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Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO_2

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Abstract

Water permeability resistant behavior and microstructure of concrete with nano-SiO_2 were experimentally studied. A water permeability test shows that, for concretes of similar 28-day strength, the incorporation of nano-SiO_2 can improve the resistance of water penetration of concrete. An ESEM test reveals that the microstructure of concrete with nano-SiO_2 is more uniform and compact than that of normal concrete. Mechanism about the effect of nano-SiO_2 on concrete is described.
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Keywords: Calcium–Silicate–Hydrate (C–S–H); Interfacial transition zone; Microstructure; Permeability; $Ca(OH)_2$; Concrete

1. Introduction

Nano-particles have been gaining increasing attention and been applied in many fields to fabricate new materials with novelty function due to their unique physical and chemical properties. If nano-particles are integrated with cement-based building materials, the new materials might possess some outstanding properties. The pozzolanic activity of nano-SiO_2 is more obvious than that of silica fume. Nano-SiO_2 can react with calcium hydroxide ($Ca(OH)_2$) crystals, which are arrayed in the interfacial transition zone (ITZ) between hardened cement paste and aggregates, and produce C–S–H gel. Thus, the size and amount of calcium hydroxide crystals are significantly decreased, and the early age strength of the hardened cement paste is increased [1–3]. Nano-SiO_2 can behave as a nucleus to tightly bond with cement hydrates. The stable gel structures can be formed and the mechanical properties of hardened cement paste can be improved when a smaller amount of nano-SiO_2 is added [4]. Nano-SiO_2 can improve the pressure-sensitive properties of cement mortar [5,6]. Fly ash concrete with nano-SiO_2 has the higher density and strength [7]. Ref. [8] indicated that high-strength concrete with nano-SiO_2 has higher flexural strength.

Penetrability in cement mortars and concrete (such as high-strength lightweight aggregate concrete, and concrete containing high-reactivity metakaolin, et al.) were studied extensively [9–14]. However, up to now, there is no published report on the durability of concrete. A water permeability test and an ESEM test were performed to investigate the durability of concrete with nano-SiO_2 in this paper. The research results reveal that nano-SiO_2 can improve the microstructure of the interfacial transition zone (ITZ) between aggregates and binding paste matrix and the water permeability resistant capacity of concrete.

2. Experimental investigation

2.1. Material properties

All materials used in these experiments are produced in China. The cement is the grade 42.5 Porland cement, and a class 1 fly ash (Chinese Standard) is used, as shown in Table 1. The superplasticizer TW-7 is naphthalene-type with a solid content of 40%. The coarse aggregates used are the continuous grading crushed gravels, with the maximum

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Table 1
Characteristics of cement and fly ash

Characteristics	Cement	Fly ash
Density (g/cm^3)	3.18	2.55
Special area (cm^2/g)	4168	6910
Bulk density (g/cm^3)	1.101	0.741
Ratio of water requirement (%)	–	84.8
Special surface mean diameter (μm)	15.32	12.33

Table 2
Properties of nano-SiO_2

Item	Diameter (nm)	Surface–volume ratio (m^2/g)	Density (g/cm^3)	Purity (%)
Target	15±5	160±20	<0.15	>99.9

particle size of 26.5 mm. The fine aggregates are river sands, with a fineness modulus of 2.7. Nano-SiO_2 is produced by Zhoushan Mingri Nanophase Material Company, Zhejian province, China. The properties of nano-SiO_2 are shown in Table 2.

2.2. Mix proportions

"NC" and "SC" are the mix proportions of normal concrete and concrete with nano-SiO_2 (called the nano-SiO_2 concrete), respectively. In the nano-SiO_2 concrete, part of cement is replaced by nano-SiO_2. Due to the vast difference between the density of nano-SiO_2 and that of cement, the wet density of each concrete was measured to adjust the mix proportions to give 1 m^3 of concrete, as reported in Table 3. The content of superplasticizer TW-7 in the nano-SiO_2 concrete is determined according to a principle that the slumps of the normal concrete and the nano-SiO_2 concrete are the same.

2.3. Concrete mixture test

2.3.1. Testing procedure

The superplasticizer TW-7 was dissolved in water, and then the nano-SiO_2 was added and stirred at a high speed for 2 min. Though nano-SiO_2 can not be dissolved in water, a smaller amount of nano-SiO_2 can be dispersed evenly by the superplasticizer TW-7.

The cement, fine aggregates, coarse aggregates and fly ash were mixed in a rotary mixer for 30 s. The ready-mixed liquid including water, TW-7 and nano-SiO_2 was poured into the rotary mixer slowly. The concrete mixture was mixed for another 1.5 min. After mixing, the slump and the slump flow of the concrete mixture were measured. The well-mixed concrete mixture was poured into molds to form the cubes of the size $15\times15\times15$ cm for the compressive strength testing. The samples were demolded after 24 h and then cured in a curing cabinet (relative humidity in excess of 95%, temperature 20 ± 3) for 28 days.

2.3.2. Testing results

Table 4 shows the slump, the slump flow and the 28-day strength of the normal concrete (NC) and the nano-SiO_2 concrete (SC). It can be seen that the slumps of NC and SC are the same, while the slump flow of NC is larger than that of SC. Namely the ratio of slump to slump flow of NC is larger than that of SC. It means that the nano-SiO_2 concrete is stickier than the normal concrete [15].

2.4. Water permeability test

2.4.1. Testing method

The HS-4 type concrete permeability device produced by Sheng Fei Testing Mechanical Factory in Zhejiang province of China was used. The testing procedure was in consistent with GBJ 82-85 [16].

The tapered cylinders with a height of 150 mm and a diameter of 175 mm at one end and 185 mm at the other end were used to determine the water permeability of NC and SC. Each of mixtures had six such tapered cylinders. The tapered cylinders were demolded after 24 h and then cured in a standard curing cabinet. The water permeability test was performed at the curing age of 28 days.

The tapered cylinders were taken out from the cabinet at the curing age of 27 days and dried in the air. The side of each tapered cylinder was sealed with moisture-insensitive

Table 3
Mix proportions

Mixture no.	Nano-SiO_2 (kg/m^3)	Cement (kg/m^3)	Fly ash (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	TW-7 (kg/m^3)	Density (kg/m^3)
NC	0	389	80	190	654	1100	5.2	2418
SC	13.9	370	79	188	647	1088	13.5	2400

Table 4
Test results

Mixture no.	Slump (mm)	Slump flow (mm)	The ratio slump to slump flow	Compressive strength of 28 days (MPa)	Water pressure *H* (MPa)	The average penetration depth (mm)	The permeability grade *S*
NC	175	420	0.417	47.5	0.5	146	S4
SC	175	405	0.432	44.0	>3.2	81	>S12

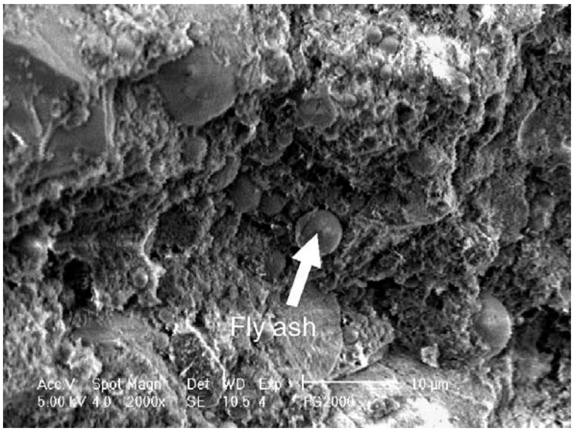

Fig. 1. Microstructure of normal concrete at curing age of 28 days.

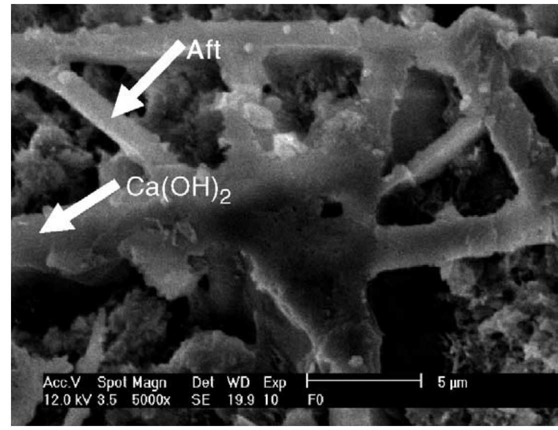

Fig. 3. Microstructure of normal concrete at curing age of 180 days.

epoxy to prevent the water leakage. The tapered cylinders were fixed into the permeability test rigs of the HS-4 type concrete permeability device pre-heated in an oven. Then the rigs were installed in the permeability device for testing.

At the beginning, the water pressure of 0.1 MPa was applied at the bottom of the specimens. Then, at interval of 8 h, the additional water pressure of 0.1 MPa was added. If the top surface of tapered cylinders is carefully observed by eyes to be wet due to water penetration, it can be said that the water penetration phenomenon rises. If three of the six cylinders had the water penetration phenomenon, the test was stopped, and the water pressure was recorded. At the end of the test, each specimen was removed from the rig and split into two halves lengthways for determining the water penetration depth. Average depth was taken from five equidistant spots along each face of the split specimens.

2.4.2. Testing results

When the water pressure H reached 0.5 MPa, three of the six cylinders of NC had the water penetration phenomenon. The average penetration depth was 14.6 cm as listed in Table 4. While for SC, when water pressure H of 3.2 MPa was applied, there were still only two cylinders having the water penetration phenomenon. Then the test was stopped. The average penetration depth of 8.1 cm was measured and reported in Table 4.

The permeability grade S (GBJ 82-89) is defined as

$$S = 10H - 1 \tag{1}$$

where H is the water pressure when the water penetration phenomenon of three of the six cylinders appears. The permeability grades of NC and SC are also listed in Table 4. It can be seen that nano-SiO_2 can improve the water permeability resistant capacity of concrete.

2.5. ESEM test

A XL30-type environmental scanning electron microscope (ESEM) produced by the Philips-FEI Company in Holland was used in the test. The resolving power of the ESEM is 3.5 nm. The specimens were cut down directly from the concrete cubes at different curing ages, and then immersed in the iso-propyl alcohol to stop hydration by removal of the free water. The diameter of specimens was approximately 5 mm. The shape of specimens should be regular, and the surface to be observed should be flat.

Figs. 1 and 2 are the electronic scanning photographs of NC and SC at curing age of 28 days, respectively, which magnify the microstructure 2000 times. Figs. 3 and 4 are the

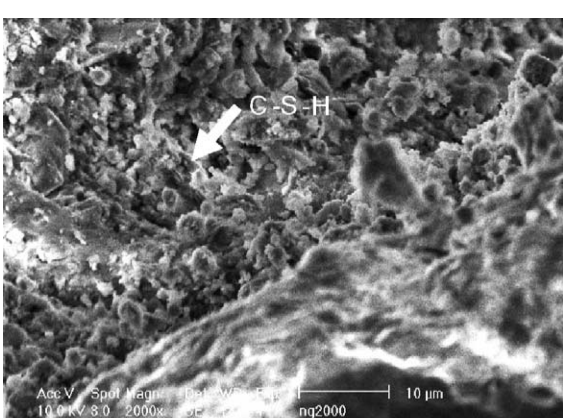

Fig. 2. Microstructure of nano-SiO_2 concrete at curing age of 28 days.

Fig. 4. Microstructure of nano-SiO_2 concrete at curing age of 180 days.

electronic scanning photographs of NC and SC at curing age of 180 days, respectively, which magnify the microstructure 5000 times. Fig. 1 shows that the fly ash particles are available in the binding paste matrix of normal concrete. Fig. 2 shows that great deals of hydration products (C–S–H) are available in nano-SiO_2 concrete, and the fly ash particles are not found. Figs. 1 and 2 reveal that the pozzolanic reaction of fly ash in SC is earlier and quicker than that in NC. Fig. 3 shows that AFt and calcium hydroxide crystals exist in the form of clusters, lapped and jointed together. Fig. 4 shows that the texture of hydrate products (C–S–H, et al.) of nano-SiO_2 concrete is very dense and compact, and big crystals such as $Ca(OH)_2$ and Aft disappeared.

3. Analysis of mechanism

The test results provided above show that the nano-SiO_2 can improve the microstructure and water permeability resistant capacity of concrete. The mechanism can be summarized as follows:

(1) A great deal of $Ca(OH)_2$ crystal is produced due to the hydration reaction between cement and water. $Ca(OH)_2$ crystal is hexagonal and is arrayed in the interfacial transition zone (ITZ) between aggregates and binding paste matrix, which is detrimental to the water permeability resistant capacity. Nano-SiO_2 has very high activity due to its galactic specific surface area. Nano-SiO_2 can react with $Ca(OH)_2$ crystal quickly, and produce C–S–H gel. Namely, the $Ca(OH)_2$ crystal can be absorbed. Then the size and amount of the calcium hydroxide crystals is reduced. The C–S–H gel fills the voids to improve the density of the interfacial transition zone (ITZ) and the binding paste matrix.

(2) About 70% hydration products is C–S–H gel. The average diameter of C–S–H gel is approximately 10 nm [4]. The nano-SiO_2 particles can fill the voids of C–S–H gel structure, making the binding paste matrix denser. In the C–S–H gel structure, a nano-SiO_2 particle can act as a nucleus to tightly bond with C–S–H gel particles. Thus the integration and stability of the hydration product structure are improved, and long-term mechanical properties and durability of concrete are expected to be increased.

4. Conclusions

(1) Nano-SiO_2 concrete is stickier than normal concrete due to the larger specific surface area.

(2) The water permeability test shows that the nano-SiO_2 concrete has better water permeability resistant behavior than the normal concrete. The ESEM test reveals that the microstructure of the nano-SiO_2 concrete is more uniform and compact than that of the normal concrete.

(3) Nano-SiO_2 can absorb the $Ca(OH)_2$ crystals, and reduce the size and amount of the $Ca(OH)_2$ crystals, thus making the interfacial transition zone (ITZ) of aggregates and binding paste matrix denser. The nano-SiO_2 particles can fill the voids of the C–S–H gel structure and act as nucleus to tightly bond with C–S–H gel particles, making binding paste matrix denser, and long-term mechanical properties and durability of concrete are expected to be increased.

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