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Environmental resistance of cement concrete modified with low dosage nano particles

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HIGHLIGHTS

- Impacts of NaCl and KAc on cement concrete materials were investigated.
- Low dosage nano particles can provide positive effects on the durability enhancement of concrete materials with exposure to aggressive environment.
- Microstructure of the cement concrete materials before and after F/T and W/D cycles were analyzed.
- Potential deterioration and modification mechanisms have been presented.

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ABSTRACT

The negative impacts of aggressive environment on the durability of concrete materials have raised great concerns in recent years. Although the nano modification has been considered as a promising approach to enhance the durability of concrete materials with exposure to synergistic attacks from complicated aggressive environment, the investigation of the impacts of various chemicals on low dosage nano modified concrete, especially along with freeze/thaw and wet/dry cycles, is still very limited. In this study, the impacts of sodium chloride (NaCl) and potassium acetate (KAc) on laboratory fabricated concrete samples, which were modified with low dosage of nano SiO_2 and nano TiO_2 particles, were investigated. The mass loss, flexural strength, compressive strength, and relative dynamic modulus of elasticity were tested to evaluate the deterioration of low dosage nano modified concrete samples after exposure to F/T along with W/D cycles in KAc and NaCl solutions. The microstructure analyses demonstrate that both NaCl and KAc have negative impacts on the durability of concrete samples after F/T and W/D cycles. However, the addition of low dosage nano particles shows a distinctive enhancement of environment resistance of concrete samples. Through the microstructure analysis, three potential reasons were presented to help elucidate the deterioration mechanisms of concrete with exposure to aggressive environment. Moreover, based on the microstructure analysis, the different modification mechanisms corresponding to various nano materials were presented. This study not only shows the possibility of low dosage nano modification on the durability enhancement of concrete, but also provides potential modification mechanisms which help to design and fabricate durable concrete materials with exposure to complicated aggressive environment.

1. Introduction

In the past decade, it has been widely noticed that the cement concrete infrastructures, such as bridge poles, beams, decks, or cement concrete pavements, have been considerably damaged with exposure to salts along with freeze/thaw (F/T) and wet/dry (W/D) cycling. Former studies have demonstrated that the deterioration of concrete infrastructures with exposure to an aggressive

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environment can be ascribed to both physical and chemical attacks [1,2]. The physical attack is mainly resulted from the F/T and W/D cycles, which will lead to scaling and cracking of concrete infrastructures [3,4]. The chemical attack, however, has detrimental effects on cement concrete materials because of the complicated chemical reactions between the salts and the C—S—H binder phase which finally lead to the reduction of the integrity and strength of concrete materials [5,6].

Numerous studies had been carried out to identify the physical and chemical attacks of salts on concrete according to salt types [7–9]. The results suggested that the deleterious process is complicated and the damage mechanism is synergistic. In a short-term laboratory study, the deleterious process of Portland cement concrete (PCC) specimens with exposure to chloride based salt solutions and combined with F/T cycling was investigated. It was found that all applied chloride based salts not only exacerbate the physical distresses but also chemically react with hydration products of cement paste, and the PCC specimens with exposure to various salt solutions exhibited different mass loss and mechanical properties, and the chemical and morphological changes of cement hydration products could be distinctively observed after one year of continuous immersion in chloride based salt solutions [10].

Other than the attack from the chloride based salts, the attack from inorganic based salts was also investigated [8]. It was found, although the inorganic salts have benefits on eliminating the negative effects of the chloride ions on the rebar corrosion, the chemical attack of the organic salts on the cementitious materials is not a negligible factor. Therefore, according to the results from previous studies, it has been widely recognized that how to clarify the effects of salts on the durability of concrete, mitigate the environmental attack problem in a cost-effective way and increase the durability of concrete infrastructures are still big challenges to achieve the sustainable development of constructions.

In the most recent decade, nano-modification is considered as a promising method to enhance the mechanical properties of cement concrete materials [11]. The most widely investigated nanomaterials include SiO_2 [12–14], TiO_2 [15,16], Al_2O_3 [17], Fe_2O_3 [18,19], nanoclay [20,21], nano kaolinite [22,23], carbon nanotubes [24] or nanofibers [25,26], and graphene oxide [27,28]. Apart from the mechanical properties, it was claimed that the F/T resistance of concrete can also be significantly improved by the addition of nano particles [29]. It was claimed that the strength loss of the concrete mixed with 5 wt% of nano particles was only 16%, while the control one showed 100% strength loss after 300F/T cycles. Salemi also proved that the nanoparticles have remarkably positive effect on the F/T resistance of concrete materials [30]. After mixing with 5 wt% of nano particles, the mechanical properties of the concrete increased only by 8%, but the F/T resistance increased by over 80% comparing with the plain concrete. This phenomenon was supported by Gonzalez that the nano material can evidently improve the F/T resistance of concrete because of the nano material can act as a supplementary cementitious material, and thus improves the density of concrete, and increases the paste quality and the aggregate-paste bond [31].

However, unlike the results presented above, in which the F/T resistance of the cement concrete can be modified by nano particles, Leòn's study denied the benefits of the nano modification [32]. It was argued that the addition of the nano particles has little or negative effects on the F/T resistance of cement mortars. The disagreement may result from two possible reasons. First, the average size of the nano particles used in Behfarnia's study was claimed less than 10 nm, while in the Leòn's study, the average size of the nano particles was much larger and in a wide range from 260 to 550 nm. Second, the dosage of the nano particles was different. In Behfarnia's study, the dosage was up to 3 wt%, while in the Leòn's study, it was 5 wt%.

Except for the disagreement of the modification results based on various types of nano modifiers, the dosages of the nano modifiers were varied in a range of 3–10 wt%, which largely limited the application of nanomaterials in concrete because of the relatively high cost of nanoparticles. Therefore, to decrease the manufacturing costs, it is necessary to find out if the low dosage modification works as well as the high dosage modification in cement concrete. More importantly, to the best of our knowledge, only limited studies have been conducted to evaluate the environment resistance of nano modified concrete when exposed to physical and chemical synergistic attacks, especially with low dosage addition of nanoparticles.

According to the results from previous studies, it can be found that the effects of the nano modification on concrete materials are determined by various factors, including the type, size, shape, dispersion methods and the dosage of nanomaterials. Although previous studies have proved that the nanomaterials have positive effects on mechanical performances and environmental resistance of concrete materials, however, to the best of our knowledge, the agreement of the nano modification mechanisms with respect to the types of nano materials on the durability of concrete is yet achieved, especially for the low dosage nano modified concrete materials with exposure to physical and chemical synergistic attacks, which means the salt along with F/T attacks, still need to be further investigated.

2. Experimental methods and materials

2.1. Materials

Ordinary Portland cement (P.O 42.5) was used as cementitious binder in this study. Natural sand and basalt rocks were used as fine and coarse aggregates, respectively. To evaluate the effects of nano particles on the environmental resistance of cement concrete materials, commercially available nano SiO_2 and nano TiO_2 (provided by Hefei Liangziyuan Co.) were chosen as the nano modifiers. The purity of the nano particles are both higher than 99.0%. The average size of the nano particles are both about 30 nm with specific surface area of 80 m^2/g. The crystal structure of the nano TiO_2 was anatase while the nano SiO_2 was amorphous. Fig. 1 gives the TEM image and the corresponding SAED pattern of the nano TiO_2 and nano SiO_2, respectively.

2.2. Preparation

To realize the well dispersion of the nano particles in water, the naphthalene water reducer (UNF-5), with concentration of 1 g/mL, was resolved in water by using magnetic stirring for 5 min with mixing speed of 1500 rpm. After adding the nano particles in the solution, the mixtures were ultrasonicated at 200 w and 40 Hz for 10 min.

The water-to-cement ratio (w/c) was 0.5, and the dosage of the nano particles was 0%, 0.05%, 0.1%, 0.5%, and 1.0% by the weight of cement. The mix design of the nano modified concrete is listed in Table 1, and the slump was tested based on ASTM C143. After sufficient mixing, the concrete mix was placed into steel molds to form samples with size of $100 \times 100 \times 400$ mm^3. After mixing, the fresh mixture was cast into molds. During the first 24 h of molding, the concrete specimens were placed on a rigid surface and stored at room temperature. Next, the specimens were de-molded and cured in a moist cure room at 25 °C and relative humidity (RH) of 95% for 27 days. Once fully cured, the concrete specimens were air-dried for 24 h at 23 ± 1.7 °C at RH 45–55% and weighed before being used for testing.

Zeta potential was used to assess the dispersion of the nano SiO_2 and nano TiO_2. The zeta potentials were measured by Beckman Coulter-Delsa Nano C particle analyzer via the suspensions of nano particles in water with addition of naphthalene water reducer as dispersion agent. Table 2 gives the tested cumulant diameters of the average agglomeration size and the zeta potential of nano SiO_2 and nano TiO_2. As demonstrated in this table, the cumulant diameters of the average agglomeration particles are 265.7 nm and 302.7 nm, while the Zeta potential are −23.78 mV and 0.61 mV with mobility of -1.48×10^{-4} and 3.82×10^{-6}, corresponding to nano SiO_2 and nano TiO_2, respectively. By combining with the TEM images, it can be claimed that the nano particles have been well dispersed in water with the help of the naphthalene water reducer.