



## EFFECT OF NANOPARTICLES ON FROST DURABILITY OF CONCRETE

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### ABSTRACT

The influence of nano-TiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub> and nano-ZnO<sub>2</sub> on durability and mechanical properties of concrete was experimentally investigated. For this purpose, compressive strength tests were conducted in order to investigate the effects of nano particles on mechanical properties of concrete. Moreover water absorption and freeze and thaw tests were conducted to explore the effect of nano particles on durability of concrete. Results of this study showed that all the examined nano particles can improve durability and mechanical properties of concrete. The contribution of nano-TiO<sub>2</sub> on improvement of mechanical properties and durability of concrete was more than the other nano particles.

**Keywords:** Nano particles; mechanical properties; frost durability.

### 1. INTRODUCTION

The freezing and thawing is one of the major problems of the concrete pavement which is mostly used for road surfaces, bridge decks, airfield runways and parking lots [1]. Numerous studies on the frost resistance of concrete have been carried out to improve the durability and to prolong the service life of concrete in the world [2-4]. As results of these studies, it is now commonly believed that mineral admixtures can significantly improve permeation-related durability of concrete and air-entrainment can enhance frost resistance, although it causes a reduction in compressive strength of concrete [5]. It is also reported that pozzolans could make microstructure of concrete more compact and improve frost resistance [6]. The effect of pozzolans is mainly to improve the interfacial transition zone, resulting in a reduction in porosity of this zone [7].

On the other hand, during the recent years nanotechnology is developing with noticeable

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rate. Due to the new potential uses of nano-particles, there is a global interest in the investigation of the influence of nano particles in construction materials especially cement mortar and concrete. The nano scale size of particles can result in dramatically improved properties from conventional grain-size materials of the same chemical composition.

As authors knowledge, there are few works on incorporating nano particles into concrete to achieve improved durability properties. There are several reports on merging nanoparticles in concrete which most of them have focused on using  $\text{SiO}_2$  nano particles [8,9]. Previously a series of works [10] have been conducted on cementitious composites by adding different nano particles evaluating the mechanical properties of the composites. Among the utilized nano particles, although adding  $\text{TiO}_2$ ,  $\text{ZnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  nano particles into cement paste is studied in few works [10,11], more detailed evaluation in order to introduce their characteristics and effects on cementitious materials are required.

Nano- $\text{TiO}_2$  has proven very effective for the self-cleaning of concrete and provides the additional benefit of helping to clean the environment [12]. Nano- $\text{TiO}_2$  containing concrete acts by triggering photocatalytic degradation of the pollutants, such as  $\text{NO}_x$ , carbon monoxide, VOCs, chlorophenols and aldehydes from vehicle and industrial emissions [13]. 'Self-cleaning' and 'de-polluting' concrete products are already being produced for use in the facades of buildings and in paving materials for roads and have been used in Europe and Japan. In addition to imparting self-cleaning properties, a few studies have shown that nano- $\text{TiO}_2$  can accelerate the early-age hydration of Portland cement, improve compressive and flexural strengths, and enhances the abrasion resistance of concrete [1,14], however it also found that aging due to carbonation may result in loss in catalytic efficiency [13].

The effects of zinc dioxide nano particles on flexural strength of self-compacting concrete were investigated by Nazari and Riahi [11]. They showed that as the content of  $\text{ZnO}_2$  nano particles is increased, the flexural strength of SCC specimens is increased. Also the pore structure of self-compacting concrete containing  $\text{ZnO}_2$  nano particles is improved [11].

It has been stated that the use of nano-alumina as a partial replacement by cement leads to the C-A-S (calcium-aluminum-silicate) gel formation in concrete. Nano-alumina reacts with calcium hydroxide produced from the hydration of calcium aluminates. The rate of this reaction is proportional to the amount of surface area available for this reaction. Therefore it is possible to add nano-alumina of a high purity and a high blain fineness value in order to improve the characteristics of concrete [9].

The investigation results show that nano-alumina particles blended concrete has higher compressive strength compare to that of the concrete without nano-alumina particles. It is found that the cement could be advantageously replaced with nano-alumina particles up to maximum limit of 2% with average particle size of 15 nm [15]. Nano-alumina has been shown to significantly increase the modules of elasticity (up to 143% at a dosage of 5%) but to have a limited effect on the compressive strength [16].

Nano-alumina improves mechanical properties of concrete such as compressive and tensile strength. It also decreases the water absorbtion and chloride penetration; improving the durability of concrete [17].

The effect of  $\text{Fe}_2\text{O}_3$  nano particles has been investigated [17]. It is reported that nano- $\text{Fe}_2\text{O}_3$  particles increase the compressive strength of concrete. Nano- $\text{Fe}_2\text{O}_3$  particles can significantly reduce the water absorption of concrete. It also enhances tensile strength of concrete [17].

Nano-Fe<sub>2</sub>O<sub>3</sub> has been found to provide concrete with self-sensing capabilities as well as to improve its compressive and flexural strengths [18,19]. The volume electric resistance of cement mortar with nano-Fe<sub>2</sub>O<sub>3</sub> was found to change with the applied load, demonstrating that mortar with nano-Fe<sub>2</sub>O<sub>3</sub> could sense its own compressive stress. Such sensing capabilities are invaluable for real-time structural health monitoring and for the construction of smart structures as they do not involve the use of embedded or attached sensors.

Incorporating of nanoparticles in order to improve the durability of concrete is rarely reported. Therefore introducing some nanoparticles which probably could improve the mechanical and durability properties of cementitious composites is inherent. The aim of this study is incorporating ZnO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles into concrete to study compressive strength and frost resistance of concrete. Several specimens with polycarboxylate superplasticizer have been prepared and their mechanical and durability properties have been considered when, instead of cement, ZnO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles were partially added to the cement paste.

## 2. MATERIALS AND EXPERIMENTAL PROGRAM

### 2.1 Materials and mixture proportion

An ordinary portland cement, conforming to the ASTM C150 [20] with a specific area of 3000 (cm<sup>2</sup>/g) and a specific gravity of 3.15 (g/cm<sup>3</sup>) is used. Its chemical composition is shown in Table 1. Fine aggregate is natural river sand with a fineness module of 2.6. The course aggregate is crushed stone with diameter of 5-12 mm. The superplasticizer (SP) admixture [polycarboxylic acid based (Glenium 51P)], is employed as much as 0.5% by the weight of cementitious materials to aid the dispersion of nano-particles in concrete and achieve good workability of concrete. According to the Dransfield research [21] in 1987, superplasticizer agents affect the frost resistance of concrete because of their property of making bubbles in cement paste; so in order to confine the effective parameters in frost resistance of concrete, the amount of superplasticizer is kept constant in all specimens. The properties of superplasticizer admixture are shown in Table 2.

Table 1: Chemical composition of Portland cement

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Loss	Insol
21.86	5.90	3.20	63.50	1.80	1.70	0.20	0.70	1.24	0.50

Table 2: Properties of superplasticizer (Glenium 51P)

Form	Liquid
Color	Light brown-clear
PH value	6.5-7.5 (23°C)
Density	1.072-1.092 (gr/cm <sup>3</sup> )
Solid content	34%-36%

The nano particles are purchased from Nanopars company. The properties of nano particles are given in Table 3.

Table 3: The properties of nanoparticles

Item	Diameter (nm)	Specific surface area (m <sup>2</sup> /g)	Density (gr/cm <sup>3</sup> )	Purity
Al <sub>2</sub> O <sub>3</sub>	8.0	200	0.12	>99.8%
ZnO <sub>2</sub>	10.0	160	0.08	99.9%
Fe <sub>2</sub> O <sub>3</sub>	10.0	200-220	0.16	>99.8%
TiO <sub>2</sub>	15.0	260	0.05	99.8%

The water to binder (the sum of cement and nano particles) ratio used for all mixtures is 0.48. Sand ratio is 0.51. The mixture proportions for cubic meter of concrete are given in Table 4. Herein PC denotes plain concrete. NTC and NAC denote the concrete containing nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> respectively. NZC and NFC denote the concrete containing nano-ZnO<sub>2</sub> and nano-Fe<sub>2</sub>O<sub>3</sub> respectively. The amount of nano particles used for all specimens was 2% by the weight of cementitious materials.

Table 4: Mix proportions of specimens (Kg/m<sup>3</sup>)

Mixture no.	Water	Cement	Sand	Coarse aggregate	nTiO <sub>2</sub>	nAl <sub>2</sub> O <sub>3</sub>	nFe <sub>2</sub> O <sub>3</sub>	nZnO <sub>2</sub>	UNF	slump (cm)
PC	168	350	960	920	-	-	-	-	1.75	12.0
NTC	168	343	960	920	7	-	-	-	1.75	6.0
NAC	168	343	960	920	-	7	-	-	1.75	7.5
NFC	168	343	960	920	-	-	7	-	1.75	7.0
NZC	168	343	960	920	-	-	-	7	1.75	9.0

In this study the amount of superplasticizer in all specimens was the same in order to make other factors such as frost resistance comparable; so it can be seen that using nanoparticles reduces the workability of concrete.

### 2.2 Specimen Preparation

To fabricate the concrete containing nano particles, superplasticizer is firstly mixed into water in a mixer, and then nano particles are added and stirred at a high speed for 5 minutes. Course aggregate, sand and cement are mixed at a low speed for 2 minutes in a concrete centrifugal blender, then the mixture of water, superplasticizer and nano particles are slowly poured in and stirred at a low speed for another 2 minutes to achieve proper workability.

To fabricate plain concrete, superplasticizer is firstly dissolved in water. After course aggregate, sand and cement are mixed uniformly in a concrete centrifugal blender, the mixture of water and superplasticizer is poured in and stirred for several minutes.

Finally the fresh concrete is poured into oiled molds to form cubes of size 100×100×100 mm. After pouring an external vibrator is used to facilitate compaction and decrease the amount of air bubbles. The specimens are demolded at 24 hours and then cured in a standard moist room at a temperature of 20±3°C.

### 2.3 Test methods

Following test were conducted in order to determine mechanical properties and frost

resistance of concrete containing nano-particles with respect to plain concrete.

a. Compressive test conducted after 7, 28 and 120 days of curing according to the standard test method of ASTM C39.

b. The percentage of water absorption in specimens measured after 28 days of curing according to the ASTM C642 procedure [22].

c. The specimens were subjected to cycles of freezing and thawing in an automatic freeze-thaw machine which can apply freezing cycles at  $-20^{\circ}\text{C}$  and thawing cycles at  $20^{\circ}\text{C}$  both in water according to ASTM C666A[23]. The loss of mass, change in length, increase in water absorption and reduction in compressive strength of specimens measured during cycles.

### 3. EXPERIMENTAL RESULT

#### 3.1 Compressive strength

Compressive strength of specimens after 7, 28 and 120 days are shown in Table 5. It can be found that the compressive strength is developed in concretes containing nano particles in every case higher than that of control concretes.

Table 5: Compressive strength of specimens (MPa)

Mixture No.	Compressive Strength (7 days)		Compressive Strength (28 days)		Compressive Strength (120 days)	
	Target (Mpa)	Enhanced extent (%)	Target (Mpa)	Enhanced extent (%)	Target (Mpa)	Enhanced extent (%)
PC	27.10	0.00	42.11	0.00	47.15	0.00
NTC	30.35	12.00	51.67	22.71	59.88	27.00
NAC	29.27	8.00	47.43	12.63	54.70	16.01
NFC	28.45	5.00	46.48	10.07	53.90	14.31
NZC	29.81	10.00	49.74	18.13	58.04	23.11

As Table 5 shows, the compressive strength of concrete is improved by using nano particles as a part of cementitious materials. The compressive strength of concrete after 28 days of curing is enhanced as much as 22.71% (in comparison to that of plain concrete) by replacing 2% cement with nano-titanium oxide particles. The enhancement of the compressive strength of concrete can be attributed to that nano particles can act as nuclei for cement phases, further promoting cement hydration due to their high reactivity, as nano reinforcement, densifying the microstructure and the interfacial transition zone, thereby, leading to a reduced porosity. Also, nano particles would fill pores to increase the compressive strength. It should be noted that using a high content of nano particles must be accompanied by adjustments to the water superplasticizer dosage in the mix in order to ensure that no agglomeration would happen and specimens do not suffer from excessive self desiccation and cracking. In addition, because nano particles are more difficult to uniformly disperse, when the content are large, the weak zone in concrete increases which results in the decrease of the strength of the concrete, which did not happen in this work.

According to Table 5, among the nano particles used in this work, nano-TiO<sub>2</sub> is the most

effective particle in enhancing the compressive strength of concrete.

### 3.2 Water Absorption

Water permeability tests are performed with several methods such as percentage of water absorption, rate of water absorption and coefficient of water absorption. In this work, to evaluate the water permeability of the specimens, percentage of water absorption is considered as a criterion of the pore volume or porosity of concrete after hardening, which is occupied by water in saturated state. Water absorption values of plain concrete and concrete containing nanoparticles were measured according to the ASTM C642 [22] after 28 days of moisture curing. Figure 1 shows the result of water absorption test.

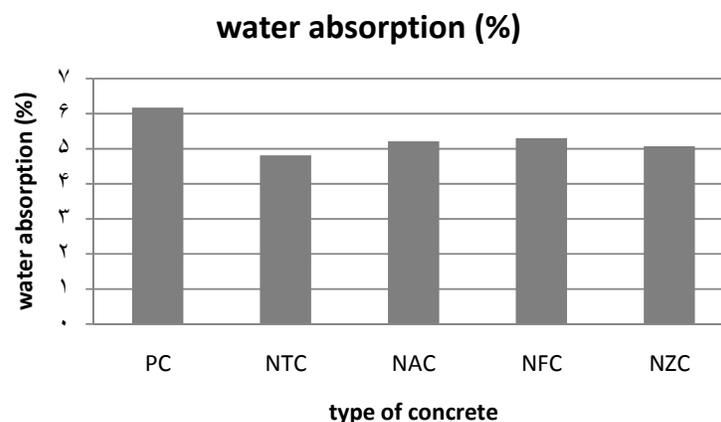


Figure 1. Water absorption of specimens

Figure 1 show that the percentage of water absorption in concrete containing nanoparticles is considerably lower than that of plain concrete. This may be due to the improved microstructure of concrete according to the use of nano particles. Nano particles recover the particle packing density of the concrete and as nano-filler improve the microstructure of it; thus the water permeability of concrete decreases by the replacement of cement with nano particles partially.

### 3.3 Frost resistance

In order to determine the frost resistance of concrete, the decrease in compressive strength, change in length, loss of mass and increase in water absorption in specimens measured during the cycles of freezing and thawing. It should be noted that the specimens were subjected to cycles of freezing and thawing in water according to the procedure of ASTM C666A.

#### 3.3.1 Compressive Strength

The compressive strength of specimens subjected to the freezing and thawing cycles, was determined after 50,150 and 300 cycles. Table 6 shows the results of compressive strength determination.

Table 6: The result of frost resistance determination in terms of strength loss for concrete using the rapid test method

Mixture No.	Residual/original compressive strength	Strength loss after 300 cycles	Cracking	Frost resistance
PC	0.00/47.15	100%	severe	poor
NTC	52.99/59.88	11.5%	slight	poor
NAC	42.06/54.70	23.1%	slight	poor
NFC	39.83/53.90	26.1%	slight	poor
NZC	49.80/58.04	14%	slight	poor

As Table 6 shows, the strength loss of concrete containing nanoparticles is much lower than that of plain concrete. For example concrete containing 2% nano-zinc oxide (by the weight of cementitious materials) showed only 14% strength loss after 300 cycles of freezing and thawing, while the strength loss of plain concrete after 300 cycles was 100%. Generally it can be said that concrete containing 2% nano-TiO<sub>2</sub> is the most frost resistant concrete among the tested samples in terms of compressive strength.

### 3.3.2 Length Change and Mass Loss

After 300 cycles of freezing and thawing, change in length and mass loss of specimens were measured in order to determine the frost resistance of concrete in terms of mass and length change. Figure 2 shows the length change and mass loss of specimens under the freezing and thawing condition.

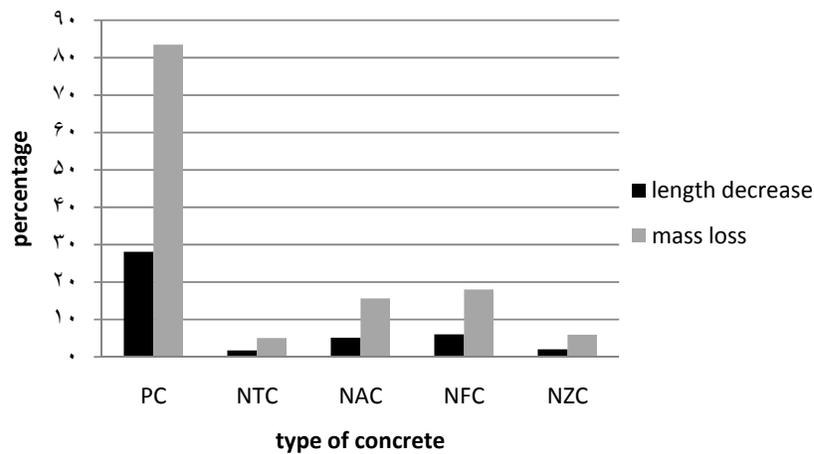


Figure 2. Length decrease and mass loss of specimens during freeze and thaw cycles

In Figure 2, it can be seen that the mass loss and length change of concrete containing nano particles have the same order as the strength loss and are much lower than that of plain concrete. Plain concrete showed 28.1% decrease in length after 300 cycles; while the decrease in length of concrete containing 2% nano-Fe<sub>2</sub>O<sub>3</sub> was 6.04%.

As far as length and mass change are concerned, among the tested concretes, concrete

containing nano-TiO<sub>2</sub> particles showed to be the most frost resistant sample.

### 3.3.3 Water Absorption

Water absorption of specimens measured after 300 cycles of freezing and thawing. Table 7 shows the water absorption of specimens after freeze and thaw cycles. It can be seen that the nano particles decrease the water absorption of specimens.

Table 7: Water Absorption of specimens during freeze and thaw cycles

Mixture no.	Water absorption after 300 cycles	Increase in water absorption after 300 cycles
PC	13.40	117.18
NTC	5.78	20.13
NAC	6.88	32.11
NFC	7.65	44.37
NZC	6.37	25.61

Table 7 shows that using nanoparticles in concrete controls the rate of increase in water absorption during the freeze and thaw cycles. The water absorption of plain concrete has been increased as much as 117% after 300 cycles of freezing and thawing; while the water absorption of concrete containing nano-Al<sub>2</sub>O<sub>3</sub> has been increased 32.11%.

The enhancement of frost resistance in terms of water absorption, is due to the rapid consuming of Ca (OH)<sub>2</sub> formed during the hydration of Portland cement, related to the high reactivity of nanoparticles. As a consequence the hydration of cement is accelerated and larger volumes of reaction products are forms. Also nanoparticles recover the particle packing density of the concrete and as nano filler improve the microstructure of it, directing to a reduced volume of larger pores in the cement paste.

## 4. DISCUSSION

The mechanical properties and frost resistance of concretes containing nano particles are improved. The mechanism of improving these properties of concrete by nano particles can be interpreted as follows: supposed that nano particles are uniformly dispersed and each particle is contained in a cube pattern, the distance between nano particles can be specified. After hydration begins, hydrate products diffuse and envelope nano particles as kernel. If the content of nano particles and the distance between them are appropriate, the crystallization will be controlled to be a suitable state through restricting the growth of Ca (OH)<sub>2</sub> crystal by nano particles. This makes the cement matrix more homogeneous and compact. Moreover some nano particles react with calcium hydroxide formed from calcium silicate hydration. It is plausible to use these nano-particles in order to produce a concrete with higher strength and considerably improved microstructure. The medium sizes of pores in concrete decreases by using nano particles. As a result concrete containing nano-particles absorbs less water in comparison to plain concrete because of a denser microstructure; so the stress, which is produced due to the volume change of frozen water, decreases and the concrete, will be more frost resistant.

## 5. CONCLUSION

The influence of nano-TiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub> and nano-ZnO<sub>2</sub> on durability and mechanical properties of concrete was experimentally investigated. For this purpose, compressive strength tests were conducted in order to investigate the effects of nano particles on mechanical properties of concrete. Moreover water absorption and freeze and thaw tests were conducted to explore the effect of nano particles on durability of concrete. Results of this study showed that all the examined nano particles can improve durability and mechanical properties of concrete. The contribution of nano-TiO<sub>2</sub> on improvement of mechanical properties and durability of concrete was more than the other nano particles.

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