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Modeling of ion diffusion coefficient in saturated concrete

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Abstract. This paper utilizes the modified Davis model and the mode coupling theory, as parts of the electrolyte solution theory, to investigate the diffusivity of the ion in concrete. Firstly, a computational model of the ion diffusion coefficient, which is associated with ion species, pore solution concentration, concrete mix parameters including water-cement ratio and cement volume fraction, and microstructure parameters such as the porosity and tortuosity, is proposed in the saturated concrete. Secondly, the experiments, on which the chloride diffusion coefficient is measured by the rapid chloride penetration test, have been carried out to investigate the validity of the proposed model. The results indicate that the chloride diffusion coefficient obtained by the proposed model is in agreement with the experimental result. Finally, numerical simulation has been completed to investigate the effects of the porosity, tortuosity, water-cement ratio, cement volume fraction and ion concentration in the pore solution on the ion diffusion coefficients. The results show that the ion diffusion coefficient in concrete increases with the porosity, water-cement ratio and cement volume fraction, while we see a decrease with the increasing of tortuosity. Meanwhile, the ion concentration produces more obvious effects on the diffusivity itself, but has almost no effects on the other ions.

Keywords: diffusion coefficient; concrete; ion; model; electrolyte solution theory.

1. Introduction

The long-term performance and durability of concrete structures is strongly influenced by chemical corrosion due to ion aggression on concrete materials under permanently aqueous or chemically aggressive environments (Marchand *et al.* 2002, Coussy *et al.* 2001, Bertron *et al.* 2005). For example, when concrete is subjected to the environmental sulfate attack, the chemical reactions between sulfate ion and aluminates in concrete result in the expansion and crack of concrete, and cause the deterioration of the material strength (Park *et al.* 1999, Lee *et al.* 2005). Under permanently chloride aggressive environments, the capacity of the concrete members such as the beam, column and plate suffer a gradual loss resulting from a combination of steel corrosion and concrete cracking (Bastidas *et al.* 2008, Ababneh *et al.* 2003). Exposed to the long-term humid or aqueous environmental conditions, the concrete materials undergo the calcium-leaching phenomenon caused by the calcium ion transport in the pore space, which results in the increasing of the porosity and the reduction of the stiffness and strength of concrete (Carde *et al.* 1997, Ulm *et al.* 2003). In

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the above process of the concrete deterioration, the chemically induced deteriorations are generally associated with the diffusivity of the ions such as sulfate, chloride and calcium ion in concrete. The ion diffusion coefficient in concrete is a significant parameter evaluating the service life of concrete structures (Clifton *et al*. 1989).

At present, the ion diffusion coefficient in concrete can be acquired by two approaches. One is the experimental methods including the rapid test or the chemical titration. For example, the rapid test methods such as ASTM C1202 (ASTM 1994), RCM (NT Build 1999) and NEL (CCES01 2004), which are standard test methods, have been applied for measuring the diffusion coefficient of chloride ion in concrete. The diffusion coefficient of sulfate and other ions in concrete cannot be established by the standard test methods, but it may be obtained by the chemical titration (Levi *et al*. 2005). The other is the theoretical modeling based on the conventional diffusion theory such as Fick's law, mass conservation law (Saetta *et al*. 1993, Suryavanshi 2002) and the basic electrochemistry laws including the Nernst-Plank and Nernst-Einstein equation (Andrade 1993, Chatterji 1994). In addition, researchers propose some multi-scale models for predicting the ion diffusion coefficient in concrete based on the diffusivity characteristics of concrete materials at a variety of length scales.

However these models are mainly suitable for the calculation of the diffusion coefficient of the chloride ion in concrete (Xi *et al*. 2000, Garboczi *et al*. 1998, Oh *et al*. 2004, Zheng *et al*. 2007). The ion diffusion coefficients obtained by the two above approaches are based on the assumptions that the ion diffusion coefficients in concrete are invariable and the effects of the pore solution in concrete on the diffusivity are neglected. The actual situation is that, besides the chloride ion, there are various ions which cause the degradation of concrete structures, and these ion diffusion coefficients change with not only the concrete mixture proportion but also with the environmental conditions such as ambient temperature, ionic species and its respective concentrations in pore solution according to the electrolyte solution theory (Barthel *et al*. 1998). Generally, the ion diffusion coefficients increase with the concrete deterioration in the process of ion aggression on concrete, so when an invariable ion diffusion coefficient is used for the concrete durability analysis, the chemical degradation of concrete is significantly underestimated, and this can lead to the overestimation of the lifetime of concrete structures.

The purpose of this study is to propose a computational model to predict the diffusion coefficient of various ions in concrete. Firstly, based on the modified Davis model and the mode coupling theory, the ionic activity and conductivity are presented and the models of the ion diffusion coefficient in the pore solution and the saturated concrete are established. Secondly, the experiments on measuring the chloride diffusion coefficient are carried out to investigate the validity of the proposed model. Finally, the effects of concrete microstructure parameters, concrete mix parameters and the ion concentration in pore solution on the ion diffusion coefficients in concrete are discussed by using numerical simulation.

2. Model

2.1 Basic assumption

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

2.2 Ion activity and conductivity in pore solution

2.2.1 Activity

The ionic diffusivity in the aqueous solution is associated with not only the ionic activity but also the ionic conductivity according to the electrolyte solution theory. The ionic activity in the solution may be represented by the ion activity coefficients which can be calculated by several models based on the theory of the thermodynamics. The Debye-Hükel model (Barthel *et al.* 1998) describe the ion-ion interaction in the electrolyte solutions such as the pore solution of concrete and is a classical model for calculating the ionic activity (coefficient) in the strong electrolyte solutions with low concentration. This model considers that every ion is surrounded by an ionic atmosphere of charges of the opposite sign, and all ions in solution as point charges having no radii. It may be expressed by

$$\ln f_i = -Az_i^2\sqrt{I} \tag{1}$$

where f_i is the ionic activity coefficient which represent the magnitude of the ion activity, z_i is the valence number of the ion i, I is the ionic strength (mmol/L or mol/m^3) and A is temperature dependent parameters, given by

$$I = \frac{1}{2}\sum_{i=1}^{N} z_i^2 c_i \tag{2}$$

$$A = \frac{\sqrt{2}eF^2}{8\pi(\varepsilon_0\varepsilon_r RT)^{3/2}} \tag{3}$$

N is the total number of ionic species, c_i is the concentration of the ion i in the solution, e is the elementary charge, $e = 1.602\times10^{-19}$C, ε_0 is the vacuum electric permittivity, $\varepsilon_0 = 8.85419\times10^{-12}$ C^2/J.m, ε_r is the water relative permittivity, $\varepsilon_r = 78.54$, R is the universal gas constant, $R = 8.31451$ J/K.mol, F is the Faraday constant, $F = 9.64853\times10^4$ C/mol, T is the temperature.

The Debye-Hükel model can efficiently calculate the activity coefficients of a 1-1 solution with an ionic strength of 10 mmol/L or less and can not be used for the calculations of the ion activity of the solution with high concentrations (Li *et al.* 1998). By considering the radii of the central ions in the cloud of ions for the Debye-Hükel model, the extended Debye-Hükel model can be used for calculating the activity coefficients of the electrolyte solution with an ionic strength of less than 100 mmol/L (Ritsema 2006, Adamson 1990).

$$\ln f_i = -\frac{Az_i^2\sqrt{I}}{1 + a_i B\sqrt{I}} \tag{4}$$

where a_i is the radius of the ion i, and the radii of parts of ions are listed in Table 1, B is temperature dependent parameters

$$B=\sqrt{\frac{2F^2}{\varepsilon_0\varepsilon_r RT}} \tag{5}$$

In order to improve the applicability of Debye-Hükel model for the high concentration solution, Davies modified the extended Debye-Hükel model by adding a composite term with proportion to the ionic strength of the solution in Eq. (4), which accounts for the salvation and short-range interactions due to high ionic concentration in the solution

$$\ln f_i=-\frac{Az_i^2\sqrt{I}}{1+a_iB\sqrt{I}}+\frac{0.2Az_i^2I}{\sqrt{1000}} \tag{6}$$

The Davies model (6) can usually predict the behavior of an electrolytic solution up to an ionic strength of 500 mmol/L (Pankow *et al.* 1994). For improving the accuracy of the Davies model over a wide range of ionic strengths, Samson modifies the Davis model by changing the composite term, and makes it fit for calculating the solution with an ionic strength of 1500 mmol/L, and the modified Davies model as follows (Samson *et al.* 1999).

$$\ln f_i=-\frac{Az_i^2\sqrt{I}}{1+a_iB\sqrt{I}}+\frac{(0.2-4.17\times 10^{-5}I)Az_i^2I}{\sqrt{1000}} \tag{7}$$

2.2.2 Conductivity

The computation of the ionic conductivity in the concentrated electrolyte solution plays an important role in estimating the ionic diffusivity. At present, many models have been derived for the calculation of the ionic conductivity (Onsager *et al.* 1932, Lee *et al.* 1979, Chandra *et al.* 1999). The Onsager model proposes a simple formula providing quantitative results for the conductivity of ions in strong electrolyte solutions with low concentration, the model considers that the ionic conductivity is proportional to the square root of the concentration by assuming that the solvent is a continuous medium and that the ion is a charged hard sphere on the basis of the Debye-Hückel theory

$$\Lambda_i=\Lambda_i^0-[Cz_i^2+Dz_i^3\Lambda_i^0]\sqrt{c_i} \tag{8}$$

where Λ_i is the conductivity of the ion i, c_i is the ionic the concentration in the solution, Λ_i^0 is the ionic conductivity at the infinite dilution which is obtained by extrapolating the concentration of the solution to zero, and the limiting conductivity of parts of ions at $T = 298$K are presented in Table 1, C and D are two constants which are determined by the temperature, the ion species and the medium, they are given by

$$C=\frac{\sqrt{2}\pi eF^2}{3\pi\eta\sqrt{1000\varepsilon_0\varepsilon_r RT}} \tag{9}$$

$$D=\frac{\sqrt{2}\pi eF^2}{3\sqrt{1000}(\varepsilon_0\varepsilon_r RT)^{\frac{3}{2}}} \tag{10}$$

The Onsager model can only calculate efficiently the ionic conductivity under the lower ionic

Table 1 Conductivity of parts of ions at the infinite dilution at $T = 298$K (Kuhl *et al.* 2003)

Species	Na^+	K^+	Ca^{2+}	SO_4^{2-}	OH^-	Cl^-
Valency z	1	1	2	2	1	1
Conductivity Λ^0($\times 10^{-3}$ Sm^2/mol)	5.01	7.60	5.95	8.00	19.92	7.64
Ionic radius a_i ($\times 10^{-10}$ m)	0.95	1.33	0.99	2.58	1.33	1.81

concentration, and produce a great error when the concentration is greater than 1mmol/L (Onsager *et al.* 1932, Huang 1983). Based on the mode coupling theory treatment of the electrolyte friction, Chandra and Bagchi modified the Onsager model for the calculation of ionic conductivity when the ion concentration attains 2000 mmol/L (Chandra *et al.* 1999).

$$\Lambda_i = \Lambda_i^0 - [Cz_i^2 + Dz_i^3 w_i \Lambda_i^0]\sqrt{c_i} \tag{11}$$

where w_i is the influence coefficient considering the mobility of the ion species

$$w_i = 2\left[1 - \left(\frac{1}{2}\sum_{j=1, j\neq i}^{N} \frac{\Lambda_i^0}{\Lambda_i^0 + \Lambda_j^0}\right)^{\frac{1}{2}}\right] \tag{12}$$

2.3 Ion diffusion coefficient in pore solution

According to the above assumptions, the pore solution, through which the ions penetrate concrete, can be regarded as an electrolyte solution. Considering the effect of the activity coefficient f_i at higher concentration, and based on the Nernst-Einstein relation (Moore *et al.* 1972), the diffusion coefficient D_{si} of the ion i in the solution with a concentration c_i can be expressed by the following equation.

$$D_{si} = \frac{RT}{z_i^2 F^2}\left(1 + \frac{\partial \ln f_i}{\partial \ln c_i}\right)\Lambda_i \tag{13}$$

It can be deduced from Eq. (7) that

$$\frac{\partial \ln f_i}{\partial \ln c_i} = -\left[\frac{1}{4\sqrt{I}(1 + a_i B\sqrt{I})^2} - \frac{0.1 - 4.17 \times 10^{-5} I}{\sqrt{1000}}\right] A c_i z_i^4 \tag{14}$$

Substituting Eqs. (11) and (14) into Eq. (13), the diffusion coefficient D_{si} of the ion i in the concrete pore solution, can be obtained

$$D_{si} = \frac{RT}{z_i^2 F^2}\left\{1 - \left[\frac{1}{4\sqrt{I}(1 + a_i B\sqrt{I})^2} - \frac{0.1 - 4.17 \times 10^{-5} I}{\sqrt{1000}}\right] A c_i z_i^4\right\} \cdot [\Lambda_i^0 - (Cz_i^2 + Dz_i^3 w_i \Lambda_i^0)\sqrt{c_i}] \tag{15}$$

2.4 Ion diffusion coefficient in saturated concrete

Let us consider the saturated concrete as an isotropic system made up of two phases having different diffusivities for a given ion, which includes the aqueous solution phase, equivalent to the electrolyte solution, and the solid phase, namely the coarse and fine aggregates in the concrete skeleton. The ion diffusion coefficient in the aqueous solution has been presented in Eq. (15). Because the solid phase is a non-porous insulator, the ionic diffusivity in the solid phase can be ignored. But the pore structure of the concrete skeleton in the system has very important influences on the ionic diffusivity in concrete. Therefore, the ion diffusion coefficient in concrete is mainly related to the ionic diffusivity in the pore solution, and also the pore structure characteristics, including the porosity and the tortuosity of the pore.

The diffusivity of a porous material such as concrete and mortar can be expressed by the following relationship with the pore structure parameters (Garboczi 1990, Promentilla *et al.* 2009).

$$D_{ci} = D_{si}\frac{\varphi}{\tau_D} \tag{16}$$

where D_{ci} is the ion diffusion coefficient in the porous material such as concrete and mortar, D_{si} is the ion diffusion coefficient in the pore solution, φ and τ_D are the porosity and tortuosity of concrete, respectively.

Tortuousity is viewed as a property of the porous materials that is expressed by the tortuousity coefficient reflecting on the complicated transport paths in the porous media, and it is defined as a ratio of the average diffusion path of fluid particle to the corresponding straight and shortest distance along the direction of macroscopic flux. In the cement-based material, the tortuousity coefficient is considered as a function of the porosity or the volume fraction of the cement (Yoon 2009, Bejaoui *et al.* 2007), and the expression related to the cement volume fraction is considered (Bejaoui *et al.* 2007)

$$\frac{1}{\tau_D} = 0.0067e^{5f_c} \tag{17}$$

where τ_D refers to the tortuousity coefficient, f_c is the volume fraction of the cement.

The porosity φ is a function of the water-cement ratio and the hydration degree of the cement. It can be determined by the following formula (Clifton *et al.* 1995)

$$\varphi = \max\left(f_c\frac{w/c-0.39h_\alpha}{w/c+0.32}, 0\right) \tag{18}$$

f_c and w/c are the volume fraction of the cement in concrete and the water-cement ratio.

h_α is the hydration degree of the cement that can be determined by (Masi *et al.* 1997)

$$h_\alpha = 1-0.5[(1+1.67t)^{-0.6}+(1+0.29t)^{-0.48}] \tag{19}$$

t is the hydration time.

With the combinations of Eqs. (15) and (16), the diffusion coefficient of the ion species i in concrete is obtained by

$$D_{ci} = \frac{\varphi RT}{\tau_D z_i^2 F^2}\left\{1-\left[\frac{1}{4\sqrt{I}(1+a_iB\sqrt{I})^2}-\frac{0.1-4.17\times10^{-5}I}{\sqrt{1000}}\right]Ac_iz_i^4\right\}\cdot[\Lambda_i^0-(Cz_i^2+Dz_i^3w_i\Lambda_i^0)\sqrt{c_i}] \tag{20}$$

3. A simple experimental validation

3.1 Materials and specimen

In this experiment, the cement is prepared by commercial Portland II 42.5 type "Jinningyang" produced by China Jiangnan Corporation, whose chemical compositions are given in Table 2. The fine aggregate is a kind of river sand with the maximum particle size being 2 mm and the apparent density 2.64 g/cm^3, and the coarse aggregate is crushed wacke stone with the maximum diameter being 10 mm and the cumulate density 1.6 g/cm^3. The mix weight proportions of concrete are shown in Table 3 and the initial concentration of the main ions in the concrete pore solution are listed in Table 4.

The cylinder concrete specimens with 100 mm diameter and 300 mm length (Φ100×300 mm) are cast according to the mixture proportions of concrete in Table 3, and are cured in 20°C water. For 20 days, a 50±2-mm-thick slice (Φ100×(50±2)mm) is taken from the center of the cylinder specimen. The slices are polished until smooth, cleaned and continue the curing process until the prescribed test period.

3.2 Experimental methods and results

The electrical method proposed by Tang and Nilsson (Tang *et al.* 1992) is adopted for the measurement of the chloride diffusivity in concrete. The experimental configuration and setup are illustrated in Fig. 1 (see also the rapid chloride penetration test of NT BUILD 492 (NT Build 1999)). The slice (Φ100×50 mm) is enclosed by the rubber sleeve as shown in Fig. 1 and it is secured with two

Table 2 Chemical compositions and mechanical properties of raw materials

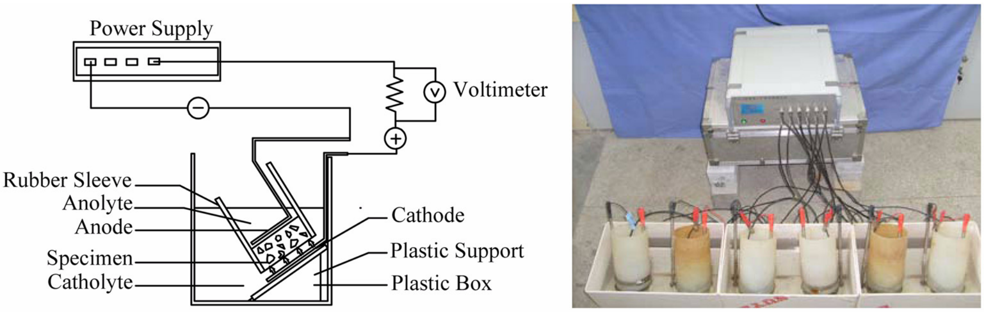
Main chemical compositions (w/%)									Stacking density (kg/m^3)	Specific area (m^2/kg)
SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	Na_2O	K_2O	LOI		
20.60	5.03	65.06	0.55	2.24	4.38	0.20	0.40	1.30	1300	417

Table 3 The mix weight proportions of concrete materials

Water-cement ratio	Cement	Water	Sand	Gravel	Cement volume fraction
0.35	1	0.35	0.743	1.816	0.381
0.45	1	0.45	1.107	2.465	0.311
0.55	1	0.55	1.561	3.028	0.283
0.65	1	0.65	2.073	3.529	0.269

Table 4 The initial concentration of main ions in concrete pore solution

Water-cement ratio	Ionic concentrations of initial pore solution (mmol/L)					
	Na^+	K^+	Ca^{2+}	SO_4^{2-}	OH^-	Cl^-
0.35	128.40	121.30	1.90	2.01	251.30	0
0.45	107.10	116.50	2.33	1.88	224.47	0
0.55	89.20	113.45	2.60	1.35	201.82	0
0.65	71.40	108.9	2.74	1.17	183.42	0



(a) (b)

Fig. 1 Experimental setup

clamps. The slice is then placed on the plastic support in the catholyte reservoir, and the anode is put into the rubber sleeve. The catholyte reservoir and the anolyte rubber sleeve are filled with about 12 litres of 10% NaCl solution and 300 ml of 0.3 M NaOH solution, respectively. The cathode and anode are connected to the negative pole and the anode to the positive pole of the power supply. The potential of 30±0.2V is applied between the cathode and anode during the test duration. After the test, the slice specimens are split axially into two pieces, and then a 0.1M silver nitrate solution is sprayed on to one of the freshly split sections. The chloride penetration depth is measured by the colorimetric method, the visible white silver chloride precipitation on the split surface, with the help of the slide caliper (NT Build 1999). Therefore, the chloride diffusion coefficient can be calculated from the measured depth.

$$D_{\mathrm{nssm}} = \frac{RT_D L}{zF(U-2)} \frac{x_d - \alpha\sqrt{x_d}}{t} \tag{21}$$

where D_{nssm} is the non-steady-state migration diffusion coefficients [m^2/s], x_d refers to the penetration depth of chloride ion [m], t is the test duration[s], and α is the test constant calculated by the following

$$\alpha = 2\sqrt{\frac{RTL}{zF(U-Z)}}\, erf^{-1}\left(1 - \frac{2c_d}{c_0}\right) \tag{22}$$

where z is the valence of chloride ion, $z = 1$, U is the applied potential, $U = 30\mathrm{V}$, T_D is the average value of the initial and final temperatures in the anolyte solution [K], L is the slice specimen thickness[m], $L = 0.05$ m, erf^{-1} is the inverse of the error function, c_0 and c_d are respectively the chloride concentrations in the catholyte solution and at the colour changes, $c_0 \approx 0.2N$ and $c_d \approx 0.07N$.

According to the above the NT BUILD 492 test method, the measured non-steady-state migration diffusion coefficients D_{nssm} of all concrete specimens at the ambient temperature 298K are summarized in Table 5. It can be seen from Table 5 that the NT BUILD 492 test method used in this paper reveals quite good precision. Its variability COV is in a range of 2~5% for the specimens with the water-cement ratios 0.35, 0.45 and 0.65, and the variability COV of the specimen C3 with the water-cement ratio 0.55 is 11.7%. However, for the other two test methods for measuring the chloride diffusion coefficient of concrete, the NT BUILD 443 and CTH rapid test methods, their variability COV is in a range of 8~14% and 5~9% respectively (Tang *et al.* 2001). Therefore, the precision of the NT BUILD 492 test method used in this paper is close to the precision of CTH rapid test

Table 5 Experimental result for chloride diffusion coefficient in specimens ($\times 10^{-12}$ m^2/s)

Specimen	Result of diffusion coefficient	Water-cement ratio	Mean diffusion coefficient	Standard deviation	Variability COV(%)
C11	2.904	0.35	2.951	0.141	4.8
C12	2.840				
C13	3.110				
C21	4.016	0.45	4.036	0.119	2.9
C22	4.186				
C23	3.905				
C31	4.150	0.55	4.614	0.538	11.7
C32	4.489				
C33	5.203				
C41	4.879	0.65	5.027	0.174	3.5
C42	4.983				
C43	5.219				

and better than the NT BUILD 443. It can be concluded that the NT BUILD 492 test method provides the better precision for measurements of the chloride diffusion coefficient, and the diffusion coefficients in Table 5 may be used for validating the results from the theoretical model in Eq. (20).

3.3 Comparison between model and experimental results

Using the model Eq. (20) for calculating the chloride diffusion coefficient in the saturated concrete, the chloride diffusion coefficients of every specimen with water-cement ratio 0.35~0.65 are obtained, and they are compared with the above NT BUILD 492 test results, as shown in Table 6. In order to evaluate the model Eq. (20) for the chloride diffusion coefficient, the error, $((D_{\mathrm{exp}}-D_{\mathrm{mod}})/(D_{\mathrm{exp}}))\times 100\%$, expressing the difference degree between the model and experimental results for the chloride diffusion coefficients, are calculated as shown in Table 6, D_{exp} and D_{mod} denote the experimental and model value of the chloride diffusion coefficient respectively. By calculation, the errors are 17.5%, 5.2%, 2.3% and -0.2% corresponding to the water-cement ratios 0.35, 0.45, 0.55 and 0.65 respectively. It can be seen from the above comparisons that the error of the model Eq. (20) for the concrete with low water-cement ratio is relatively high. It is known that the concrete with the low water-cement ratio have a little porosity and fill with less pore solution under the saturated states. The theoretical model Eq. (20) is established by using the electrolyte solution theory, and the more pore solution

Table 6 Comparisons between the modeling and experimental results of the chloride diffusion coefficient ($\times 10^{-12}$ m^2/s)

Specimen	Water-cement ratio	Experimental results	Calculating results	Error (%)
C1	0.35	2.951	2.434	17.5
C2	0.45	4.036	3.828	5.2
C3	0.55	4.614	4.508	2.3
C4	0.65	5.027	5.036	-0.2

(Regarded as an electrolyte solution), there is more high precision of the model Eq. (20) for calculating the chloride diffusion coefficient. This might be one of the reasons for the relatively high error of the theoretical model Eq. (20) for calculating the chloride diffusion coefficient of concrete with low water-cement ratio when compared with the experimental results. On basis of the above comparisons between the proposed model values and NT BUILD 492 test results for the chloride diffusion coefficients, the model in Eq. (20) are in agreement with the experimental results, so the proposed model Eq. (20) can used for predicting the ion diffusivity in the saturated concrete.

4. Numerical results and discussion

There are several influencing factors on ion diffusivity in concrete such as the ionic concentration in pore solution, microstructure and mixture of concrete, but every factor has a different influence on ionic diffusivity in concrete. Based on the above proposed model Eq. (20), the effect of the ionic concentration, microstructure and mixture of concrete on the diffusion coefficient are investigated, and the concrete material, with the water-cement ratio 0.45, the cement volume fraction 0.311 and the initial concentration of Na^+, K^+, Ca^{2+}, SO_4^{2-}, OH^-, Cl^- in the concrete pore solution: 107.10, 116.50, 2.33, 1.88, 224.47, 0 mmol/L, are considered.

4.1 Effects of ionic concentration on ion diffusion coefficient

At present, the standard models for evaluating the concrete diffusivity mainly consider the effects of the constitutes and microstructures of the concrete material itself and the environmental temperature (Xi *et al.* 2000, Saetta *et al.* 1993), but not consider the effects of the concentration of every ion in the pore solution, which is the ionic activity, on the diffusivity. Due to existing many ions in pore solution such as Na^+, K^+, Ca^{2+}, SO_4^{2-}, OH^-, Cl^-, every ion concentration has an influence on the diffusivity of one of them in concrete. The two following cases are analyzed for evaluating the influence of ion concentration on the its diffusivity in concrete. Firstly, the influences of each of ion concentrations in pore solution on an ionic diffusion coefficient are considered. As an

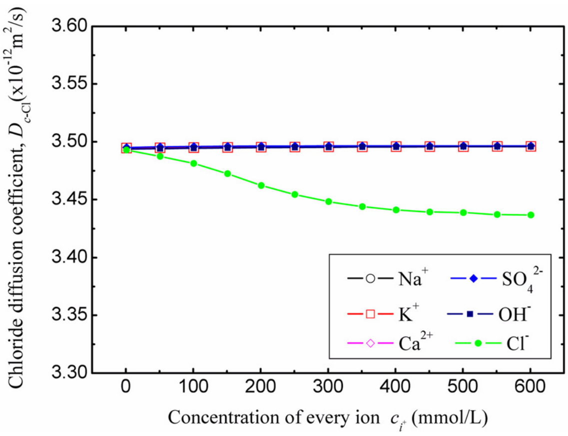


Fig. 2 Effects of the respective concentration of every ion on Cl^- diffusion coefficient

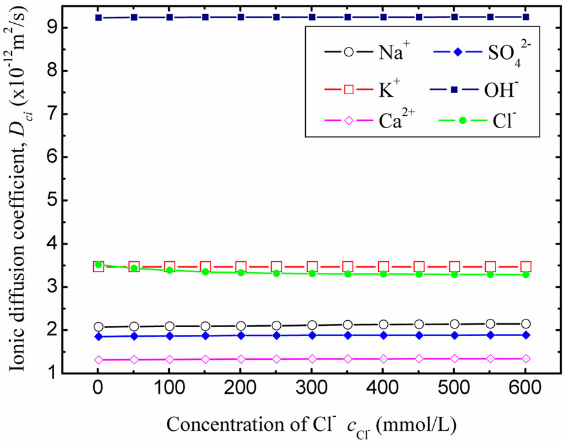


Fig. 3 Effects of Cl^- concentration on the diffusion coefficient of every ion

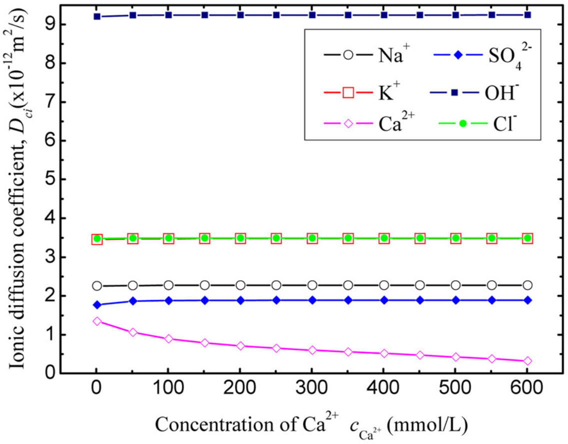


Fig. 4 Effects of Ca^{2+} concentration on the diffusion coefficient of every ion

example, Fig. 2 describes the relation between the chloride diffusion coefficient and the respective concentration of every ion. It is seen from Fig. 2 that, when the concentrations of every ion change respectively from 0 to 600 mmol/L, very low concentration, the chloride concentration has the most evident effect on the diffusivity itself in concrete, and the chloride diffusion coefficient decreases with the concentration, and yet the concentration variations of the other ion have little effect on the chloride diffusity. In the same analysis, it is obtained that the relation between the other ion diffusion coefficient and the concentration of every ion is similar to the chloride diffusivity. Secondly, the effects of the concentration of an ion on the diffusion coefficient of every ion in the pore solution are presented. Figs. 3 and 4 present respectively the effects of the concentration of Cl^- and Ca^{2+} on the diffusion coefficient of every ion in concrete. It can be seen from Fig. 3 that, with the increase of the chloride concentration, the diffusion coefficients of the other ion have basically no changes, and yet the chloride diffusion coefficient has an obvious decrease. The same results are obtained from Fig. 4 that the increase of the calcium ion concentration reduces the diffusivity itself and has almost no effects on the diffusivity of the other ions. In summary, it is concluded from above analysis that under the low concentration, the variations of the ion concentration produce more obvious effects on the diffusivity itself, but has almost no effects on the diffusivity of the other ions.

Generally, in practical engineering environment, the concentration of every ion is very low, so the effect of the other ion concentrations on the diffusivity of the harmful ion such as chloride ion may not be taken into account in the life time prediction of concrete structures, but for the harmful ion itself, its concentration has a certain impact on its diffusivity. Due to not considering the effects of the ion concentrations, the standard diffusion model gets a high diffusion coefficient compared to the model in Eq. (20). This means, that the life time of concrete structures is underestimated by the standard diffusion model, and it is very conservative for design of concrete structures under chemical attack.

4.2 Effects of microstructure parameters on ion diffusion coefficient

The microstructure parameters associated with the ionic diffusivity in concrete are mainly referred as the pore structure parameters such as the porosity and tortuosity. Fig. 5 presents the effects of the porosity on the diffusion coefficient of every ion in concrete. It is seen from Fig. 5 that, under the

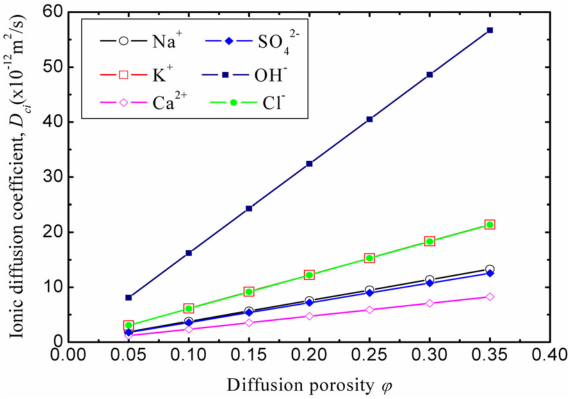


Fig. 5 Effects of the concrete porosity on the ionic diffusion coefficients

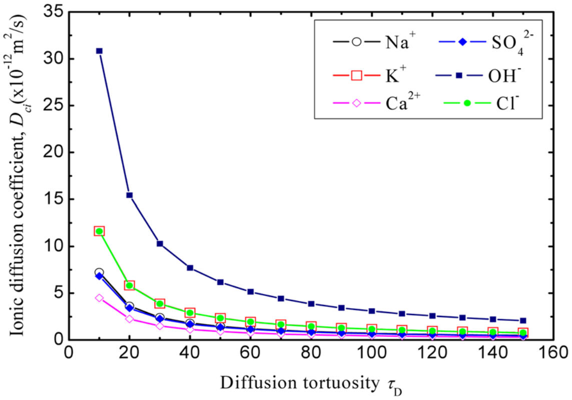


Fig. 6 Effects of the concrete tortuosity on the ionic diffusion coefficients

same porosity, the diffusion coefficient of OH^- in concrete is the largest while the diffusion coefficient of Ca^{2+} is the smallest, and with the increasing of the porosity, the diffusion coefficients of every ion in concrete increase linearly. This is because, according to Table 1, the conductivity of OH^- is the largest, and the conductivity of Ca^{2+} is relatively smaller, and the larger the conductivity and porosity there is, the more diffusivity for the ion transportation in concrete. Fig. 6 illustrates the effects of the tortuosity on the ion diffusion coefficients in concrete. Fig. 6 shows that the diffusion coefficient of every ion in concrete decreases with the increasing of the tortuosity. The diffusion coefficients of every ion decrease significantly when the tortuosity begins to increase. The trend is gradually stable after the tortuosity reaches a certain value. This is a logical result because the larger tortuosity leads to the longer transport path of ions in concrete. But when the tortuosity goes up to a certain value, the ion diffusion coefficient becomes stable which means that the change is much less.

4.3 Effects of concrete mix parameters on ion diffusion coefficient

The model developed for the ion diffusion coefficient can handle the effects of the concrete mix parameters such as water-cement ratio and volume fraction of cement. Fig. 7 gives the effects of the water-cement ratio on the ion diffusion coefficients in concrete. It is seen from Fig. 7 that the ion diffusion coefficients in concrete increase with the increasing of water-cement ratio. This is because, with the increasing of the water-cement ratio, the concrete porosity increase, and the higher porosity not only leads to the smaller tortuosity (Yoon 2009), but also cause the better connectivity of the pore system (Nakarai *et al.* 2006). According to Figs. 2 and 3, under a high porosity and small tortuosity, concrete possesses a good diffusivity. Furthermore, the improvement of the connectivity of the pore system results in a reduction in the resistance to the diffusions of every ion. Fig. 8 presents the effects of the cement volume fraction in concrete on the ion diffusion coefficients, and it is seen from the figure that the higher cement volume fraction in concrete, the higher ion diffusion coefficients. It is a reason that with the increase of cement volume fraction in concrete, the tortuosity of the concrete pore has an obvious decrease and the porosity has a linear increase, as shown in Fig. 9, which is obtained from Eqs. (17) and (18). Both of the decrease of tortuosity and the increase of porosity cause a more obvious increase of the ion diffusion coefficients in concrete. In addition, the relative increase of the cement volume fraction results in a relative decrease of the

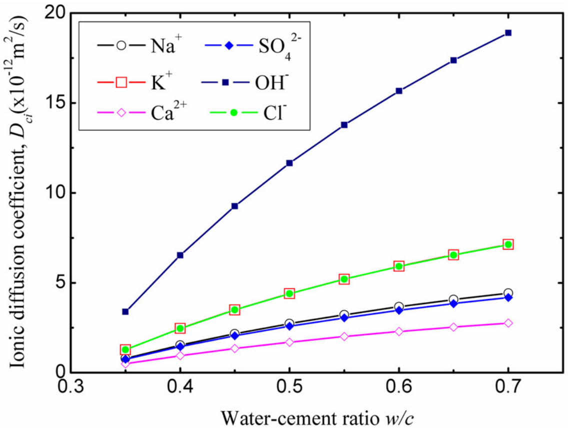


Fig. 7 Effects of the water-cement ratio on the ionic diffusion coefficients

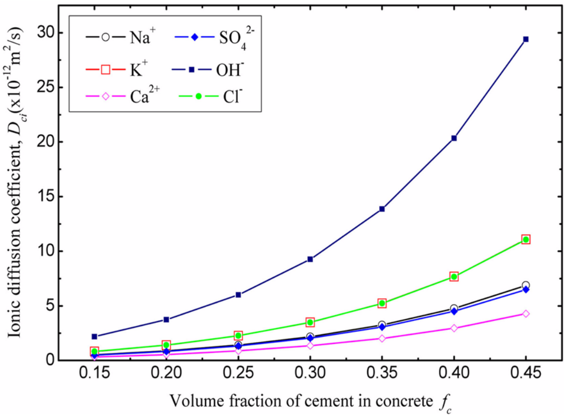


Fig. 8 Effects of the cement volume fraction on the ionic diffusion coefficients

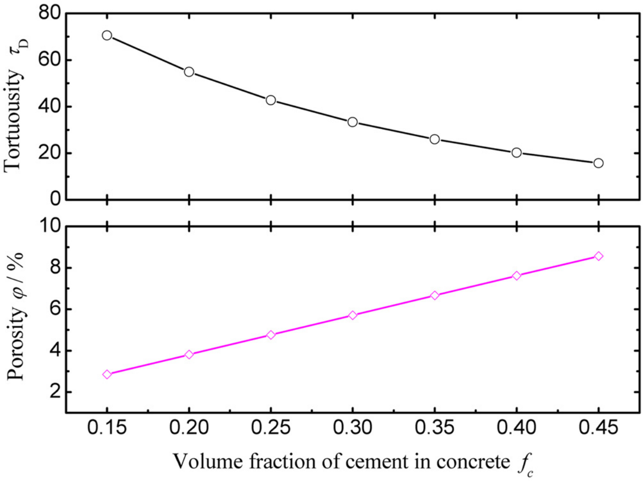


Fig. 9 Relations between the cement volume fraction and porosity and tortuousity

aggregate volume fraction in concrete. Due to the low diffusivity of aggregate, the decrease of the aggregate volume fraction causes the increase of the ionic diffusivity.

5. Conclusions

1. Based on the modified Davis model and mode coupling 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, water-cement ratio, cement volume fraction, porosity and tortuosity are considered.

2. Using the rapid chloride penetration test proposed by Tang and Nilsson, the chloride diffusion coefficients in the concrete specimens with different water-cement ratios are measured. The chloride diffusion coefficients obtained by the proposed model are in agreement with the measured results.

3. Numerical simulations are carried out to investigate the effects of the porosity, tortuosity, water-cement ratio, cement volume fraction and the concentration of ion in the pore solution on the ion diffusion coefficients when single ion concentration changes from 0 to 600 mmol/L. The numerical results show that the ion diffusion coefficients in concrete increase with the porosity, water-cement ratio and cement volume fraction, but decrease with the increasing of tortuosity. The ion concentration produces more obvious effects on the diffusivity itself, but has almost no effects on the diffusivity of the other ions.

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