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Concentration dependence of diffusion and migration of chloride ions
Part 1. Theoretical considerations

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Abstract

This paper series includes two parts: (1) theoretical considerations and (2) experimental evaluations. In Part 1, the chloride ion diffusion and migration processes in concentrated solutions are theoretically analyzed. The quantitative relationship between diffusion coefficient and migration coefficient is established. Two important parameters that are inherent in the cement based materials (i.e., ion-selective semipermeability and chloride binding) are discussed. The theoretical analysis shows that the “effective” chloride diffusion coefficient determined from the conventional diffusion or migration tests is not a constant, but rather is a complicated function of concentration. This function contains four main factors: (1) the parameter K_T, describing the effect of counter-electrical potential; (2) the ratio of cation velocity to anion velocity β_v; (3) the friction coefficient f, which reflects the ionic interaction; and (4) the activity coefficient γ, which is also a function of concentration. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Chloride transport in concrete has drawn much attention due to the problem of chloride-induced corrosion of reinforcement in concrete structures. Despite of the complicated transport mechanisms of chloride ions in concrete, in many cases diffusion is still considered as one of the major transport processes. Therefore, the measurement of chloride diffusivity has been interesting topic. There are many methods for determining chloride diffusivity. A number of literature reviews can be found elsewhere [1–4]. In the past years, some rapid methods based on electrical migration have been developed [5–10]. However, the diffusion coefficients reported in the literature are in general not comparable due to different test methods, conditions, and even calculation equations. It is well known that the ion transport is concentration-dependent. Chloride diffusion or migration through cement-based materials is not in an infinite dilute solution, but an ion-enriched pore solution [2,8,11,12]. In many methods a chloride diffusion coefficient is usually calculated simply by using equations similar to those used for an infinite dilute solution. A number of researchers have tried to establish a relationship between diffusion coefficient and concentration. Andrade [8] simply replaced the concentration term in the migration equation with an activity term. Chatterji [11] suggested a square-root rule. Zhang & Gjørv [12] introduced a correction factor for the ionic interaction. Recently, Zhang [13] proposed a cubic root relationship. In this paper some basic theories of ion transport in concentrated solutions will be used to find the relationships between diffusion coefficients obtained from different test methods. It should be noted that the theories deduced in this study are limited to binary electrolytic solutions, which are often used as external source solutions for chlorides penetrating into concrete. Further study is needed to extend the theories to multicomponent solutions if other ions such as alkali coexist.

2. Ion diffusion and migration functions in general

Diffusion is the movement of substance under a gradient of concentration, or more strictly speaking, chemical potential, from a high concentration zone to a low concentration zone, while migration is the movement of charged substance under the action of an electrical field.

In general, chlorides exist in concrete in two forms: free chlorides and bound chlorides. The total chloride content in concrete is a sum of free and bound chlorides. It should be kept in mind that only free chloride ions in a solution are

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movable and could contribute to a concentration or chemical potential.

Under a gradient of chemical potential, the ions will move along the gradient. It has been found that the cations (e.g., Na^+, K^+, Li^+, Cs^+, etc.) have a lower diffusion rate than Cl^- in cement paste, as reported by Ushiyama and Goto [14] and Roy et al. [15]. Because chloride ions cannot exist alone, there must be some cations around to keep the solution electrically neutral. Once chloride ions move forward, a counter-electrical field between the chloride ions and the surrounding slower cations will be formed. This counter-electrical field tends to redraw the chloride ions [10]. The combination of driving force (chemical potential) and draw-back force (counter-electrical field) is called "electrochemical potential." The actual movement of ionic species is in fact under the gradient of electrochemical potential, as expressed by Eq. (1) [16,17]

$$J = -\frac{D}{RT}c\nabla\mu = -D\frac{\partial c}{\partial x}\left(1+\frac{\partial \ln\gamma}{\partial \ln c}\right) - cD\frac{zF}{RT}\cdot\frac{\partial\phi}{\partial x} \tag{1}$$

where J is the flux of ions, D denotes the diffusion coefficient, c is the molar concentration, R is the gas constant, T is the absolute temperature, $\nabla\mu$ represents the gradient of electrochemical potential, x is the distance, γ is the activity coefficient, z is the valence of ions, F is the Faraday constant, and ϕ is the counter-electrical potential.

It should be emphasized that, if not otherwise specifically stated, the symbol c in Eq. (1) and hereinafter represents the ion concentration but not the ion activity, because the effect of ion activity has already been considered in Eq. (1) in the form of $1 + \partial\ln\gamma/\partial\ln c$.

In the literature the terms $1 + \partial\ln\gamma/\partial\ln c$ and $\partial\phi/\partial x$ are often neglected. Thus Eq. (1) becomes a general form of Fick's law, or Fick's first law, as in Eq. (2):

$$J = -D\frac{\partial c}{\partial x} \tag{2}$$

or under the action of an external potential [6], as in Eq. (3):

$$J = -D\left(\frac{\partial c}{\partial x} + c\frac{zF}{RT}\cdot\frac{\partial\phi}{\partial x}\right) \tag{3}$$

where the potential ϕ may represent the combination of the external potential and the counter-electrical potential. If the external potential is sufficiently large, the counter-electrical potential as well as the diffusion term could be negligible. Thus Eq. (3) can be simplified as [7] Eq. (4):

$$J = -cD\frac{zF}{RT}\cdot\frac{\partial\phi}{\partial x} \tag{4}$$

Andrade [8] also proposed a similar equation but with c as the ion activity, which is not a direct simplified form of Eq. (1).

Since the coefficient D in Eq. (3) and Eq. (4) is obtained from migration tests, it is sometimes called "migration coefficient" [8] to differentiate it from the one in Eq. (2) obtained from diffusion tests.

3. Ion diffusion and migration in concentrated solutions

In a concentrated solution, ions are so close to each other that the friction effect, or interaction, between moving ions should not be ignored. A multicomponent diffusion equation [17] can be used to describe the mass transfer in concentrated electrolytic solutions. For a binary electrolytic solution composed of anions, cations, and solvent, the equation for anions is as shown in Eq. (5)

$$\begin{aligned} c_-\nabla\mu_- &= RT\frac{c_-c_+}{(c_- + c_+ + c_{0+})D_{-+}}(\nu_+ - \nu_-) \\ &\quad + RT\frac{c_-c_0}{(c_- + c_+ + c_0)D_{-0}}(\nu_0 - \nu_-) \end{aligned} \tag{5}$$

where μ_- is defined as the "electrochemical potential" of anions; v_+, v_-, and v_0 are the average drift velocity of cations, anions, and solvent, respectively; c_0 is the solvent concentration; D_{-0} is the diffusion coefficient of anions in the infinite dilute solution; and D_{-+} is the diffusion coefficient of anions with the interaction of cations and its reciprocal could be regarded as a friction coefficient [17]. Without convection, v_0 can be ignored. Let [See Eq. (6)]

$$\beta_\nu = \frac{\nu_+}{\nu_-} \qquad \text{and} \qquad f = \frac{D_{-0}}{D_{-+}} \tag{6}$$

The following flow equation for anions in a 1:1 salt solution could be derived as shown in Eq. (7):

$$J_- = -\mathcal{D}\frac{\partial c}{\partial x}\left(1+\frac{\partial\ln\gamma}{\partial\ln c}\right) - \frac{z_-\mathcal{D}F}{RT}\cdot c\frac{\partial\phi}{\partial x} \tag{7}$$

where [see Eq. (8)]

$$\mathcal{D} = \frac{2c + c_0}{f(1-\beta_\nu)c + c_0}\cdot D_{-0} \tag{8}$$

The solvent concentration c_0 can be estimated by using Eq. (9):

$$c_0 = \frac{\rho - cM}{M_0} = \frac{\rho_0}{M_0} - c \tag{9}$$

where ρ and ρ_0 are the density of the solution and solvent in g/dm^3, respectively, and M and M_0 are the molar weight of electrolyte and solvent, respectively.

3.1. Diffusion process

As previously mentioned, without any external potential the ϕ in Eq. (7) represents the counter-electrical potential, which is caused by the difference in drift velocity between cations and anions in an electrolytic solution, as shown in Eq. (10):

$$\phi \propto -\frac{RT}{F}(\tau_{+0} - \tau_{-0})\ln(\gamma c) = -\frac{RT}{F}K_{\tau 0}\ln(\gamma c) \tag{10}$$

or as shown in Eq. (11):

$$\begin{aligned} \frac{\partial\phi}{\partial x} &= -\frac{RT}{F}K_{\tau 0}\left(\frac{\partial\ln\gamma}{\partial x} + \frac{\partial\ln c}{\partial x}\right) \\ &= -\frac{RT}{F}\frac{K_{\tau 0}}{c}\left(1+\frac{\partial\ln\gamma}{\partial\ln c}\right)\frac{\partial c}{\partial x} \end{aligned} \tag{11}$$

where τ_{+0} and τ_{-0} are the transference number of cations and anions in the solution, respectively. Since [see Eq. (12)],

$$\tau_{\pm} = \frac{\nu_{\pm}}{\nu_{+} + \nu_{-}} = \frac{u_{\pm}}{u_{+} + u_{-}} = \frac{\lambda_{\pm}}{\lambda_{+} + \lambda_{-}} \tag{12}$$

therefore [see Eq. (13)],

$$\begin{aligned} K_{\tau 0} &= (\tau_{+0} - \tau_{-0}) = \frac{\nu_{+0} - \nu_{-0}}{\nu_{+0} + \nu_{-0}} = \frac{u_{+0} - u_{-0}}{u_{+0} + u_{-0}} \\ &= \frac{\lambda_{+0} - \lambda_{-0}}{\lambda_{+0} + \lambda_{-0}} \end{aligned} \tag{13}$$

where u_{+0} and u_{-0} are the mobility and λ_{+0} and λ_{-0} are the conductivity of cations and anions in the infinite dilute solution. Thus Eq. (7) becomes Eq. (14)

$$J_{-} = -\mathcal{D}(1 - z_{-}K_{\tau 0})\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right)\frac{\partial c}{\partial x} = D_{\mathrm{d}}\frac{\partial c}{\partial x} \tag{14}$$

where D_{d} represents the "effective" diffusion coefficient determined from conventional diffusion tests simply by using Fick's law [see Eq. (15)],

$$D_{\mathrm{d}} = \mathcal{D}(1 - z_{-}K_{\tau 0})\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right) \tag{15}$$

Inserting Eq. (8) into Eq. (15) gives Eq. (16):

$$\frac{D_{\mathrm{d}}}{D_{-0}} = (1 - z_{-}K_{\tau 0})\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right) \cdot \frac{2c + c_0}{f(1 - \beta_{\nu})c + c_0} \tag{16}$$

Eq. (16) shows the concentration dependence of an "effective" diffusion coefficient. For pure solutions, β_{ν} can be estimated by Eq. (17).

$$\beta_{\nu} = \frac{\nu_{+0}}{\nu_{-0}} = \frac{u_{+0}}{u_{-0}} = \frac{\lambda_{+0}}{\lambda_{-0}} \tag{17}$$

Thus the parameters $K_{\tau 0}$ and β_{ν} in Eq. (16) can easily be obtained by using the mobility or conductivity data from chemistry textbooks or handbooks. The term $\partial\ln\gamma/\partial\ln c$ can be estimated by applying the Debye-Hückel equations, while the friction coefficient f could be estimated by curve-fitting some measured data of "effective" diffusion coefficient. Some examples will be given in Part 2 of this work.

3.2. Migration process

If the external potential ϕ is sufficiently large, Eq. (7) can be simplified as Eq. (18)

$$J_{-} = -\frac{z_{-}\mathcal{D}F}{RT} \cdot c\frac{\partial \phi}{\partial x} = -\frac{z_{-}D_{\mathrm{m}}F}{RT} \cdot c\frac{\partial \phi}{\partial x} \tag{18}$$

where D_{m} represents the "effective" diffusion coefficient determined from migration tests, or the so-called "effective migration coefficient." It is obvious that $D_{\mathrm{m}} = \mathcal{D}$. Since the flow direction of cations in a migration process is opposite that of anions(i.e. $\beta_{\nu} < 0$), thus [see Eq. (19)]

$$\frac{D_{\mathrm{m}}}{D_{-0}} = \frac{2c + c_0}{f(1 - \beta_{\nu})c + c_0} = \frac{2c + c_0}{f(1 + |\beta_{\nu}|)c + c_0} \tag{19}$$

By comparing Eq. (16) with Eq. (19), one can find that [see Eq. (20)]

$$\frac{D_{\mathrm{d}}}{D_{\mathrm{m}}} = (1 - z_{-}K_{\tau 0})\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right) \cdot \frac{f(1 + |\beta_{\nu}|)c + c_0}{f(1 - |\beta_{\nu}|)c + c_0} \tag{20}$$

It can be seen that the relationship between D_{d} and D_{m} is not simple, but contains many parameters. This might be why in the literature diffusion coefficients determined from a steady-state migration test can rarely be directly compared with those determined from a steady-state diffusion test. A comparison between D_{d} and D_{m} will be given, theoretically and experimentally, in Part 2 of this work.

4. Diffusion and migration through a concrete specimen

4.1. Solution-concrete system

The theories discussed above are based on a homogeneous pure solution system. For chloride ions diffusing into concrete, however, in most cases there exists a solution-concrete interface across which the physical meanings of the dimension area or volume are different. For water-saturated concrete, the following relations could be used to keep the dimensions consistent [10; see Eq. (21)]

$$D_{\mathrm{d}} = \frac{D_{\mathrm{ssd}}}{\varepsilon} \qquad \text{and} \qquad D_{\mathrm{m}} = \frac{D_{\mathrm{ssm}}}{\varepsilon} \tag{21}$$

where ϵ is the volumetric porosity of concrete and D_{ssd} and D_{ssm} are the "effective" diffusion coefficient of concrete from a steady-state diffusion test and a steady-state migration test, respectively.

4.2. Steady-state process

Under a steady state, the chloride binding or reaction should be completed and the chloride flux becomes constant. Since cement paste in the concrete behaves as an electronegative permeable semimembrane [11,14], when cations and anions from the external source solution diffuse into concrete the semimembrane will selectively reduce the transference number of cations to increase the difference in the average drift velocity between cations and anions. This large difference between v_{+} and v_{-} in the pore solution will result in a counter-electrical field larger than that in the external source solution. The phenomenon can be described by a membrane potential [18], which is expressed as Eq. (22) [19,20],

$$\begin{aligned} \Delta\phi_{\mathrm{m}} &= \phi_2 - \phi_1 = -\frac{RT}{F}(\tau_{+\mathrm{m}} - \tau_{-\mathrm{m}})\ln\frac{a_2}{a_1} \\ &= -\frac{RT}{F}K_{\tau \mathrm{m}}\ln\frac{\gamma_2 c_2}{\gamma_1 c_1} \end{aligned} \tag{22}$$

where $\Delta\phi_{\mathrm{m}}$ is the membrane potential or the potential difference between two diffusion cells with the activity a_1 and

a_2, and $\tau_{+\mathrm{m}}$ and $\tau_{-\mathrm{m}}$ are the transference number of cations and anions through the membrane, respectively. The symbol $K_{\tau\mathrm{m}}$ denotes the difference in transference number or drift velocity caused by the semimembrane effect [see Eq. (23)],

$$K_{\tau\mathrm{m}} = (\tau_{+\mathrm{m}} - \tau_{-\mathrm{m}}) = \frac{\nu_{+\mathrm{m}} - \nu_{-\mathrm{m}}}{\nu_{+\mathrm{m}} + \nu_{-\mathrm{m}}} \tag{23}$$

The differential form of the membrane potential can be written as Eq. (24)

$$\begin{aligned}\frac{\partial\phi_\mathrm{m}}{\partial x} &= -\frac{RT}{F}K_{\tau\mathrm{m}}\left(\frac{\partial \ln c}{\partial x} + \frac{\partial \ln\gamma}{\partial x}\right)\\ &= -\frac{RT}{F}\frac{K_{\tau\mathrm{m}}}{c}\left(1 + \frac{\partial\ln\gamma}{\partial\ln c}\right)\frac{\partial c}{\partial x}\end{aligned} \tag{24}$$

Owing to this extra counter-electrical field, the chloride diffusion in concrete becomes [see Eq. (25)]

$$\begin{aligned}J_\mathrm{concrete} &= \varepsilon \cdot J_- = -\varepsilon\mathscr{D}(1 - z_-K_\tau)\\ &\quad\cdot\left(1 + \frac{\partial\ln\gamma}{\partial\ln c}\right)\frac{\partial c}{\partial x} = -D_\mathrm{ssd}\frac{\partial c}{\partial x}\end{aligned} \tag{25}$$

where K_τ is the total effect of counter-electrical potential, as shown in Eq. (26).

$$K_\tau = K_{\tau 0} + K_{\tau\mathrm{m}} = \frac{\nu_+ - \nu_-}{\nu_+ + \nu_-} \tag{26}$$

In the above equation v_+ and v_- represent the net drift velocity of cation diffusates and anion diffusates through the concrete specimen, respectively.

Similar to Eq. (16), the relationship between the effective chloride diffusion coefficient of concrete D_ssd and the chloride diffusion coefficient in the infinite dilute solution D_{-0} is shown in Eq. (27).

$$\begin{aligned}\frac{D_\mathrm{ssd}}{D_{-0}} &= \varepsilon(1 - z_-K_{\tau 0} - z_-K_{\tau\mathrm{m}})\left(1 + \frac{\partial\ln\gamma}{\partial\ln c}\right)\\ &\quad\cdot\frac{2c + c_0}{f(1-\beta_\mathrm{v})c + c_0}\end{aligned} \tag{27}$$

Compared with an external electrical field, however, this membrane potential is also negligible. Therefore, it does not affect the migration function. According to Eq. (19) and Eq. (21), the relationship between the effective migration coefficient D_ssm and D_{-0} is as shown in Eq. (28).

$$\frac{D_\mathrm{ssm}}{D_{-0}} = \varepsilon\frac{2c + c_0}{f(1-\beta_\mathrm{v})c + c_0} = \varepsilon\frac{2c + c_0}{f(1+|\beta_\mathrm{v}|)c + c_0} \tag{28}$$

Thus the relationship between D_ssd and D_ssm is that shown in Eq. (29).

$$\begin{aligned}\frac{D_\mathrm{ssd}}{D_\mathrm{ssm}} &= (1 - z_-K_{\tau 0} - z_-K_{\tau\mathrm{m}})\left(1 + \frac{\partial\ln\gamma}{\partial\ln c}\right)\\ &\quad\cdot\frac{f(1+|\beta_\mathrm{v}|)c + c_0}{f(1-|\beta_\mathrm{v}|)c + c_0}\end{aligned} \tag{29}$$

According to the definition of β_v and Eq. (26) [see Eq. (30)]

$$\beta_\mathrm{v} = \frac{\nu_+}{\nu_-} = \frac{1 + K_\tau}{1 - K_\tau} = \frac{1 + K_{\tau 0} + K_{\tau\mathrm{m}}}{1 - K_{\tau 0} - K_{\tau\mathrm{m}}} \tag{30}$$

In this case, the parameters $K_{\tau\mathrm{m}}$ and f reflect the characteristics of the pore solution in concrete, while the parameters c, $K_{\tau 0}$, and γ reflect the characteristics of the external source solution, especially under the steady state.

4.3. Nonsteady-state process

It is well known that when chloride ions diffuse or migrate into concrete under a nonsteady state, some of the chlorides will be bound on the pore surfaces or react with the hydrates. Therefore, it is the increment of total chlorides that results in a difference in the flux [21], that is [see Eq. (31)]

$$\frac{\partial C_\mathrm{t}}{\partial t} = \varepsilon\frac{\partial c}{\partial t} + \frac{\partial C_\mathrm{b}}{\partial t} = \frac{\partial c}{\partial t}\left(\varepsilon + \frac{\partial C_\mathrm{b}}{\partial c}\right) = -\frac{\partial J_\mathrm{concrete}}{\partial x} \tag{31}$$

where C_t and C_b are the total and bound chlorides, respectively, with the dimension $\mathrm{kg_{Cl}/m^3_{concrete}}$, while the free chlorides c has the dimension $\mathrm{kg_{Cl}/m^3_{solution}}$.

Differentiating Eq. (2) and Eq. (3), respectively, yields Eq. (32)

$$-\frac{\partial J_\mathrm{concrete}}{\partial x} = \frac{\partial}{\partial x}\left(D_\mathrm{ssd}\frac{\partial c}{\partial x}\right) = \frac{\partial D_\mathrm{ssd}}{\partial c}\left(\frac{\partial c}{\partial x}\right)^2 + D_\mathrm{ssd}\frac{\partial^2 c}{\partial x^2} \tag{32}$$

for a diffusion process, and Eq. (33)

$$\begin{aligned}-\frac{\partial J_\mathrm{concrete}}{\partial x} &= \frac{\partial}{\partial x}\left(D_\mathrm{ssm}\frac{\partial c}{\partial x} + D_\mathrm{ssm}\frac{zF}{RT}\frac{\partial\phi}{\partial x}c\right)\\ &= \frac{\partial D_\mathrm{ssm}}{\partial c}\left(\frac{\partial c}{\partial x}\right)^2 + D_\mathrm{ssm}\frac{\partial^2 c}{\partial x^2}\\ &\quad + \frac{zF}{RT}\left(c\frac{\partial\phi}{\partial x}\frac{\partial D_\mathrm{ssm}}{\partial c}\frac{\partial c}{\partial x} + D_\mathrm{ssm}c\frac{\partial^2\phi}{\partial x^2} + D_\mathrm{ssm}\frac{\partial\phi}{\partial x}\frac{\partial c}{\partial x}\right)\end{aligned} \tag{33}$$

for a migration process. According to Tang and Nilsson [6], an inflection point exists in the nonsteady-state migration process where $\partial c/\partial x$ as one of the driving forces at its maximum and $\partial^2 c/\partial x^2 = 0$. Thus, under the assumption that the potential gradient $\partial\phi/\partial x$ is constant, Eq. (33) can be reduced to Eq. (34)

$$-\frac{\partial J_\mathrm{concrete}}{\partial x} = \left[\left(\frac{\partial c}{\partial x} + ac\right)\frac{\partial D_\mathrm{ssm}}{\partial c} + aD_\mathrm{ssm}\right]\frac{\partial c}{\partial x} \tag{34}$$

where $a = zF/RT \times \partial\phi/\partial x$ is a constant. Combining Eq. (31) with Eq. (32) and with Eq. (34), respectively, one can obtain Eq. (35)

$$\frac{\partial c}{\partial t}\left(\varepsilon + \frac{\partial C_\mathrm{b}}{\partial c}\right) = \frac{\partial D_\mathrm{ssd}}{\partial c}\left(\frac{\partial c}{\partial x}\right)^2 + D_\mathrm{ssd}\frac{\partial^2 c}{\partial x^2} \tag{35}$$

and Eq. (36).

$$\frac{\partial c}{\partial t}\left(\varepsilon + \frac{\partial C_b}{\partial c}\right) = \left[\left(\frac{\partial c}{\partial x} + ac\right)\frac{\partial D_{ssm}}{\partial c} + aD_{ssm}\right]\frac{\partial c}{\partial x} \tag{36}$$

In the literature, the following equations are often used for nonsteady-state diffusion [22, see Eq. (37)] and migration [6, see Eq. (38)]

$$\frac{\partial c}{\partial t} = D_{nssd}\frac{\partial^2 c}{\partial x^2} \tag{37}$$

$$\frac{\partial c}{\partial t} = D_{nssm}\left(\frac{\partial^2 c}{\partial x^2} + a\frac{\partial c}{\partial x}\right) \approx aD_{nssm}\frac{\partial c}{\partial x} \tag{38}$$

where D_{nssd} and D_{nssm} are the "apparent" diffusion coefficients determined from conventional nonsteady-state diffusion and migration tests, respectively. Comparing Eq. (35) with Eq. (37), one can find that the relationship between D_{nssd} and D_{ssd} is complicated, unless the term $(\partial c/\partial x)^2$ or $\partial D_{ssd}/\partial c$ is negligible. In this case [see Eq. (39)],

$$D_{nssd} = \frac{D_{ssd}}{\varepsilon + \frac{\partial C_b}{\partial c}} = \frac{D_{ssd}}{\varepsilon\left(1 + \frac{\partial c_b}{\partial c}\right)} = \frac{D_{ssd}}{\varepsilon + (1-\varepsilon)\frac{\partial S_b}{\partial c}} \tag{39}$$

where c_b and S_b are the bound chlorides with the dimension $\mathrm{kg_{Cl}/m^3_{solution}}$ and $\mathrm{kg_{Cl}/m^3_{solid}}$, respectively. However, the assumption of negligible $(\partial c/\partial x)^2$ or $\partial D_{ssd}/\partial c$ seems very week, because $\partial c/\partial x$ is the only driving force in a diffusion process and D_{ssd} is a function of c as shown in Eq. (27). The relationship between D_{nssd} and D_{ssd} in Eq. (39) has previously been reported by Atkinson and Nickerson [23] as well as by Nilsson [21], although the above assumption was not mentioned in their papers.

On the other hand, it is possible to obtain the relationship between D_{nssm} and D_{ssm} by comparing Eq. (36) with Eq. (38), although it looks complicated [see Eq. (40)]:

$$D_{nssm} = \frac{D_{ssm} + \left(\frac{1}{a}\frac{\partial c}{\partial x} + c\right)\frac{\partial D_{ssm}}{\partial c}}{\varepsilon + \frac{\partial C_b}{\partial c}} = \frac{D_{ssm} + \left(\frac{1}{a}\frac{\partial c}{\partial x} + c\right)\frac{aD_{ssm}}{\partial c}}{\varepsilon\left(1 + \frac{\partial c_b}{\partial c}\right)} \tag{40}$$

However, more experimental data are needed to verify the above relationship.

In reality, chloride penetration into concrete is a nonsteady-state process. For the concrete structures submerged in seawater, it could be described by Eq. (35), which involves three important parameters: porosity, chloride-binding capacity, and effective diffusion coefficient D_{ssd}. The latter is expressed by Eq. (27).

A few years ago, Garboczi [24] proposed an equation to describe D_{ssd} [see Eq. (41)]:

$$D_{ssd} = \varepsilon\xi D_{-0} \tag{41}$$

where the parameter ξ lumps all the interesting features of the pore structure, including "tortuosity" and connectivity of the pore network, according to Garboczi [24]. Comparing Eq. (41) with Eq. (27), one finds that [see Eq. (42)]

$$\xi = (1 - z_- K_{\tau 0} - z_- K_{\tau m}) \cdot 1 + \left(\frac{\partial \ln\gamma}{\partial \ln c}\right) \cdot \frac{2c + c_0}{f(1-\beta_v)c + c_0} \tag{42}$$

It is obvious that ξ involves not only the features of the pore structure ($K_{\tau m}$ and f), but also the features of the external source solution (c, $K_{\tau 0}$, and γ). Here the "features of pore structure" mean both physical and chemical characteristics of the pore structure, such as tortuosity, semipermeability, pore solution chemistry, etc.

5. Concluding remarks

It can be seen from the above theoretical analysis that the "effective" chloride diffusion coefficient determined from the conventional diffusion or migration tests is not a constant, but rather is a complicated function of concentration. This function contains four main factors: (1) the parameter K_τ, describing the effect of counter-electrical potential; (2) the ratio of cation velocity to anion velocity β_v; (3) the friction coefficient f, which reflects the ionic interaction; and (4) the activity coefficient γ, which is also a function of concentration.

When chloride ions diffuse into concrete, an extra counter-electrical field, caused by the ion-selective semimembrane effect, will be introduced. Therefore, the counter-electrical field in a solution-concrete system consists of two parts: one from the external source solution, $K_{\tau 0}$, and another from the concrete, $K_{\tau m}$.

According to the theoretical analysis, the following relationships between different diffusion coefficients could be found:

- the relationship between steady-state diffusion and migration tests [Eq. (29)],
- the relationship between steady-state diffusion and nonsteady-state diffusion tests Eq. (39)],
- the relationship between steady-state migration and nonsteady-state migration tests [Eq. (40)], and
- the relationship between "effective" diffusion or migration coefficient and the diffusion coefficient at an infinite diluted solution Eq. (27) and Eq. (28)].

The quantitative influences of various parameters on chloride diffusion coefficient and some experimental evidences will be given in Part 2 of work.

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