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Instantaneous chloride diffusion coefficient and its time dependency of concrete exposed to a marine tidal environment

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HIGHLIGHTS

- 9 concrete mixtures with different W/B ratios and admixtures were designed, exposed up to 600 d.
- The analytical method of instantaneous diffusion coefficients was studied.
- Influence of W/B ratio, admixture and exposure time on the age reduction factors were analyzed.
- Time dependent model of instantaneous diffusion coefficients of chloride was validated.
- The chloride diffusivity of concrete tends to be stable basically after 360 d exposure time.

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ABSTRACT

Based on the field exposure test in a marine tidal environment, the free chloride concentrations of nine concrete mixtures at different exposed times were obtained. Then the apparent chloride diffusion coefficients in concrete were calculated by Fick's second law, according to the calculated values and the time dependent characteristic, the method for analyzing the instantaneous chloride diffusion coefficient of concrete was studied. Furthermore, effects of water to binder (W/B) ratio, admixture and exposure time on the age reduction factor of apparent diffusion coefficient and instantaneous diffusion coefficient have been analyzed respectively. The suggested time dependent model of instantaneous chloride diffusion coefficient was verified by the measured chloride concentrations. Results show that the convection zone has been appeared in test concrete at 120 d exposure time, and the addition of admixtures can reduce the free chloride concentrations effectively. Besides, the instantaneous chloride diffusion coefficients are all less than the corresponding apparent chloride diffusion coefficients, the difference between them decreases with W/B ratio, but increases with admixture, except silica fume. In addition, at 360 d exposure time, the age reduction factor of instantaneous diffusion coefficients tend to be stable generally. Based on the time dependent model of instantaneous chloride diffusion coefficient in concrete at 360 d exposure time, the derived instantaneous chloride diffusion coefficients can be well coincident with the fitted calculated by the measured chloride concentrations. In addition, the relative error of chloride concentration between the values predicted by the time dependent model of instantaneous diffusion coefficients and the measured values is less than that predicted by the time dependent model of apparent diffusion coefficients.

1. Introduction

As a composite porous material, the diffusivity of concrete is affected by many factors, such as the characteristics of raw materials, surrounding temperature and relative humidity, mix ratio and hydrate process, etc. [1,2]. Nowadays, the research of chloride diffusivity in concrete mainly relies on experiments [3], or theoretical analysis based on experiments [4,5]. Experiments include the long term exposure tests in a site environment [6–8] and the accelerated simulation tests in an artificial simulated environment [9]. Due to the effect of test environment, there is an obvious difference of diffusivity in concrete with different experiment methods, although the diffusivity obtained by the accelerated simulation tests, in which the environmental parameters can be controlled

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[10,11]. Corrosion of reinforcing steel due to chloride attack is the main cause of deterioration of RC structures in a tidal environment. In addition, the chloride diffusivity and its time dependency of concrete are important parameters to reflect the durability of concrete, but influenced by many factors [1,12]. Therefore, the results of diffusivity and its time dependency of concrete by accelerated simulation tests need to be verified by long-term field test in different environments [7,9,13] and by different test methods [14].

Previous research showed that the chloride diffusion coefficient of concrete decreased with exposure time [15,16], due to the continuous hydration of cementitious materials in concrete and chemical combination or physical absorption of chlorine inside concrete [17,18]. Moreover, the decrease degree is influenced by water-to-binder (W/B) ratio [15], admixture [16] and exposure time [15,17,18]. Thus the chloride diffusivity in concrete is time dependent, which is generally expressed by power function based on the reference period (eg. 28 d) and the time of cement hydration [19,20]. However, it is impossible to obtain the chloride diffusion coefficient of concrete at 28 d curing period directly by fitting the measured chloride concentrations based on Fick's second law. It can only be estimated by the fitted time dependent relationship of diffusion coefficient [2,3,15].

It is worth noting that an exposure test in the chloride environment usually lasts from several months to years. The chloride concentrations in concrete at different exposure times are measured respectively, and then the apparent diffusion coefficients of concrete are analyzed by the accumulated chloride concentrations. Therefore, the diffusion coefficients fitted by Fick's second law are the apparent chloride diffusion coefficients of concrete, which are the average diffusion coefficients during the whole testing period [4,6,9], not the instantaneous diffusion coefficients. The instantaneous chloride diffusion coefficients in concrete are the diffusion coefficients at the sampling time in the exposure test [2,11,17]. Since there are different time dependent characteristics between apparent chloride diffusion coefficient and instantaneous chloride diffusion coefficient [4,21,22], a certain error will occur if the time dependent model of apparent chloride diffusion coefficient is used to predict chloride concentrations and service life of concrete structure after the long-term exposure [8,19,20]. Therefore, it is necessary to determine the differences between apparent chloride diffusion coefficient and instantaneous chloride diffusion coefficient of concrete and establish the time dependent model of instantaneous chloride diffusion coefficient.

Based on Fick's second law, Frederiksen et al. [21] deduced the relationship between apparent chloride diffusion coefficient ($D_{app}(t)$) and instantaneous chloride diffusion coefficient ($D_{ins}(t)$) of concrete. They suggested that there is a linear relationship between apparent diffusion coefficient and instantaneous diffusion coefficient, i.e., $D_{ins}(t) \approx (1 - m_{app})\, D_{app}(t)$ (m_{app} is the age reduction factor of apparent chloride diffusion coefficient) [21]. Stanish and Thomas [4] provided a relative simple way to establish the correlation between apparent diffusion coefficient and instantaneous diffusion coefficient by solving a certain time t_{eff}. That is to say, the instantaneous diffusion coefficient at t_{eff} is equal to the apparent diffusion coefficient of concrete exposed to the chloride environment begins at time t_1 and continues for time t, i.e., $D_{ins}(t_{eff}) = D_{app}(t)$. However, in the process of calculation, there are still some problems. The instantaneous diffusion coefficient can be quickly solved when the apparent diffusion coefficient of concrete is known, but it is still necessary to estimate the apparent diffusion coefficient at the beginning of exposure time according to the obtained time dependent relationship of diffusion coefficient, such as the apparent diffusion coefficient after curing 28 d. Song et al. [22] believed that these two diffusion coefficients have different meanings and suggested to discuss and verify their relationship through a large number of effective experimental results. Nokken et al. [2] designed an indoor simulation experiment of chloride ingress into concrete and discussed the differences between m_{app} and m_{ins} (m_{ins} is the age reduction factor of instantaneous chloride diffusion coefficient). However, their experiment did not consider the binding effect of chlorine ions when testing the chloride content. The tested chloride concentrations were not the free chloride concentrations, but the total chloride concentrations. As mentioned above, currently there are still lack of the research conclusions based on the field exposure test about the differences between D_{ins} and D_{app}, m_{ins} and m_{app}.

In addition, the maturity of concrete depends on its constitutes, thus, the reduction of diffusion coefficients is inconsistent during the whole exposure period, usually showing an early rapid decline and gradual slow down trend. In general, the addition of admixtures in concrete can effectively improve the resistance to chloride, however, the effects are different [16,23]. Moreover, the time that chloride diffusivity tends to be stable is also related to the types of admixtures [2,3,24]. Since cement hydration is a continuous process, the chloride diffusivity can decrease and gradually become stable with exposure time [24–26]. Irrespective of the reduction of chloride diffusivity of concrete with different admixtures may lead to an unreliable result of chloride diffusion coefficient and the final life prediction of concrete structure [25,27,28]. In consideration that only limited environmental factors can be simulated in the indoor test [9,29], the chloride concentrations in concrete exposed to natural environment can better reflect the influence of admixtures on chloride diffusion [2,7]. Therefore, the time dependent model of instantaneous chloride diffusion coefficient in concrete based on the field exposure test can predict the time that the chloride diffusion performance tends to be stable more accurately.

In this paper, nine concrete mixtures with different W/B ratios and admixtures were designed and exposed to a natural tidal environment. First, the free chloride concentrations were measured from the specimens at different exposure times, and apparent chloride diffusion coefficients in concrete were fitted by Fick's second law on the basis of removing the influence of convective zone. Second, considering the time dependency of apparent chloride diffusion coefficients in concrete, the analytical method of instantaneous diffusion coefficients was studied. Furthermore, the influences of W/B ratio, admixture and exposure time on the age reduction factors of apparent diffusion coefficients and instantaneous diffusion coefficients were analyzed respectively. At last, based on the measured chloride concentrations, the proposed time dependent model of instantaneous chloride diffusion coefficients was validated.

2. Exposure test in marine tidal environment

2.1. Raw materials and mix proportion of concrete

All tested concrete is prepared using coarse aggregates of the maximum size 40 mm with an apparent density of 2700 kg/m^3, fine aggregates (sand) of the fineness modulus 2.4 with an apparent density of 2600 kg/m^3. The water used in the mix as well as for curing is the laboratory tap water, and the cement is Qian-Chao complex Portland cement (P.C. 32.5). The admixtures used in tested concrete include chopped basalt fiber (BF) with filament diameter 17–20 μm, length 17–24 mm, tensile strength 390–450 MPa and density of 2800 kg/m^3, silica fume (SF) with Bertrand specific area 21, 000 m^2/kg and fineness of 350 mesh, and grade I fly ash (FA) with Bertrand specific area 540 m^2/kg. Table 1 lists the chemical compositions and mineralogical components of cement and mineral admixtures in the test concrete.

In total, five kinds of W/B ratios were designed, which were 0.40, 0.45, 0.50, 0.55 and 0.60, respectively, and the W/B ratio of