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Kirchhoff transformation analysis for determining time/depth dependent chloride diffusion coefficient in concrete

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Abstract This article uses the Kirchhoff transformation method to solve a non-steady one-dimensional diffusion equation when the apparent diffusion coefficient is expressed as a function of time, depth, and concentration of chloride for concrete exposed to chloride environment. The analytical results obtained by the proposed method, which are coincided with those calculated from the Boltzmann–Matano methodology under specific condition, can be used to conveniently predict the chloride diffusion process physically and chemically so that the traditional natural diffusion test to obtain time/depth dependent apparent diffusion coefficient may be greatly simplified. Two new simplified methods to effectively process the experimental results from the natural diffusion test are proposed: one is called the long-specimen-at-one-specific-time method using fewer specimens at one time and the other the short-specimen-at-long-elapsed-time method using more specimens at various service times. Two numerical examples are provided to illustrate the application of these two proposed methods.

Introduction

Transport of chloride ions in concrete plays an important role in the durability prediction of a reinforced concrete (RC) structure. Ion transport in concrete is a rather complicated process, which involves diffusion, capillary suction, and convective flow with exposure to marine environment, accompanied by chloride binding relationship of free chlorides and bound chlorides. It is very important to use apparent chloride diffusion coefficients for prediction of the initiation period of rebar corrosion and service life for an RC structure.

In most cases, chloride as the penetrated material does not behave as an inert and stable solid with uniform pores. A variety of different physical and chemical mechanisms may govern the transport of chloride into the concrete, such as the substance mobility, concentration, environmental conditions, etc. As a consequence, the pore structure of concrete may alter, chemical absorption may occur, and a multiple transport mechanism may take place during diffusion process [1]. Therefore, the development of reliable model to measure chloride penetrating into concrete is essential for durability design.

Several researches [2–6] did steady-state experiments using the so-called diffusion or migration cell to obtain effective chloride diffusion coefficients. However, when chloride diffuses into concrete, the chloride concentration C may change at any time t in every point x of the concrete, i.e., it is a non-steady state of diffusion. In order to simplify the problem, most frequently the diffusion coefficient is

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assumed constant in a solution of Fick's 2nd law of diffusion [7–9]. Many different mathematical models for diffusion behavior prediction have been presented and described as follows. Tumidajski et al. [10] applied the Boltzmann–Matano methodology to solve one-dimensional diffusion equation for the non-steady state. Černý et al. [11] used the double integration method and the Matano method to analyze chloride profiles and the apparent diffusion coefficient. Dhir et al. [12] modeled the chloride concentration by an exponential decay function of Boltzmann's variable. Midgley and Illston [13] showed that the pore size distribution of the hardened cement paste is altered because the penetrating chloride reacted with tricalcium aluminate (C_3A) will reduce the sizes of the small pores thus reducing the permeability.

To date, however, no studies have attempted to solve a complete problem of one-dimensional non-steady-state diffusion equation employing Kirchhoff transformation technique. This is a notable shortcoming, because the use of Kirchhoff transformation approach may easily transfer a non-linear partial differential equation into a linear one.

The main purpose of this article is aimed at presenting a practical mathematical model for determining apparent diffusion coefficients by two process-simplified experiments. The mathematical model expressed in this study is based on one-dimensional diffusion equation in non-steady state, from which the Kirchhoff transformation methodology is applied to solve the non-linear diffusion equation and to calculate the non-steady-state chloride diffusion coefficients of concrete specimens. The results of this study can be provided as an important reference basis for damage evaluation and service life prediction for the existing concrete or RC structures.

Mathematical modeling for apparent chloride diffusion coefficients

The process of chloride ingress

Fundamentally, for non-steady state of diffusion, chloride diffuses into the concrete that changes the chloride concentration C at different time t and different location x of the concrete. According to Fick's second law of diffusion [14], the chloride diffusion in concrete can be modeled as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C (kg/m^3 or % by mass of concrete) is the total chloride concentration, t (s) is the exposure period, x (cm) is the space coordinate, and D (cm^2/s) is the apparent diffusion coefficient.

By assuming one-dimensional diffusion into semi-infinite space, the analytical solution of Eq. 1 can be given as

$$C(x,t) = C_\mathrm{i} + (C_\mathrm{s} - C_\mathrm{i})\mathrm{erfc}\left(\frac{x}{\sqrt{4tD}}\right) \tag{2}$$

where $C(x,t)$ is the chloride concentration at time t and point x, C_i is the initial chloride concentration of the concrete, C_s is the surface concentration, and erfc is the complementary error function. Note that Eq. 2 is valid for a constant diffusion coefficient.

For concrete structure, in principle, the transport properties of chloride depend on two factors: (1) the intrinsic permeability of the concrete, which is changing during the process of cement hydration with time, and (2) the chloride concentration level in the pore solution, which is also changing due to the continuous chemical reaction of chloride with the dilute solution of cement and the amount of diffused chloride ion. On the other hand, the variation of capillary pore structure of concrete depends on w/c ratio, degree of hydration (age), cement type, pozzolanic admixture, severity of exposure, etc., and is also changing with time at various locations. As a result, both the chloride ion concentration and diffusivity are time and space variables. During the process of chloride diffusion, some of the free chloride ions in the pore solution will be chemically bound either by adsorption on the calcium silicate hydrate (C–S–H) gel of cement hydration products or by chemical reaction with the calcium sulfoaluminates in aluminate phases. Both mechanisms accumulate the chloride ion concentration in the pore solution. As the level of concentration increases with the increasing amount of accumulated ingressed chloride, the mobility of free chloride ion gradually becomes difficult such that the diffusion coefficient decreases. As a result, it is postulated that the diffusion coefficient is concentration dependent, as also indicated by other literatures [15–20]. Therefore, in this study, it is assumed that $D = D(C(x,t))$.

The solution of the differential equation of diffusion

The one-dimensional partial differential equation for non-steady-state diffusion and its initial (IC) and boundary conditions (BC) for a solid can be written as

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D(C(x,t))\frac{\partial C(x,t)}{\partial x}\right) \tag{3a}$$

$$\mathrm{IC}: C(x,0) = C_\mathrm{i} \tag{3b}$$

$$\mathrm{BC}: C(0,t_\mathrm{m}) = C_\mathrm{s} \tag{3c}$$

$$C(x\to\infty,t_\mathrm{m}) = C_\mathrm{i} \tag{3d}$$

where x is the penetration depth from the structure surface, t is the exposure time, $C(x,t)$ is the total chloride concentration, $D(C(x,t))$ is the apparent diffusion coefficient dependent on chloride concentration $C(x,t)$, C_i is the initial chloride concentration of the concrete, C_s is the surface concentration, and, t_m is a large number of time period, since diffusion is a slow process which needs longer time to proceed. Equation 3a is a non-linear partial differential equation. To solve this equation, first, the Kirchhoff transformation is used to render the non-linear problem into a linear one [21–23]. For the purpose of brevity, the state variables in $C(x,t)$ and $D(C(x,t))$ will be omitted hereinafter. A new variable ψ is defined such that

$$\frac{d\psi(x,t)}{dC} = D(C) \tag{4}$$

Equation 4 can also be written in integral form as follows,

$$\psi(x,t) = \int_{C_{sm}}^{C_r} D(C)dC = K(C_r) = K_r \tag{5}$$

where C_r is an arbitrary reference value of concentration, C_{sm} is a nominal chloride surface concentration at t_m, and Eq. 5 is called the Kirchhoff transformation. By applying the concepts of chain rule and Leibnitz's rule to Eqs. 4 and 5, the following three equations can be obtained, respectively,

$$\frac{\partial\psi}{\partial t} = \frac{\partial\psi}{\partial C}\frac{\partial C}{\partial t} = D\frac{\partial C}{\partial t} \tag{6}$$

$$\frac{\partial\psi}{\partial x} = D\frac{\partial C}{\partial x} \tag{7a}$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{7b}$$

Equation 2a is multiplied by D and changed as

$$D\frac{\partial C}{\partial t} = D\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{8}$$

Substituting Eqs. 6–7b into Eq. 8, we get the following linear partial differential equation

$$\frac{\partial\psi}{\partial t} = D\frac{\partial^2\psi}{\partial x^2} \tag{9a}$$

The initial condition (IC) and boundary conditions (BC) mentioned above are also transferred as

$$\text{IC}: \psi(x,0) = K(C_i) = \int_{C_{sm}}^{C_i} D(C)dC = K_i \tag{9b}$$

$$\text{BC}: \psi(0,t) = K(C_s) = \int_{C_{sm}}^{C_s} D(C)dC = K_s \tag{9c}$$

$$\psi(x \to \infty, t_m) = K(C_i) = \int_{C_{sm}}^{C_i} D(C)dC = K_i \tag{9d}$$

The method of Laplace transformation is used to solve Eq. 9a. The definition of Laplace transformation of $\psi(x,t)$ [24] is given as

$$\Omega(x,s) = L[\psi(x,t)] = \int_0^\infty \psi e^{-st}dt \tag{10}$$

Thus, the Laplace transformation of Eq. 9a is given as follows,

$$\Omega(x,s) = \frac{K_0}{s} - K_0\frac{e^{-\sqrt{\frac{s}{D}}x}}{s} \tag{11}$$

The inverse Laplace transformation for the first term in Eq. 11 equals to K_0 and the second term [24] is given as,

$$L^{-1}\left\{\frac{e^{-\sqrt{\frac{s}{D}}x}}{s}\right\} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) = \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{12}$$

where erf is the error function. Thus, by taking the inverse transform on both sides of Eq. 11, we have

$$\psi(x,t) = K_i + (K_s - K_i)\operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{13}$$

The substitution of Eqs. 4 and 9b into Eq. 13 yields

$$\frac{\int_{C_{sm}}^{C_r} D(C)dC - \int_{C_{sm}}^{C_i} D(C)dC}{\int_{C_{sm}}^{C_s} D(C)dC - \int_{C_{sm}}^{C_i} D(C)dC} = \frac{\int_{C_i}^{C_r} D(C)dC}{\int_{C_i}^{C_s} D(C)dC} = \operatorname{erfc}\frac{x}{\sqrt{4Dt}} \tag{14}$$

Equation 14 provides the relationship among diffusion coefficient D, chloride concentration C, penetration depth x, and time t. The left side of Eq. 14 is purely the area ratio between areas under the D–C curve from C_s to C_r and C_s to C_i, respectively. From Eq. 14, the relationship among depth, time, and diffusion coefficient is shown in Fig. 1 by using a commercial computer package named "Mathematica" [25]. It is found that the diffusion coefficient D increases with increasing depth x, and decreases with increasing duration of exposure time t as experimentally verified by several other researchers [9–11].

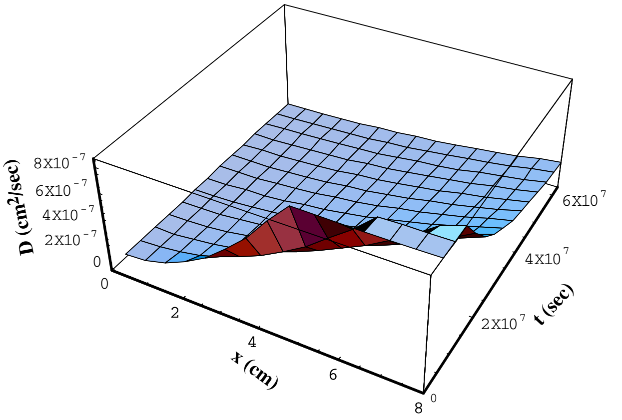


Fig. 1 Variation of the diffusion coefficient with both depth x and time t under chloride penetration conditions

Application

In order to verify the applicability of present theory, the results of analytical solution are compared with experimental results and analysis of so-called natural diffusion test (ponding test) previously obtained by Tumidajski et al. [10], who used 75 × 75 × 300 mm beams. The beams were waxed on five sides and immersed into two different baths. After 3, 6, 12, 18, and 24 months, the beams were removed from the baths. The chloride contents were determined at various penetration depths by measuring total chloride in specimens every 6 mm depth. In order to theoretically calculate the apparent diffusion coefficients varied with both distance x and time t obtained from experimental results, Tumidajski et al. [10] substituted the Boltzmann variable $u = xt^{-\frac{1}{2}}$ [26, 27] into Eq. 2a to get a solvable homogenous differential equation. After integrating the equation between $C = 0$ and $C = C^*$, $(0 < C^* < C_s)$, they obtained

$$D(C^*) = -\frac{1}{2t}\left(\frac{\mathrm{d}x}{\mathrm{d}C}\right)_{C^*}\int_0^{C^*} x \cdot \mathrm{d}C \tag{15}$$

Tumidajski et al. [10] named the method “Boltzmann–Matano methodology” to determine apparent diffusion coefficients as a function of time and distance/concentration for concrete exposed to chloride solution.

Relationship between apparent chloride diffusion coefficient (D) and time (t)

At various fixed depths, Tumidajski et al. [10] applied Boltzmann–Matano methodology to calculate apparent diffusion coefficients. The relation between apparent diffusion coefficients and chloride concentration (%) at different depths for the experimental data [10] can be fitted through the following equation

$$D(x) = \alpha \cdot e^{-\beta C(x)} \tag{16}$$

where α and β are constants. Figure 2 illustrates the fitting equation and curve at 12 months from 0.2 to 4.4 cm depth for specimens with 3-days cured and exposed to bath 1. The composition of the bath 1 is given in Table 1. The apparent chloride diffusion coefficients in Fig. 2 calculated by Eq. 2 are relatively lower than those by Eq. 15 from the Boltzmann–Matano methodology. In this example, α and β are 8.63×10^{-8} and 1.4, respectively. Subsequently, Eq. 16 was applied to Eq. 14 to calculate the values of apparent diffusion coefficient and time at certain depth. These results are compared with results by Boltzmann–Matano methodology [10] and shown in Fig. 3, in which the apparent diffusion coefficient (D) is exponential decay to the time t. Both results show a satisfactory agreement.

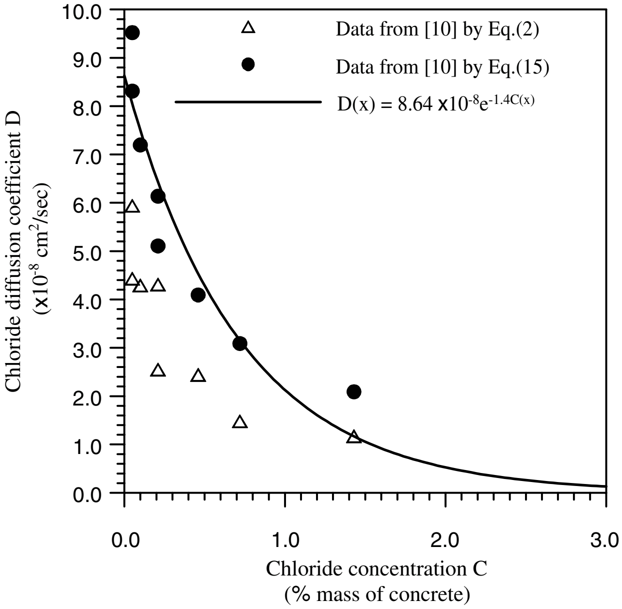


Fig. 2 *D–C* data and fitting curve of various depths at 12 months for 3-days cure exposed to bath 1

Table 1 Ion concentrations of bath (% by weight of solution) [10]

	K^+	Cl^-	SO_4^{-2}	Ca^{+2}	Mg^{+2}	Na^+
Bath 1	4.68	16.82	0.18	0.134	0.107	7.76

Relationship between apparent chloride diffusion coefficient (D) and depth (x)

At various fixed times, Tumidajski et al. [10] applied Boltzmann–Matano methodology to calculate apparent diffusion coefficients. The relationship between apparent diffusion coefficients and chloride concentration (%) for the experimental data [10] at various time periods and a fixed depth can be fitted by the following equation

$$D(t) = \delta \cdot e^{-\gamma C(t)} \tag{17}$$

where δ and γ represent constants.

Figure 4 demonstrates the fitting curve at depth of 2.0 cm from 3 to 24 months for the specimens 3-day cured and exposed to bath 1. The apparent chloride diffusion coefficients in Fig. 4 calculated by Eq. 2 are relatively lower than those by Eq. 15 from the Boltzmann–Matano methodology. The properties of concrete keep changing simultaneously with hydration process of concrete which results in different fitting curves at different time durations. Table 2 gives the values of δ and γ for this example. Subsequently, such fitting curves were applied to Eq. 14 to calculate the values of apparent diffusion coefficient and depth at certain time. These results are compared with

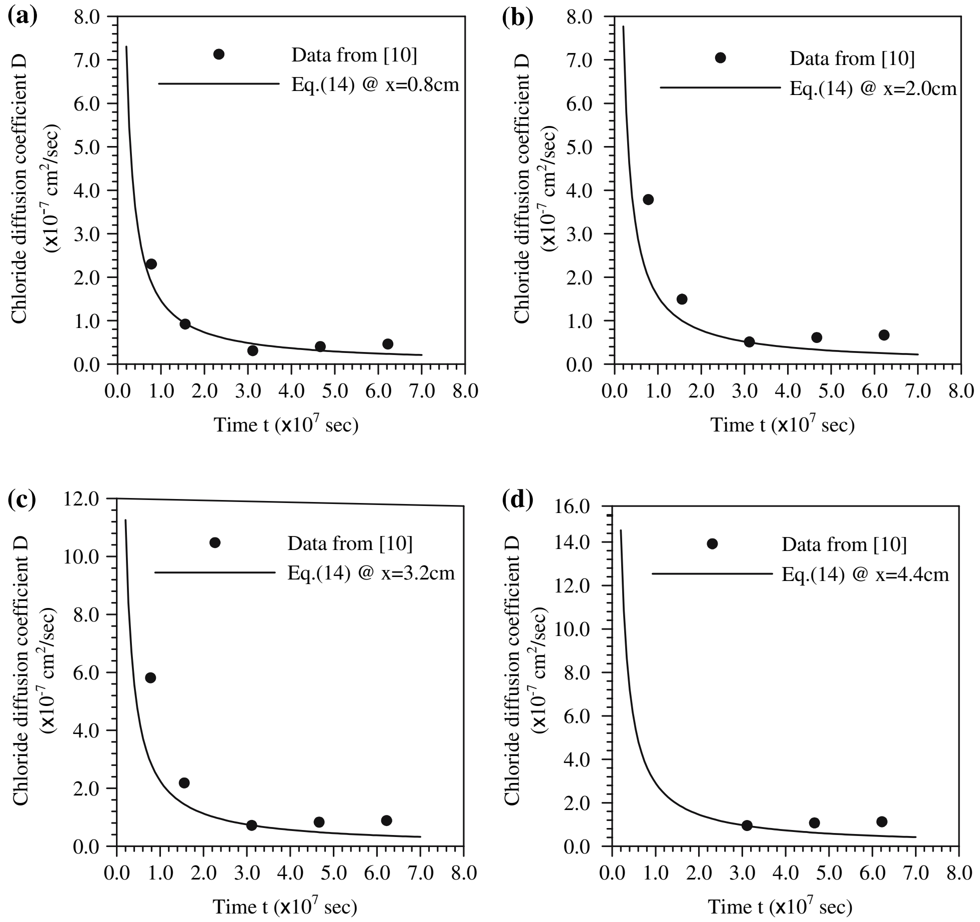


Fig. 3 Relationship between apparent chloride diffusion coefficient and time at certain depth (**a**) x = 0.8 cm, (**b**) x = 2.0 cm, (**c**) x = 3.2 cm, (**d**) x = 4.4 cm

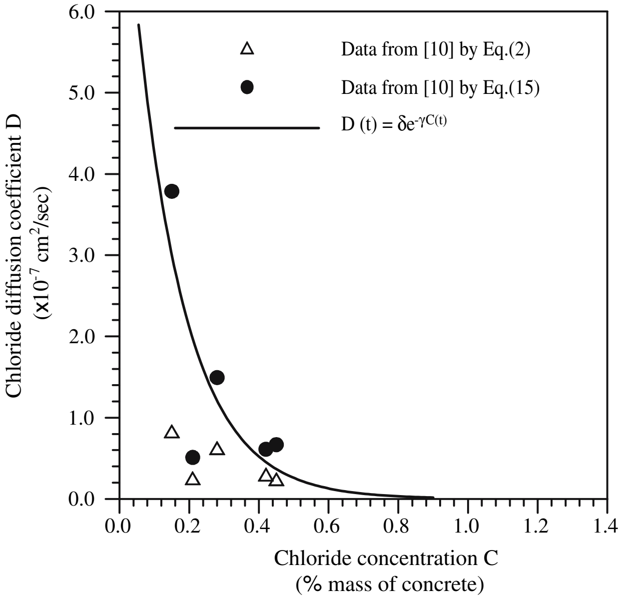


Fig. 4 *D*–*C* data and fitting curve of various time at depth of 2.0 cm for 3-days cure exposed to bath 1

those obtained by the Boltzmann–Matano methodology [10] and shown in Fig. 5, in which the apparent diffusion coefficient (D) is nearly exponential growth of the depth x. The resulting values are in good agreement with those results calculated by the Boltzmann–Matano methodology.

Discussion

Physical phenomena

In the real situation, the apparent diffusion coefficient D, is actually varied with both depth x and time t. This fact can be revealed from Eq. 3a and Fig. 1. Such experiments as for measuring chloride diffusion coefficient that varied simultaneously with both depth and time are in general very costly and time-consuming. Through the proposed concepts in this study, those lengthy and costly experiments can be substantially reduced to merely measure the chloride concentration at different fixed depths and fixed times as done by Tumidajski et al. [10]. It is equivalent to conducting the several experiments only at some sections of Fig. 1 for either x = constant or t = constant. For such cases, the physical phenomena may be described by the diffusion equation of Fick's second law [27–31] with initial and boundary conditions written as Eq. 3a–d and the analytical solution as Eq. 14.

Table 2 Values of δ and γ in fitting Eq. 17 of apparent chloride diffusion coefficient calculation

Time	6 months	12 months	18 months	24 months
δ	8.58×10^{-7}	1.75×10^{-6}	7.06×10^{-7}	4.59×10^{-7}
γ	7	11	6	4

Rearrangement of Eq. 14 gives

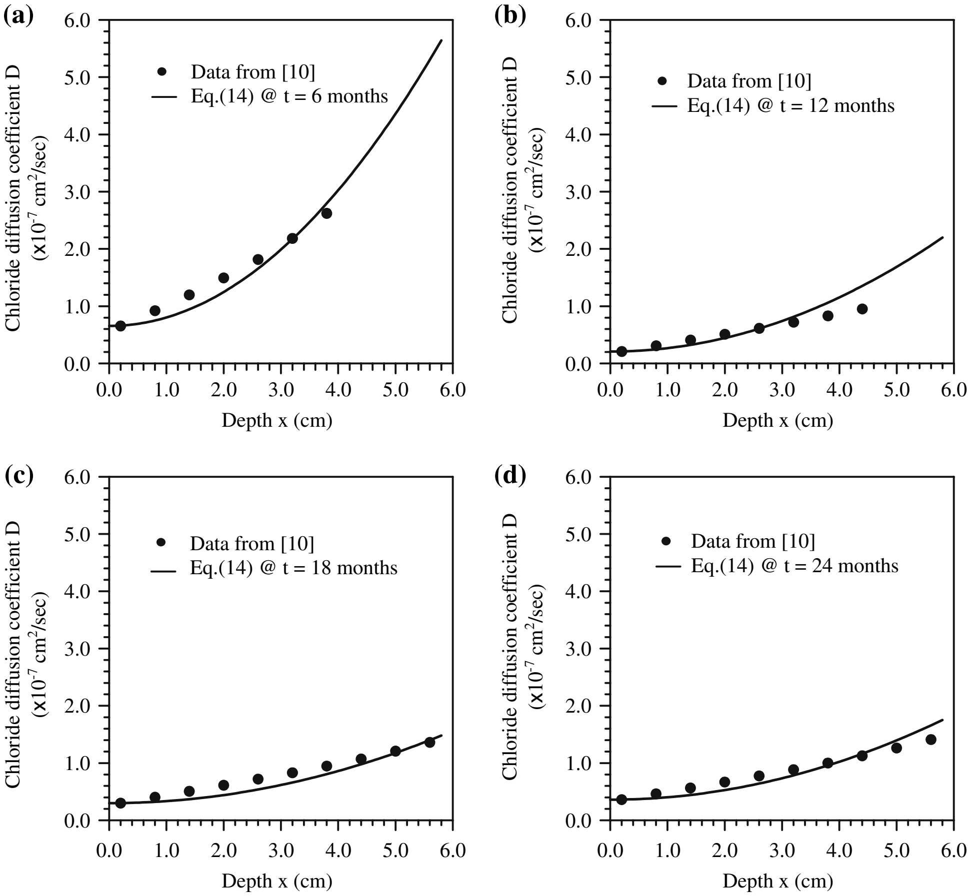
$$D = \frac{1}{4t}\left\{\frac{x}{\mathrm{erfc}^{-1}\left[\frac{\int_{C_i}^{C_r} D(C)dC}{\int_{C_i}^{C_s} D(C)dC}\right]}\right\}^2 \tag{18}$$

Equation 18 reveals that the chloride diffusion coefficient is inversely proportional to the duration of exposure time t and is proportional to the square of depth. When the duration of exposure time increases twice, the chloride diffusion coefficient decreases by half under the same penetration depth. This trend is also illustrated by Fig. 3(a–d) which provides the relationship between the chloride diffusion coefficient and time under certain depth. When the penetration depth of concrete doubly increases the chloride diffusion coefficient increases four times under a fixed time as also denoted in Fig. 5(a–d).

Two new methods to determine time/depth dependent apparent chloride diffusion coefficient

Important factors in typical transport processes of chloride ion ingress of concrete include transport of water under a hydrostatic pressure head, transport of water by capillary suction, the diffusion of ions under an applied concentration gradient, and the transport of ions by moving water, ion exchange reactions with other compounds of concrete, etc. These factors may result in changes of chemical binding in the microstructure of concrete such that its pore size and connectivity in the microstructure control how the spatial geometry of microstructure affects transport properties. As the apparent chloride diffusion coefficient is the main parameter used to measure the concrete property of diffusion, it may be expected that once the value of D is known, some related information about the microstructure and the chemical binding characteristics of concrete may be inferred [27]. From the satisfactory comparison between theoretical and experimental results mentioned above, the proposed mathematical model seems to be proper to serve this purpose. As stated previously, the major advantage of applying the model to the determination of apparent chloride diffusion coefficient at non-steady state is the reduction of the duration of test and the amount of test

Fig. 5 Relationship between apparent chloride diffusion coefficient and depth at certain time (**a**) t = 6 months, (**b**) t = 12 months, (**c**) t = 18 months, (**d**) t = 24 months



specimens. By using this model, there are two ways to determine apparent chloride diffusion coefficient in a simple natural diffusion test.

1. *Long-specimen-at-one-specific-time method*: At a certain exposure time *t*, say, 6 months, the chloride contents *C* were determined experimentally at various penetration depths of a relatively long specimen and used to get the relevant apparent diffusion coefficients *D* mathematically by the Boltzmann–Matano methodology through Eq. 15. Then these resulting data of *D* and *C* at various depths are substituted into Eq. 14 to determine the apparent diffusion coefficients of concrete at any times and depths. This approach may reduce the test period and require only one set of specimens.

2. *Short-specimen-at-long-elapsed-time method*: The chloride concentrations *C* at two certain depths *x*, say, top surface and 2.0 cm underneath, of a relatively short specimen were measured experimentally at various elapsed times and used to get the apparent diffusion coefficients *D* by Crank's solution to Fick's second law of diffusion as given by Eq. 2. Then, these resulting data of *D* and *C* at various time periods are plugged into Eq. 14 to determine the apparent diffusion coefficients at all time periods and depths. It should be noted that *D* may be underestimated by Eq. 2, but it is acceptable for simplifying the test process. This method may use only one or two slices of sample from shorter specimens but require a longer time interval. In practice, in order to properly account for the actual changes of material properties for a fully matured concrete under the environmental variations during its service period, a reasonably longer period of inspections is normally required.

Illustrations for proposed methods

Example 1: Long-specimen-at-one-specific-time method: In the following, it is grateful to use the natural diffusion experiment results published by Dhir et al. [12] who used concrete specimens, which were made of a grade 40 normal Portland cement, being immersed in a 5 M NaCl solution at 20 °C for an exposure period of 6 months. Table 3 shows the results of both chloride concentration *C* (% by mass of concrete) at different penetration depths *x* (cm) and apparent diffusion coefficients *D* (cm^2/s) calculated by applying *C* and *x* to Eq. 15. These data of apparent diffusion coefficients and concentrations at the same time (s) but different depths were fitted by the following equation and shown in Fig. 6:

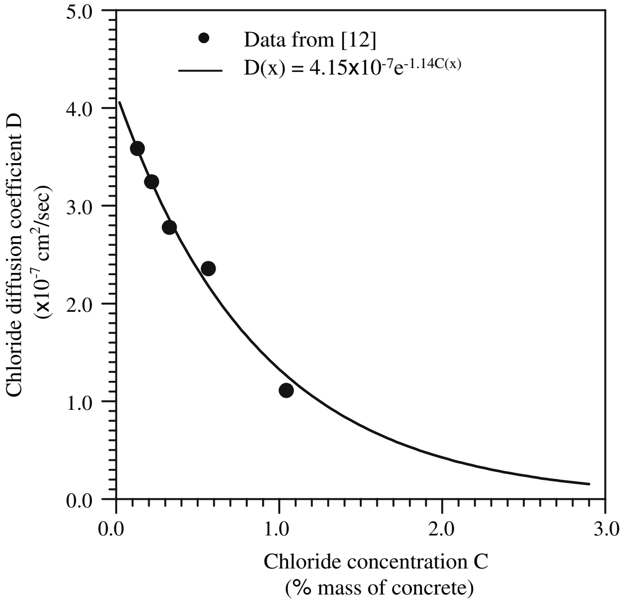


Fig. 6 *D–C* data and fitting curve for example 1

$$D(x) = 4.15 \times 10^{-7} e^{-1.14C(x)} \tag{19}$$

The fitting equation of Eq. 19 was applied to Eq. 14 to calculate apparent diffusion coefficient and time at certain depth. Figure 7 shows the resulting relationship between apparent chloride diffusion coefficient and time at different penetration depths, from which Table 4 shows the calculation results of apparent diffusion coefficients for 1, 5, 10, 15, and 20 years at 0.7, 1.7, 2.7, 3.7, and 4.7 cm, respectively.

Example 2: Short-specimen-at-long-elapsed-time method: In the second illustrated example, it is also grateful to use the experimental results published by Nokken et al. [32] who performed the natural diffusion test on some 5-cm thick, 10-cm diameter cylindrical concrete samples with different concrete mixtures for 3 years. For one set of concrete specimens 1B (w/cm = 0.4, 8% high-reactivity metakaolin cement replacement), its surface concentrations and apparent diffusion coefficients at various chloride exposure periods are shown in Table 5. These data were used to obtain the fitting curves between *C* and *D* and to predict surface concentrations and surface apparent

Table 3 Chloride concentration *C* at different penetration depths and corresponding apparent chloride diffusion coefficients *D* (*t* = 6 months) for example 1 [12]

Depth *x* (cm)	0.7	1.7	2.7	3.7	4.7
C (% by mass of con.)	1.043	0.565	0.326	0.217	0.130
D (cm^2/s)	1.11×10^{-7}	2.36×10^{-7}	2.78×10^{-7}	3.24×10^{-7}	3.59×10^{-7}

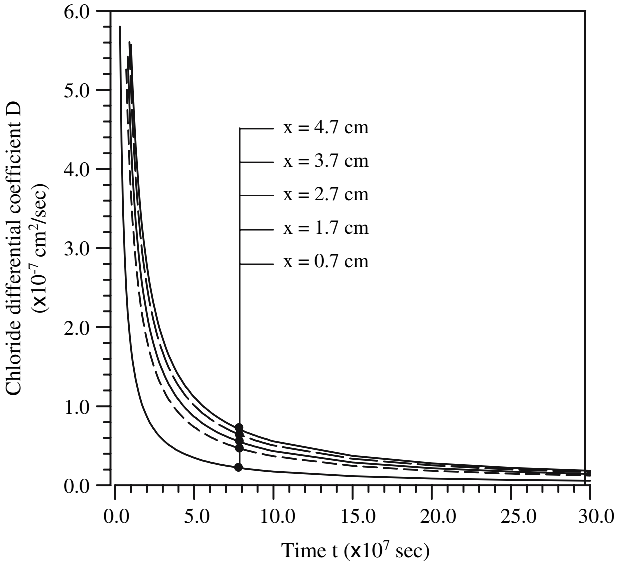


Fig. 7 Time/depth dependant apparent chloride diffusion coefficient for example 1

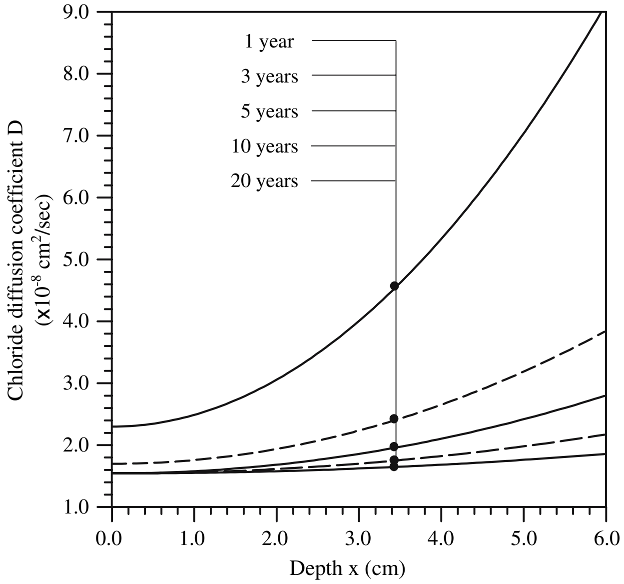


Fig. 8 Time/depth dependant apparent chloride diffusion coefficient for example 2

diffusion coefficients at future longer time, respectively. The latter two values were applied to Eq. 14 to calculate apparent diffusion coefficient and depth at certain future time. Figure 8 shows the predicted relationship between apparent diffusion coefficient and depth at different penetration times.

Incidentally, either Tables 3 or 5 provides five sets of test data for the prediction of apparent diffusion coefficient at any time and depth. Both Figs. 7 and 8 indicate that the apparent diffusion coefficients decrease as the time increases, while the apparent diffusion coefficients increase as the depth increases. Such phenomenon may be explained by the fact that the apparent diffusion coefficients decrease when the pore size of concrete is decreasing due to the penetrated chloride ions being bound and accumulated to the pore walls of concrete microstructure. In addition, the chemical interaction of chloride in the concrete microstructure and the increasing amount of hydration products of C–S–H gel have blocked up the paths of water and reduced the size of pores gradually as the time elapsed.

Conclusions

The approach to obtaining the analytical solution of one-dimensional non-steady-state diffusion equation by the Kirchhoff transformation technique has been described and

Table 4 Apparent chloride diffusion coefficient prediction results for example 1

Depth x (cm)	Apparent chloride diffusion coefficient D (cm^2/s)				
	Time t (years)				
	1	5	10	15	20
0.7	5.52×10^{-8}	1.10×10^{-8}	5.52×10^{-9}	3.68×10^{-9}	2.76×10^{-9}
1.7	1.17×10^{-7}	2.34×10^{-8}	1.17×10^{-8}	7.78×10^{-9}	5.84×10^{-9}
2.7	1.37×10^{-7}	2.75×10^{-8}	1.37×10^{-8}	9.17×10^{-9}	6.87×10^{-9}
3.7	1.60×10^{-7}	3.20×10^{-8}	1.60×10^{-8}	1.07×10^{-8}	8.00×10^{-9}
4.7	1.77×10^{-7}	3.54×10^{-8}	1.77×10^{-8}	1.18×10^{-8}	8.84×10^{-9}

Table 5 Surface chloride concentration C and corresponding apparent chloride diffusion coefficients D at various chloride exposure periods for specimen 1B from [32]

Exposure period (days)	28	90	140	365	1095
C (% by mass of con.)	0.690	0.580	0.610	0.680	0.130
D (cm^2/s)	8.25×10^{-8}	5.73×10^{-8}	3.79×10^{-8}	2.30×10^{-8}	1.70×10^{-8}

the resulting outcomes were compared satisfactorily with those results calculated by the Boltzmann–Matano methodology. This proposed method allows the prediction of non-steady-state and non-constant apparent diffusion coefficients that are dependent on both time and penetration depths by just using the experimental data of some natural diffusion tests with a short period of test time or less work in test process.

The time/depth dependence of chloride concentration and the apparent chloride diffusion coefficients on the concentration content can be well modeled by the proposed solution. It is found that the apparent diffusion coefficient is proportional to the square of penetration depth and inversely proportional to exposure time.

The physical phenomenon implied in this proposed method may coincide with the trend of progress of hydration products of concrete microstructure and some other chemical interactive reactions with concrete such that the permeability of concrete is reducing with increasing exposure time and the age of concrete specimen. However, in principle, this model cannot describe the increase in apparent chloride diffusion coefficients after a longer exposure time if any alkali materials exist in the concrete or solution to cause microcracks or more porous microstructures [10]. It is obvious that further efforts are certainly required to have a robust prediction model of concrete chloride diffusion that is valid and reliable even when there are cracks occurred in the concrete system during its service life.

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