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Pore structure and chloride diffusivity of recycled aggregate concrete with nano-SiO_2 and nano-TiO_2

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HIGHLIGHTS

- Effect of nanoparticles on the pore structure of RAC is explored.
- Chloride diffusivity of RAC is found to be reduced by nanoparticles.
- A three-phase model considering the microstructures of RAC is verified.

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ABSTRACT

Nano-SiO_2 and nano-TiO_2 particles were mixed into recycled aggregate concrete (RAC) to enhance its properties. Mercury intrusion porosimetry was used to test the pore structure of the mortar in RAC, and the rapid chloride migration instrument was selected to investigate the diffusivity of RAC. It is found that the addition of nanoparticle refines the pore structure of RAC and enhances the resistance to chloride diffusivity of RAC. Furthermore, a three-phase composite sphere model for the matrix in RAC was proposed by considering the new mortar, old attached mortar and original aggregate as continuous phases. The three-phase model considering the microstructure of RAC was verified by experiment results, which can be applied to predict the chloride diffusivity of RAC with nanoparticles.

1. Introduction

With the global challenge of a shortage of natural resources in the 21st century, the recycling of waste concrete is one of the most important means for the implementation of sustainable construction development strategies. Over the past several decades, recycled aggregate concrete (RAC) has been used in many applications such as concrete pavements [1,2] and building structures [3]. RAC has a highly complex composition, which leads to significant uncertainties in its mechanical properties and structural behaviors. As a result, it is a great challenge to evaluate the durability of RAC structures.

In fact, durability has attracted much attention from many researchers because it has a critical influence on the service life of concrete structures [4]. Similar to ordinary concrete, chloride diffusivity is one of the important factors affecting the durability of RAC structures and is influenced by many parameters. In recent years, a wide range of research has led to significant advances in an understanding of the chloride diffusion properties in RAC, both experimentally [5] and numerically [6,7]. For example, Wang et al. [5] designed and fabricated a setup to test chloride diffusion in RAC, and the result showed that the diffusivity presents a trend of firstly decreasing and then increasing as the compressive stress ratio increases. Moreover, Srubar [7] introduced the development and implementation of a stochastic service-life model for chloride-induced corrosion in reinforced RAC. The results suggested that certain levels of contamination may be permissible in the design of reinforced RAC structures. As a porous material, the pore size distribution influences the chloride diffusivity of cement-based materials significantly [8]. There is a relationship between pore structure and chloride diffusivity in cement-based materials [9], and some researchers [10–13] have investigated the pore structure which influences the properties of RAC. For example, Xiao et al. [11] tested the pore structures of the new

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mortar and old adhesive mortar in RAC to explain the effects of recycled aggregate replacement ratio (R_{RA}) on the chloride concentration distribution in RAC subjected to long-term immersion. Moreover, Guo et al. [10,12] proved that the pore structure plays a significant role in the drying shrinkage of RAC. With the increase of R_{ra}, the drying shrinkage value increases gradually, and pores with the greatest impact on concrete shrinkage are those whose sizes ranging from 2.5 nm to 100 nm [12]. In addition, Gomez-Soberon [13] concluded that the porosity of RAC increases considerably with increasing R_{RA}, and a reduction in the mechanical properties of RAC is found compared with ordinary concrete when the porosity increases. Whereas, nanoparticles are considered as a potential solution which has been investigated in the literature [14–17] to improve the pore structure and durability of concrete.

Nano-particles are among most promising materials for improving the durability of concrete. Because nanoparticles possess many unique properties such as huge specific surface area and high activity due to their small size [4], much attention has been paid to the application of nano-materials in civil engineering in recent years. Mukharjee and Barai [14,15] addressed the effect of incorporation of colloidal nano-silica on the behavior of RAC. The results depicted that the compressive strength, tensile strength and non-destructive parameters were enhanced due to the addition of nano-silica. Moreover, some researcher proved that the characteristics of natural aggregate concrete resembled with that of RAC with the addition of little amount (3%) of nano-silica [14,16,17]. Despite the effort in the literature, there is a lack of knowledge about effect of nano-particles on pore structure and durability of RAC. Therefore, investigating the effects of nano silica and nano TiO_2 on pore structure and durability should be highlighted.

Taking RAC as a three-phase material, the difference between the pore structure of new mortar and that of old mortar, and the interactions between the phases in RAC matrix should all be taken into account. In this study, the pore structure of RAC and chloride diffusivity in RAC containing nanoparticles (TiO_2 and SiO_2) with a lower water-to-cement ratio (w/c) will be experimentally investigated. Considering the microstructure of RAC, a three-phase model will be developed and verified to predict the chloride diffusivity in RAC with nanoparticles.

2. Experimental program

2.1. Materials and mixture proportions

The cement used was Portland cement (P.O 42.5). The fine aggregate was natural river sand with a fineness modulus of 2.6. The natural coarse aggregates (NCAs) used were crushed limestone with a diameter of 5–32 mm. The recycled coarse aggregates (RCAs) with a diameter of 5–32 mm were crushed from cubic concrete specimens with original compressive strength 35–45 MPa. Both two kinds of aggregates are continuous gradation according to aggregate gradation curves and satisfy the *Chinese Standard* (*JGJ 52-2006*) [18]. Table 1 presents the physical properties of NCA and RCA tested by the standard test procedure [18]. Table 2 gives the properties of nanoparticle (TiO_2 and SiO_2). Table 3 presents the mixture proportions of concrete per cubic meter. For all mixtures, the water-to-binder (the sum of cement and nanoparticles) ratio is 0.30, and the sand ratio is 45%. The NCA and RCA were in the saturated surface-dry condition; the defoamer with 0.11 kg/m^3 was used to decrease the number of air bubbles. The dosage of water reducer, namely polycarboxylate superplasticizer, was adjusted to obtain the required slump ranging from 100 to140 mm. The symbol RO1, RO2 and RO3 in Table 3 denote the RAC containing nano-SiO_2 in the amount of 1%, 2% and 3% by weight of the binder, respectively. Other symbols of mixture type in Table 3 have the similar meanings as RO1, RO2 and RO3.

2.2. Specimen preparation

To prepare the RAC, nanoparticle dispersed solution and nanoparticle dispersed agent were firstly mixed into water and dispersed by using ultrasonic wave with 40 kHz and homogenizer with 10,000–12,000 r/min discontinuously for 30 min. Cement and sand were mixed at a low speed for 2 min in a concrete centrifugal blender, then the mixture of nano-particle suspension, coarse aggregate, water-reducing agent and defoamer were slowly poured in and stirred for another 2 min to achieve excellent workability. Finally, the fresh concrete was poured into molds to cast cubes of size 100 × 100 × 100 mm to be used for compressive strength, and into PVC tubes with Ø101 × 300 mm to be used for chloride diffusion coefficient testing and pore structure testing. After pouring, an external vibrator was used to facilitate compaction and reduce the number of air bubbles. The plastic film and PVC cap were used to prevent water evaporation.

The cubic specimens were de-molded after 24 h. Meanwhile, the cylinder specimens were filled with about 50 mm depth water for curing. All samples were cured in a standard curing room (temperature of 20 ± 3 °C, relative humidity above 95%) until the prescribed period. For all mixes, three specimens were fabricated and tested to ensure the statistical reliability of test results.

2.3. Test methods

2.3.1. Pore structure

The pore structure can be measured by many methods such as optics method, mercury intrusion porosimetry (MIP), helium flow and gas adsorption. MIP technique has been extensively adopted to characterize the pore structure in a porous material due to its simplicity, quickness and wide measuring range of pore diameter [19,20]. MIP also provides the information about pore connectivity [20]. In this study, MIP was used to determine the pore structure of RAC. To prepare the samples for MIP measurement, round sheets with a thickness of about 3 mm were cut from the concrete specimen after the specified curing ages then broken into smaller pieces. The fragments of old mortar and new mortar selected from the center of cylinders were used to measure pore structure, respectively. Before testing, the samples were immersed in ethanol to stop further cement hydration by removal of the free water. The freeze-drying technique [21] was used to dry the samples prior to MIP test.

Mercury intrusion measurements were performed with a Micrometrics AutoPore IV 9500 (American Michael Instruments Corp., USA) with a maximum pressure up to 30,000 Psia, which determined pore sizes in the range from 6 nm to 302 μm. Measurements were conducted in two stages: a manual low pressure that injecting the mercury into dilatometer, and an automated high pressure that injecting the mercury into the pores of a sample under increasing pressure. Data were collected and handled by a computer acting as a control module. After low-pressure testing, the penetrometer was removed and weighed. High-pressure testing was then initiated. The machine was set to equilibrate for 10 s at a contact angle of 130°. The density of mercury is 13.5335 g/ml. The surface tension of mercury is taken as 485 dynes/cm.

2.3.2. Chloride diffusion

To evaluate the chloride diffusivity of cement-based materials, researchers have developed a series of testing methods [22]. The Rapid Chloride Migration (RCM) method proposed by Tang and Nilsson [23] was applied in this study. The principle of this method is to generate chloride penetration through the sample by a solution concentration gradient and accelerate the movement of chloride using an electrical field. A migration cell was set up with a specimen 50 mm thick and 101 mm in diameter. The relationship between the applied initial current and the testing time is listed in Table 4. After a specified duration (depending on the applied current), the specimens were removed and split. Then a 0.1 N silver nitrate solution was sprayed onto the surface of the split samples. If chloride ion rises to the surface after spraying the solution on the surface for 15 min, it will create a whitish color. Otherwise, it will become brown. The color change border indicates the chloride penetration depth. The depth of the chloride penetration was measured. Then the depth was used to determine the diffusion coefficient through the Nernst-Einstein equation, which is described as follows [24].

Table 1
Properties of aggregate.

Aggregate	Bulk density/(kg·m^{-3})	Apparent density/(kg·m^{-3})	Water absorption/%	Crushing index/%	Flakiness content%
Sand	1600	2590	3.88	–	–
NCA	1350	2700	0.45	11.1	7.5
RCA	1250	2520	4.40	17.2	12.4