91 days | 180 days |
| CON         | 0                        | 0                        | 32.7                                      | 48.5    | 55.5    | 61.9     |
| NS2.25/SF0  | 0                        | 18                       | 36.3                                      | 51.9    | 59.9    | 64.1     |
| NS0.75/SF3  | 12                       | 6                        | 38.0                                      | 55.5    | 61.1    | 66.7     |
| NS0/SF4.5   | 18                       | 0                        | 35.9                                      | 50.9    | 53.4    | 54.5     |
| NS1.5/SF4.5 | 18                       | 12                       | 36.7                                      | 55.1    | 60.3    | 60.0     |
| NS0.75/SF6  | 24                       | 6                        | 41.5                                      | 58.7    | 61.7    | 63.0     |
| NS0/SF7.5   | 30                       | 0                        | 37.6                                      | 56.9    | 58.7    | 60.1     |

Mixtures NS0.75/SF3 and NS0.75/SF6 have higher compressive strength than other mixtures. The NS0.75/SF6 at 7 and 28 days had respectively, 27 and 21% increase in compressive strength compared to the control mixture. The NS0.75/SF3 had a higher strength at 180 days in comparison with other mixtures. The development of compressive strength with an age of 7 to 91 days of all mixes that contained CS were higher than that of the control mixture.

As seen in Fig 2, replacement of SF with CS in the NS2.25/SF0, NS0.75/SF3 and NS0.75/SF6 mixes, improved compressive strength in comparison to the mixes that only contained SF at all ages (7 to 180 days). In fact, nano-SiO<sub>2</sub> is thought to be more effective in pozzolanic reaction than silica fume (except in NS1.5/SF4.5). Also the nano-SiO<sub>2</sub> would fill pores to increase the concrete strength, as silica fume does. The incorporating of 0.75% CS and 3% by weight of cement, higher compressive strength compare to other ratio (for example, 9%, 14% and 22% at ages of 28, 91 and 180 days compared to the NS0/SF4.5).

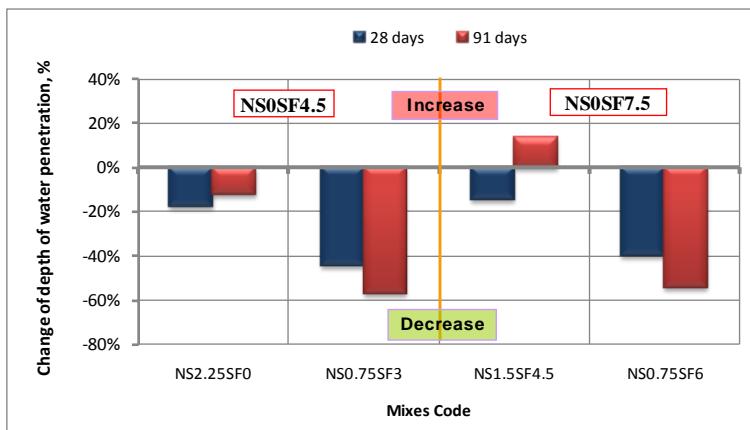


**Fig 2. Change of compressive strength of mixes, in comparison to SF alone**

### Depth of Water penetration under pressure (DWPT)

The permeability characteristics of the concrete are one of its most important durability parameters. As noted before, this parameter was tested by using the EN 12390-8 standard. The test results for the concrete mixes are shown in Table 4. As seen in this table, and according to the classification in the DIN standard, all mixtures are in the low permeability range (< 30mm), but the NS0.75/SF3 and NS0.75/SF6 concretes had lower permeability at both ages in comparison to the control concrete samples (and other mixes). All mixes that contain CS and/or SF, had lower permeability at 91 days, in comparison to the CON.

As seen in fig 3, performance of CS and SF to improve the DWPT of concrete is very similar to the effect of CS and SF, in improvement of compressive strength. The NS0.75/SF3 had higher decreased in the water permeability, in comparison to the other mixes. These result confirmed that incorporating of 0.75% CS and 3% by weight of cement, can optimize the mix ratio of CS and SF.



**Fig 3. Change of DWPT of mixes, in comparison to SF alone**

### Rapid Chloride Permeability Test (RCPT)

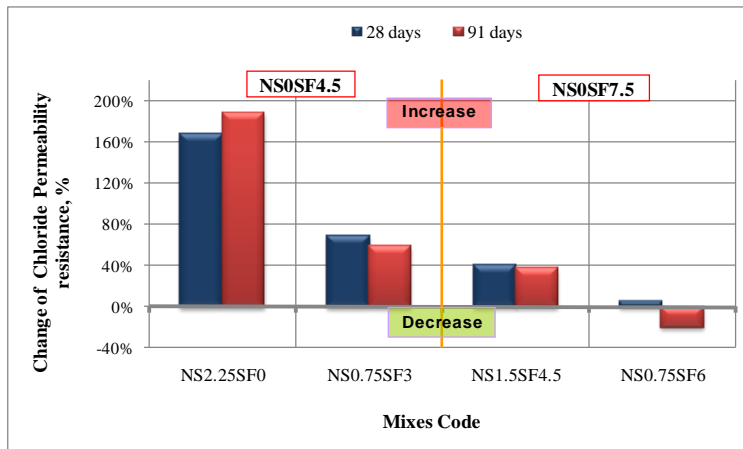
The chloride penetration test was carried out according to the ASTM C 1202 standard after 28 and 91 days, the results are shown in Table 4. These results show that with an increase in the amount of silica fume, the chloride penetration resistance was decreased. This reduction

in chloride ion diffusion can be attributed to the fact that, pozzolanic activity of NS is higher than CS. In General, the NS0.75/SF6 and NS0/SF7.5 mixes had lower chloride permeability than other concrete mixtures.

**Table 4. Compressive strength of all concrete mixtures**

| Sample      | SF, Kg/m <sup>3</sup> | CS, Kg/m <sup>3</sup> | DWPT, mm |         | RCPT, coulomb |         |
|-------------|-----------------------|-----------------------|----------|---------|---------------|---------|
|             |                       |                       | 28 days  | 91 days | 28 days       | 91 days |
| CON         | 0                     | 0                     | 14.7     | 19.0    | 5221          | 4264    |
| NS2.25/SF0  | 0                     | 18                    | 16.0     | 12.3    | 4795          | 4672    |
| NS0.75/SF3  | 12                    | 6                     | 10.7     | 6.0     | 3030          | 2569    |
| NS0/SF4.5   | 18                    | 0                     | 19.3     | 14.0    | 1794          | 1618    |
| NS1.5/SF4.5 | 18                    | 12                    | 16.5     | 14.0    | 1739          | 1718    |
| NS0.75/SF6  | 24                    | 6                     | 11.7     | 5.7     | 1311          | 992     |
| NS0/SF7.5   | 30                    | 0                     | 19.3     | 12.3    | 1246          | 1244    |

Effect of CS in the RCPT is very different from the compressive strength and water permeability testes results. It can be seen in fig 4, that the resistance to chloride permeability of concrete, were increased with increasing of the silica fume content. According to these results, the filling ability of CS is more than pozzolanic reaction. Therefore, the silica fume is more effective to enhance chloride permeability than nano-SiO<sub>2</sub>.



**Fig 4. Change of RCPT of mixes, in comparison to SF alone**

## CONCLUSIONS

In the present study, effects of the one type colloidal nano silica, was investigated by compressive strength, water permeability and rapid chloride penetration tests. The results and conclusions are summarized as follows:

- The used of NS and/or SF, in short-term (up to 28 days), were improved compressive strength and reduced chloride ion permeability.
- The accelerating effects of NS on compressive strength and RCPT were demonstrated.

- In the ages of 91 and 180 days, dependent to amount of consumption and the percentage of CS or NS, and their composition, the compressive strength development was different. In a way, the compressive strength of CON mixture in 180 days more than any other mixture. The mixtures that containing 0.75% wt, NS, and 3% or 6% wt, silica fume, in the ages 180 days, have the most strength, respectively.
- Although, compressive strength and water penetration tests results shows that the nano-SiO<sub>2</sub> have better performance than the silica fume (in the same condition), but the combination of NS and SF has better performance than the mixtures that contained NS or SF alone.
- Review of compressive strength, RCPT and DWPT results, shows the influence of NS in improving concrete properties, both due to filling ability (Filler) is and the Pozzolanic activity, but based on the results of RCPT, it is expected that nano SiO<sub>2</sub> behave more as filler.

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