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Prediction of chloride diffusion coefficients in concrete using meso-scale multi-phase transport models

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Abstract – 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 is developed. The model explains how the shape of aggregates affects the chloride diffusion in concrete. By using the present model the effects of aggregates and corresponding ITZs on chloride diffusion in concrete and mortar are examined. Comparisons of the present model with other models published in literature, experimental and numerical data are also provided.

Keywords: chloride, concrete, diffusion-coefficient, aggregates, ITZs

1. Introduction

Corrosion of reinforcing steel due to chloride attack is the most significant threat to reinforced concrete structures, which 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, building and structures exposed to marine environments. To prevent the corrosion of reinforcing steel being induced by dissolved chloride ions, one has to know the mechanism of chloride penetration in concrete and the factors that affect the chloride penetration.

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 no 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 et al. 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 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 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 compositions 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 et al. 2012, Zheng and Zhou 2007). The popular analytical prediction models include the two-phase series and two-phase parallel models developed by Hobbs (Hobbs 1999), the two-phase spherical model developed by Xi and Bazant (Xi and Bazant 1999), and the n-phase spherical model developed by Caré and Hervé (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 the chloride diffusion by Zheng and Zhou (Zheng and Zhou 2007), Yang and Weng (Yang and Weng 2003), Ying et al. (Ying et al. 2013). In this paper a combined series and parallel multi-phase transport model is 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. The present model explains how the shape of aggregates and the model dimension affect the chloride diffusion in concrete. By using the present model the effects of aggregates and corresponding ITZs on chloride diffusion in concrete and mortar are examined. Comparisons of the present model with other models published in literature, experimental and numerical data are also provided.

2. 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 flux is expressed as follows,

$$J = -D\nabla C \quad (1)$$

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. Eq. (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 (see Fig. 1a). The other is the series model in which the two materials are assumed to be aligned in series (see Fig. 1b). 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 follows,

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

where ε_{upper} and ε_{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, C_l 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 be expressed in terms of the bulk effective diffusion coefficient of ions in the composite as follows,

$$J = -D_p \nabla C \quad (3)$$

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

$$D_p = \frac{\varepsilon_{upper}D_{upper} + \varepsilon_{lower}D_{lower}}{\varepsilon_{upper} + \varepsilon_{lower}} \quad (4)$$

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 follows,

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

where ε_{left} and ε_{right} are the volumetric fractions of the two materials, D_{left} and D_{right} are the effective diffusion coefficients of ions in the two materials, C_l and C_r are the concentrations of ions at the left and right boundaries of the specimen, 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 follows,

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

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

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

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

3. 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 materials. In reality, however, the transport of ions in a composite material may not exactly follow the series model or the parallel model. It is more likely to follow a combined series and parallel model as shown in Fig. 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 Fig. 2 can be expressed as follows,

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

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, 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 the dimensions used to model the transport of ions in the composite, which will be discussed in the subsequent sections.

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

It is understood from SEM analysis of concrete that a phase of ITZs of large pores exists around aggregates. The thickness of the ITZs varies from 20 to 50 μm and is compounded by anhydrous and hydrated cement. It has been reported that chloride ions diffuse much quicker in ITZs than in the bulk cement paste (Caré 2003, Delagrave et al., 1997, 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 uniaxial diffusion of ions, the aggregate together with ITZs surrounding it can be modelled as an isotropic shape composite shown in Fig. 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 $\varepsilon_{ITZ} \ll \varepsilon_{agg}$ one can assume $\varepsilon_{1p} = 2\varepsilon_{ITZ}/3$, $\varepsilon_{1s} = \varepsilon_{ITZ}/3$, $\varepsilon_{2p} = 0$, $\varepsilon_{2s} = \varepsilon_{agg}$, $D_1 = D_{ITZ}$ and $D_2 = D_{agg} = 0$, where ε_{agg} and ε_{ITZ} are the volumetric fractions of aggregates and ITZs, D_{agg} and D_{ITZ} are the diffusion coefficients of ions in aggregates and ITZs, respectively. By using Eq. (8) the overall effective diffusion coefficient of ions in the mixed aggregates and ITZs can be expressed as follows,

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

Eq. (9) can be also derived from the two-phase spherical model by using the assumption of $\varepsilon_{ITZ} \ll \varepsilon_{agg}$ (Caré and Hervé 2004, Xi and Bazant 1999). This indicates that if the composite is isotropic shape and the individual materials are uniformly distributed in the three directions of the material then the present model gives the same result as the spherical model does. Eq.

(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,

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

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 the r and h are taken as the average values for all aggregates involved in the REV. Substituting Eq. (10) into (9), it yields,

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

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

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

5. Effective diffusion coefficients of ions in three-phase composite materials

Concrete is a composite material, consisting of aggregates, cement paste, and ITZs, which 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 Eq. (9) or Eq. (11). Therefore the three-phase model of concrete can be simplified into the two-phase model which consists of a cement paste phase and a mixed aggregates and ITZs phase. Let $\varepsilon_{lp} = k\varepsilon_{cem}$, $\varepsilon_{ls} = (1-k)\varepsilon_{cem}$, and $D_1 = D_{cem}$, 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 $\varepsilon_{2p} = 0$, $\varepsilon_{2s} = \varepsilon_{agg} + \varepsilon_{ITZ}$, and $D_2 = D_{mix}$. Note that $\varepsilon_{cem} + \varepsilon_{agg} + \varepsilon_{ITZ} = 1$. Hence, Eq. (8) can be expressed as follows,

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

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 be in an isotropic shape then k depends on only the dimensions. For example, in the two-dimensional model the thicknesses of the vertical and horizontal panels representing the cement paste should be identical (see **Fig. 5**) for the

isotropic shape of aggregates. Therefore $\varepsilon_{lp} = 1t = k\varepsilon_{cem}$ and $\varepsilon_{ls} = (1-t)t = (1-k)\varepsilon_{cem}$ where t is the width of the ε_{cem} panels, from which the following expression can be obtained,

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

Similarly, in the 3-D isotropic shape model the shape factor can be calculated from the volumes of ε_{lp} and ε_{ls} and can be expressed as

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

where k_2 and k_3 represent the shape factor k in 2-D and 3-D problems, respectively. Fig. 6 and 7 show the detailed comparisons of the bulk diffusion coefficients calculated from the present combined series and parallel model, the 3-D n-phase spherical model (Caré and Hervé 2004) and the 2-D three-phase circular model (Zheng and Zhou 2007). Note that for the 2-D model the prefactor “2/3” in Eq. (9) need be replaced with “1/2” because all phases have an identical dimensional length in the direction normal to the 2-D plain. It is evident from the results shown in Figs. 6 and 7 that the present model agrees very well with both the 2-D circular and 3-D spherical models. However, the benefit of using the present model is obvious since it creates further options for investigating the shape factor effect of aggregates on the ionic diffusion in concrete. For instance, if the aggregate is ellipsis shape then 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 Eq. (12) with the shape factor defined by Eq. (14) reduces to

$$D_{con} = \frac{2\varepsilon_{cem}D_{cem}}{3 - \varepsilon_{cem}} \quad (15)$$

This is the result of the effective diffusion coefficient in a composite material where the solid grains are considered as spherical inclusions in a fluid phase of $\phi = \varepsilon_{cem}$ (Dormieux and Lemarchand 2000, Garboczi 1990, Van Brakel and Heetjes 1974).

6. Numerical validation

To further demonstrate the model described above both 2-D and 3-D numerical simulations are performed (Liu et al. 2012, 2014, 2015a, 2015b). In the 2-D model a plain concrete of 50 mm x 50 mm is considered, which consists of impermeable circular aggregates, ITZs surrounding aggregates, and a cement paste matrix phase. Analyses are carried out for the concrete with different volume fractions of aggregates under a steady state case, in which the concentration boundary conditions are specified at $x = 0$ mm and $x = 50$ mm and zero flux boundary conditions are specified at $y = 0$ mm and $y = 50$ mm. The bulk effective diffusion coefficient of the concrete is 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 3-D model a concrete cube of 50 mm x 50 mm x 50 mm is analysed, which also consists of spherical aggregates, ITZs surrounding the aggregates, and a cement paste matrix phase. Analyses are carried out for the concrete cube with different volume fractions of aggregates under a steady state case. The concentration boundary conditions are specified at surfaces of $x = 0$ mm and $x = 50$ mm and zero flux boundary conditions are 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 is obtained based on the flux calculated at the surface $x = 500$ mm. **Figs. 8** and **9** display the geometrical models of the 2-D and 3-D simulations employed herein. **Figs. 10** and **11** show the detailed comparisons of the present analytical solutions with the numerical solutions obtained from the 2-D and 3-D models, and the experimental data obtained from the chloride migration tests in mortars (Yang and Weng 2013). It can be seen from the figures that in both the 2-D and 3-D cases the present predictions are in good agreement with the numerical data and/or experimental data. This demonstrates that the present 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.

7. 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 follows,

$$D_{eff} = \phi D_{app} \quad (16)$$

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 it is excluded in Eq. (16). If there is no ionic reaction involved, then the apparent diffusion coefficient gives the measure of amount of ions pass through unit area of pore solution in unite time; whereas the effective diffusion coefficient gives the measure of amount of ions pass through unit area of concrete in unite time. Since the transport of ions can occur only in the pore solution one is more interested in the apparent diffusion coefficient. Let ϕ_{cem} and ϕ_{ITZ} be the porosities of the cement paste and ITZs. Thus the ratio of the apparent diffusion coefficients of ions in concrete and in cement can be expressed as follows,

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

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

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

where $D_{mix}^* = D_{mix}/D_{cem}$. It is obvious that if $(D_{con}/D_{cem})_{app} < 1$ holds then the addition of aggregates in concrete will reduce the diffusivity of the concrete. Of particular interest is the critical case of $(D_{con}/D_{cem})_{app} = 1$. Solve Eq. (18) for the critical case, yielding

$$D_{mix}^{cr} = \frac{3\varepsilon_{cem} D_{cem}}{3 + \varepsilon_{cem}} \approx \varepsilon_{cem} D_{cem} \quad (19)$$

where D_{mix}^{cr} is the critical value of the effective diffusion coefficient of ions in the mixed aggregates and ITZs composite. Eq. (19) indicates that if the effective diffusion coefficient of

ions in the mixed aggregates and ITZs composite is greater than this critical value, then the addition of aggregates in concrete will increase the diffusivity of concrete. Otherwise, the 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.

8. 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 is derived. By using the present model the effects of aggregates and corresponding ITZs on chloride diffusion in concrete and mortar are examined. Comparisons of the present model with other models published in literature, experimental and numerical data are also provided. From the present study the following conclusions can be drawn:

- Comparisons of the present model with other models published in literature, experimental and numerical data have demonstrated that the present model is rational and suitable for calculating the chloride diffusion coefficient in concrete.
- The use of combined series and parallel models can well describe the transport behaviour of ions in multi-phase composite materials.
- The dimension employed to model the transport of ions in a multi-phase composite material may affect the simulation results. Thus caution should be taken, particularly when one uses a 2-D computer model to simulate a 3-D experiment.
- The effects of ITZs and aggregates on the chloride diffusion in concrete can be examined effectively by using the present analytical solution for the effective diffusion coefficients.
- The concrete diffusivity should be assessed based on the apparent diffusion coefficient. There exists a critical value for the effective diffusion coefficient of ions in the mixed aggregates and ITZs composite, from which whether the addition of aggregates in concrete will increase the concrete diffusivity can be identified.

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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, A.K. (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., Thiery, 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, D.P. and Garboczi, E.J. (1991), "Percolation of phases in a three-dimensional cement paste microstructural model", *Cement and Concrete Research*, **21**(2-3), 325-344.
- Bentz, D.P., Garboczi, E.J. and Lagergren, E.S. (1998), "Multi-scale microstructural modeling of concrete diffusivity: identification of significant variables", *Cement and Concrete Composites*, **20** (1), 129-139.
- Bentz, D.P., Jensen, O.M., Coats, A.M. and Glasser, F.P. (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, J.P. (1995), "Modeling of the transition zone porosity", *Cement and Concrete Research*, **25**(4), 741-751.
- Byung, H.O. and Seung, Y.J. (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, H.J., Huang, S.S., Tang, C.W., Malek, M.A. and Ean, L.W. (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, J.P., Ollivier, J.P., 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, R.K., Jones, M.R. and Ng, S.L.D. (1998), "Prediction of total chloride content profile and concentration/time-dependent diffusion coefficients for concrete", *Magazine of Concrete Research*, **50**(1), 37-48.
- Dormieux, L. and Lemarchand, E. (2000), "Modélisation macroscopique du transport diffusif, apport des méthodes de changement d'espace", *Oil Gas Sci. Technol. – Rev. IFP*, **55**(1), 15-34.
- Garboczi, E.J. (1990), "Permeability, diffusivity and microstructural parameters: a critical review", *Cement and Concrete Research*, **20**(4), 591-601.
- Garboczi, E.J. and Bentz, D.P. (1992), "Computer simulation of the diffusivity of cement-based materials", *Materials Science*, **27**(8), 2083-2092.
- Garboczi, E.J. and Bentz, D.P. (1997), "Analytical formulas for interfacial transition zone properties", *Advanced Cement Based Materials*, **6**(3-4), 99-108.
- Garboczi, E.J. and Bentz, D.P. (1998), "Multiscale analytical/numerical theory of the diffusivity of concrete", *Advanced Cement Based Materials*, **8**(2), 77-88.
- Garboczi, E.J., Schwartz, L.M., Bentz, D.P. (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, R.J., Bentz, D.P. and Garboczi, E.J. (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.
- Hobbs, D.W. (1999), “Aggregate influence on chloride ion diffusion into concrete”, *Cement and Concrete Research*, **29**(12), 1995–1998.
- Jiang, L.H., Song, Z.J., 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, L.Y. and Page, C.L. (1998), “Modelling of electrochemical chloride extraction from concrete: influence of ionic activity coefficients”, *Computational Material Science*, **9**(3-4), 303-308.
- Li, L.Y. and Page, C.L. (2000), “Finite element modelling of chloride removal from concrete by electrochemical method”, *Corrosion Science*, **42**(12), 2145-2165.
- Li, L.Y., Xia, J. and Lin, S.S. (2012), “A multi-phase model for predicting the effective diffusion coefficient of chlorides in concrete”, *Construction and Building Materials*, **26**(1), 295-301.
- Liu, Q.F., Li, L.Y., 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, Q.F., Xia, J., Easterbrook, D., Yang, J. and Li, L.Y. (2014), “Three-phase modelling of electrochemical chloride removal from corroded steel-reinforced concrete”, *Construction and Building Materials*, **70**, 410–427.
- Liu, Q.F., Easterbrook, D., Yang, J. and Li, L.Y. (2015a), “A three-phase, multi-component ionic transport model for simulation of chloride penetration in concrete”, *Engineering Structures*, **86**, 122-133.
- Liu, Q.F., Yang, J., Xia, J., Easterbrook, D., Li, L.Y. and Lu, X.Y. (2015b), “A numerical study on chloride migration in cracked concrete using multi-component ionic transport models”, *Computational Materials Science*, **99**, 396–416.
- Liu, Y.J. and Shi, X.M. (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, J.G. (2004), “A semi-closed-form solution for chloride diffusion in concrete with time-varying parameters”, *Magazine of Concrete Research*, **56**(6), 359-366.
- 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, S.W., Jung, M.S., Song, H.W., Kim, S.H. and Ann, K.Y. (2010), “Prediction of time dependent chloride transport in concrete structures exposed to a marine environment”, *Cement and Concrete Research*, **40**(2), 302-312.
- Page, C.L., Short, N.R. 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, S.W. and Page, C.L. (1992), “Diffusion of chloride and hydroxyl ions in cementitious materials exposed to a saline environment”, *Magazine of Concrete Research*, **44**(158), 63-69.

- Shane, J.D., Mason, T.O., Jennings, H.M., Garboczi, E.J. and Bentz, D.P. (2000), “Effect of the interfacial transition zone on the conductivity of Portland cement mortars”, *American Ceramic Society*, **83**(5), 1137-1144.
- Spiesz, P., Ballari, M.M. and Brouwers, H.J.H. (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.
- Spiesz, P. and Brouwers, H.J.H. (2013), “The apparent and effective chloride migration coefficients obtained in migration tests”, *Cement and Concrete Research*, **48**, 116-127.
- Spiesz, P. and Brouwers, H.J.H. (2012), “Influence of the applied voltage on the rapid chloride migration (RCM) test”, *Cement and Concrete Research*, **42**(8), 1072-1082.
- 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.
- 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, P.M. (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, Z.P. (1999), “Modeling chloride penetration in saturated concrete”, *Journal of Materials in Civil Engineering*, **11**(1), 58–65.
- Xia, J. and Li, L.Y. (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, C.C. (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, C.C. and Su, J.K. (2002), “Approximate migration coefficient of interfacial transition zone and the effect of the aggregate content on the migration coefficient of mortar”, *Cement and Concrete Research*, **32**(10), 1559–1565.
- Yang, C.C. and Weng, S.H. (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.
- Ying, J.W., Xiao, J.Z., Shen, L.M. and Bradford, M.A. (2013), “Five-phase composite sphere model for chloride diffusivity prediction of recycled aggregate concrete”, *Magazine of Concrete Research*, **65**(9), 573-588.
- Zheng, J.J. and Zhou, X.Z. (2007), “Prediction of the Chloride Diffusion Coefficient of Concrete”, *Materials and Structures*, **40**(7), 693-701.
- Zheng, J.J., Zhou, X.X., Wu, Y.F. and Jin, X.X. (2012), “A numerical method for the chloride diffusivity in concrete with aggregate shape effect”, *Construction and Building Materials*, **31**, 151–156.

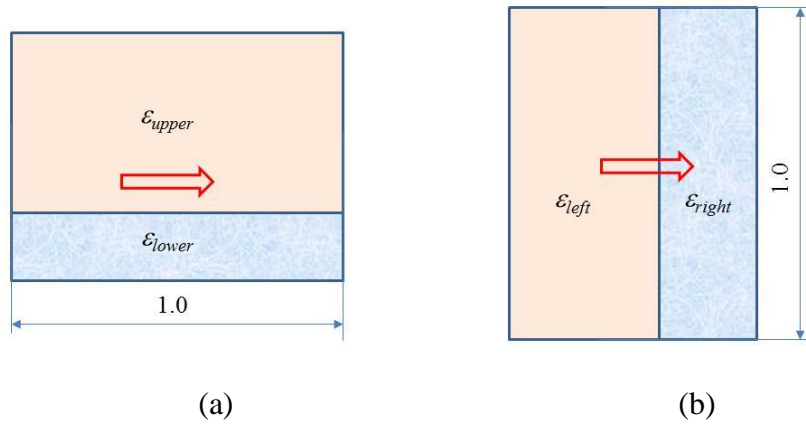


Figure 1. Two-phase ionic transport models. (a) The parallel and (b) series models.

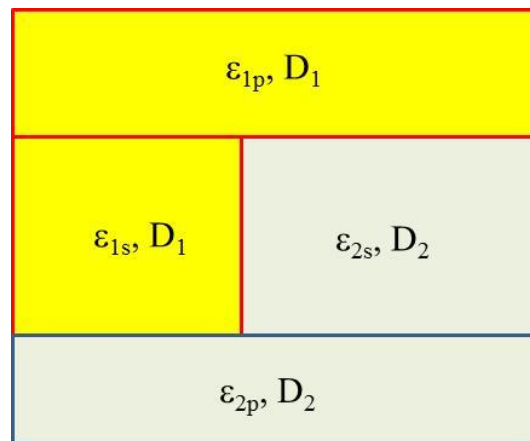


Figure 2. A combined series and parallel transport model.

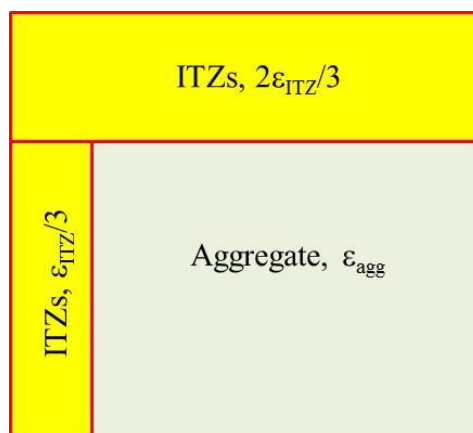


Figure 3. The two-phase model for the composite of aggregates and ITZs.

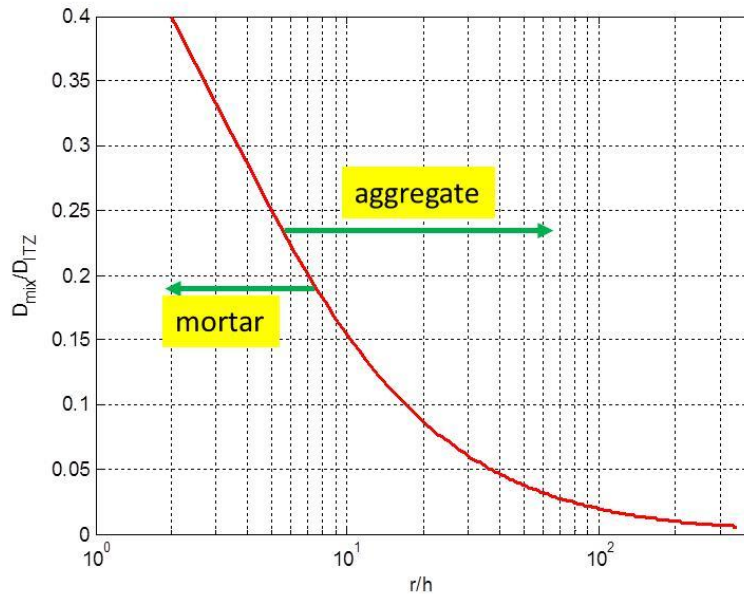


Figure 4. Variation of diffusion coefficient in the composite of aggregates and ITZs with aggregate size.

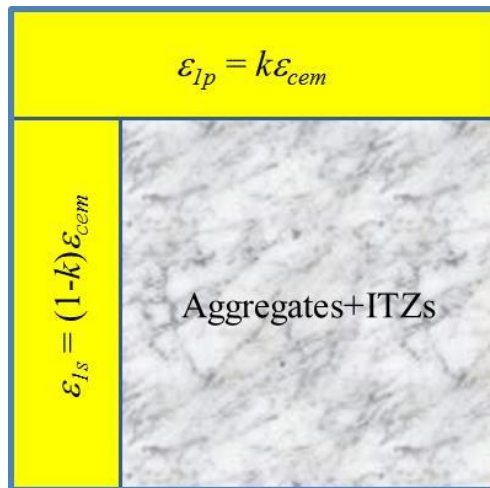


Figure 5. Relationship between volumetric fractions in the parallel and series zones in a 2-D isotropic shape model.

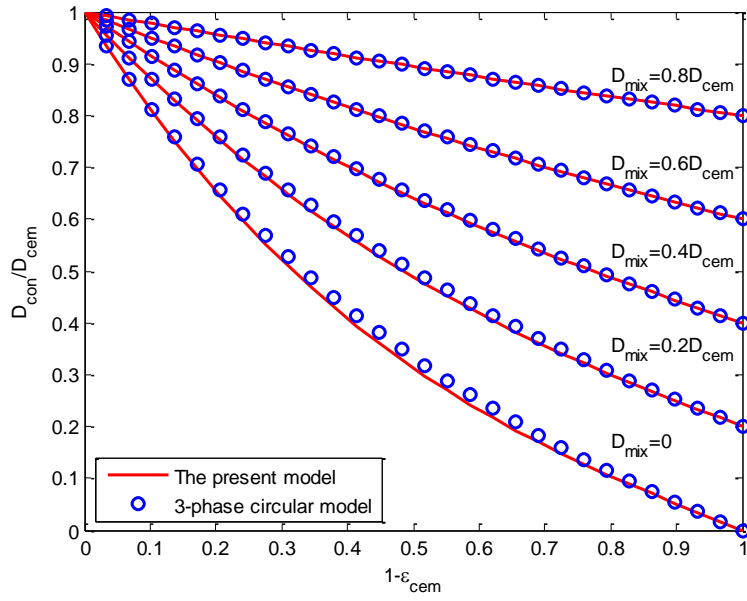


Figure 6. Comparison of diffusion coefficients between the combined series and parallel model and the 2-D three-phase circular model.

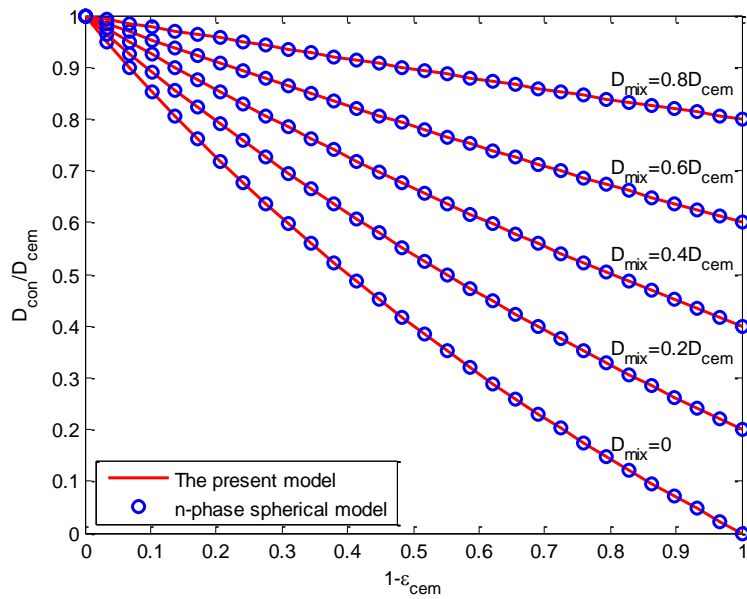


Figure 7. Comparison of diffusion coefficients between the combined series and parallel model and the 3-D n-phase spherical model.

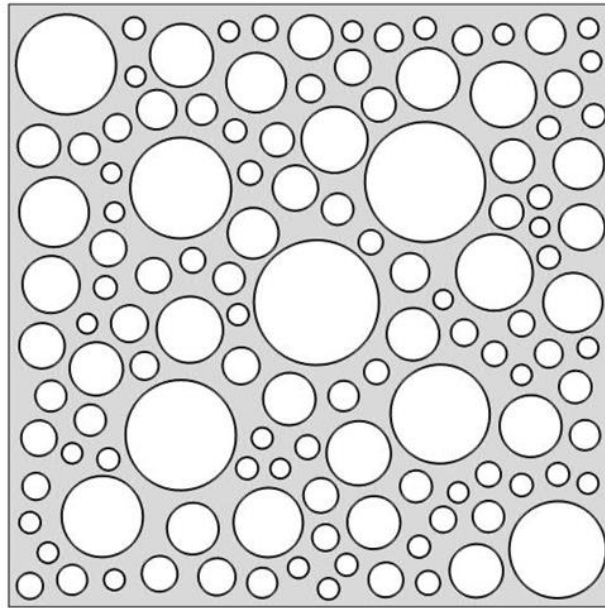


Figure 8. The numerical simulation model of ionic transport in two-dimensional problems (the radii of aggregates vary from 0.5 to 3.5 mm).

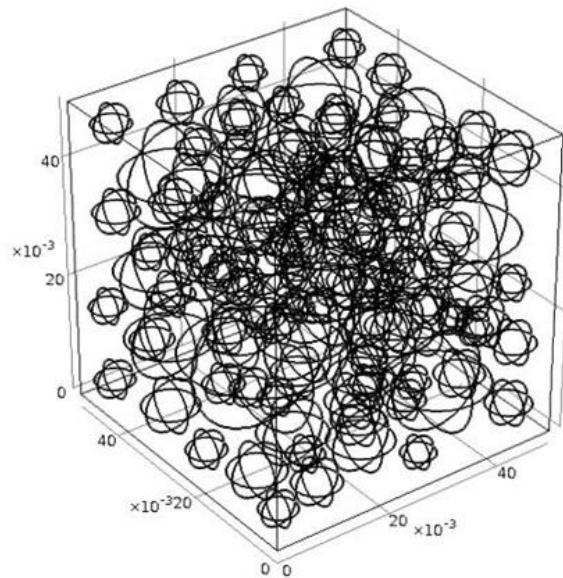


Figure 9. The numerical simulation model of ionic transport in three-dimensional problems (the radii of aggregates vary from 0.5 to 3.0 mm).

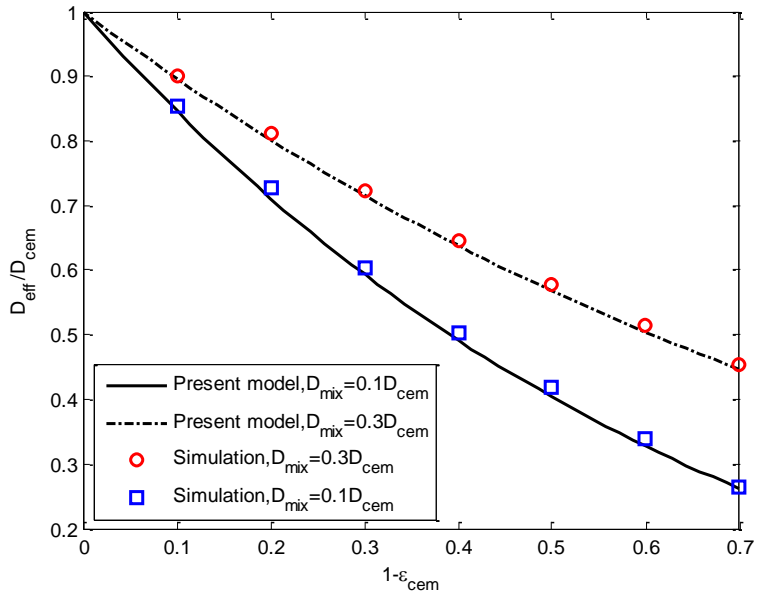


Figure 10. Comparison of diffusion coefficients between the combined series and parallel model and the 2-D simulation model.

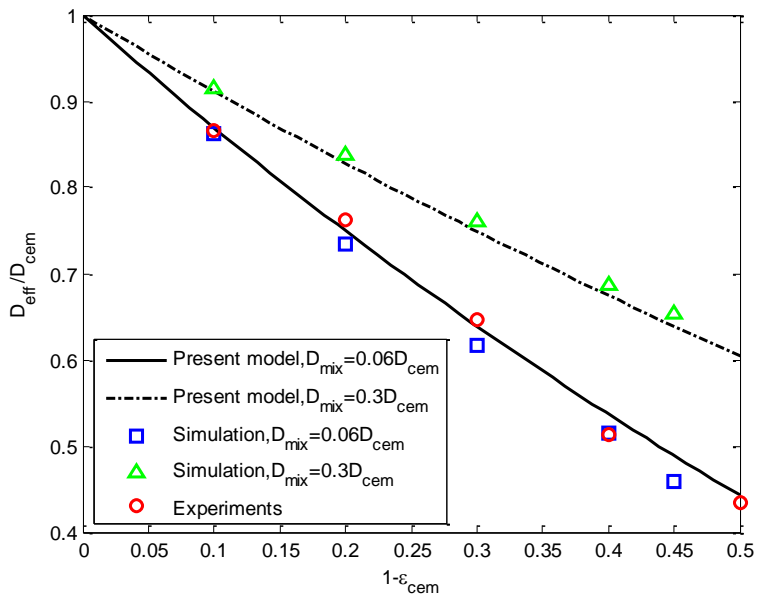


Figure 11. Comparison of diffusion coefficients between the combined series and parallel model and the 3-D simulation model and experimental data.