



# Chloride diffusion in concrete containing nano-TiO<sub>2</sub> under coupled effect of scouring



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## ABSTRACT

The advantage of concrete containing nano-TiO<sub>2</sub> in resisting the coupled effects of chloride diffusion and scouring with respect to pure concrete was studied in this paper. Because of the movement in exposed concrete surface induced by scouring and the deterioration in concrete microstructure caused by chloride salt accumulation, an increasing mutual accelerative effect between the chloride diffusion and the scouring abrasion was experimental observed, which agreed with the theoretical simulation results. Benefited from the improvement in microstructure and porosity compared with the pure concrete, concrete containing 1% nano-TiO<sub>2</sub> in the weight of cement showed a better impermeability as well as the abrasability. Correspondingly, a better performance in resisting the coupled effects of chloride diffusion and scouring was founded for the concrete containing nano-TiO<sub>2</sub> compared to the pure concrete, and this advantage increased upon the time.

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## 1. Introduction

Durability of concrete is one of the important factors determining the serving life of infrastructures. Durability involves the degradation of concrete and structures caused by environmental or loading impacts [1]. Among the durability problems, steel bar corrosion is considered as the most harmful factor that makes the structure lose the loading capacity and even leads to a undesired collapse. [2–6]. Corrosion of steel bar is often caused by the ingress of chloride in concrete. When sufficient chloride has invaded the concrete and accumulated around steel bar, the protective film of the steel bar will be destroyed and the reinforcing steel becomes active. Corrosion in the form of rust formation and/or loss in cross section of the rebar occur and cause the cover concrete cracking [7–9]. In the past decade years, most of the studies on chloride diffusion, included laboratory experimentation [10–12] and theoretical modeling [13–15], focused on ordinary reinforced concrete in normal constant state. Recently, increasing attention has contributed to chloride diffusion in stressed concrete [16–18], cracked concrete [19,20] and coupled humidity or pressure [21,22]. By considering the couple effect of other environmental or loading factors, these studies were consisted with the real engineering environments.

Progress achieved on chloride diffusion coupled environmental or loading factors is giving us a comprehensive understanding of the durability of a engineering concrete structure in the real servicing condition. However, it is still at a starting stage and many important couple factor have not been studied yet. In particular, for marine concrete structures such as a pier, it is under a chloride attack coupled with water scouring. However, effect of scouring was not considered in the previously reports. In the case of diffusion coupled scouring, surfacial concrete will be washed away [23–25], i.e., the boundary condition of the chloride diffusion will move inwards upon time, which may cause the chloride ingress more quickly compared with the pure diffusion and lead to a early corrosion of reinforcing bar. On the other hand, invasion and crystallization of chloride may cause a degradation of concrete [26,27] that results in a adverse effect on the abrasion resistance. Therefore, the coupled effects of chloride invasion and scouring are necessary to be studied for designing and evaluating the concrete structures built in that environment. Furthermore, the recently developed concrete containing nano-particles was found to have the advantages in resisting chloride penetration [28,29] and abrasion [30]. Compared with the traditional additives such as silica powder, fly ash and fiber, nano-particles have a higher efficiency in simultaneously enhancing the mechanical properties and durability of concrete, which was considered to be benefited from the improvement in microstructures induced by the nano-particles [31–33]. Hence, compared with a normal concrete, better performance can be expected for concrete containing nano-particles under the chloride invasion coupled scouring and was investigated in this paper.

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## 2. Materials and experimental methods

### 2.1. Materials and specimens

According to the requirement of marine concrete structures, C45 concrete was designed. The cement used was Portland cement P.O32.5. The fine aggregate was natural river sand with a fineness modulus of 2.94. The coarse aggregate was crushed diabase with a maximum radius of 20 mm. FDN-water-reducing agent (one kind of  $\beta$ -naphthalene sulfonic acid and form aldehyde condensates) was used. The defoamer, tributyl phosphate (made in China) was used to decrease the amount of air bubbles.

The nano-TiO<sub>2</sub> used in this study was purchased from Zhoushan Hongsheng Nano-phase Material Co. (Zhejiang, China). According to the supplier's report, the as-received nano-TiO<sub>2</sub> has an average diameter of 15 nm, a purity of 99.7%, a specific surface area of  $240 \pm 50 \text{ m}^2/\text{g}$  and a density of  $0.04\text{--}0.06 \text{ g}/\text{cm}^3$ , and the micrograph picture of the nano-TiO<sub>2</sub> is shown in Fig. 1. The ratio of water to cement used for all mixtures is 0.42. The mixture proportions are given in Table 1. Herein, PC denotes plain concrete and NC denotes concrete containing nano-TiO<sub>2</sub>, respectively.

Concrete prisms were cast with molds of  $100 \times 100 \times 200 \text{ mm}$  for chloride diffusion testing and  $100 \times 100 \times 100 \text{ mm}$  for compressive testing. For casting a PC, FDN was first dissolved in a half volume of water and mixed with cement, sand, and coarse aggregate in a concrete centrifugal blender for 2 min. The remainder of the FDN solution and water were poured into the mixture and mixed for another 2 min to achieve good workability. Finally, the fresh concrete was poured into oiled molds to form prisms. After pouring, an external vibrator was used to facilitate compaction. For casting a NC, nano-TiO<sub>2</sub> and FDN were first dissolved in a half volume of water and hand-stirred. Then, the mixture was stirred in a shear blender at a high speed of 1600 rpm for 10 min. Subsequently, the mixture was sonicated in a sonicator (400 W and 40 KH) for 1 h. Except that the nano-TiO<sub>2</sub> dispersed FDN solution was taken to replace the pure FDN solution, other fabrication procedure for NC was the same with that of PC. The specimens were demolded at 24 h and then cured in a standard moist room at room temperature for 28 days.

Three cubic specimens with a size of  $100 \times 100 \times 100 \text{ mm}$  were tested using a Materials Testing System (MTS) to obtain the compressive strength of PC and NC, respectively.

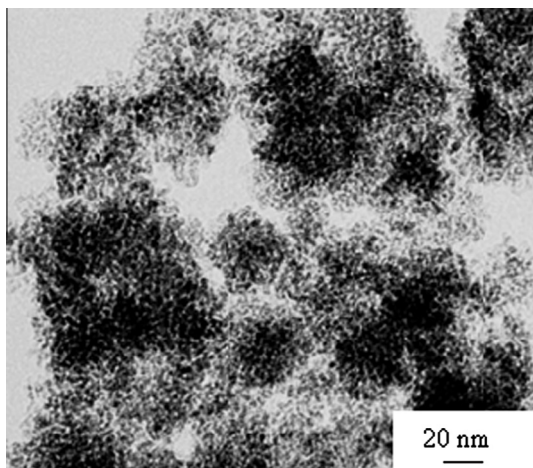


Fig. 1. Morphology characteristic of the nano-TiO<sub>2</sub> provided by Zhoushan Hongsheng Nano-phase Material Co.,  $1 \times 10^8 \times$ .

### 2.2. Chloride concentration measurement for pure diffusion

For comparison, pure chloride penetrating test was first conducted. Chloride concentration was measured according to the specified method of ASTM C1556. The cured concrete specimens were sealed with epoxy resin, leaving only one surface ( $100 \times 200 \text{ mm}$ , the vertical side during casting) exposed. Then, the prepared concrete specimens were immersed in distilled water for 24 h to ensure that it was water saturated. After that, the specimens were immersed in 10.24% sodium chloride solution for chloride penetrating test. The temperature of chloride solution was controlled at  $40 \text{ }^\circ\text{C}$  during penetrating test.

After immersed in sodium chloride solution for 48 h, 96 h and 144 h, respectively, concrete powder at various depths were sampled in the concrete prisms. Fig. 2 shows the positions of sampling. To get enough concrete powder for testing, powder was sampled from the segments with depth range of 0–3 mm, 3–6 mm, 6–9 mm, 9–12 mm, 12–15 mm, 15–20 mm, 20–25 mm, 25–30 mm and 30–40 mm, respectively, to profile the chloride concentrations at the depth of 1.5 mm, 4.5 mm, 7.5 mm, 10.5 mm, 13.5 mm, 17.5 mm, 22.5 mm, 27.5 mm and 35 mm. Seven sample holes were dryly drilled using a 20 mm diameter rotary impact drill. At each depth, powdered samples from seven holes were mixed to give a test sample representing the average chloride concentration at that depth. The powdered concrete samples obtained were further milled and fined by a sieve with pore size of 0.63 mm. Then, 20 g prepared concrete powder of each sample was used to extract acid-soluble chloride contents [22]. Mohr titration was used to determine the chloride concentration in the solution.

### 2.3. Chloride concentration measurement for diffusion coupled scouring

Scouring test was conducted with a home-made experimental set-up. Turbine blade was connected with a stepping motor and fixed at the center of a container which filled with standard sand mixed 10.24% chloride solution. Actuated by the motor, the blade can stir the chloride solution at a control speed of 400 rpm. The cured concrete prisms were sealed (leaving one of the vertical sides during casting exposed) and distilled water saturated using the same method as described in the pure chloride diffusion test. Then, the weight of each specimen was measured with an electric balance with a resolution of 0.001 g. After that, the concrete prisms were placed in the container to be immersed in the chloride solution, with the exposed surface towards the blade as shown in Fig. 3. During the test process of chloride diffusion coupled scouring, the temperature of chloride solution was controlled at  $40 \text{ }^\circ\text{C}$ . The exposed surface facing blade was wash abraded and penetrated by chloride solution simultaneously. After scouring for 48 h, 96 h and 144 h, the concrete specimens were taken out to measure the weight. The average scouring depth was calculated based on the amount of weight loss. The chloride concentration was measured using the same method as described in the pure diffusion test, where the depth was defined as the distance from the measured point to the initial exposed surface before scouring.

To investigate the effect of chloride diffusion on scouring, scouring test using pure water as scouring medium was also conducted and the results were compared with that using chloride solution as scouring medium.

## 3. Numerical simulation method

Based on Fick's 2nd Law of Pure Diffusion [34], the one-dimensional penetration of chloride into concrete can be described as:

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