



## Pore structure and chloride permeability of concrete containing nano-particles for pavement

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### ABSTRACT

Pore structure and chloride permeability of concrete containing nano-particles ( $\text{TiO}_2$  and  $\text{SiO}_2$ ) for pavement are experimentally studied and compared with that of plain concrete, concrete containing polypropylene (PP) fibers and concrete containing both nano- $\text{TiO}_2$  and PP fibers. The test results indicate that the addition of nano-particles refines the pore structure of concrete and enhances the resistance to chloride penetration of concrete. The refined extent of pore structure and the enhanced extent of the resistance to chloride penetration of concrete are increased with the decreasing content of nano-particles. The pore structure and the resistance to chloride penetration of concrete containing nano- $\text{TiO}_2$  are superior to that of concrete containing the same amount of nano- $\text{SiO}_2$ . However, for the concrete containing PP fibers, the pore structure is coarsened and the resistance to chloride penetration is reduced. The larger the content of PP fibers, the coarser the pore structure of concrete, and the lower the resistance to chloride penetration. For the concrete containing both nano- $\text{TiO}_2$  and PP fibers, the pore structure is coarser and the resistance to chloride penetration is lower than that of concrete containing the same amount of PP fibers only. A hyperbolic relationship between chloride permeability and compressive strength of concrete is exhibited. There is an obvious linear relationship between chloride permeability and pore structure of concrete.

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### 1. Introduction

Concrete durability has attracted a lot of attention from many researchers, because it has critical influence on the service life of concrete structure. Pavement is subjected to a harsh environment because of exposure in air and endures dynamic fatigue loads due to passing vehicles, and thus the durability of pavement concrete has received more attention. The durability properties of pavement concrete include many aspects such as permeability, impact resistance, abrasion resistance and frost resistance. In this study, the durability of pavement concrete is measured through permeability.

Permeability, which can be defined as the ease with which external media such as liquids, gases, various aggressive ions and other pollutants penetrate concrete [1,2], is considered to be one of the most important properties affecting concrete durability [3]. A lower permeability reduces the ingress and movement of fluid media in concrete and is therefore beneficial. Concrete with higher permeability allows faster penetration of fluid media, resulting in rapid deterioration of concrete.

Concrete is a heterogeneous and porous material, in which there are many pores with different sizes and shapes. It is well known that the pore structure of concrete strongly influences its physical properties. Many important properties, such as strength and permeability, are directly or indirectly related to the pore structure of concrete [4,5]. It is generally agreed that the pore structure of concrete is one of its most important characteristics and strongly affects both its durability and mechanical properties [6]. Therefore, study of the pore structure of concrete is essential to understand the nature of this complex material.

The permeability of concrete, which is strongly affected by the pore structure of concrete, is now accepted mainly to be a function of pore size distribution [4]. The permeability of concrete is intimately related to the pore connectivity, but the compressive strength of concrete is governed by the total porosity [5,7].

The permeability of concrete mostly lies on the pore structure and its development and change. There are three types of factors affecting the permeability of concrete [8]. The first one is the factors that influence the original pore structure of concrete such as water-to-binder ratio, mineral admixtures (such as silica fume, fly ash and blast furnace slag) and additive agents (such as water-reducing agent, air-entraining agent and expansive agent). The second one is the factors that affect the development of pore structure of concrete including the curing condition, age and the

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activity of binder. The third one is the penetration condition such as hydraulic gradient, penetration time and chemistry component of penetration media.

There are two types of arguments regarding the relationship between compressive strength and permeability of concrete. Some researchers consider that compressive strength is a crucial factor affecting the permeability of concrete, and the permeability of concrete decreases with increasing compressive strength. For instance, Mohr et al. [1] described the relationship between compressive strength and permeability of concrete by a power function, and a similar trend was found by Armaghani et al. [9]. While other researchers consider that there is no significant relationship between compressive strength and permeability of concrete, and the compressive strength of concrete cannot reflect its permeability, especially for high-performance concrete [7].

Many studies have shown that the addition of PP fibers is harmful to the impermeability of concrete. Toutanji et al. [10,11] found that the permeability of concrete containing PP fibers is enhanced, and this was attributed to that PP fibers increased the void content in concrete due to the lack of cohesiveness of cement matrix and poor dispersion of PP fibers. However, there are also many researchers who argued that the impermeability of concrete was significantly improved by the addition of PP fibers [12,13].

By the addition of mineral admixtures such as silica fume, the impermeability of concrete is increased to some extent. Toutanji [11] and Oh et al. [14] reported that the permeability of concrete containing silica fume was remarkably reduced because of the denser pore structure. Toutanji et al. [10] also indicated the addition of silica fume improved the dispersion of PP fibers in cement matrix, causing a marked reduction in the permeability of PP fiber-reinforced concrete.

Nano-materials have been considered as the most promising materials in 21 century by scientists. In recent years, much attention has been paid to the applications of nano-materials in civil engineering, because nano-particles possess many special properties such as huge specific surface area and high activity due to their small size.

Li et al. [15,16] investigated the improvement in compressive and flexural strengths, abrasion resistance, and flexural fatigue performance of concrete containing nano-particles. Li et al. [17,18] also studied the microstructure and self-sensing properties of mortar containing nano-particles. The results show good prospects of concrete (or mortar) containing nano-particles.

In cold area, deicing salt is often used to sprinkle on pavement after snowing and icing. Pavement concrete may fail due to the penetration of chloride, so the permeability measured by chloride ion is more consistent with the practical condition of pavement concrete. In this work, the pore structure and chloride permeability of concrete containing nano-particles ( $\text{TiO}_2$  and  $\text{SiO}_2$ ) for pavement is experimentally studied and compared with that of plain concrete, concrete containing PP fibers and concrete containing both nano- $\text{TiO}_2$  and PP fibers.

## 2. Experimental program

### 2.1. Materials and mixture proportions

The cement used is Portland cement (P.O42.5). The fine aggregate is natural river sand with a fineness modulus of 2.4. The coarse aggregate used is crushed diabase with a diameter of 5–30 mm. The properties of nano-particles ( $\text{TiO}_2$  and

**Table 1**  
Properties of nano-particles.

Item	Diameter (nm)	Specific surface area ( $\text{m}^2/\text{g}$ )	Density ( $\text{kg}/\text{m}^3$ )	Purity (%)	Phase
$\text{SiO}_2$	$10 \pm 5$	$640 \pm 50$	<120	99.9	–
$\text{TiO}_2$	15	$240 \pm 50$	40–60	99.7	Anatase

**Table 2**  
Properties of modified PP fibers.

Elongation (%)	Titer (D)	Diameter ( $\mu\text{m}$ )	Length (mm)
$40 \pm 3$	$11 \pm 0.5$	84–92	$15 \pm 1$

$\text{SiO}_2$ ) are given in Table 1. The properties of modified PP fibers used are shown in Table 2. The water-reducing agent (UNF-5, one kind of  $\beta$ -naphthalene sulfonic acid and formaldehyde condensates) is employed to aid the dispersion of nano-particles in cement paste and achieve good workability of concrete. The defoamer (tributyl phosphate) is used to decrease the amount of air bubbles.

The water-to-binder (the sum of cement and nano-particles) ratio used for all mixtures is 0.42, and the sand ratio is 34%. The mixture proportions of concretes per cubic meter are given in Table 3. Here, PC denotes plain concrete. PPC6 and PPC9 denote the concrete containing PP fibers in the content of 0.6 and 0.9  $\text{kg}/\text{m}^3$ , respectively. NSC1 and NSC3 denote the concrete containing nano- $\text{SiO}_2$  in the amount of 1% and 3% by weight of binder, respectively. NTC1, NTC3 and NTC5 denote the concrete containing nano- $\text{TiO}_2$  in the amount of 1%, 3% and 5% by weight of binder, respectively. NTPC denotes the concrete containing both nano- $\text{TiO}_2$  in the amount of 1% by weight of binder and PP fibers in the content of 0.9  $\text{kg}/\text{m}^3$ .

### 2.2. Specimen preparation

To prepare the concrete containing nano-particles, water-reducing agent is firstly mixed into water in a mortar mixer, and then nano-particles are added and stirred at a high speed for 5 min. Defoamer is added as stirring. Cement, sand and coarse aggregate are mixed at a low speed for 2 min in a concrete centrifugal blender, and then the mixture of water, water-reducing agent, nano-particles and defoamer is slowly poured in and stirred at a low speed for another 2 min to achieve good workability.

To prepare plain concrete and the concrete containing PP fibers, water-reducing agent is firstly dissolved in water. After cement, sand, coarse aggregate and PP fibers (if used) are mixed uniformly in a concrete centrifugal blender, the mixture of water and water-reducing agent is poured in and stirred for several minutes.

Finally, the fresh concrete is poured into oiled molds to form cubes of size  $100 \times 100 \times 100$  mm to be used for compressive strength and permeability testing, prisms of size  $100 \times 100 \times 400$  mm for flexural strength and pore structure testing. After pouring, an external vibrator is used to facilitate compaction and reduce the amount of air bubbles. The specimens are de-molded at 24 h and then cured in a room at a temperature of  $20 \pm 3$  °C and a relative humidity of 95% until the prescribed period.

### 2.3. Test methods

Both compressive and flexural tests are performed according to JTG E30-2005 (Test Methods of Cement and Concrete for Highway Engineering, China).

#### 2.3.1. Pore structure measurement

There are many methods usually used to measure the pore structure, such as optics method, mercury intrusion porosimetry (MIP), helium flow and gas adsorption [19]. MIP technique is extensively used to characterize the pore structure in porous material due to its simplicity, quickness and wide measuring range of pore diameter [5,19]. MIP also provides the information about pore connectivity [19]. In this study, the pore structure of concrete is determined by using MIP.

To prepare the samples for MIP measurement, the concrete specimens after the specified curing ages are first broken into smaller pieces, and then the cement paste fragments selected from the center of prisms are used to measure pore structure. The samples are immersed in acetone to stop hydration as fast as possible. Before mercury intrusion test, the samples are dried in an oven at about 105 °C to remove moisture in the pores until a constant weight is achieved.

MIP is based on the assumption that the nonwetting liquid mercury (the contact angle between mercury and solid is greater than 90°) will only intrude in the pores of porous material under pressure [5,19]. Each pore size is quantitatively determined from the relationship between volume of intruded mercury and applied pressure [5]. The relationship between pore diameter and applied pressure is generally described by Washburn equation as follows [5,19].

$$D = -4\gamma \cos \theta / P \quad (1)$$

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