A novel short-term immersion test to determine the chloride ion diffusion coefficient of cementitious materials

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HIGHLIGHTS

- This study proposes a new method to determine the chloride ion diffusion coefficient.
- The diffusivity is calculated from the concentration change in a source solution.
- The concentration change in the source solution is employed as a boundary condition.
- A series of tests was performed to validate the proposed method.
- The proposed method can estimate the diffusion coefficient within two weeks.

ARTICLE INFO

ABSTRACT

The chloride ion diffusion coefficient is a crucial factor in the durability of concrete structures exposed to seawater. A number of test methods have been developed to determine the chloride ion diffusion coefficient of concrete. Most of these test methods require an excessive test duration or represent a chloride ion penetration mechanism that applied an electrical potential to accelerate chloride ion penetration. This study proposes a new test method to determine the chloride ion diffusion coefficient while avoiding these deficiencies. The proposed method incorporates a new analytical approach that calculates the diffusion coefficient from the change in chloride ion concentration in a source solution. The proposed method can be called a short-term immersion test in comparison with traditional long-term immersion tests. The short-term immersion test was validated by comparison with a long-term immersion test and an electrical migration–diffusion test. It was found that the proposed test method and analytical solution can estimate the chloride ion diffusion coefficient within two weeks.

1. Introduction

Although concrete is known to be a very durable material, as time goes by, degradation by physical and chemical factors is inevitable. This deterioration may threaten the functionality and safety of concrete structures during their service lives. In particular, durability design against chloride ion penetration should be performed for concrete structures exposed to the marine environment since steel corrosion caused by chloride ion penetration into concrete is a major cause of durability degradation of concrete structures. Steel corrosion decreases steel area and causes cracking due to expansion by corrosion products. With the recent increase in the number of concrete structures built in the marine environment, such as bridges linking islands to land and off-shore structures, steel corrosion caused by chloride ion penetration has become an important issue. To attain durability against chloride ion attack, thereby ensuring the target service life, it is necessary to reliably predict chloride ion penetration.

A number of methodologies based on mathematical models have been proposed to predict chloride ion penetration [1–18]. In these methods, the diffusion coefficient is considered to be a major parameter affecting chloride ion transport in concrete. So, it is important to accurately evaluate the chloride ion diffusion coefficient to predict chloride ion penetration in concrete. Currently two kinds of test methods, long-term immersion tests and electrical migration–diffusion tests, are the most widely used to determine the diffusion coefficient. However, a long-term immersion test requires such a long period of time to determine the chloride ion diffusion coefficient that it may have changed due to the

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cement hydration process. The electrical migration–diffusion test can measure determine the chloride ion diffusion coefficient in a short period of time [4–11,14–18]; nevertheless, the diffusion coefficient obtained by the electrical migration–diffusion test is not the same as the actual value, because the chloride ion penetration mechanism simulated in the electrical migration–diffusion test is different from that occurs in real concrete structures [19].

In this paper, a new test method which overcomes these deficiencies in measuring the chloride ion diffusion coefficient quickly and accurately is proposed. The test method developed in this study is a rapid immersion test in which the chloride ion diffusion coefficient can be obtained using only the known change in the chloride ion concentration of the source solution. To calculate the diffusion coefficient using the short-term immersion test proposed in this study, we present a new mathematical model in which the decrease in chloride ion concentration in the source solution during the test is considered a boundary condition. The validation test was performed for mortar specimens with two W/C ratios and two different initial chloride ion concentrations. In addition, the diffusion coefficient estimated using the proposed method was compared with those from long-term immersion and electrical migration–diffusion test.

2. Existing test methods

2.1. Long-term immersion test

The long-term immersion test is a fundamental and widely-used method to determine the chloride ion diffusion coefficient in concrete. In this test, a concrete specimen is immersed in a chloride ion solution for 35–90 days, and the diffusion coefficient is calculated from the chloride ion concentration measured along the depth of the immersed specimen. The long-term immersion test is standardized as AASHTO T 259 [1] and NT Build 443 [2]. NT Build 443 is used in the Life-365 Service Life Prediction Model [20] for predicting the service life and life-cycle costs of reinforced concrete exposed to chlorides.

The chloride ion penetration mechanism in the long-term immersion test can be explained using Fick's 2nd law as follows [20]:

$$\frac{\partial C_t}{\partial t} = D_{LT} \frac{\partial^2 C_t}{\partial x^2} \tag{1}$$

where C_t is the total chloride ion concentration (mass% of sample), t is time (s), x is distance (m), D_{LT} is the apparent diffusion coefficient determined during the long-term immersion test and is defined as Eq. (2) [8].

$$D_{LT} = \frac{D_{ssd}}{\theta + \frac{\partial C_b}{\partial c}} \tag{2}$$

where D_{ssd}, θ, C_b, and c are the steady-state diffusion coefficient ($m^3_{pore} \, m_x/m^2_{concrete} \, s$), porosity ($m^3_{pore}/m^3_{concrete}$), concentration of binding chloride ion ($kg_{Cl}/m^3_{concrete}$), and concentration of free chloride ion (kg_{Cl}/m^3_{pore}), respectively. Assuming that the concentration ratio between the free chloride ion and the binding chloride ion, the surface chloride ion concentration and the diffusion coefficient are constant, the chloride ion concentration can be calculated using Eq. (3) [2].

$$C_t = C_{ts} - (C_{ts} - C_{ti}) \cdot erf\left(\frac{x}{2\sqrt{D_{LT} \cdot t}}\right) \tag{3}$$

where C_{ts} is the surface chloride ion concentration (mass% of sample) and C_{ti} is the initial chloride ion concentration (mass% of sample) in concrete. Finally, the diffusion coefficient is obtained by curve-fitting between the total concentration profile measured along the depth of the immersed concrete and the concentration profile estimated by Eq. (3).

Although the long-term immersion test simulates the real chloride ion penetration mechanism, it requires a long immersion time of at least 35–90 days. Because the pore structure of the concrete varies during the hydration process, the long test period affects the diffusion coefficient. Therefore, the assumption, employed in the derivation of Eq. (3), that the diffusion coefficient is constant throughout the test is not in accord with the actual test conditions. Besides, the complicated procedure to measure the chloride ion concentration in concrete, consisting of collecting concrete powder along the depth and extracting chloride ions from the powder, is a deficiency of the long-term immersion test [8]. So, a new test method to determine the chloride ion diffusion coefficient while avoiding these deficiencies is needed.

2.2. Electrical migration–diffusion test

An electrical migration–diffusion test was developed to shorten the test period by accelerating chloride ion penetration using electrical equipment. The most widely used method of the electrical migration–diffusion tests is the CTH (Chalmers Tekniska Hogskola) test proposed by Tang [8]. The chloride ion diffusion coefficient can be obtained within 6–96 h using the CTH test. The CTH test is standardized as NT Build 492 [11], and is used as a standard test method in the European durability test specifications, Duracrete [21]. Because chloride ions are transported by ion migration as well as by diffusion in the CTH test, chloride ion transport is represented by the Nernst–Plank equation (Eq. (4)) [8].

$$\frac{\partial c}{\partial t} = D_{nssm}\left(\frac{\partial^2 c}{\partial x^2} - \frac{zFU}{RTL} \cdot \frac{\partial c}{\partial x}\right) \tag{4}$$

where z is ion valence, F is Faraday constant, U is electrical potential difference, R is gas constant, T is temperature, and L is thickness of the specimen. The parameter D_{nssm} is the apparent diffusion coefficient determined by the CTH test and is defined as in Eq. (5) [22].

$$D_{nssm} = \frac{D_{ssm}}{\theta + K_b \cdot W_{gel}} \tag{5}$$

where D_{ssm} is the steady-state migration coefficient, θ is porosity, K_b is the chloride binding factor in a non-steady state migration test, and W_{gel} is the hydrate gel content in concrete [22]. The value $K_b \cdot W_{gel}$ represents the quantity of chloride ion binding and is assumed to be a constant determined by the cement hydration ratio and the chloride ion concentration in the source solution, irrespective of the chloride ion concentration in concrete.

Although the CTH test is the most widely used due to its short test duration and relatively simple test procedure, some researchers have pointed out deficiencies of the test caused by its reliance on electrical equipment. Chloride ion transport in concrete is affected by electrochemical reactions between various ions in the pore solution [23]. When the chloride ions are accelerated by an electrical field, the resulting electrochemical reactions, such as ion interactions and ion binding, might be different from those in an actual marine environment. This phenomenon might lead to an incorrect estimation of the chloride ion diffusion coefficient [23].

Some research also indicates that the mathematical model for chloride ion binding in the CTH test is problematic. Some specimens had a chloride ion concentration profile different from that predicted by the mathematical model used in the CTH test [16,19,24]. Spiesz et al. proposed that this phenomenon is due to the non-equilibrium caused by the limited mass transfer between the pore solution and the cement hydrate [19]. While the binding reaction between the chloride ions and the cement hydrate is sustained for 7–14 days [8,25], the CTH test is commonly completed within 24 h. This time difference means that chloride ion transport occurs with imperfect binding reactions. Consequently, the chloride ion penetration mechanism in the mathematical model used in CTH would be different from reality. This deficiency may cause error in the estimation of the diffusion coefficient.

Another electrical migration–diffusion test, a steady-state migration test method, has been reported by Truc [18]. In this test, the diffusion coefficient is determined from the concentration gradient of the external solution, and chloride ion is accelerated by an electrical field until the concentration gradient of the external solution stabilizes. However, this penetration mechanism does not adequately reflect chloride ion transport in real concrete structures, because the electrical field can affect ionic interactions and binding mechanisms [22]. Tang has also reported that diffusion coefficients obtained by the electrically accelerated test show large difference from those by NT Build 443 and 492 tests [14].

3. A new test method and mathematical model

3.1. The proposed test and mathematical model

Fig. 1(a) shows the test setup for the short-term immersion test proposed in this study. In the long-term immersion test, it is assumed that the concentration of the source solution in which a specimen is totally immersed remains constant during the test. On the other hand, in the short-term immersion test proposed in this study, a small container filled with solution is placed on the surface of a specimen disc (Fig. 1(b)). This scheme allows the chloride ions to penetrate into the specimen in one direction, and the concentration of the solution in the container continuously decreases. Fig. 2 shows the transport mechanism of chloride ions in the short-term immersion test. As seen in Fig. 2(a), the actual test configuration uses a specimen of finite height, but for the purposes of the mathematical modeling, the specimen height is assumed to be infinite (Fig. 2(b)).