

Prediction of chloride diffusion coefficients using multi-phase models

Qing-feng Liu

State Key Laboratory of Ocean Engineering, School of Naval Architecture, Ocean and Civil Engineering, Shanghai Jiao Tong University, Shanghai, China; Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration (CISSE), Shanghai, China

Dave Easterbrook

School of Marine Science and Engineering, University of Plymouth, Plymouth, UK

Long-yuan Li

School of Marine Science and Engineering, University of Plymouth, Plymouth, UK (corresponding author: long-yuan.li@plymouth.ac.uk)

Dawang Li

Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen, China

Chloride-induced reinforcing steel corrosion is a worldwide problem. In order to design durable concrete structures, one has to understand the diffusion mechanism of chlorides in concrete. Unfortunately, most of the experimental data obtained from laboratory studies are for chloride diffusion in cement paste. Thus, it is important to discuss and examine the difference between chloride diffusion in cement paste and in concrete. This paper presents a theoretical study on chloride diffusion in concrete. By treating the concrete as a composite consisting of aggregates, interfacial transition zones and cement paste, a combined series and parallel multi-phase transport model was developed. The model explains how the shape of aggregates affects the chloride diffusion in concrete. Using the model, the effects of aggregates and corresponding interfacial transition zones on chloride diffusion in concrete and mortar were examined. Comparisons of the model with other models published in the literature and with experimental and numerical data are also provided.

Notation

C	concentration of free chlorides in unit volume of pore solution	D_{left}	effective diffusion coefficient of ions in the left part of materials
C_1	concentration of ions at the left boundary of a specimen	D_{lower}	effective diffusion coefficient of ions in the lower part of materials
C_0	concentration of ions at the interface between two materials	D_{mix}	effective diffusion coefficient of ions in mixed aggregates and ITZ composite
C_r	concentration of ions at the right boundary of a specimen	D_{mix}^*	$= D_{\text{mix}}/D_{\text{cem}}$
D	effective diffusion coefficient of chloride ions in concrete	$D_{\text{mix}}^{\text{ct}}$	critical value of the effective diffusion coefficient of ions in mixed aggregates and ITZ composite
D_1	effective diffusion coefficient of ions in material 1	D_p	bulk effective diffusion coefficient of ions in composite material in the parallel model
D_2	effective diffusion coefficient of ions in material 2	D_{right}	effective diffusion coefficient of ions in the right part of materials
D_{agg}	effective diffusion coefficient of chloride ions in aggregates	D_s	bulk effective diffusion coefficient of ions in composite material in the series model
D_{app}	apparent diffusion coefficient of chloride ions in concrete	D_{upper}	effective diffusion coefficient of ions in the upper part of materials
D_{cem}	effective diffusion coefficient of ions in cement paste	h	thickness of ITZs
D_{com}	bulk effective diffusion coefficient of ions in composite material	J	diffusion flux of chlorides passing through a unit cross-sectional area of concrete
D_{con}	bulk effective diffusion coefficient of ions in concrete	k	shape factor
D_{eff}	effective diffusion coefficient of chloride ions	k_2	shape factor k in the 2D problem
D_{ITZ}	effective diffusion coefficient of chloride ions in ITZs	k_3	shape factor k in the 3D problem
		r	radius of aggregates
		t	width of ε_{cem} panels

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

ε_1	$=\varepsilon_{1p} + \varepsilon_{1s}$ is the volumetric fraction of material 1 in composite material
ε_2	$=\varepsilon_{2p} + \varepsilon_{2s}$ is the volumetric fraction of material 2 in composite material
ε_{1p}	partial volumetric fraction of material 1
ε_{2p}	partial volumetric fraction of material 2
ε_{1s}	partial volumetric fraction of material 1
ε_{2s}	partial volumetric fraction of material 2
ε_{agg}	volumetric fraction of aggregates in concrete
ε_{cem}	volumetric fraction of the cement paste phase in concrete
ε_{ITZ}	volumetric fraction of ITZs in concrete
ε_{left}	volumetric fraction of the left part of materials
ε_{lower}	volumetric fraction of the lower part of materials
ε_{right}	volumetric fraction of the right part of materials
ε_{upper}	volumetric fraction of the upper part of materials
ϕ	volumetric water content of porous material
ϕ_{cem}	porosity of cement paste
ϕ_{ITZ}	porosity of ITZs

Introduction

The corrosion of reinforcing steel due to chloride attack is the most significant threat to reinforced concrete structures, and may lead to early repair or premature replacement of the structure. Typical examples include bridges subjected to the application of de-icing salts, tunnels exposed to saline groundwater, and buildings and structures exposed to marine environments. To prevent the corrosion of reinforcing steel being induced by dissolved chloride ions, knowledge of the mechanism of chloride penetration in concrete and the factors that affect the chloride penetration is essential.

Intensive research on chloride penetration in cement and concrete-related materials started in the early 1980s. Laboratory and site experimental investigations (Atkinson and Nickerson, 1984; Audenaert *et al.*, 2010; Chen *et al.*, 2012; Dhir *et al.*, 1998; Maheswaran and Sanjayan, 2004; Page *et al.*, 1981; Petcherdchoo, 2013; Sergi *et al.*, 1992; Spiesz and Brouwers, 2013; Tang and Gulikers, 2007; Yang, 2004) were carried out on the diffusion and migration of chloride ions using both steady-state and non-steady-state testing methods. Various prediction models (Andrade *et al.*, 2011, 2013; Baroghel-Bouny *et al.*, 2012; Bentz *et al.*, 1998; Garboczi and Bentz, 1992; Garboczi *et al.*, 1995; Halamickova *et al.*, 1995; Jiang *et al.*, 2013; Li and Page, 1998, 2000; Liu and Shi, 2012; Maheswaran and Sanjayan, 2004; Mercado *et al.*, 2012; Pack *et al.*, 2010; Spiesz and Brouwers, 2012; Spiesz *et al.*, 2012; Xia and Li, 2013) were also developed to examine the influence of the concrete mixture, water-to-cement ratio, porosity, pore sizes, interfacial transition zones (ITZs), concrete saturation rate, ionic interactions, ionic binding and ionic strength on the penetration of chlorides in cement, mortar and concrete materials.

In general, the penetration of chloride ions in concrete can be treated as a diffusion process, which can be described by Fick's second law using a single bulk diffusion coefficient (Audenaert *et al.*, 2010; Garboczi *et al.*, 1995; Maheswaran and Sanjayan, 2004; Pack *et al.*, 2010; Stanish and Thomas, 2003). This simplified approach requires the bulk diffusion coefficient to be able to reflect the features of individual components and the influence of the composition of concrete. Existing experimental data showed that the addition of aggregates and the corresponding ITZs generated surrounding the aggregates have significant influence on chloride penetration in concrete (Caré, 2003; Delagrave *et al.*, 1997; Yang and Su, 2002). To quantify the effect of aggregates and ITZs on the bulk diffusion coefficient of chloride ions in concrete, analytical and numerical prediction models have been developed by using the concepts of micro-scale and meso-scale modelling (Bentz and Garboczi, 1991; Bentz *et al.*, 2000; Bourdette *et al.*, 1995; Byung and Seung, 2004; Caré and Hervé, 2004; Garboczi and Bentz, 1997, 1998; Hobbs, 1999; Li *et al.*, 2012; Shane *et al.*, 2000; Xi and Bazant, 1999; Yang and Weng, 2013; Ying *et al.*, 2013; Zheng and Zhou, 2007; Zheng *et al.*, 2012). Popular analytical prediction models include the two-phase series and two-phase parallel models developed by Hobbs (1999), the two-phase spherical model developed by Xi and Bazant (1999), and the n -phase spherical model developed by Caré and Hervé (2004). The two-phase models can be used to predict the effect of aggregates, but not ITZs, on the diffusivity of concrete. In the n -phase model the concrete is treated as a three-phase composite, consisting of a cement continuous phase, an aggregate dispersed phase and an ITZ phase. The effective diffusion coefficient of ions in concrete is expressed analytically in terms of the volumetric fractions and ionic diffusion coefficients defined in individual phases. This n -phase spherical model was further developed and applied to mortars and concrete to investigate the effects of aggregates and ITZs on chloride diffusion by Zheng and Zhou (2007), Yang and Weng (2013) and Ying *et al.* (2013).

This paper reports on a combined series and parallel multi-phase transport model developed for predicting chloride diffusion in concrete, in which the concrete is treated as a composite consisting of three phases, namely aggregates, ITZs and the cement paste phase. This model explains how the shape of aggregates and the model dimension affect chloride diffusion in concrete. Using the model, the effects of aggregates and the corresponding ITZs on chloride diffusion in concrete and mortar were examined. Comparisons of the model with other models published in literature and with experimental and numerical data are also provided.

Effective diffusion coefficients of ions in two-phase series and parallel models

Chloride penetration in cement and concrete-related materials is usually treated as a diffusion process, in which the chloride

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

flux is expressed as

$$1. \quad J = -D\nabla C$$

where J is the diffusion flux of chlorides passing through the unit cross-sectional area of concrete, D is the effective diffusion coefficient of chloride ions in concrete and C is the concentration of free chlorides in the unit volume of pore solution. Equation 1 is normally used to determine the effective diffusion coefficient of chlorides in the steady-state diffusion test, in which the diffusion flux J is calculated using the chloride mass flow across the sample divided by the cross-sectional area of the sample, and the concentration gradient ∇C is calculated by the concentration difference between the two surfaces of the sample divided by the length of the sample (Atkinson and Nickerson, 1984; Page *et al.*, 1981).

Consider a composite specimen assembled with two porous materials. The transport of ions in the composite can be described using two different approaches. One is the parallel model, in which the two materials are assumed to be aligned in parallel (Figure 1(a)). The other is the series model, in which the two materials are assumed to be aligned in series (Figure 1(b)). Consider the uniaxial diffusion of ions in the composite. In the parallel model, the bulk ionic flux, J , through the composite can be expressed in terms of the sum of fluxes of two individual materials as

$$2. \quad J = \frac{(\varepsilon_{\text{upper}}D_{\text{upper}} + \varepsilon_{\text{lower}}D_{\text{lower}})(C_1 - C_r)}{\varepsilon_{\text{upper}} + \varepsilon_{\text{lower}}}$$

where $\varepsilon_{\text{upper}}$ and $\varepsilon_{\text{lower}}$ are the volumetric fractions of the two materials, D_{upper} and D_{lower} are the effective diffusion coefficients of ions in the two materials, and C_1 and C_r are the concentrations of ions at the left and right boundaries of the specimen, respectively. Note that the bulk ionic flux can also

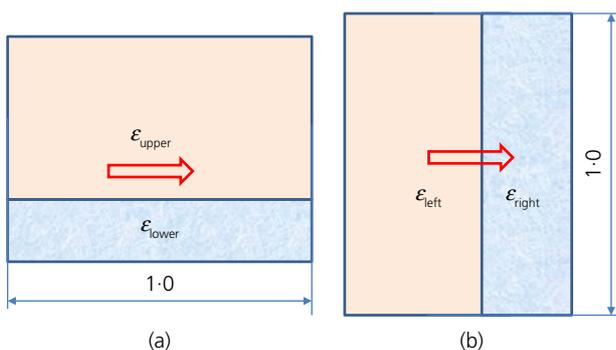


Figure 1. Two-phase ionic transport models: the (a) parallel and (b) series models

be expressed in terms of the bulk effective diffusion coefficient of ions in the composite as

$$3. \quad J = -D_p\nabla C$$

where D_p is the bulk effective diffusion coefficient of ions in the composite and $\nabla C = -(C_1 - C_r)/1.0$ is the concentration gradient (note that in Figure 1(a) the specimen length is assumed to be unity). The bulk effective diffusion coefficient of ions in the parallel model can be obtained by eliminating J and $(C_1 - C_r)$ in Equations 2 and 3, which yields

$$4. \quad D_p = \frac{\varepsilon_{\text{upper}}D_{\text{upper}} + \varepsilon_{\text{lower}}D_{\text{lower}}}{\varepsilon_{\text{upper}} + \varepsilon_{\text{lower}}}$$

In the series model, the ionic flux is perpendicular to the material layer. Owing to the continuity of flux, the bulk ionic flux through the composite can be expressed in terms of the flux of either material as

$$5. \quad J = \frac{D_{\text{left}}(C_1 - C_o)}{\varepsilon_{\text{left}}} = \frac{D_{\text{right}}(C_o - C_r)}{\varepsilon_{\text{right}}}$$

where $\varepsilon_{\text{left}}$ and $\varepsilon_{\text{right}}$ are the volumetric fractions of the two materials, and D_{left} and D_{right} are the effective diffusion coefficients of ions in the two materials. C_o is the concentration of ions at the interface between the two materials. Note that the bulk ionic flux can also be expressed in terms of the bulk effective diffusion coefficient of ions in the composite as

$$6. \quad J = -D_s\nabla C = \frac{D_s(C_1 - C_r)}{\varepsilon_{\text{right}} + \varepsilon_{\text{left}}}$$

where D_s is the bulk effective diffusion coefficient of ions in the composite and $(\varepsilon_{\text{left}} + \varepsilon_{\text{right}})$ represents the length of the specimen in Figure 1(b). It is obvious from Equations 5 and 6 that the bulk effective diffusion coefficient of ions in the series model can be expressed as

$$7. \quad D_s = \frac{\varepsilon_{\text{left}} + \varepsilon_{\text{right}}}{(\varepsilon_{\text{left}}/D_{\text{left}}) + (\varepsilon_{\text{right}}/D_{\text{right}})}$$

Equations 4 and 7 provide a framework for the calculation of the diffusion coefficient of ions in a porous composite material.

Effective diffusion coefficients of ions in a combined series and parallel model

The two-phase series and parallel models described above are the idealised transport models for ionic transport in composite

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

materials. In reality, however, the transport of ions in a composite material may not follow the series model or the parallel model exactly. It is more likely to follow a combined series and parallel model, as shown in Figure 2. By using the series transport model for ε_{1s} and ε_{2s} , followed by the parallel transport model for ε_{1p} , $(\varepsilon_{1s} + \varepsilon_{2s})$ and ε_{2p} , the overall effective diffusion coefficient of ions in the combined model of Figure 2 can be expressed as

$$8. \quad D_{\text{com}} = \frac{\varepsilon_{1p}D_1 + \varepsilon_{2p}D_2 + [(\varepsilon_{1s} + \varepsilon_{2s})^2 D_1 D_2 / (\varepsilon_{1s}D_2 + \varepsilon_{2s}D_1)]}{\varepsilon_{1s} + \varepsilon_{1p} + \varepsilon_{2s} + \varepsilon_{2p}}$$

where D_{com} is the bulk effective diffusion coefficient of ions in the composite material, ε_{1p} and ε_{1s} are the partial volumetric fractions of material 1, ε_{2p} and ε_{2s} are the partial volumetric fractions of material 2, and D_1 and D_2 are the effective diffusion coefficients of ions in material 1 and material 2, respectively. Note that $\varepsilon_{1p} + \varepsilon_{1s} = \varepsilon_1$ and $\varepsilon_{2p} + \varepsilon_{2s} = \varepsilon_2$, where ε_1 and ε_2 are the volumetric fractions of materials 1 and 2 in the composite. The ratios between ε_{1p} and ε_{1s} and between ε_{2p} and ε_{2s} are dependent upon the shapes of materials 1 and 2 as well as on the dimensions used to model the transport of ions in the composite, which will be discussed in the subsequent sections.

Effective diffusion coefficient of ions in the composite made of aggregates and ITZs

It is known from scanning electron microscopy analyses of concrete that an ITZ phase comprising large pores exists around aggregates. The thickness of this ITZ varies from 20 to 50 μm and it consists of anhydrous and hydrated cement. It has been reported that most harmful substances, including chloride ions, diffuse much quicker in ITZs than in the bulk cement paste (Caré, 2003; Delagrave *et al.*, 1997; Su *et al.*, 2015; Yang and Su, 2002). Therefore, it is necessary to take into account the effect of ITZs on chloride penetration in concrete. Assume that the aggregate is represented by a cubic unit surrounded by an ITZ layer of equal thickness. For the case of

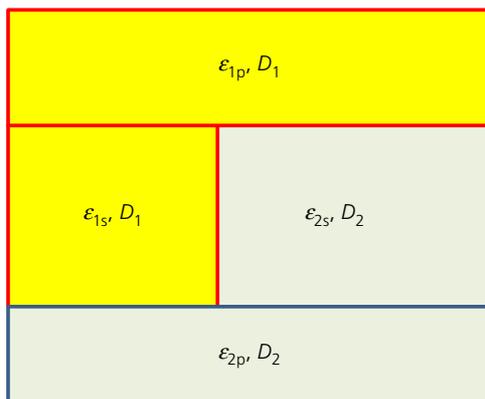


Figure 2. A combined series and parallel transport model

the uniaxial diffusion of ions, the aggregate together with ITZs surrounding it can be modelled as an isotropic shape composite, as shown in Figure 3. Note that in the model the volume of the horizontal panel is assumed to be double that of the vertical panel for the ITZs. This is because there are six surfaces for a cube, and four are treated as the parallel transport model and two are treated as the series transport model. Moreover, since $\varepsilon_{\text{ITZ}} \ll \varepsilon_{\text{agg}}$, one can assume $\varepsilon_{1p} = 2\varepsilon_{\text{ITZ}}/3$, $\varepsilon_{1s} = \varepsilon_{\text{ITZ}}/3$, $\varepsilon_{2p} = 0$, $\varepsilon_{2s} = \varepsilon_{\text{agg}}$, $D_1 = D_{\text{ITZ}}$ and $D_2 = D_{\text{agg}} = 0$, where ε_{agg} and ε_{ITZ} are the volumetric fractions of aggregates and ITZs, and D_{agg} and D_{ITZ} are the diffusion coefficients of ions in aggregates and ITZs, respectively. Using Equation 8, the overall effective diffusion coefficient of ions in the mixed aggregates and ITZs can be expressed as

$$9. \quad D_{\text{mix}} = \frac{2\varepsilon_{\text{ITZ}}D_{\text{ITZ}}}{3(\varepsilon_{\text{ITZ}} + \varepsilon_{\text{agg}})}$$

Equation 9 can be also derived from the two-phase spherical model by using the assumption of $\varepsilon_{\text{ITZ}} \ll \varepsilon_{\text{agg}}$ (Caré and Hervé, 2004; Xi and Bazant, 1999). This indicates that if the composite is isotropic in shape and the individual materials are uniformly distributed in the three directions of the material, then the developed model gives the same result as the spherical model. Equation 9 shows that, due to the contribution of ITZs, the bulk diffusion coefficient, D_{mix} , in the mixed aggregates and ITZs is proportional to the effective diffusion coefficient of ions in ITZs and the relative volume of the ITZs in the mixture.

Consider a single aggregate of spherical shape and a thin layer of ITZs surrounding the sphere. The relative volume of the ITZs in the mixture can be expressed as

$$10. \quad \frac{\varepsilon_{\text{ITZ}}}{\varepsilon_{\text{ITZ}} + \varepsilon_{\text{agg}}} = \frac{4\pi r^2 h}{4\pi r^2 h + (4\pi r^3/3)} = \frac{3h}{3h + r}$$

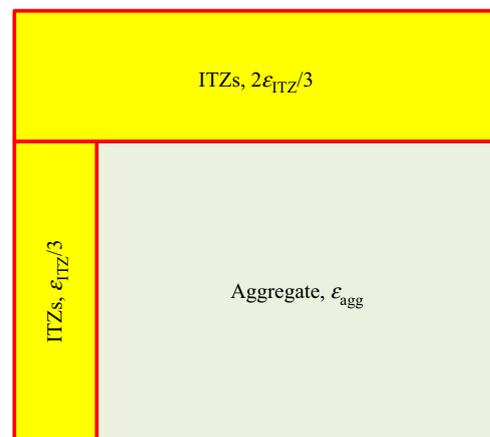


Figure 3. The two-phase model for the composite of aggregates and ITZs

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

where r is the radius of the aggregate and h is the thickness of the ITZs. This volume fraction can be applied to the representative elementary volume (REV) of aggregates and ITZs that involves a number of aggregates provided that r and h are taken as the average values for all aggregates involved in the REV. Substituting Equation 10 into 9 yields

$$11. \quad D_{\text{mix}} = \frac{2D_{\text{ITZ}}}{3 + r/h}$$

Figure 4 plots the variation of $D_{\text{mix}}/D_{\text{ITZ}}$ with r/h . It can be seen from the figure that the value of $D_{\text{mix}}/D_{\text{ITZ}}$ is much higher in the mixture of sands and ITZs composite than in the mixture of aggregates and ITZ composite. This probably explains why the diffusion coefficient of ions is greater in mortar than in concrete.

Note that if the aggregate is not in the isotropic shape, $\varepsilon_{1p} = 2\varepsilon_{\text{ITZ}}/3$ and $\varepsilon_{1s} = \varepsilon_{\text{ITZ}}/3$ will no longer hold, and the partial volumetric fractions ε_{1p} and ε_{1s} defined for the ITZs should be amended based on its actual shape.

Effective diffusion coefficients of ions in three-phase composite materials

Concrete is a composite material, consisting of aggregates, cement paste and ITZs, that requires the use of three-phase transport models. However, the aggregates, cement paste and ITZs in a real concrete are neither in parallel nor in series. This means that the modelling of ionic transport in concrete should use the combined series and parallel model. Note that the effective diffusion coefficient of ions in the mixture of aggregates and ITZs can be described using Equation 9 or 11. Therefore, the three-phase model of concrete can be simplified

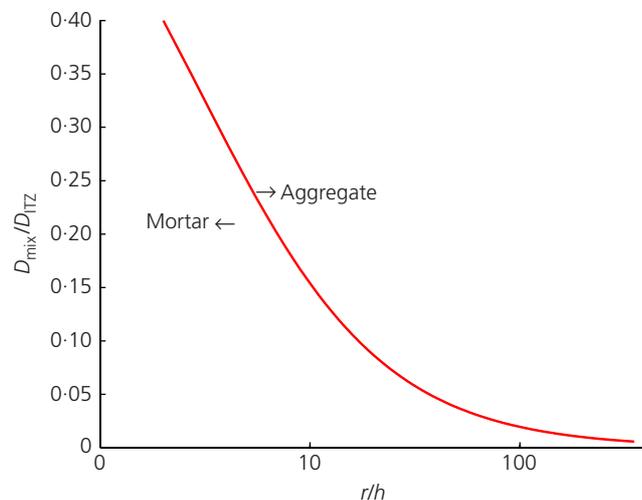


Figure 4. Variation of the diffusion coefficient in the composite of aggregates and ITZs with aggregate size

into the two-phase model, which consists of a cement paste phase and a mixed aggregate and ITZ phase. Let $\varepsilon_{1p} = k\varepsilon_{\text{cem}}$, $\varepsilon_{1s} = (1-k)\varepsilon_{\text{cem}}$, and $D_1 = D_{\text{cem}}$, where ε_{cem} is the volumetric fraction of the cement paste phase, D_{cem} is the effective diffusion coefficient of ions in the cement paste and k is a shape factor. If individual aggregates are assumed to be isolated, then $\varepsilon_{2p} = 0$, $\varepsilon_{2s} = \varepsilon_{\text{agg}} + \varepsilon_{\text{ITZ}}$ and $D_2 = D_{\text{mix}}$. Note that $\varepsilon_{\text{cem}} + \varepsilon_{\text{agg}} + \varepsilon_{\text{ITZ}} = 1$. Hence, Equation 8 can be expressed as

$$12. \quad D_{\text{con}} = k\varepsilon_{\text{cem}}D_{\text{cem}} + \frac{(1-k\varepsilon_{\text{cem}})^2 D_{\text{cem}} D_{\text{mix}}}{(1-k)\varepsilon_{\text{cem}}D_{\text{mix}} + (1-\varepsilon_{\text{cem}})D_{\text{cem}}}$$

where D_{con} is the bulk effective diffusion coefficient of ions in concrete.

The shape factor k is dependent on the shape of aggregates and the dimension used in the model. If the aggregates are assumed to have an isotropic shape, then k depends on only the dimensions. For example, in the two-dimensional model (2D) the thicknesses of the vertical and horizontal panels representing the cement paste should be identical (Figure 5) for the isotropic shape of aggregates. Therefore $\varepsilon_{1p} = 1t = k\varepsilon_{\text{cem}}$ and $\varepsilon_{1s} = (1-t)t = (1-k)\varepsilon_{\text{cem}}$, where t is the width of the ε_{cem} panels, from which the expression

$$13. \quad k = k_2 = \frac{1}{1 + \sqrt{1 - \varepsilon_{\text{cem}}}} \approx \frac{1 + \varepsilon_{\text{cem}}^2}{2}$$

can be obtained. Similarly, in the three-dimensional (3D) isotropic shape model the shape factor can be calculated from the volumes of ε_{1p} and ε_{1s} , and can be expressed as

$$14. \quad k = k_3 = \frac{1 + (1 - \varepsilon_{\text{cem}})^{1/3}}{1 + (1 - \varepsilon_{\text{cem}})^{1/3} + (1 - \varepsilon_{\text{cem}})^{2/3}} \approx \frac{2}{3 - \varepsilon_{\text{cem}}}$$



Figure 5. Relationship between volumetric fractions in the parallel and series zones in a 2D isotropic shape model

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

where k_2 and k_3 represent the shape factor in the 2D and 3D problems, respectively. Figure 6 and Figure 7 show detailed comparisons of the bulk diffusion coefficients calculated from the developed combined series and parallel model, the 3D n -phase spherical model (Caré and Hervé, 2004) and the 2D three-phase circular model (Zheng and Zhou, 2007). Note that for the 2D model, the prefactor '2/3' in Equation 9 needs to be replaced with '1/2' because all phases have an identical dimensional length in the direction normal to the 2D plane. It is evident from the results shown in Figure 6 and Figure 7 that

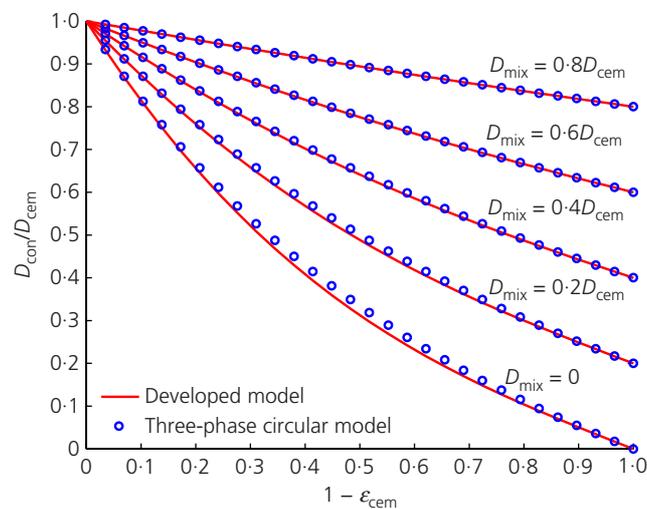


Figure 6. Comparison of diffusion coefficients between the combined series and parallel model and the 2D three-phase circular model

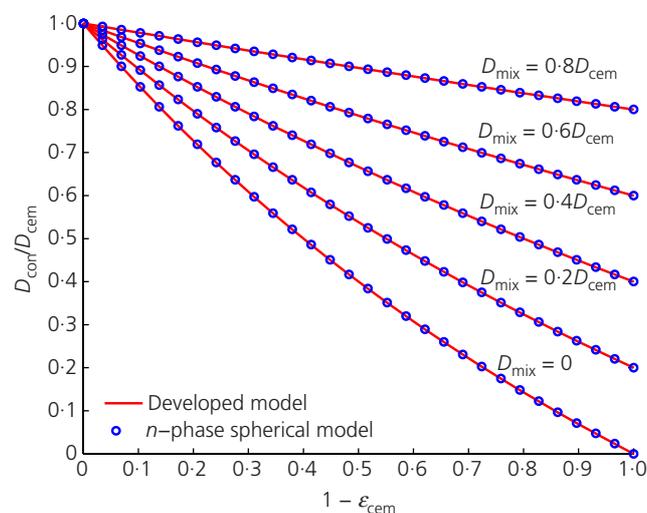


Figure 7. Comparison of diffusion coefficients between the combined series and parallel model and the 3D n -phase spherical model

the developed model agrees very well with both the 2D circular and 3D spherical models. However, the benefit of using the developed model is obvious, since it creates further options for investigating the shape factor effect of aggregates on ionic diffusion in concrete. For instance, if the aggregate is elliptical in shape then k_2 and k_3 will depend on the lengths of the major and minor axes of the ellipse.

Furthermore, if the diffusion of ions in ITZs is ignored, then Equation 12 with the shape factor defined by Equation 14 reduces to

$$15. \quad D_{\text{con}} = \frac{2\epsilon_{\text{cem}}D_{\text{cem}}}{3 - \epsilon_{\text{cem}}}$$

This is the result of the effective diffusion coefficient of ions in a composite material where the solid grains are considered as spherical inclusions in a fluid phase of $\phi = \epsilon_{\text{cem}}$ (Dormieux and Lemarchand, 2000; Garboczi, 1990; Van Brakel and Heetjes, 1974). Equation 15 indicates that $D_{\text{con}}/D_{\text{cem}}$ is proportional to ϵ_{cem} and $2/(3 - \epsilon_{\text{cem}})$. The former reflects the effect of porosity, whereas the latter represents the effect of tortuosity. The latter is also demonstrated by the curve shown in Figure 6 or Figure 7 with $D_{\text{mix}} = 0$, where the predicted value is marginally below the diagonal line defined by the two points (0, 0) to (1, 1).

Figure 6 and Figure 7 also highlight the effect of the high diffusivity of ITZs on the ratio $D_{\text{con}}/D_{\text{cem}}$. As D_{mix} increases, not only does $D_{\text{con}}/D_{\text{cem}}$ increase, but also the effect of tortuosity on $D_{\text{con}}/D_{\text{cem}}$ becomes small.

Numerical validation

To further demonstrate the model developed above, both 2D and 3D numerical simulations were undertaken (Feng *et al.*, 2016; Liu *et al.*, 2012, 2014, 2015a, 2015b). In the 2D model, a concrete plane of 50 mm \times 50 mm was considered, consisting of impermeable circular aggregates, ITZs surrounding aggregates, and a cement paste matrix phase. Analyses were carried out for concrete with different volume fractions of aggregates under steady-state conditions, in which the concentration boundary conditions were specified at $x=0$ mm and $x=50$ mm, and zero flux boundary conditions were specified at $y=0$ mm and $y=50$ mm. The bulk effective diffusion coefficient of the concrete was obtained based on the flux calculated at the boundary $x=50$ mm, the principle of which is exactly the same as that performed in the steady-state diffusion test. In the 3D model, a concrete cube of 50 mm \times 50 mm \times 50 mm was analysed, which also consisted of spherical aggregates, ITZs surrounding the aggregates, and a cement paste matrix phase. Analyses were carried out for the concrete cube with different volume fractions of aggregates under steady-state conditions. The concentration boundary conditions were specified at surfaces of $x=0$ mm and $x=50$ mm, and zero flux

Offprint provided courtesy of www.icevirtuallibrary.com
 Author copy for personal use, not for distribution

boundary conditions were specified at surfaces $y=0$ mm, $y=50$ mm, $z=0$ mm and $z=50$ mm. The bulk effective diffusion coefficient of the concrete cube was obtained based on the flux calculated at the surface $x=500$ mm. Figure 8 and Figure 9 show the geometrical models of the 2D and 3D simulations employed therein. Figure 10 and Figure 11 show detailed comparisons of the analytical solutions with the

numerical solutions obtained from the 2D and 3D models, and with experimental data obtained from chloride migration tests in mortars with a water-to-cement ratio of 0.35 (Yang and Wong, 2013). It can be seen from the figures that in both the 2D and 3D cases the predictions are in good agreement with the numerical data and/or experimental data. This demonstrates that the developed model is rational and suitable for calculating the bulk effective diffusion coefficient of chloride ions in concrete based on the volumetric fractions, and the diffusion coefficients of ions in individual components in the concrete.

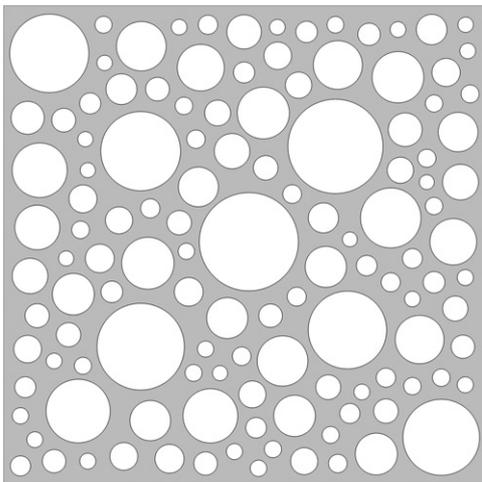


Figure 8. The numerical simulation model of ionic transport in 2D problems (the radius of the aggregates varies from 0.5 to 3.5 mm)

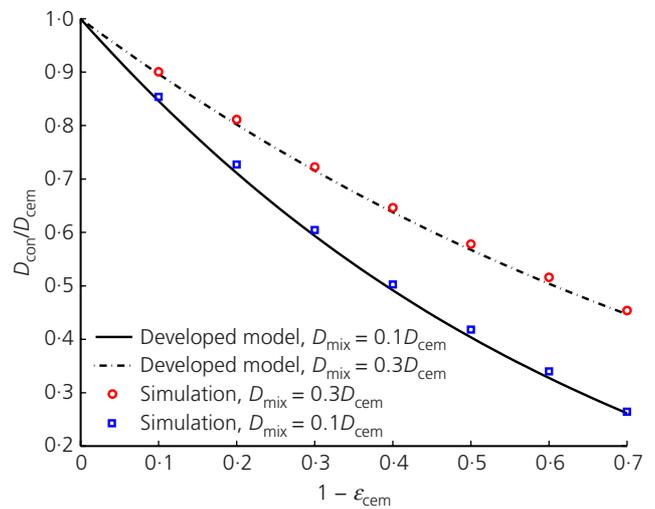


Figure 10. Comparison of diffusion coefficients between the combined series and parallel model and the 2D simulation model

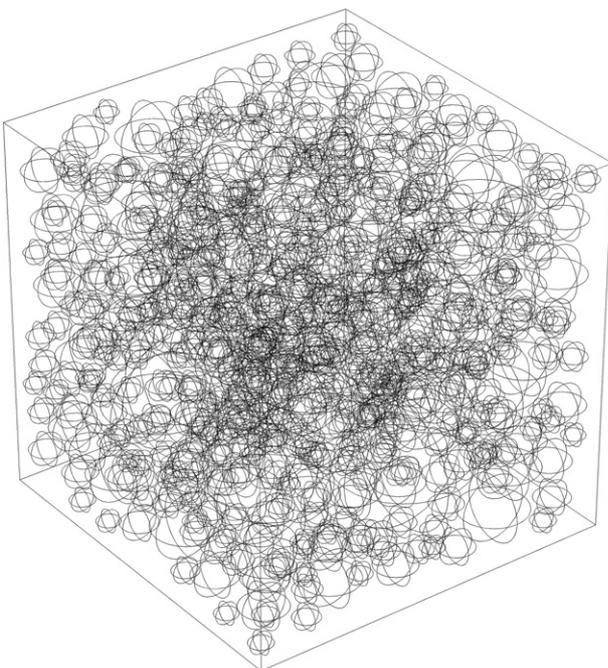


Figure 9. The numerical simulation model of ionic transport in 3D problems (the radius of the aggregates varies from 0.5 to 3.0 mm)

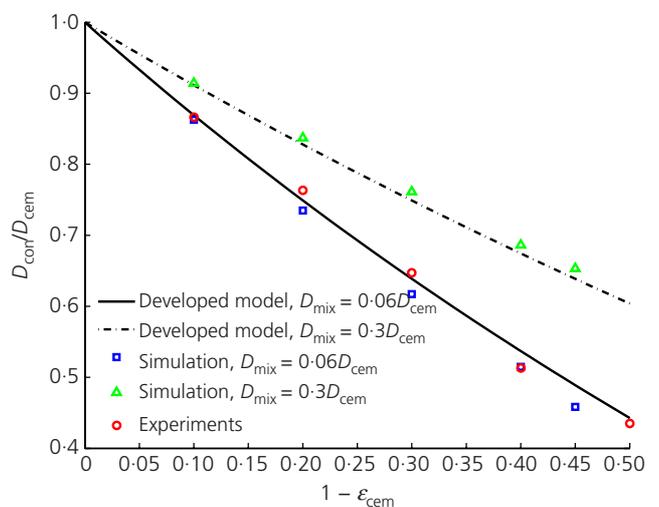


Figure 11. Comparison of diffusion coefficients between the combined series and parallel model and the 3D simulation model and experimental data (the experimental value of D_{cem} is $7.8 \times 10^{-12} \text{ m}^2/\text{s}$)

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

Diffusivity of concrete

It should be noted that the diffusion coefficient used in the diffusion equation under transient conditions (i.e. Fick second law) is not the effective diffusion coefficient but the apparent diffusion coefficient. These two different diffusion coefficients are linked by the volumetric water content as

$$16. \quad D_{\text{eff}} = \phi D_{\text{app}}$$

where D_{eff} is the effective diffusion coefficient, D_{app} is the apparent diffusion coefficient and ϕ is the volumetric water content of the porous material. Note that both D_{eff} and D_{app} include the effect of material tortuosity on ionic transport, and thus this is excluded in Equation 16. If there is no ionic reaction involved, then the apparent diffusion coefficient gives a measure of the amount of ions passing through unit area of pore solution in unit time, whereas the effective diffusion coefficient gives a measure of the amount of ions passing through unit area of concrete in unit time. Since the transport of ions can occur only in the pore solution, we are more interested in the apparent diffusion coefficient. Let ϕ_{cem} and ϕ_{ITZ} be the porosities of the cement paste and ITZs, respectively. Thus, the ratio of the apparent diffusion coefficients of ions in concrete and in cement can be expressed as

$$17. \quad \left(\frac{D_{\text{con}}}{D_{\text{cem}}}\right)_{\text{app}} = \frac{\phi_{\text{cem}}}{\phi_{\text{cem}}\varepsilon_{\text{cem}} + \phi_{\text{ITZ}}\varepsilon_{\text{ITZ}}} \left(\frac{D_{\text{con}}}{D_{\text{cem}}}\right)_{\text{eff}} \\ \approx \frac{1}{\varepsilon_{\text{cem}}} \left(\frac{D_{\text{con}}}{D_{\text{cem}}}\right)_{\text{eff}}$$

It can be seen from Equation 17 that $(D_{\text{con}}/D_{\text{cem}})_{\text{app}}$ is approximately proportional to $(D_{\text{con}}/D_{\text{cem}})_{\text{eff}}$ but inversely proportional to the cement paste volumetric fraction. Therefore, although $(D_{\text{con}}/D_{\text{cem}})_{\text{eff}}$ decreases with the increased aggregate volumetric fraction as demonstrated in Figure 6 and Figure 7, $(D_{\text{con}}/D_{\text{cem}})_{\text{app}}$ may not necessarily exhibit the same feature. Substituting Equations 12 and 14 into 17 yields

$$18. \quad \left(\frac{D_{\text{con}}}{D_{\text{cem}}}\right)_{\text{app}} = \frac{1}{3 - \varepsilon_{\text{cem}}} \left(2 + \frac{9(1 - \varepsilon_{\text{cem}})D_{\text{mix}}^*}{(3 - \varepsilon_{\text{cem}})\varepsilon_{\text{cem}} + \varepsilon_{\text{cem}}^2 D_{\text{mix}}^*}\right)$$

where $D_{\text{mix}}^* = D_{\text{mix}}/D_{\text{cem}}$. Note that if $(D_{\text{con}}/D_{\text{cem}})_{\text{app}} < 1$ held, then the addition of aggregates in concrete would reduce the diffusivity of the concrete. Of particular interest is the critical case of $(D_{\text{con}}/D_{\text{cem}})_{\text{app}} = 1$. Solve Equation 18 for the critical case, yielding

$$19. \quad D_{\text{mix}}^{\text{cr}} = \frac{\varepsilon_{\text{cem}} D_{\text{cem}}}{3 + \varepsilon_{\text{cem}}}$$

where $D_{\text{mix}}^{\text{cr}}$ is the critical value of the effective diffusion coefficient of ions in the mixed aggregates and ITZ composite. Equation 19 indicates that if the effective diffusion coefficient

of ions in the mixed aggregates and ITZ composite is greater than this critical value, then the addition of aggregates to concrete will increase the diffusivity of the concrete. Otherwise, concrete diffusivity will reduce. The former is due to the large diffusion coefficient of ions in the ITZs, which exceeds the tortuosity effect of aggregates on ionic diffusion, while in the latter the tortuosity effect of added aggregates exceeds the effect of the ITZs. As indicated by Equation 9, the effective diffusion coefficient of ions in the mixed aggregates and ITZ composite is dependent on the relative volume fraction of ITZs in the composite and the effective diffusion coefficient of ions in the ITZs. The reported values of $D_{\text{ITZ}}/D_{\text{cem}}$ in the literature are in the range 5–10 (Liu *et al.*, 2015a; Yang and Weng 2013; Ying *et al.*, 2013; Zheng and Zhou, 2007). If, for example, $D_{\text{ITZ}}/D_{\text{cem}} = 5$, $\varepsilon_{\text{cem}} = 0.3$ and $h = 20 \mu\text{m}$ are used, the estimated critical radius of aggregates obtained from Equations 11 and 19 is 2.54 mm. This indicates that the increase in the volume of aggregates will lead to an increase in the apparent diffusion coefficient (but not the effective diffusion coefficient), provided that the size of the aggregates is less than 2.54 mm.

Note that the developed model does not consider directly the ageing effect of concrete on chloride diffusion. It has been reported in the literature that chloride diffusion decreases with concrete age (Maheswaran and Sanjayan, 2004). The ageing effect on chloride diffusion could be due to many factors, including both physical and chemical aspects. Although some physical aspects such as porosity and tortuosity could be included in the developed model, a full consideration of the ageing effect must also include chemical aspects such as ionic interactions, which is beyond the scope of the present study.

Conclusions

This paper has presented a combined series and parallel multi-phase transport model for predicting chloride penetration in concrete. By treating the concrete as a composite consisting of aggregates, ITZs and cement paste, an analytical expression for calculating the effective diffusion coefficient of chloride ions in concrete was derived. Using the model, the effects of aggregates and the corresponding ITZs on chloride diffusion in concrete and mortar were examined. Comparisons of the developed model with other models published in the literature and with experimental and numerical data were also undertaken. The following conclusions can be drawn from this study.

- Comparisons of the developed model with other models published in the literature and with experimental and numerical data demonstrated that the developed model is rational and suitable for calculating the chloride diffusion coefficient in concrete.
- The use of combined series and parallel models can accurately describe the transport behaviour of ions in multi-phase composite materials.

Offprint provided courtesy of www.icevirtuallibrary.com
 Author copy for personal use, not for distribution

- The dimension employed to model the transport of ions in a multi-phase composite material may affect the simulation results. Thus, caution is required, particularly when using a 2D computer model to simulate a 3D experiment.
- The effects of ITZs and aggregates on chloride diffusion in concrete can be examined effectively by using the developed analytical solution for the effective diffusion coefficients.
- Concrete diffusivity should be assessed based on the apparent diffusion coefficient. There is a critical value for the effective diffusion coefficient of ions in mixed aggregates and ITZ composite that will indicate whether the addition of aggregates in concrete will increase concrete diffusivity.

Acknowledgements

This work was supported by the European Union Research Council via a research grant (FP7-PEOPLE-2011-IRSES-294955) and the Chinese National Natural Science Foundation (grant 51508324, 51520105012 and 51278303).

REFERENCES

- Andrade C, Castellote M and d'Andrea R (2011) Measurement of ageing effect on chloride diffusion coefficients in cementitious matrices. *Journal of Nuclear Materials* **412(1)**: 209–216.
- Andrade C, Prieto M, Tanner P, Tavares F and d'Andrea R (2013) Testing and modelling chloride penetration into concrete. *Construction and Building Materials* **39**: 9–18.
- Atkinson A and Nickerson AK (1984) The diffusion of ions through water-saturated cement. *Journal of Materials Science* **19(9)**: 3068–3078.
- Audenaert K, Yuan Q and De Schutter G (2010) On the time dependency of the chloride migration coefficient in concrete. *Construction and Building Materials* **24(3)**: 396–402.
- Baroghel-Bouny V, Wang X, Thierry M, Saillio M and Barberon F (2012) Prediction of chloride binding isotherms of cementitious materials by analytical model or numerical inverse analysis. *Cement and Concrete Research* **42(9)**: 1207–1224.
- Bentz DP and Garboczi EJ (1991) Percolation of phases in a three-dimensional cement paste microstructural model. *Cement and Concrete Research* **21(2–3)**: 325–344.
- Bentz DP, Garboczi EJ and Lagergren ES (1998) Multi-scale microstructural modeling of concrete diffusivity: identification of significant variables. *Cement and Concrete Composites* **20(1)**: 129–139.
- Bentz DP, Jensen OM, Coats AM and Glasser FP (2000) Influence of silica fume on diffusivity in cement-based materials, I. experimental and computer modeling studies on cement pastes. *Cement and Concrete Research* **30(6)**: 953–962.
- Bourdette B, Ringot E and Ollivier JP (1995) Modeling of the transition zone porosity. *Cement and Concrete Research* **25(4)**: 741–751.
- Byung HO and Seung YJ (2004) Prediction of diffusivity of concrete based on simple analytical equations. *Cement and Concrete Research* **34(3)**: 463–480.
- Caré S (2003) Influence of aggregates on chloride diffusion coefficient into mortar. *Cement and Concrete Research* **33(7)**: 1021–1028.
- Caré S and Hervé E (2004) Application of a *n*-phase model to the diffusion coefficient of chloride in mortar. *Transport Porous Media* **56(2)**: 119–135.
- Chen HJ, Huang SS, Tang CW, Malek MA and Ean LW (2012) Effect of curing environments on strength, porosity and chloride ingress resistance of blast furnace slag cement concretes: a construction site study. *Construction and Building Materials* **35**: 1063–1070.
- Delagrave A, Bigas JP, Ollivier JP, Marchand J and Pigeon M (1997) Influence of the interfacial zone on the chloride diffusivity of mortars. *Advanced Cement Based Materials* **5(3–4)**: 86–92.
- Dhir RK, Jones MR and Ng SLD (1998) Prediction of total chloride content profile and concentration/time-dependent diffusion coefficients for concrete. *Magazine of Concrete Research* **50(1)**: 37–48, <http://dx.doi.org/10.1680/macrc.1998.50.1.37>.
- Dormieux L and Lemarchand E (2000) Modélisation macroscopique du transport diffusif, apport des méthodes de changement d'espace. *Oil and Gas Science Technology – Revue d'IFP* **55(1)**: 15–34.
- Feng GL, Li LY, Kim B and Liu QF (2016) Multiphase modelling of ionic transport in cementitious materials. *Computational Materials Science* **111**: 339–349.
- Garboczi EJ (1990) Permeability, diffusivity and microstructural parameters: a critical review. *Cement and Concrete Research* **20(4)**: 591–601.
- Garboczi EJ and Bentz DP (1992) Computer simulation of the diffusivity of cement-based materials. *Materials Science* **27(8)**: 2083–2092.
- Garboczi EJ and Bentz DP (1997) Analytical formulas for interfacial transition zone properties. *Advanced Cement Based Materials* **6(3–4)**: 99–108.
- Garboczi EJ and Bentz DP (1998) Multiscale analytical/numerical theory of the diffusivity of concrete. *Advanced Cement Based Materials* **8(2)**: 77–88.
- Garboczi EJ, Schwartz LM and Bentz DP (1995) Modelling the influence of the interfacial zone on the conductivity and diffusivity of concrete. *Journal of Advanced Cement-Based Materials* **2(5)**: 169–181.
- Halamickova P, Detwiler RJ, Bentz DP and Garboczi EJ (1995) Water permeability and chloride ion diffusion in Portland cement mortars: relationship to sand content and critical pore diameter. *Cement and Concrete Research* **25(4)**: 790–802.

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

- Hobbs DW (1999) Aggregate influence on chloride ion diffusion into concrete. *Cement and Concrete Research* **29**(12): 1995–1998.
- Jiang LH, Song ZJ, Yang H, Pu Q and Zhu Q (2013) Modeling the chloride concentration profile in migration test based on general Poisson Nernst Planck equations and pore structure hypothesis. *Construction and Building Materials* **40**: 596–603.
- Li LY and Page CL (1998) Modelling of electrochemical chloride extraction from concrete: influence of ionic activity coefficients. *Computational Material Science* **9**(3–4): 303–308.
- Li LY and Page CL (2000) Finite element modelling of chloride removal from concrete by electrochemical method. *Corrosion Science* **42**(12): 2145–2165.
- Li LY, Xia J and Lin SS (2012) A multi-phase model for predicting the effective diffusion coefficient of chlorides in concrete. *Construction and Building Materials* **26**(1): 295–301.
- Liu QF, Li LY, Easterbrook D and Yang J (2012) Multi-phase modelling of ionic transport in concrete when subjected to an externally applied electric field. *Engineering Structures* **42**: 201–213.
- Liu QF, Xia J, Easterbrook D, Yang J and Li LY (2014) Three-phase modelling of electrochemical chloride removal from corroded steel-reinforced concrete. *Construction and Building Materials* **70**: 410–427.
- Liu QF, Easterbrook D, Yang J and Li LY (2015a) A three-phase, multi-component ionic transport model for simulation of chloride penetration in concrete. *Engineering Structures* **86**: 122–133.
- Liu QF, Yang J, Xia J et al. (2015b) A numerical study on chloride migration in cracked concrete using multi-component ionic transport models. *Computational Materials Science* **99**: 396–416.
- Liu YJ and Shi XM (2012) Ionic transport in cementitious materials under an externally applied electric field: finite element modelling. *Construction and Building Materials* **27**: 450–460.
- Maheswaran T and Sanjayan JG (2004) A semi-closed-form solution for chloride diffusion in concrete with time-varying parameters. *Magazine of Concrete Research* **56**(6): 359–366, <http://dx.doi.org/10.1680/mac.2004.56.6.359>.
- Mercado H, Lorente S and Bourbon X (2012) Chloride diffusion coefficient: a comparison between impedance spectroscopy and electrokinetic tests. *Cement and Concrete Composites* **34**(1): 68–75.
- Pack SW, Jung MS, Song HW, Kim SH and Ann KY (2010) Prediction of time dependent chloride transport in concrete structures exposed to a marine environment. *Cement and Concrete Research* **40**(2): 302–312.
- Page CL, Short NR and El-Tarras A (1981) Diffusion of chloride ions in hardened cement pastes. *Cement and Concrete Research* **11**(3): 395–406.
- Petcherdchoo A (2013) Time dependent models of apparent diffusion coefficient and surface chloride for chloride transport in fly ash concrete. *Construction and Building Materials* **38**: 497–507.
- Sergi G, Yu SW and Page CL (1992) Diffusion of chloride and hydroxyl ions in cementitious materials exposed to a saline environment. *Magazine of Concrete Research* **44**(158): 63–69, <http://dx.doi.org/10.1680/mac.1992.44.158.63>.
- Shane JD, Mason TO, Jennings HM, Garboczi EJ and Bentz DP (2000) Effect of the interfacial transition zone on the conductivity of Portland cement mortars. *Journal of the American Ceramic Society* **83**(5): 1137–1144.
- Spiesz P and Brouwers HJH (2012) Influence of the applied voltage on the rapid chloride migration (RCM) test. *Cement and Concrete Research* **42**(8): 1072–1082.
- Spiesz P and Brouwers HJH (2013) The apparent and effective chloride migration coefficients obtained in migration tests. *Cement and Concrete Research* **48**: 116–127.
- Spiesz P, Ballari MM and Brouwers HJH (2012) RCM: a new model accounting for the non-linear chloride binding isotherm and the non-equilibrium conditions between the free- and bound-chloride concentrations. *Construction and Building Materials* **27**(1): 293–304.
- Stanish K and Thomas M (2003) The use of bulk diffusion tests to establish time-dependent concrete chloride diffusion coefficients. *Cement and Concrete Research* **33**(1): 55–62.
- Su H, Yang J, Ling TC et al. (2015) Properties of concrete prepared with waste tyre rubber particles of uniform and varying sizes. *Journal of Cleaner Production* **91**: 288–296.
- Tang L and Gulikers J (2007) On the mathematics of time-dependent apparent chloride diffusion coefficient in concrete. *Cement and Concrete Research* **37**(4): 589–595.
- Van Brakel J and Heetjes PM (1974) Analysis of diffusion in macroporous media in terms of a porosity, a tortuosity and a constrictivity factor. *International Journal of Heat and Mass Transfer* **17**(9): 1093–1103.
- Xi Y and Bazant ZP (1999) Modeling chloride penetration in saturated concrete. *Journal of Materials in Civil Engineering* **11**(1): 58–65.
- Xia J and Li LY (2013) Numerical simulation of ionic transport in cement paste under the action of externally applied electric field. *Construction and Building Materials* **39**: 51–59.
- Yang CC (2004) The relationship between migration coefficient of chloride ions for concrete and charge passed in steady state using the accelerated chloride migration test. *ACI Materials Journal* **101**(2): 124–130.
- Yang CC and Su JK (2002) Approximate migration coefficient of interfacial transition zone and the effect of the aggregate

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

content on the migration coefficient of mortar. *Cement and Concrete Research* **32(10)**: 1559–1565.

Yang CC and Weng SH (2013) A three-phase model for predicting the effective chloride migration coefficient of ITZ in cement-based materials. *Magazine of Concrete Research* **65(3)**: 193–201, <http://dx.doi.org/10.1680/mac.12.00052>.

Ying JW, Xiao JZ, Shen LM and Bradford MA (2013) Five-phase composite sphere model for chloride diffusivity prediction of recycled aggregate concrete. *Magazine of Concrete*

Research **65(9)**: 573–588, <http://dx.doi.org/10.1680/mac.12.00180>.

Zheng JJ and Zhou XZ (2007) Prediction of the chloride diffusion coefficient of concrete. *Materials and Structures* **40(7)**: 693–701.

Zheng JJ, Zhou XX, Wu YF and Jin XX (2012) A numerical method for the chloride diffusivity in concrete with aggregate shape effect. *Construction and Building Materials* **31**: 151–156.

HOW CAN YOU CONTRIBUTE?

To discuss this paper, please submit up to 500 words to the editor at journals@ice.org.uk. Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editorial board, it will be published as a discussion in a future issue of the journal.