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The influence of admixture on chloride time-varying diffusivity and microstructure of concrete by low-field NMR

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ABSTRACT

The permeability of chloride can be used as an important indicator of durability. In this article, based on the ingress test in an artificial simulating dry-wet cycling chloride environment, the influence of four minerals, namely basalt fiber (BF), fly ash (FA), silica fume (SF), and combined FA and SF mixture on the penetration of chloride ions and microstructure in concrete were examined. In addition, the chloride diffusion coefficients of concrete were fitted with Fick's diffusion law, and pore characteristic parameters and pore-size distribution with exposure time were measured by a nuclear magnetic resonance (NMR) technology. The results show that the addition of these mineral admixtures can increase anti-permeability and decrease properties of concrete at the same exposure time. Moreover, the addition of SF has the most obvious decreasing effect on porosity, and the decreased effect of FA on chloride diffusion coefficient of concrete is the most significant, especially at the later stage. Minerals can refine the pore-size distribution in concrete, in which the content of aperture radius 100 ~1000 nm pores decreases after the same exposure time. At last, we can also see that the influence of contributive porosity of aperture radius 100–1000 nm in concrete on chloride diffusion coefficient is more than that of total porosity of concrete, there is a better positive correlation between contributive porosities of radius 100~ 1000 nm in concrete and chloride diffusion coefficients.

1. Introduction

Chloride ingress into concrete is an issue of the durability of reinforced concrete (RC) structures (Yu et al., 2015). The corrosion of reinforcing steel is the most common cause of premature deterioration and failure of concrete, leading to a reduction of its service life, particularly for structures exposed to deicing salt or marine environment (Papakonstantinou and Shinozuka, 2013). The study on the reinforcing steel corrosion in concrete is a complex process, depending on many factors, including not only the concrete materials itself (e.g. the admixture, the quality of concrete and the type of reinforcement) but also the environmental factors (e. g. exposure condition, temperature and humidity) (Valipour et al., 2014). Pore microstructure in concrete plays an important role for its mechanical and durability properties (Pipilikaki and Beazi-Katsion, 2009). The transport properties of cement-based materials are related to many factors such as the porosity, size and connectivity of capillary pores. Decreasing the porosity is the most important issue to improve the durability of RC structures (Gao et al., 2013). Therefore, many researchers have focused their studies on the porosity of concrete materials (Jia et al., 2016). Various methods, such as reducing water to binder ratio and adding mineral admixtures etc., have been employed to decrease the permeability of concrete by reducing the porosity (Mohammed et al., 2014; Camacho et al., 2014). However, the durability failure of a RC structure is a long and slow process and can be affected by many factors, most of which are time-dependent (Simčič et al., 2015; Song et al., 2013). Costa and Appleton (1999) calibrated the parameters of Fick's second law of diffusion by using a long term chloride ion penetration experiment of concrete in the marine environment, in which an age factor was defined to express the time-dependent characteristic of chloride diffusion coefficients in concrete (Boddy et al., 1999; Mangat and Molloy, 1994; Audenaert et al., 2010). Mangat and Molloy (1994) and Tang and Nilsson (1995) used rapid diffusivity tests and field data to obtain the variation of the diffusion coefficient with time, respectively. Zhang and Ye (2010) studied the influences of age and w/c ratio on the chloride diffusion coefficient. Existing results revealed that the chloride diffusion coefficient has a decrease trend with the increased exposure time or the decreased w/c ratio when the concrete is exposed to the chloride environment (Costa and Appleton, 1999; Boddy et al., 1999; Mangat and Molloy, 1994; Audenaert et al., 2010; Tang and Nilsson, 1995; Zhang and Ye, 2010; Khanzadeh-Moradllo et al., 2015).

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It is well-known that the resistance of concrete to chloride ingress is largely related to the chloride diffusion coefficient and the porosity of concrete. Some methods, such as the mercury intrusion porosimetry (MIP), electric flux and ASTM C1202, were often used to investigate the chloride diffusion coefficient and the micro-structure of concrete. It was reported that MIP measurements are useful to provide threshold diameters and intrudable pore space measurements, which can be served as comparative indices for the connectivity and capacity of the pore systems in hydrated cements (Cook and Hover, 1999; Loukili et al., 1999; Zhang, 1998; Diamond, 2000). However, it is difficult to provide precisely quantitative relation or correlation between micro-structure and diffusion performance of concrete by using these methods. Recently, nuclear magnetic resonance (NMR) technology has been used to determine the quantitative relation between ionic diffusion coefficient and pore micro-structure parameters (Wang et al., 2015). Today, the low field NMR can be used as a useful way for the traditional methods to characterize the pore structure of concrete.

In the present study, a new method based on the low field NMR is developed to study the time-varying relationship between the porosity and pore-size distribution and the chloride diffusion coefficient in concrete. Based on an artificial simulation experiment, the effects of three represented mineral admixtures of basalt fiber (BF), fly ash (FA), silica fume (SF) and a ternary mixture of FA and SF on penetration of chloride ions in concrete were analyzed. NMR was used to investigate the porosity and micro-pore size distribution in tested concrete. In addition, the effects of exposure time and the amount of mineral admixtures on chloride diffusion coefficient and micro-pore size distribution in concrete were analyzed. The results showed that NMR is very effective in examining the micro-pore structure of large size concrete specimen. Moreover, it can be used to study the relationship between time-varying diffusivity and microstructure in concrete.

2. Materials and testing methods

2.1. Materials and mix proportion of tested concrete

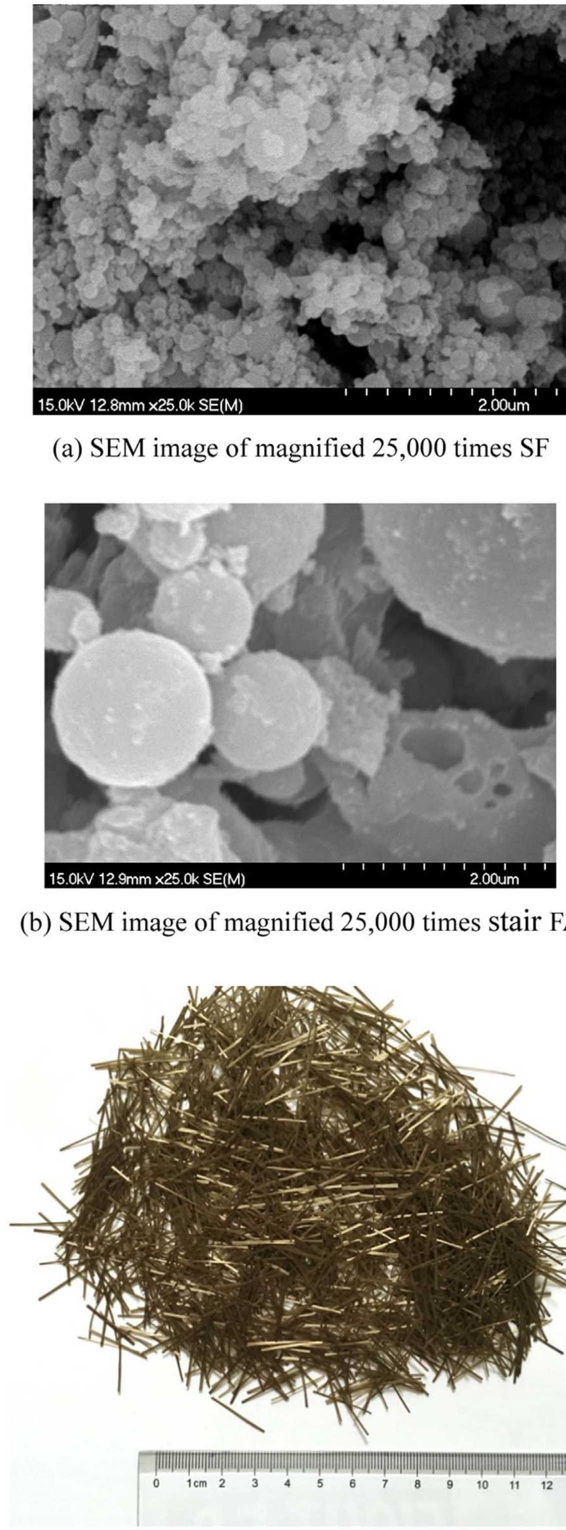
Common river sand is used as fine aggregates in this experiment. The fineness modulus of the sand is 2.4 with an apparent density of 2600 kg/m^3. The maximum size of coarse aggregates is 31.5 mm with an apparent density of 2700 kg/m^3. The cement used in the tested concrete is Qian-Chao complex Portland cement (PC 32.5) with a density of 3100 kg/m^3. The water used in the mix as well as for curing is the laboratory tap water.

The admixtures used in tested concrete include the chopped basalt fiber (BF) with filament diameter 17–20 μm and tensile strength 390–450 MPa, the silica fume (SF) with Bertrand specific area 21,000 m^2/kg, 350 mesh and 91.3% SiO_2, and the fly ash (FA) with fineness 4.6% and apparent density of 2240 kg/m^3 and specific surface area 454 m^2/kg. Fig. 1 shows the SEM images of SF with particle size 0.01–0.03 μm and stair FA with particle size 1–10 μm, and the photo of BF with length 17–24 mm.

The weight of water used in the tested concrete mixes is 190 kg/m^3, which gives the constant water-to-binder ratio 0.5. The ratio of fine to coarse aggregates used in the mixes is purposely kept to be 32% for reducing the influence of raw material randomness on the experimental results. The details of the mixture proportions of tested concrete are summarized in Table 1.

2.2. Concrete producing

The specimen of the tested concrete was made in accordance with the Chinese standards of SL352-2006. Five cylindrical specimens of size Φ100 × 50 mm were used for chloride ingress test and nuclear magnetic resonance (NMR) test for each concrete mixture. After 24 h of the specimens being cast, they were demoulded placed into a standard curing room for a period of 28 days with the temperature of 20 °C ± 5 °C and relative humidity of 95%. After the 28 days curing, the cylindrical specimens were used for chloride exposure test to examine the variation of pore structure of the mixed concrete.



(a) SEM image of magnified 25,000 times SF

(b) SEM image of magnified 25,000 times stair FA

(c) Photo of BF with length 17~24 mm

Fig. 1. SEM images and photo of materials used in the test.