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The effect of superhydrophobic nano-silica particles on the transport and mechanical properties of hardened cement pastes

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HIGHLIGHTS

- Superhydrophobic nano-silica (SNS) particles were added into the cement pastes
- Compressive strength and water sorptivity of hardened cement pastes were measured
- Cement hydration and pore structure of hardened cement pastes were investigated
- The roles of SNS particles and superplasticizer were discussed

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ABSTRACT

The water permeability of hardened cement pastes (HCP) is closely related to the durability of cement-based materials since most deteriorations of cement-based materials result from the ingress of foreign ions. In this study, superhydrophobic nano-silica (SNS) particles with a dosage of 1%, 2%, and 4% (by cement mass) were added into cement pastes (water cement ratio is 0.3) to take advantage of the pozzolanic reactivity and hydrophobicity of SNS particles, and their influence on the water sorptivity and compressive strength of the HCP were investigated. In addition, the techniques of isothermal calorimetry, mercury intrusion porosimetry, and X-ray diffraction were combined to reveal the reinforcement mechanism of SNS particles. The results showed that the compressive strength was increased by 42%, 61%, and 71%, respectively, and that the water sorptivity was reduced by 4.2%, 13.8%, and 25.1%, respectively. Moreover, the increment of compressive strength and decrement of water sorptivity were positively proportional to the dosage of SNS particles. The improvement was attributed to the pozzolanic reaction between SNS and Portlandite produced by cement hydration, which can not only refine the pore structure of HCP, but also increase the hydrophobicity of calcium silicate hydrates. Furthermore, the dosage of superplasticizer also played a significant role in the development of HCP microstructure. The results indicated that addition of SNS particles is a promising method to enhance the durability of cement-based materials.

1. Introduction

The durability of concrete is one of the most concerned issues for researchers and engineers, in which the permeability of concrete plays a critical role since the ingress of foreign ions contributes to most the deteriorations of concrete like alkali silica reaction, sulfate attack and chloride attack [1]. Therefore, extensive investigations have been made on the reduction in the permeability of concrete, which can be basically divided into two categories: the treatment of concrete surface and concrete bulk. In regard to the first method, polymers like epoxy resins [2], polymer nanocomposite like polymer/clay nanocomposite [3], small organic molecules like silane and siloxane [4], and inorganic solutions like sodium silicate solution have been applied on the surface of concrete to improve its impermeability [5]. However, this type of method was frequently subject to some problems such as the aging of organic polymers, bonding strength between the coating and concrete substrate, penetration depth and so on [6]. The second method was the refinement of the microstructure of the cement matrix by the addition of fine particles [7] such as hydrophilic nano silica [8]. However, the two methods maybe become much less effective when the integrity of concrete materials is broken by micro-cracks. As a brittle material, concrete frequently services in the presence of cracks or micro-cracks caused by thermal stress or heavy loads. In certain cases, the cracks or micro-cracks were

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inevitable. These cracks would provide channels for the transport of foreign ions by capillary action. Therefore, hydrophobization of concrete materials themselves can be an effective way to improve their impermeability. In line with this thought, several organic admixtures were added into the cement pastes. Agus Maryoto [9] found the addition of calcium stearate ($Ca(C_{18}H_{35}O_2)_2$) would reduce the permeability of concrete. Tkach et al. [10] prepared a complex of hydrophobization modifiers and found this complex would not only increase the strength of concrete but also reduce the water absorption of concrete. Falchi et al. [11] investigated the influence of several water-repellent admixtures on the properties of Portland limestone cement mortars and showed that both siloxane products and zinc stearates presented good water-repellent effectiveness though they would slow down the hydration of cement more or less. Different from the researches above, in this study, superhydrophobic nano silica (SNS) particles were added into the cement pastes in order to improve the impermeability and mechanical properties for the first time to the best knowledge of the authors. The significant advantage of the this treatment is that, the reaction between SNS particles and the hydration product of cement, Portlandite (CH), can not only increase the hydrophobicity of calcium silicate hydrate (C-S-H) gels, the principal component of HCP [12], but also refine the microstructure of HCP. The innovation of this study is to reduce the permeability by the increase of hydrophobicity of C-S-H gels themselves not by the addition of hydrophobization modifiers or by the treatment of HCP surface.

In this study, SNS particles with a dosage of 1%, 2%, and 4% (by cement mass) were added into the cement paste with a water cement ratio (w/c) of 0.3 in order to disperse the SNS better, and the compressive strength and water sorptivity of the HCP with different dosages of SNS particles were measured. In addition, the techniques of mercury intrusion porosimetry (MIP), isothermal calorimetry, and X-ray diffraction (XRD) were combined to explore the mechanism of the influence of SNS particles on cement hydration and formation of microstructure of HCP.

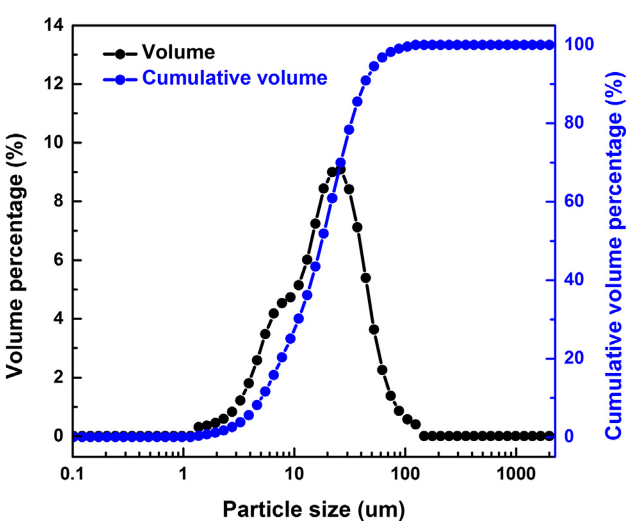

Fig. 1. The particle size distribution of Portland cement.

2. Materials and methods

2.1. Materials

Chinese P·II 52.5 Portland cement (Jiangnan-Xiaoyetian Co., Ltd), tap water, AEROSIL R974 SNS (EVONIK, Germany), and a Polycarboxylate water-reducing admixture (PCA) (Subote Co., China) with a solids content of 40% was purchased and used as received in this study. Fig. 1 presents the particle size distribution of the cement, which was determined on a laser diffraction particle size analyzer (Microtrac S3500, Microtrac, America). The chemical and mineral compositions of the cement are given in Table 1, which was determined by X-ray fluorescence (XRF) and XRD respectively. The infrared spectra of SNS and a hydrophilic nano silica are given in Fig. 2. It can be seen that the two spectra are almost the same, except for that there is an additional band at around 2968 cm^{-1} in the spectrum of SNS as shown in the inset of Fig. 2. This band corresponds to the asymmetric stretching vibration of –CH in the methyl group [13], which is responsible to the hydrophobicity of SNS.

2.2. Preparation of samples

SNS particles with a dosage of 0%, 1%, 2%, and 4% (by cement mass) were added into the cement pastes with a water cement ratio of 0.3. This lower water cement ratio was chosen because it is very difficult to mix SNS particles with water at a higher water cement ratio. Due to their hydrophobicity and high specific surface area, the addition of SNS particles would reduce the fluidity of cement pastes, therefore, additional PCA were added for the samples with SNS particles and the amount of the additional admixture is proportional to the mass of added SNS particles, to obtain an appropriate workability. The mixture proportion of the cement pastes in this study is given in Table 2. The **SNS-2L** was prepared in order to investigate the influence of PCA.

During the preparation of the samples with SNS particles, the SNS particles were first mixed with cement powder manually before mixing. Then, they were poured into a mixer as specified in ASTM C305-14 [14], following which mixing water with PCA was added into the mixer. Then, a process of 90 s slow mixing, 60 s fast mixing, and finally 60 s slow mixing allowed the formation of a uniform paste. About 20 g of the pastes were used for calorimetric tests, and the rest were cast into molds of 40 × 40 × 160 mm^3. All the samples were demolded after one day of standard curing (20 °C, RH > 95%), and then they were steam-cured at 40 °C for seven days, ready for the tests of XRD, MIP, water sorptivity and compressive strength.

2.3. Methods

2.3.1. Isothermal calorimetry

The heat evolution of all the cement pastes was measured on an eight-channel isothermal calorimeter (TAM Air, Thermometric, Sweden). The calorimeter was placed in a constant temperature room at 20 °C and the chamber temperature of the calorimeter was set to 20 °C as well. In this test, right after the mixing process

Table 1
Chemical and mineral compositions of Portland cement.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	LOI[1]
wt%	19.70	4.45	2.93	63.62	1.28	2.93	0.68	0.12	0.27	1.09
Minerals[2]	C_3S	C_2S	C_3A	C_4AF	Calcite	Bassanite	Quartz			
wt%	59.8	15.4	7.6	7.1	5.5	4.2	0.4			

[1] Loss on ignition.
[2] Minerals composition of cement is obtained by a TOPAS software.