

Calculation of ion diffusion coefficient related to concrete deterioration based on Debye-Hückel-Onsager theory

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Abstract: This paper applies the Debye-Hückel-Onsager electrolyte solution theory to investigate the diffusivity of ions in concrete pore solutions. First, a model of the diffusion coefficient associated with the ionic species, solution concentration and ambient temperature is proposed in the saturated concrete. Secondly, as an example, the effects of sodium chloride solution concentration, which are associated with influencing factors such as the ionic cloud radius, electrophoresis and relaxation, on the chloride diffusion coefficient are analyzed. It is found that the diffusion coefficient decreases with the increase in solution concentration, and the electrophoresis and ionic cloud radius are two important factors influencing the ionic diffusivity. Finally, the experiments, in which the chloride diffusion coefficients in specimens under different water-cement ratios are measured by the rapid chloride migration (RCM) method, are carried out to validate the effectiveness of the proposed model, and the results indicate that there is a generally reasonable agreement between the experimental and the proposed model results.

Key words: ion; diffusion coefficient; Debye-Hückel-Onsager theory; rapid chloride migration (RCM) method; concrete

The long-term performance and durability of concrete structures are strongly influenced by chemical corrosion due to ion aggression on concrete materials under permanently aqueous or chemically aggressive environments^[1-2]. For example, when concrete is subjected to external sulfate attack, the chemical reactions between sulfate ions and aluminates in concrete result in the expansion and cracking of concrete, and cause the deterioration of the material strength^[3]. Under permanent chloride environments, the capacity of concrete members such as beam, column and plate suffers a gradual loss resulting from a combination of steel corrosion and concrete cracking^[4]. Exposed to long-term humid or aqueous environmental conditions, concrete materials undergo the calcium-leaching phenomenon caused by calcium ion transport in the pore space, which results in the increase of porosity and the reduction of concrete stiffness

and strength^[5]. In the above process of concrete deterioration, the chemically induced deteriorations are generally associated with the diffusivity of the ions such as sulfate, chloride and calcium ions in concrete. The ion diffusion coefficient in concrete is a significant parameter evaluating the service life of concrete structures^[6].

The electrolyte solution theory offers a promising way to study the ionic diffusivity in concrete, and it can be used to establish a model to theoretically obtain the ionic diffusion coefficient^[7]. Based on the Debye-Hückel-Onsager electrolyte solution theory, this paper investigates the ionic diffusivity in electrolyte solutions similar to concrete pore solutions, and proposes a model of the concentration dependent diffusion coefficient in concrete to evaluate the concrete structure lifetime.

1 Model

1.1 Basic assumption

When concrete structures are permanently exposed to humid or aqueous environments, the ion transportation in concrete is related not only to the ionic species and concentrations in concrete pore solutions but also to the concrete microstructures such as the porosity, distribution, connectivity and tortuosity of the pores, and the properties of interface transition zones (ITZ). Two assumptions for modeling the ion diffusion coefficient are considered due to the complexity and randomness of the concrete microstructures. The first one is that concrete is in a saturated state and its pore solution is regarded as an electrolyte solution. The second one is that concrete is an isotropic and homogeneous porous material, and the porosity is the main microstructure parameter that influences the ionic diffusivity.

1.2 Ion activity and conductivity in pore solution

According to the above assumptions, the ionic diffusivity in aqueous solutions is associated not only with the ionic molar activity but also with the ionic conductivity. If there exists an electrolyte E such as chlorate or sulfate in a concrete pore solution, the ions including chloride or sulfate ions are produced by chemical reactions. One mole of an electrolyte E is dissociated into ν^+ mole cations E^+ and ν^- mole anions E^- (Cl^- or SO_4^{2-}).

$$E \rightleftharpoons \nu_+ E_+^{z_+} + \nu_- E_-^{z_-}, \quad \nu_+ z_+ - \nu_- z_- = 0 \quad (1)$$

where E , $E_+^{z_+}$, and $E_-^{z_-}$ are the electrolyte and the corresponding dissociated cations and anions, respectively; z_+ and z_- are the valencies of cations and anions, respectively; ν_+ and ν_- are the stoichiometric coefficients.

Depending on the ionic cloud model of the Debye-Hückel

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theory, for the concentration c of the electrolyte E in the solution, the approximation of the average molar activity coefficient of ions f_{\pm} is

$$\ln f_{\pm} = - \frac{|z_+ z_-| e^2}{8\pi\epsilon_0\epsilon_r kT} \frac{\kappa}{1 + \kappa a} \quad (2)$$

where f_{\pm} is the average activity coefficient of ions; e is the elementary charge, $e = 1.602 \times 10^{-19}$ C; ϵ_0 is the vacuum electric permittivity, $\epsilon_0 = 8.854 \times 10^{-12}$ C²/(J · m); ϵ_r is the water relative permittivity, $\epsilon_r = 78.54$; k is the Boltzmann constant, $k = 1.380 \times 10^{-23}$ J/K; T is the temperature; a is the ionic radius; κ represents the reciprocal of the ionic cloud radius, and it is given by

$$\kappa = \sqrt{\frac{F^2}{\epsilon_0\epsilon_r RT} (v_+ z_+^2 + v_- z_-^2) c} \quad (3)$$

where F is the Faraday constant, $F = 9.648 \times 10^4$ C/mol; R is the universal gas constant, $R = 8.314$ J/(K · mol); c is the solution concentration.

According to the Onsager theory of conductivity, and taking the electroporetic and relaxation effects on the molar conductivity of ions in the solution into account, the molar conductivity Λ_m of the electrolyte E solution associated with the concentration c is^[8]

$$\Lambda_m = \Lambda_m^0 - (A' + B'\Lambda_m^0) \sqrt{(v_+ z_+^2 + v_- z_-^2) c} + C'(v_+ z_+^2 + v_- z_-^2) c \quad (4)$$

where Λ_m , Λ_m^0 are the molar conductivity of the electrolyte E solution with the concentration c and an infinitely diluted solution, respectively; A' , B' and C' are the parameters related to the temperature.

$$A' = \frac{(|z_+| + |z_-|) peF^2}{6\pi\eta_0(1 + \kappa a)}, \quad B' = \frac{(|z_+ z_-|) p q e F^2}{12\pi\epsilon_0\epsilon_r RT(1 + \sqrt{q})}$$

$$C' = \frac{\sqrt{2} z^2 peF^2}{3\pi\eta_0}$$

where η_0 is the water viscosity, $\eta_0 = 8.91 \times 10^{-4}$ kg/ms.

$$p = \sqrt{\frac{1}{\epsilon_0\epsilon_r RT}}, \quad q = \frac{|z_+ z_-|}{|z_+| + |z_-|} \frac{\lambda_+^0 + \lambda_-^0}{|z_+| \lambda_+^0 + |z_-| \lambda_-^0} \quad (5)$$

where λ_+^0 and λ_-^0 are the limiting equivalent conductivity of cation and anion.

Generally, concrete structures are subjected to an environment with a low ion concentration, so the ionic concentration penetrating into the concrete is diluted. For the diluted electrolyte solution, there is $1 + \kappa a \approx 1$ in Eq. (2), so Eq. (4) can be simplified as

$$\Lambda_m = \Lambda_m^0 - (A'' + B''\Lambda_m^0) \sqrt{c} + C''c \quad (6)$$

where

$$A'' = \frac{(|z_+| + |z_-|) peF^2 \sqrt{v_+ z_+^2 + v_- z_-^2}}{6\pi\eta_0}$$

$$B'' = \frac{|z_+ z_-| p q e F^2 \sqrt{v_+ z_+^2 + v_- z_-^2}}{12\pi\epsilon_0\epsilon_r RT(1 + \sqrt{q})}$$

$$C'' = \frac{(|z_+| + |z_-|) |z_+ z_-| p^2 q e^2 F^4 (v_+ z_+^2 + v_- z_-^2)}{72\pi^2 \eta_0 \epsilon_0 \epsilon_r RT(1 + \sqrt{q})}$$

Eqs. (4) and (6) are used to calculate the molar conductivity of the electrolyte E dissolving into cations and anions in the pore water. Considering damage analysis and lifetime evaluation of the concrete structure subjected to the attack of ions such as chloride and sulfate ions, the diffusivity of single ion in concrete is paid more attention. In order to obtain the diffusion coefficient of an ion in concrete, its molar conductivity in Eqs. (4) and (6) can be simplified as

$$\Lambda_m = \Lambda_m^0 - (A''' + B'''\Lambda_m^0) \sqrt{c} + C'''c \quad (7)$$

where A''' , B''' and C''' are the parameters related to the temperatures,

$$A''' = \frac{\sqrt{2} z^2 peF^2}{3\pi\eta_0}, \quad B''' = \frac{(\sqrt{2} - 1) z^3 peF^2}{12\pi\epsilon_0\epsilon_r RT}, \quad C''' = \frac{(2 - \sqrt{2}) z^5 p^2 e^2 F^4}{36\pi^2 \eta_0 \epsilon_0 \epsilon_r RT}$$

In Eqs. (4), (6) and (7), $A^{(','',''')}\sqrt{c}$, $B^{(','',''')}\Lambda_m^0\sqrt{c}$ and $C^{(','',''')}c$ represent the effects of electroporetics, relaxation and the interactions between them on ion molar conductivity.

1.3 Ionic diffusion coefficient in pore solution

Depending on basic assumptions, the ion penetrates concrete through the pore solution which can be regarded as an electrolyte solution. Considering the effects of the molar activity coefficient f_{\pm} , the ionic diffusion coefficient D_s in the electrolyte E solution with a concentration c is^[9]

$$D_s = \frac{RT}{|z_+ z_-| F^2} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c} \right) \Lambda_m \quad (8)$$

where D_s is the ionic diffusion coefficient in the electrolyte E solution with a concentration c .

It can be deduced from Eqs. (2) and (3) that

$$\frac{\partial \ln f_{\pm}}{\partial \ln c} = - \frac{|z_+ z_-| e^2}{16\pi\epsilon_0\epsilon_r kT} \frac{\kappa}{(1 + \kappa a)^2} \quad (9)$$

Substituting Eq. (9) into Eq. (8), the ion diffusion coefficient D_s can be written as

$$D_s = \frac{RT}{|z_+ z_-| F^2} \left(1 - \frac{|z_+ z_-| e^2}{16\pi\epsilon_0\epsilon_r kT} \frac{\kappa}{(1 + \kappa a)^2} \right) \Lambda_m \quad (10)$$

For the ion solution with the valence z and concentration c , its diffusion coefficient D_s is

$$D_s = \frac{RT}{z^2 F^2} \left(1 - \frac{z^2 e^2}{16\pi\epsilon_0\epsilon_r kT} \frac{\kappa}{(1 + \kappa a)^2} \right) \Lambda_m \quad (11)$$

In Eq. (11), the reciprocal of the ionic cloud radius κ is

$$\kappa = zF \sqrt{\frac{2c}{\epsilon_0\epsilon_r RT}} \quad (12)$$

where c is the molar activity or concentration of the erosive

ion.

1.4 Ion diffusion coefficient in concrete

The ion diffusion coefficient in concrete is mainly associated with its porosity according to the assumption. The relationship between the ionic diffusion coefficient D in concrete and the porosity φ is^[10]

$$D = D_s \eta(\varphi) \quad (13)$$

where D is the ionic diffusion coefficient in saturated concrete; D_s is the ionic diffusion coefficient in the electrolyte solution corresponding to the pore solution of the concrete, which can be calculated by Eq. (11); $\eta(\varphi)$, as a correction coefficient reflecting the effect of porosity, and it can be expressed as^[11]

$$\eta(\varphi) = 0.001 + 0.07\varphi^2 + H(\varphi - 0.18)0.18(\varphi - 0.18)^2$$

where H is the Heaviside function, and φ is the porosity that can be determined by^[12]

$$\varphi = \max\left(f_c \frac{w/c - 0.39h_\alpha}{w/c + 0.32}, 0\right)$$

where f_c and w/c are the cement volume fraction and the water-cement ratio in the concrete, and h_α is the hydration degree of the cement that can be determined by^[13]

$$h_\alpha = 1 - 0.5[(1 + 1.67t)^{-0.6} + (1 + 0.29t)^{-0.48}]$$

where t is the hydration time.

2 Analysis of Ion Diffusion Coefficient in Pore Solution

As an example, the effects of the solution concentration on the chloride diffusion coefficient in sodium chloride solutions is analyzed. The main parameters of chloride ion Cl^- and sodium ion Na^+ are given^[7]: the valences $z = z^- = z^+ = 1$, the limiting equivalent conductivity $\lambda_-^0 = 7.635 \times 10^{-3} \text{ Sm}^2/\text{mol}$ and $\lambda_+^0 = 5.010 \times 10^{-3} \text{ Sm}^2/\text{mol}$; the radius $a_- = 1.81 \times 10^{-10} \text{ m}$ and $a_+ = 0.95 \times 10^{-10} \text{ m}$; the temperature $T = 298 \text{ K}$, and the other parameters related to the analysis are the same as above.

Fig. 1 presents the effects of the chloride ion concentration in pore solutions with sodium chloride on its diffusion coefficient at $T = 298 \text{ K}$. It can be seen from Fig. 1 that the chloride diffusion coefficient is $2.03 \times 10^{-9} \text{ m}^2/\text{s}$ in the infinitely diluted solution and it decreases gradually with the increase in the solution concentration. When the chloride concentration increases from the infinitely diluted solution to $150 \text{ mol}/\text{m}^3$, the diffusion coefficients decrease from 2.03×10^{-9} to 1.18×10^{-9} and $1.09 \times 10^{-9} \text{ m}^2/\text{s}$ according to the electrolyte solution in Eq. (4) and the single ion solution in Eq. (7), respectively, and the decrease ratios are 41.87% and 46.3%. When the solution concentration is comparatively high, the diffusion coefficient decreases slowly. For example, when the solution concentration increases from 350 to $500 \text{ mol}/\text{m}^3$, according to Eqs. (4) and (5), the chloride diffusion coefficient decreases from 9.30×10^{-10} , 7.56×10^{-10} to 8.19×10^{-10} , $5.95 \times 10^{-10} \text{ m}^2/\text{s}$, respectively, and the corresponding decrease ratios are 11.94% and 21.30%, respectively, which are obviously

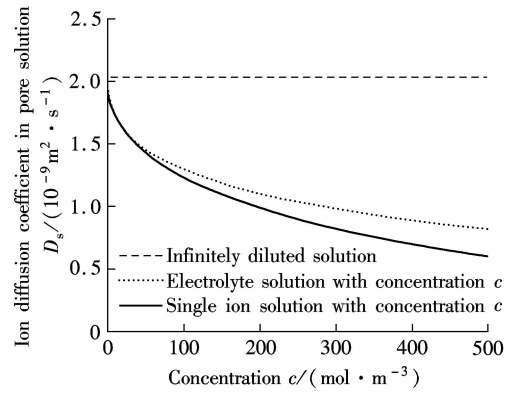


Fig. 1 Effects of concentration on chloride diffusion coefficient

less than the decrease ratio of the preceding $150 \text{ mol}/\text{m}^3$.

The influences of the concentration of the sodium chloride solution on the diffusion coefficient are mainly related to the ionic cloud radius, the electrophoretic effect, the relaxation effect and the interaction between electrophoresis and relaxation. Fig. 2 presents the change in the chloride diffusion coefficient with the sodium chloride solution concentration. It can be obtained from the figure that the diffusion coefficient decreases with the increase in the solution concentration; and compared with the infinitely diluted solution, the electrophoresis, relaxation and their interaction have more obvious influences on the chloride diffusion coefficient. This is because the increase of the solution concentration can strengthen the electrophoresis, relaxation and their interactions and decrease the ionic molar conductivity. In addition, the higher concentration causes a larger ionic cloud radius. Both decreasing the conductivity and increasing the ionic cloud radius result in the decrease of the ionic diffusion coefficient, but the conductivity has more obvious effects on the diffusion coefficient than the ionic cloud radius. For example, when the concentration is $500 \text{ mol}/\text{m}^3$, the ion diffusion coefficient decreases from $2.03 \times 10^{-9} \text{ m}^2/\text{s}$ in an infinitely diluted solution to $5.95 \times 10^{-10} \text{ m}^2/\text{s}$ in the coefficient and $1.61 \times 10^{-9} \text{ m}^2/\text{s}$ in only considering the ionic cloud radius, respectively, and the corresponding decreasing ratios are 70.69% and 20.68%, respectively.

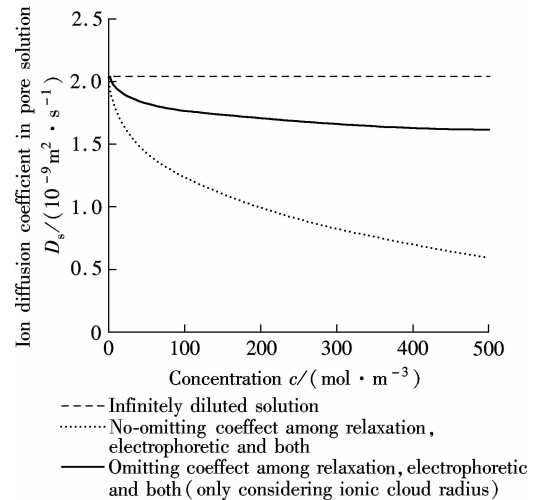


Fig. 2 Effect of ion cloud radius, electrophoresis, and relaxation on chloride diffusion coefficient

3 Experimental Validation

3.1 Materials and specimen

In this experiment, the cement is prepared by commercial P II 42.5 type “Jinningyang” produced by China Jiangnan Corporation, whose compositions are given in Tab. 1. The fine aggregate is a kind of river sand with a maximum particle size of 2 mm and an apparent density of 2.64 g/cm^3 , and the coarse aggregate is crushed wacke stone with a maximum diameter of 10 mm and a cumulate density of 1.6 g/cm^3 . The mix weight proportions of concrete are shown in Tab. 2 and the initial concentrations of the main ions in the concrete pore solution are listed in Tab. 3.

The cylinder specimens with 100 mm in diameter and 300 mm in length ($\phi 100 \times 300 \text{ mm}$) were cast according to the concrete mix proportions in Tab. 3, and cured in 20°C water. After 20 d, a (50 ± 2) -mm-thick slice ($\phi 100 \times (50 \pm 2) \text{ mm}$) was taken from the cylinder specimen center. The slices were polished until smooth, cleaned and continued the curing process until the prescribed test period.

Tab. 1 Chemical composition content of raw materials %

$w(\text{SiO}_2)$	$w(\text{Al}_2\text{O}_3)$	$w(\text{CaO})$	$w(\text{MgO})$	$w(\text{SO}_3)$	$w(\text{Fe}_2\text{O}_3)$
20.60	5.03	65.06	0.55	2.24	4.38

Tab. 2 Concrete mix weight proportions of concrete

w/c	Cement	Water	Sand	Stone
0.35	1	0.35	0.743	1.816
0.45	1	0.45	1.107	2.465
0.55	1	0.55	1.561	3.028
0.65	1	0.65	2.073	3.529

Tab. 3 Initial concentrations of ions in pore solution mol/m^3

w/c	Na^+	K^+	Ca^{2+}	SO_4^{2-}	OH^-	Cl^-
0.35	128.4	121.3	1.9	2.0	251.3	0
0.45	107.1	116.5	2.3	1.9	224.5	0
0.55	89.2	113.5	2.6	1.4	201.8	0
0.65	71.4	108.9	2.7	1.2	183.4	0

3.2 Experimental methods and results

The RCM method was adopted for measuring the chloride diffusivity in the concrete^[14], and the experimental configuration and setup are illustrated in Fig. 3. The slice ($\phi 100 \times 50 \text{ mm}$) was enclosed by the rubber sleeve as shown in Fig. 3, and then it was placed on the plastic support in the catholyte reservoir filled with 12 L of 10 % NaCl solution, and the anode was put into the rubber sleeve filled with 300 mL of 0.3 mol NaOH solution. The cathode and anode were respectively connected to the negative and positive pole of the power supply with a potential of $(30 \pm 0.2) \text{ V}$ during the tests. After the tests, the slices were split axially into two pieces, and a 0.1 mol silver nitrate solution was sprayed on one of the freshly split sections. The chloride penetration depth was measured by the colorimetric method. Therefore, the chloride diffusion coefficients can be calculated from the measured depth. According to the experimental method, the measured non-steady-state migration diffusion coefficients of all the specimens at the temperature 298 K are given in Tab. 4.

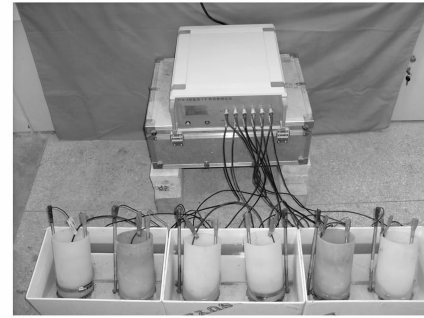
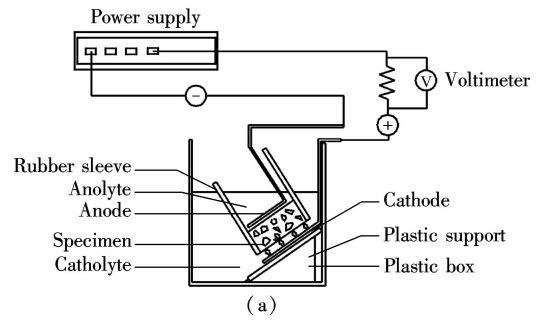


Fig. 3 Experimental setup. (a) Schematic; (b) Test setup

Tab. 4 Experimental results of chloride diffusion coefficient $10^{-12} \text{ m}^2/\text{s}$

Specimens	w/c	Experiment	Average
C11, C12, C13	0.35	2.904, 2.840, 3.110	2.951
C21, C22, C23	0.45	4.016, 4.186, 3.905	4.036
C31, C32, C33	0.55	4.150, 4.489, 5.203	4.614
C41, C42, C43	0.65	4.879, 4.983, 5.219	5.027

3.3 Comparison

Using Eq. (13), the chloride diffusion coefficient in concrete can be calculated to be 3.278×10^{-12} , 4.125×10^{-12} , 4.754×10^{-12} , $5.201 \times 10^{-12} \text{ m}^2/\text{s}$ corresponding to the water-cement ratios 0.35, 0.45, 0.55 and 0.65, respectively. The comparisons between the calculation and the experimental results are shown in Fig. 4. In order to evaluate the model of the ion diffusion coefficient in Eq. (13), the deflection ratios between the calculation values and the experimental results of the chloride diffusion coefficient are calculated by the formula $\delta_D = |D_{\text{exp}} - D_{\text{mod}}|/D_{\text{exp}}$, in which δ_D , D_{exp} and D_{mod} denote the deflection ratios, the experimental and calculation values of the chloride diffusion coefficients in

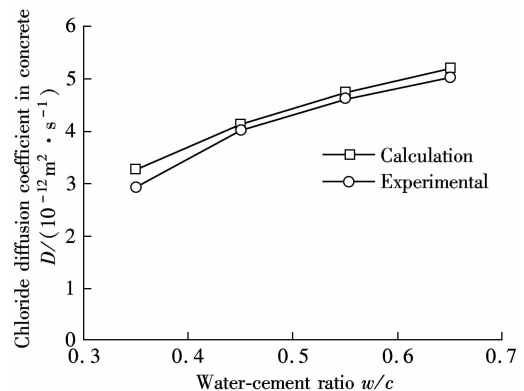


Fig. 4 Comparisons of calculation and experimental results

the concrete, respectively. The deflection ratios δ_D are 11.1%, 2.2%, 3.1% and 3.52% corresponding to the water-cement ratios 0.35, 0.45, 0.55 and 0.65, respectively. It can be obtained from Fig. 4 and the deflection ratios that, the calculation results of the chloride diffusion coefficient obtained by Eq. (13) are in agreement with the experimental results in the concrete.

4 Conclusions

1) Based on the Debye-Hückel-Onsager theory, a comprehensive model for predicting the ion diffusion coefficient in the saturated concrete is proposed, in which the main parameters such as ion species, pore solution concentration and temperature are considered.

2) Based on the supposed model of ion diffusion coefficients, as an example, the effects of the chloride concentration in sodium chloride solutions, which are related to the influencing factors such as the ionic cloud radius, electrophoresis, relaxation and interaction between electrophoresis and relaxation, on the diffusion coefficient are analyzed. The results show that the chloride diffusion coefficient decreases with the increase in the concentration, and the main influencing factors related to the solution concentration are the electrophoresis and the ionic cloud radius.

3) Using the RCM method, the chloride diffusion coefficients in concrete specimens with different water-cement ratios are measured. The chloride diffusion coefficients obtained by the proposed model based on the Debye-Hückel-Onsager theory are in agreement with the measured results by the RCM method.

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基于 Debye-Hückel-Onsager 理论的混凝土中离子扩散系数的计算

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摘要: 将 Debye-Hückel 理论和 Onsager 电导理论用于研究混凝土孔溶液中离子的扩散规律. 首先, 建立了饱和混凝土中离子扩散系数的计算模型, 该模型考虑了离子的种类、孔溶液中离子的浓度、环境温度等因素对离子扩散系数的影响. 其次, 以孔溶液中氯化钠的浓度变化为例分析了离子氛半径、松弛效应、电泳效应等对孔溶液中氯离子扩散系数的影响规律, 发现氯离子的扩散系数随氯化钠溶液浓度的增加而减小, 离子氛半径和电泳效应是影响氯离子扩散性能的重要参数. 最后, 通过 RCM 法测定了不同水灰比混凝土的氯离子扩散系数, 并将模型的计算结果与实测结果进行了对比, 以验证模型的合理性, 结果表明所建立的模型与实测结果较为符合.

关键词: 离子; 扩散系数; Debye-Hückel-Onsager 理论; RCM 法; 混凝土

中图分类号: TU528