EXPLORING THE POTENTIAL OF NANO-SIO2 TO PREVENT EARLY-AGE FROST DAMAGE IN PORTLAND CEMENT PASTE

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Abstract

The purpose of this study is to explore the potential of nano-SiO_2 (NS) to prevent early frost damage, and the effect of nano-SiO_2 (NS) on cement pastes subjected to early-age freezing was investigated regarding the macro properties (strength and durability) and micro properties (hydration and microstructure). The specimens were prepared with NS content of 0%, 0.6%, 0.9% and 1.2% by weight of cement. The results indicated that nano-SiO_2 has a positive impact on the macro properties of cement pastes frozen at early ages, compared with reference specimen. The cement pastes containing 0.9% NS achieved the best enhancements of 22.6% and 30.9% in compressive strength and chloride ion penetration, respectively. The TG results indicated that the additional nano-SiO_2 particles can increase the hydration degree of cement paste and the MIP data indicated that nano-SiO_2 particles reduced the total porosity and other pore structure parameters. This is because the additional C-S-H gels produced by the pozzolanic effect of nano-SiO_2, and nano-filling of nano-SiO_2 particles refine the pore structure of cement matrix. Moreover, XRD results showed that nano-SiO_2 also reduce the $Ca(OH)_2$ orientation in cement matrix.

Keywords: Cement paste, Nano-SiO_2, Early-age frost damage, Strength, Microstructure

1. INTRODUCTION

In the north of China, the climate is characterized by the duration of wintertime up to 5 months a year and the minimum temperature in winter can reach approximately -30 ~ -40 °C. In the construction industry, this extremely cold environments require development of technologies for preventing the frost damage.

Nanomaterial is being adopted to improve the performance of cement-based building materials, such as nano-metakaolin [1], nano-TiO_2 [2], nano-Fe_2O_3 [3], nano-Al_2O_3 [4]. Among them, nano-SiO_2 has been gaining increasing attention and turned into an effective material to improve the properties of cement-based building materials. Due to the high specific surface areas and activities of nano-SiO_2 [5, 6], it can significantly improve the mechanical and durability properties of cement-based material, even at small dosage [7,8,9,10,11,12,13]. Zhang et al. [14] suggested that the 2.0% addition of nano-SiO_2 achieved the maximum increase of strength. The compressive strengths increased 48.1% and 48.7% at the age of 3d and 28d, respectively. Salemi and Behfarnia [15] used 5% nano-silica to achieve 84% reduction in deterioration of concrete after 300 cycles of freezing and thawing. Quercia et al. [16] proposed that nano-SiO_2 modified self-compacting concrete has a high resistance to the freeze-thaw cycles, owing to the formation of highly stiff C-S-H gel and the refined pore structure. Moreover, Nano-SiO_2 can also behave as a filler to improve microstructure, as an activator to accelerate pozzolanic reaction and as the nuclear agent to tightly bond with hydration products [17,18,19]. The size and amount of calcium hydroxide ($Ca(OH)_2$) crystals are significantly decreased by means of pozzolanic reaction [20]. And forming additional C-S-H phase make the cement paste more stable and more strongly bonded [21]. These improvements lead to a longer lifespan of concrete structures, thus reduce the cost of repairing such structures. Considering the excellent performance of nano-SiO_2 in improving the properties, it is expected that nano-SiO_2 can improve the performance of cement composites to prevent the early frost damage.

Accordingly, this paper explored the effect of nano-SiO_2 on the mechanical properties and durability of cement pastes suffered early-age frost damage. Using the XRD, TG, and MIP techniques, the influence of the nano-SiO_2 on microstructure and cement hydration was investigated. The results provide the experimental and theoretical support for applying nano-SiO_2 in concrete structures serving in extremely cold environments.

2. MATERIALS AND EXPERIMENTAL METHODOLOGY

2.1 Material

P.O.42.5 used as binder material was provided by Harbin Yatai Cement Company. The nano-SiO2 were purchased from Taihong Yuda New Material Co., Ltd. The properties of nano-SiO2 are listed in Table 1.

Table 1: Properties of nano-SiO_2

Item	Purity (%)	Diameter (nm)	SSA (BET) (m^2/g)	Density (g/cm3)
Target	99.0	20	100.53	≤0.12

2.2 Mix procedures

A Scientz SB-5200DT sonicator (40 KHz, 300 W) was applied to disperse the nano-SiO_2 particles in the water. The sonication process was carried out three times, with the duration of each stage being 60 mins. The suspensions needed to be placed in ice water after each sonication stage in order to eliminate the heat and foam caused by sonication. Mixing procedures were carried out in a multifunctional mixer (TZJBJ-001, Wuxi City Construction Test Equipment Co., Ltd.), as follows:

1. Weighed all raw materials according to the mixture proportions.
2. Added the 4/5 of prepared nano-SiO2 suspensions into cement and simultaneously stirred at a low speed of 72 r/min for 2 min, then held for 1 min.
3. Added the remaining suspensions into mixture and mixed at a high speed of 200 r/min for 4 min.
4. Put the mixtures into molds and demold after 24 hours.

2.3 Curing method

The samples were immediately stored in automatic temperature-controlled freezer at -15 ℃ for 7 days, and then were cured in standard curing room (20 ℃) for 28 days to carry out macro performance tests, so as to reflect the warming conditions encountered after winter. The normal cement paste and cement paste with nano-SiO_2 (nano-SiO_2 cement paste) are referred to as "Freezing-PC'' and ''Freezing-NS", respectively. In the nano-SiO2 cement paste, nano-SiO2 is added at the amounts of 0.6%, 0.9% and 1.2% by the weight of cement, as shown in Table 2.

Table 2: Experimental design

Sample Name	Weight Fraction /(wt.%)	Water-cement ratio	Freezing ages /(d)	Standard curing ages /(d)
Freezing-PC	0	0.35	7	28
Freezing-NS06	0.6	0.35	7	28
Freezing-NS09	0.9	0.35	7	28
Freezing-NS12	1.2	0.35	7	28

2.4 Testing methods

The compressive strength was evaluated on cubic samples, 40-mm side and the average strength of six samples was used as an index according to the Chinese standard GB/T 17671-1999 [22]. The test was performed using a 2000 kN compression testing machine (WHY-2000) under displacement control and the rate of loading was kept as 0.6 kN/s. And the non-steady state migration test in accordance with NT BUILD 492 [23] were used to evaluate the chloride-ion penetration.

The AutoPore IV 9500 Mercury Porosimeters, able to determine a broad pore size distribution (0.003 to 1100 μm), was used for mercury intrusion porosimetry (MIP). By assuming a contact angle of 130° and a mercury surface tension of 485 dynes/cm, the minimum pore access diameter reached is about 5.65 nm. The MIP samples were taken from the fracture pieces of the prism. To stop the hydration, samples were soaked in ethanol for 7 days, and then were further oven-dried at 60 ℃ until the weight of samples were accurate to 0.001 g.

Thermal analysis was investigated by a thermogravimetric apparatus (TG; NETZSCH STA449F3). All experiments were performed from 60 up to 1000 ℃ and with a 10 ℃/min heating rate under flowing nitrogen.

The X-ray diffraction analysis (X'PERT, PANalytical B.V.)) were applied for determining the amount and change tendency of calcium hydroxide crystal. The samples were scanned from 5° to 90° at a scanning speed of 8°/min.

3. RESULTS

3.1 Compressive strength

The compressive strengths of cement pastes with nano-SiO_2 and reference sample are presented in Fig. 1. It is found that the compressive strengths of Freezing-NS samples are higher than the reference samples (Freezing-PC). Especially, the compressive strength of Freezing-NS sample at dosage of 0.9 wt.% reached the maximum, which increases by 22.6%/10MPa.

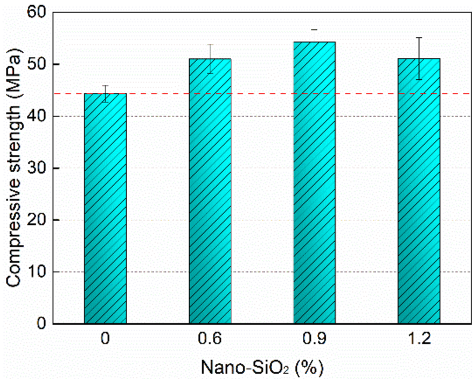

Figure 1: Compressive strengths of the samples.

3.2 Chloride ion penetration

The 35-day D_{nssm} (Fig. 2) indicate the addition of the nano-SiO_2 can effectively enhance the resistance of cement matrix to the intrusion of chlorides. At 0.6 wt.%, 0.9 wt.%, and 1.2 wt.% nano-SiO_2 content, the non-steady-state migration coefficient (D_{nssm}) were decreased by 18.2%, 30.9%, and 29.7%, respectively, compared with the reference samples (Freezing-PC).

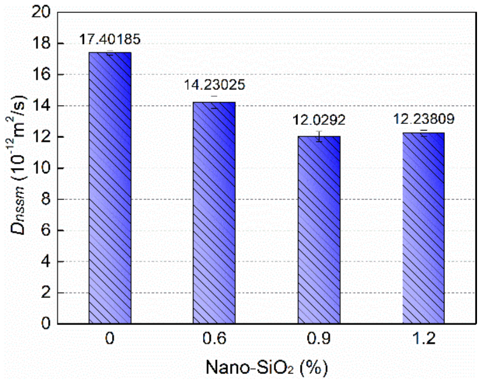

Figure 2: The non-steady-state migration coefficient (D_{nssm}) of the samples.

3.3 Pore structure

The MIP results are shown in Table 3 and it can be seen that the addition of nano-SiO_2 obviously decreased the median pore diameter (by volume), which is reduced from 106.2 nm (for the reference, Freezing-PC) to 73.6. The average pore diameter and the critical pore diameter were decreased and the reductions of 7.4 nm and 100.8 nm was found in the average pore diameter and critical pore diameter, respectively.

Table 3: MIP data

Parameters	Freezing-PC	Freezing-NS09
Median pore diameter (volume) (nm)	106.2	73.6
Median pore diameter (area) (nm)	10.1	9.8
Average pore diameter (4V/A) (nm)	38.8	31.4
Critical pore diameter (nm)	283.9	183.1
Porosity (%)	20.3	18.1

3.4 Hydration degree

Based on the TG results (Fig. 3), non-evaporable water contents of the hydrated cement pastes were calculated to estimate the hydration degree. As shown in Table 4, the hydration degrees of Freezing-NS09 sample is higher than that of Freezing-PC sample.

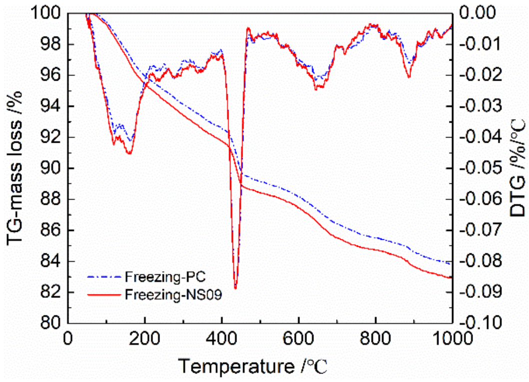

Figure 3: TG and DTG curves of cement paste with 0.9 wt.% nano-SiO_2 (Freezing-NS09) and reference sample (Freezing-PC).

Table 4: Hydration degree (%)

Sample	Freezing-PC	Freezing-NS09
Hydration degree	61.0	63.9

3.5 XRD

The X-ray diffraction analysis (XRD) were used to qualitatively determine the pozzolanic activity of nano-silica. The X-ray patterns of cement pastes containing 0% and 0.9% nano-SiO_2 contents are shown in Fig. 4. The $Ca(OH)_2$ consumption, which is obtained by the intensity change of the main diffraction peaks, was used as an indicator to the pozzolanic activities. As shown in Table 5, the intensity of main diffraction peaks of $Ca(OH)_2$ in cement paste with nano-SiO_2 (Freezing-NS09) is significantly lower than those in reference specimen (Freezing-PC), which means that nano-SiO_2 can consume calcium hydroxide to some extent. And nano-SiO_2 can also reduce the $Ca(OH)_2$ orientation in cement matrix. Moreover, it is found that no special diffraction peaks appear in Freezing-NS09 samples compared with Freezing-PC sample, which means the addition of nano-SiO_2 cannot produce new substances.

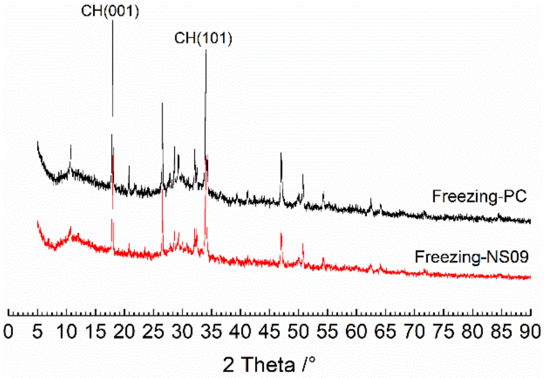

Figure 4: XRD patterns of Freezing-PC and Freezing-NS09.

Table 5: Diffraction intensity

Sample Name	CH (001)	CH (101)	CH orientation
Freezing-PC	2066	1784	1.56
Freezing-NS09	1275	1274	1.35

4. DISCUSSION

For the compressive strength of cement pastes suffered early-age freezing, it is found that the incorporation of nano-SiO_2 can significantly enhance the compressive strength of the matrix. In terms of cement hydration, TG results show that the addition of nano-SiO_2 increases the degree of hydration of cement due to the ultra-high specific surface of nano-SiO_2 particles [24]. Using quantitative (TG) and qualitative (XRD) methods, it is proved that nano-SiO_2 can consume $Ca(OH)_2$ to reduce the weak points Moreover, additional C-S-H gel, produced by the chemical reaction of nano-SiO_2 with $Ca(OH)_2$, is the main constituent for strength improvement of cement matrix. It is called pozzolanic reaction. It is known that strength is also closely related to the compactness of pore structure. The denser the pore structure form, the less internal defects are, and the higher the strength gains. These additional C-S-H gels make hydration products formed more compact with less voids, which generate higher strength. According to the Fig. 2, it can be observed that nano-SiO_2 can improve the permeability, thus enhancing the durability of cement paste. It is widely known that the pore structure is a critical factor to influence the durability of cement-based materials. MIP results indicate that the incorporation of nano-SiO_2 reduces the total porosity and other pore structure parameters. In other word, the incorporation of nano-SiO_2 can refine the pore structure of cement matrix.

5. CONCLUSIONS

The incorporation of nano-SiO_2 can significantly improve the macro properties of cement pastes suffered early-age frost damage. This improvement is due to the pozzolanic activity of nano-SiO_2, which can consume calcium hydroxide to reduce the weak points in the matrix and produce additional C-S-H gels to increase the compactness of pore structure.

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