Available online at www.sciencedirect.com

ScienceDirect

Cement & Concrete Composites 29 (2007) 559–565

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Modeling of chloride diffusion in hetero-structured concretes by finite element method

Yanwei Zeng *

School of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China

Received 10 October 2005; received in revised form 24 September 2006; accepted 5 April 2007
Available online 14 April 2007

Abstract

With a two-dimensional structure model, the finite element method was used to simulate the chloride diffusion behavior in a heterogeneous concrete composed of two phases with distinct diffusivities, compared with its derived homogeneous medium that was given a single effective diffusion coefficient by the mean field theory. In contrast to the smooth chloride concentration profiles for the homogeneous medium, a three-dimensional concentration distribution network has been found in the hetero-structured concrete, characterized by a complicated band-like profile along the diffusion depth. Moreover, it features an undulating and narrowing width as the diffusion time and diffusion depth increase. The modeling results also manifest that the chloride diffusion in hetero-structured concretes appears to lag behind that for the homogeneous ones, showing an increasingly notable discrepancy between the two chloride concentration profiles as the diffusion proceeds. Nonetheless, such a concentration difference may be remarkably reduced when the chloride binding and time-reducing effect of diffusivity are supposed to happen within the cement paste phase of the hetero-structured concrete and its derived homogeneous medium.

Keywords: Chloride diffusion; Heterogeneous concrete; Modeling; Finite element method

1. Introduction

Chloride ion ingression and thereby induced reinforcement corrosion in steel-reinforced concretes have attracted much research interest due to their significance in the durability enhancement and service-life prediction of the concrete structures that are exposed to marine environments or de-icing salts. It has been well recognized that as one of the primary causes of structural deteriorations, chloride-induced corrosion of steel in concrete generally involves two stages: initiation of the corrosive reaction and the reaction's propagation. During the first stage, chlorides penetrate the concrete surface exposed to chloride-containing media and migrate progressively through the concrete cover layer to the steel reinforcement. When the chloride concentration at the surface of steel exceeds a certain threshold value, reinforcement corrosions may be provoked and then propagated on condition that adequate oxygen and moisture are present. Since the chloride-induced corrosion of steels usually results from the formation of iron hydroxide without continual consumption of chlorides, whether or not the chloride concentration around reinforcing steels reaches a corrosion-triggering level is mainly determined by chloride transport behavior in concrete, which is a rather complex nonlinear dynamic phenomenon involving several physical and chemical processes including ionic diffusion, liquid flow due to convection, capillary sorption, ionic dispersion and binding onto the hydration products of cements, etc [1–3].

In recent years, a wide range of experimental and theoretical researches have led to significant advances in the understanding of chloride transport in various concretes prepared from different cements or under different conditions or used in different circumstances [4–10]. It seems

---

* Tel.: +86 25 83587254; fax: +86 25 83588316.
E-mail address: zengyanwei@tom.com

0958-9465/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2007.04.003

that, however, few researches have ever been reported of the details of chloride diffusion behavior associated with structural heterogeneity of concretes composed of multiple phases with different chloride diffusivities. In some researches, the concretes were often consciously or unconsciously treated as homogeneous diffusion media and characterized by a single apparent value of diffusion coefficient [4,9,11,12]. Some other researches indeed took into account the influence of aggregates as well as interfacial phases formed between aggregates and cement paste on the chloride diffusion. Nonetheless, the use of a single effective diffusion coefficient determined by experimental measurements or theoretical considerations can only lead to an averaged description of the chloride diffusion and gives no particular details about the chloride concentration distribution in a real hetero-structured concrete [13,14], which should be practically useful for the better understanding of reinforcement corrosions in concretes. In this paper, the finite element method was utilized to simulate the chloride diffusion behavior in a hetero-structured model concrete comprising two phases: cement paste and aggregates, in an attempt to reveal the particulars of chloride diffusion in a hetero-structured concrete of multiple phases as against its derived homogeneous one by the mean field theory. The present work is not aimed to put forth a sophisticated model for chloride diffusion in real concretes, but is expected to enrich the understanding of chloride diffusion in real concretes with complex hetero-structures and help the establishment of more robust models for concrete service-life predictions.

2. Hetero-structure of concretes

It is well known that a real concrete belongs to the multi-phased heterogeneous materials. Its typical interior structure, as schematically illustrated in Fig. 1, is mainly composed of cement paste, aggregates and voids. The aggregates constitute a dense phase discretely and randomly distributed in a continuous cement paste matrix that actually contains numerous uniformly distributed nanosized gel pores and capillary pores [3]. Compared with the sizes of aggregates (usually larger than a few millimeters in diameter), however, all the pores in cement paste are so small and uniformly distributed that it can be usually regarded as a homogeneous phase for the evaluation of concrete's engineering properties. Therefore, a real concrete can be represented by a hetero-structure composed of two main phases: cement paste matrix and aggregates embedded in it. For a more comprehensive structural description, the interfacial phase formed between aggregate and paste matrix is the third phase to take into account. When the concrete of such a structure is saturated with water, all the pores in the paste matrix are full of water and a continuous porous medium for fast diffusion of chlorides is formed, with the chloride diffusivity mainly depending upon its porosity. In contrast, the aggregates within cement paste are usually of very poor diffusivity due to their dense rock structures [2,13] and, thus, great heterogeneities of chloride diffusion in such a system are generated.

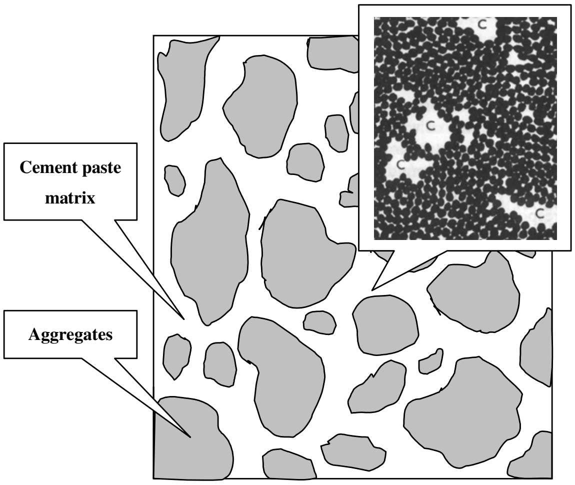

Fig. 1. Schematic illustration of typical interior structure of concrete. The inset: microstructure of cement paste, comprising gel particles, gel pores and capillary pores (marked with C).

To obtain a phenomenological description of the chloride diffusion in the above hetero-structural concrete, the usual method is to experimentally measure the chloride concentrations in the concrete specimens and then figure out an apparent value of diffusion coefficient in terms of Fick's law. This approach is theoretically analogous to a useful treatment based on the mean field theory [15] to calculate the effective diffusion coefficient for a two-phased concrete by the following formula:

$$D_{\text{eff}} = D_{\text{c}} \frac{D_{\text{a}} + K_{\text{a}} D_{\text{c}} + K_{\text{a}} \phi (D_{\text{a}} - D_{\text{c}})}{D_{\text{a}} + K_{\text{a}} D_{\text{c}} - \phi (D_{\text{a}} - D_{\text{c}})} \tag{1}$$

where D_{c} refers to the chloride diffusion coefficient of cement paste, D_{a} to that of aggregates, ϕ and K_{a} are, respectively, the volume fraction and the shape factor of the used aggregates. When the aggregates are spherically shaped and $D_{\text{a}} \ll D_{\text{c}}$, as in the usual case, $K_{\text{a}} = 2$ and then Eq. (1) may be simplified into:

$$D_{\text{eff}} = D_{\text{c}} \frac{2(1 - \phi)}{2 + \phi} \tag{2}$$

This approximation formula is identical with the one used by Sabine Care [11], where it served as a basic equation to take into account the additional contribution to D_{eff} from the interfacial phase. To achieve an accurate comparison, Eq. (1) was adopted in this paper to derive a homogeneous medium with a single effective chloride diffusion coefficient from the hetero-structural model concrete.

With the aim to reveal the particulars of chloride diffusion in a hetero-structural concrete, a simple two-dimensional and two-phased structure model was constructed and used in this paper. As schematically illustrated in Fig. 2, a rectangular plane dimensioned by 100 × 10 mm is supposed to be taken from a semi-infinite concrete body with its surface exposed to a chloride-containing medium.

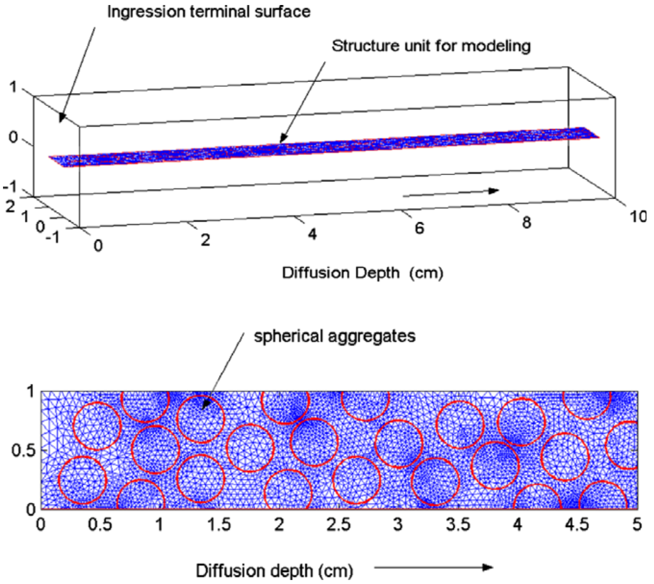

Fig. 2. Hetero-structure model of concrete for diffusion modeling. Upper: rectangular structure model and lower: meshed rectangle (half) with aggregates in it.

Table 1
Relevant parameters used for diffusion modeling

Parameter	Value
Maximum longitudinal diffusion depth	100 mm
Maximum local transverse diffusion distance	10 mm
Surface layer thickness	2 mm
Aggregate diameter	4 mm
Aggregate volumetric fraction	0.5027

It is assumed that the chloride diffusion is solely carried out inwards in the direction normal to the concrete surface, i.e., along the longitudinal direction of the model, while the possible local transverse diffusions due to the presence of structural heterogeneity are rather limited and confined within the dimension of the rectangle's short side in this paper. In the rectangular plane, the circular areas designate the cross-sections of aggregates in the concrete and the rest part represents the cement paste matrix. To imitate the macroscopic isotropy and homogeneity in the structure of a real concrete, 46 spheres with a diameter of 4 mm were randomly and uniformly distributed and positioned within the rectangle except in its front area with a depth of 2 mm, where no probability was taken into account for aggregates to occupy in the very surface layer of real concretes. Such a two-phased structure model is characterized by an equivalent volume fraction of aggregates, 0.5027, and the other geometric parameters, as given in Table 1.

3. PDEs for diffusion in hetero-structure

It is well known that the chloride transport in a porous medium containing water generally involves chloride ions diffusion in the medium as well as convection flow of water in the micro-pores, depending on the saturation degree and wetting–drying status of concrete. For a fully saturated concrete, chloride diffusion driven by the concentration gradient should be the dominant process for chloride migration and is determined by Fick's law with the following generic partial differential equation (PDE):

$$\frac{\partial C_\mathrm{t}}{\partial t} = D\vec{\nabla}^2 C_\mathrm{f} \tag{3}$$

where $\vec{\nabla}$ is the Laplace differential operator, D the chloride diffusion coefficient, C_t and C_f refer to the total concentration of chlorides and the concentration of free diffusing chlorides, respectively.

However, the chloride diffusion in cement paste is usually not a simple diffusion process but a mass transport accompanied by chloride dissipation along diffusion path due to the chloride binding onto the hydration products [16,17]. In addition, the microstructural fractality [18] and chemical evolution of the cement paste also causes a time-reduction of diffusion coefficient for the chlorides in cement paste matrix [11]. Taking into account these effects and assuming that the chloride diffusion coefficient is reduced as an exponential function of time [19,20]: $D \propto t^{-m}$ and the chloride binding to hydration products is entirely controlled by its thermodynamics, a specific PDE for chloride diffusion in cement paste for a two-dimensional system can be written as:

$$\frac{\partial C_\mathrm{f}}{\partial t} = \frac{D_{\mathrm{c}0}}{1+k}\left(\frac{t_0}{t}\right)^m \left[\frac{\partial^2 C_\mathrm{f}}{\partial x^2} + \frac{\partial^2 C_\mathrm{f}}{\partial y^2}\right] \tag{4}$$

where $D_{\mathrm{c}0}$ is the chloride diffusion coefficient of cement paste measured at the age of t_0, m is a time-reducting exponent describing how fast the diffusion coefficient reduces with time, and k is defined by $C_\mathrm{b} = kC_\mathrm{f}$, measuring the dependence of bound chloride concentration C_b on the free chloride concentration C_f. With reference to the published data related to the chloride diffusion in various concretes, the parameters involved in Eq. (4) for the diffusion profile modeling in this paper were evaluated as: $m = 0.5$, $k = 2$, $D_{\mathrm{c}28} = 2.5\ \mathrm{cm}^2/\mathrm{a}$, where $D_{\mathrm{c}28}$ is the chloride diffusion coefficient of the cement paste aged for 28 days. These evaluations are suitable for ordinary Portland cement pastes with a water/cement ratio of around 0.5 when the free chloride concentration is not very high [11,14,16,17,19,20].

In contrast, the aggregates in concrete are usually of homogeneous and dense microstructures, and no chloride binding is expected to occur. Therefore, the PDE for chloride diffusion within the aggregates should be:

$$\frac{\partial C_\mathrm{f}}{\partial t} = D_\mathrm{a}\left(\frac{\partial^2 C_\mathrm{f}}{\partial x^2} + \frac{\partial^2 C_\mathrm{f}}{\partial y^2}\right) \tag{5}$$

where D_a is the chloride diffusion coefficient of aggregates. In this paper, it was evaluated with $5 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{a}$, about two orders of magnitude smaller than $D_{\mathrm{c}28}$ to demonstrate the impact of the difference in chloride diffusivity on the chloride diffusion behavior in concrete. Obviously, it can be noted that the partial differential Eqs. (4) and (5) are mathematically of the same kind except for the different diffusion coefficients. The former holds a chloride diffusion coefficient as a function of time while the latter's diffusion coefficient is a constant. Accordingly, Eq. (5) may be applied to the homogeneous media with constant diffusivity, such as the cement paste when the chloride binding and time-reducing effect are not involved.

4. Modeling procedure

The present chloride diffusion modeling work was fulfilled using the PDE toolbox/MATLAB R13 based on the finite element method. In the modeling calculation, the rectangular plane was meshed into more than 16,000 triangles, giving an average distance between any two neighboring calculation points of around 0.3 mm. The relative and absolute tolerances for iteration control were set to be smaller than 0.001 and 0.0001, respectively. To fully understand the chloride diffusion behavior in the hetero-structural model concrete, the following four different cases have been studied:

1. The chloride concentration profiles in the homogeneous medium derived from the hetero-structured model concrete were simulated by Eq. (5), in which the effective diffusion coefficient $D_{\text{eff}} = 0.9973\ \text{cm}^2/\text{a}$ was determined from Eq. (1) by using $D_{\text{c28}} = 2.500\ \text{cm}^2/\text{a}$, $D_{\text{a}} = 5 \times 10^{-3}\ \text{cm}^2/\text{a}$ and $\phi = 0.5027$.
2. Eq. (5) was applied to both the cement paste matrix and the aggregates defined in the hetero-structural model with their respective diffusion coefficients in the corresponding domains. In this case, no chloride binding and time-reduction of diffusion coefficient were taken into account for the cement paste.
3. Eqs. (4) and (5) were applied, respectively, to the cement paste matrix and aggregates in the structural model. In this case, the chloride binding to hydration products of cement and the time-reduction of diffusion coefficient were included.
4. Eq. (4) was applied to the homogeneous medium with a single effective diffusion coefficient derived from the hetero-structural concrete with an assumption that the chloride binding and the time-reduction of diffusion coefficient also happen to the homogeneous concrete in the same manner as in the cement paste.

As the boundary and initial conditions for the modeling calculation, it was assumed for the above four cases that no chlorides were present initially inside the rectangle but a constant chloride concentration at the surface of concrete C_{s} was consistently maintained and thus, for convenience, a relative chloride concentration $C_{\text{f}}/C_{\text{s}}$ was used to describe chloride concentration profiles. In addition, during the whole diffusion no chlorides were allowed to migrate across the longitudinal sides of the structure model due to the limited local transverse diffusion, as mentioned above. As to the boundary conditions for the rectangle's far short edge, the following equation was used with D_{eff} being the averaged chloride diffusion coefficient:

$$[\vec{\nabla} C_{\text{f}}]_{\text{b}} = \frac{\text{d}}{\text{d}x}\left[1 - \text{erf}\left(\frac{x}{2\sqrt{D_{\text{eff}} t}}\right)\right]_{x=100\ \text{mm}} \tag{6}$$

5. Results and discussion

As the modeling results for Case 1, three chloride concentration profiles with respect to the diffusion times: 12 months, 3 years and 5 years, are shown in Fig. 3. It can be seen that they are all characterized with smooth curves decaying across the whole diffusion depth as in the usual cases one can see in literature where homogeneous diffusion conceptions were utilized. As illustrated in Fig. 4, in contrast, a three-dimensional concentration network for Case 2 with respect to a diffusion time of 3 years demonstrates a number of funnel-like pits instead of a smooth surface, whose positions appear to be spatially corresponding to the aggregates embedded in the cement paste. Moreover, it is easy to find that the funnel pits have their profundities reduced with the increasing diffusion depth and diffusion time. A closer observation also reveals that for each aggregate there is a conspicuous widened pit mouth on the three-dimensional concentration network profile. Obviously, these modeling results indicate that the great chloride diffusivity difference between aggregates and cement paste matrix may remarkably complicate the chloride diffusion behavior in a hetero-structural concrete although the complexity as against the smooth profile for a homogeneous medium may diminish gradually as the diffusion depth increases.

To get a clearer picture of chloride distribution in the hetero-structural concrete, the three-dimensional concentration networks were projected on the coordinate plane of concentration versus diffusion depth to form the concen-

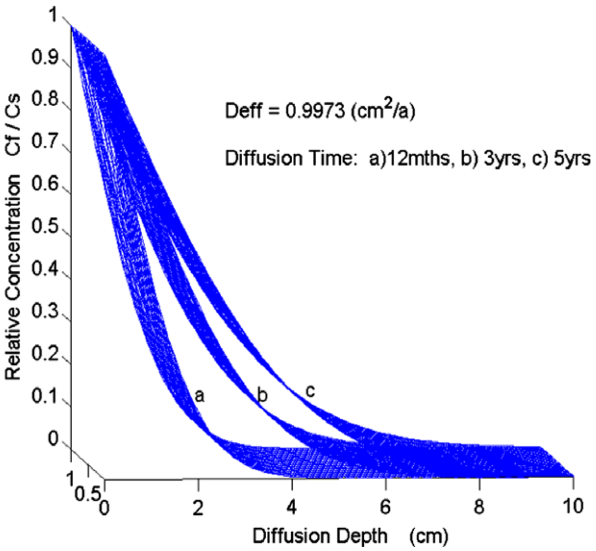

Fig. 3. Chloride concentration profiles by a single effective diffusion coefficient with diffusion time: (a) 12 months, (b) 3 years and (c) 5 years.

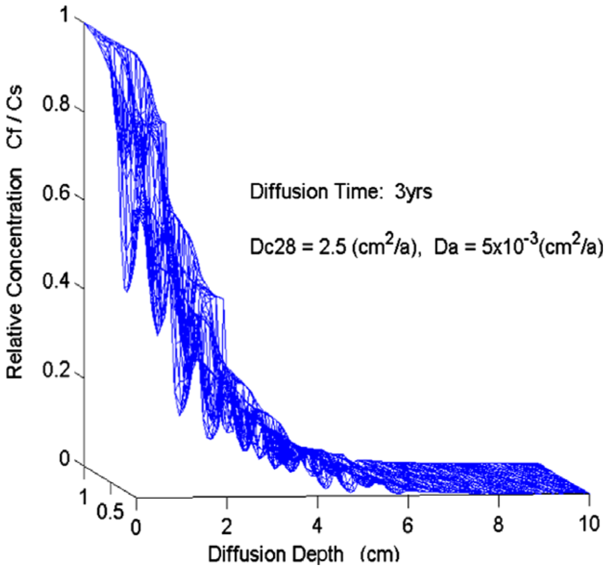

Fig. 4. Three-dimensional chloride concentration profile network for the hetero-structured model concrete at diffusion time: 3 years.

tration profiles along the diffusion depth, as shown in Fig. 5. These graphs clearly show that owing to the presence of hetero-structure, a smooth concentration curve across the diffusion depth from a homogeneous medium is now turned into a concentration "band" with an undulating and gradually narrowing width as the diffusion time and diffusion depth increase. What is more, it can be noted that when the diffusion time is relatively short, the chloride concentration curve given by the homogeneous medium is rather close to the front of the concentration band contour from the hetero-structured model, see the white curve in Fig. 5-1, for instance. As the diffusion proceeds, however, the concentration curve for the homogeneous medium appears to shift inwards deeper than does the concentration band for the hetero-structural model, resulting in an evident discrepancy between the two concentration profiles across the diffusion depth. Moreover, the longer the diffusion time is, the more remarkable such a concentration difference becomes. It has been estimated that, for example, their discrepancy after a 5-year diffusion may reach as much as around 20% at the diffusion depth 50 mm (see Fig. 5-3), where the reinforcing steels may be set if a concrete cover thickness of 50 mm is used. This result suggests that in a hetero-structured concrete, the chloride diffusion appears to lag behind that in its derived homogeneous medium.

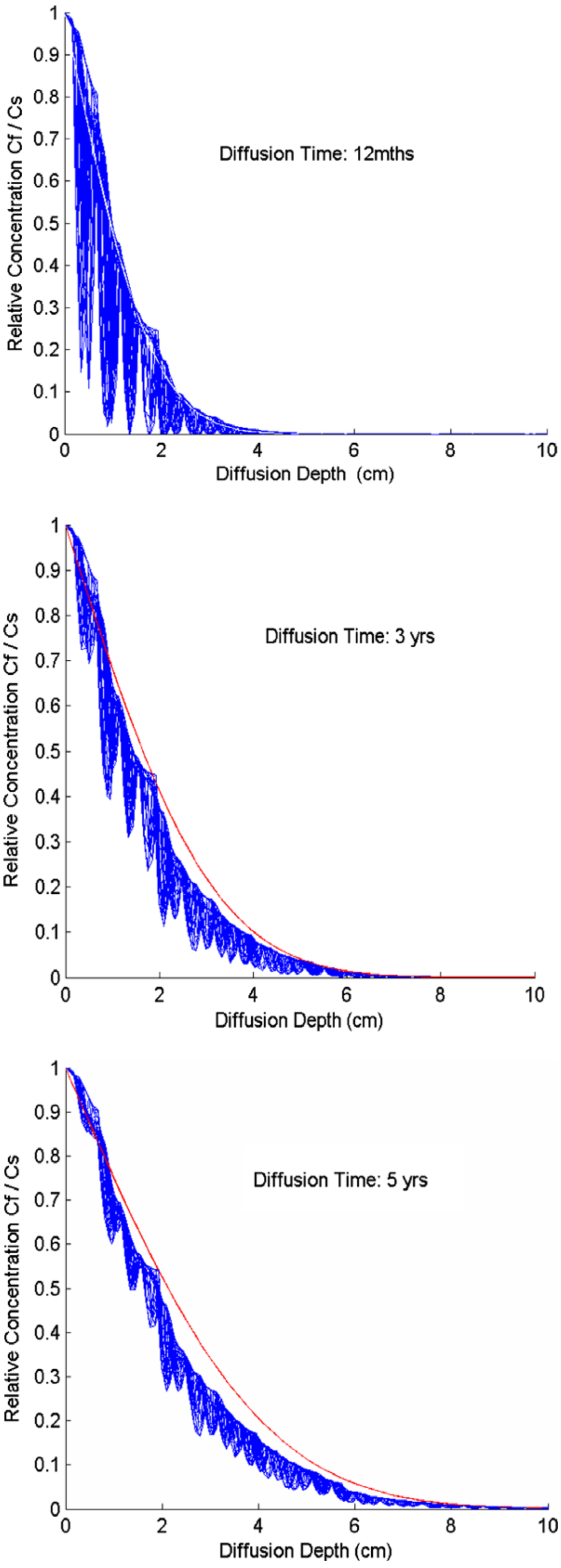

Fig. 5. Projected chloride concentration profiles for the hetero-structured model concrete and its derived homogeneous one at diffusion times: 12 months, 3 years and 5 years.

As regards Case 3, where the chloride binding and the time-reducing effect of chloride diffusion coefficient in the cement paste matrix were taken into account, the modeling results are shown in Fig. 6. It is clearly evident that owing to these additional effects, the band-like chloride concentration profile for Case 3 is much lower than that for Case 2, where the chloride binding and time-reducing effect of diffusion coefficient are not involved. Naturally, such a result is easy to understand because either the chloride binding or the reduction of chloride diffusion coefficient is actually equivalent to a significant decrease in the chloride diffusivity. Nevertheless, as shown in Fig. 7, it is interesting to note that the chloride concentration profiles for

Case 3 are so close to the concentration curves for Case 4, in which the chloride binding and time-reducing effect of diffusion coefficient are applied to the homogeneous medium with a starting effective diffusion coefficient for Case 1. Moreover, it can be seen that the closeness between the two concentration profiles is remarkably enhanced as the diffusion time increases, especially for those when the diffusion time is as long as 50 or 100 years. These results clearly suggest that the chloride binding and time-reducing effect of chloride diffusivity in the cement paste can make the hetero-structural concrete behave more or less like a homogeneous medium and thus greatly reduce the difference between their chloride concentration profiles. Furthermore, it should be reasonable to infer that the stronger the chloride binding and time-reducing effect of diffusion coefficient is, the hetero-structural concrete would behave more like a homogeneous one. Perhaps, it is because of this, at least partially, that the chloride diffusion models based on homogeneous medium conceptions were often used with no big errors to describe the chloride concentration profiles in real concretes. Certainly, in those cases the chloride binding and the time-reduction effect of diffusion coefficient were almost always involved and no separate treatments of

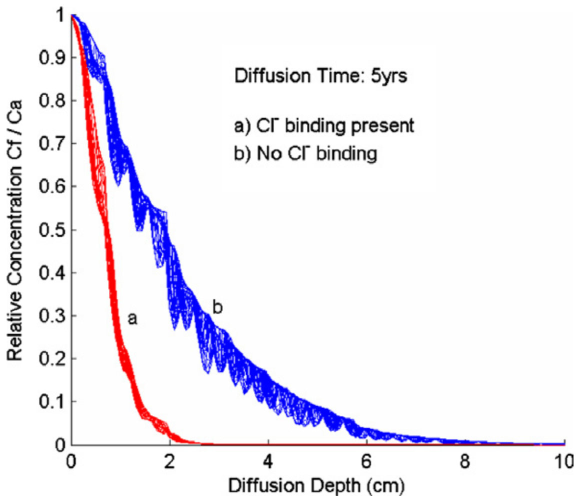

Fig. 6. Chloride concentration profiles after 5 years diffusion for Case 3 and Case 2.

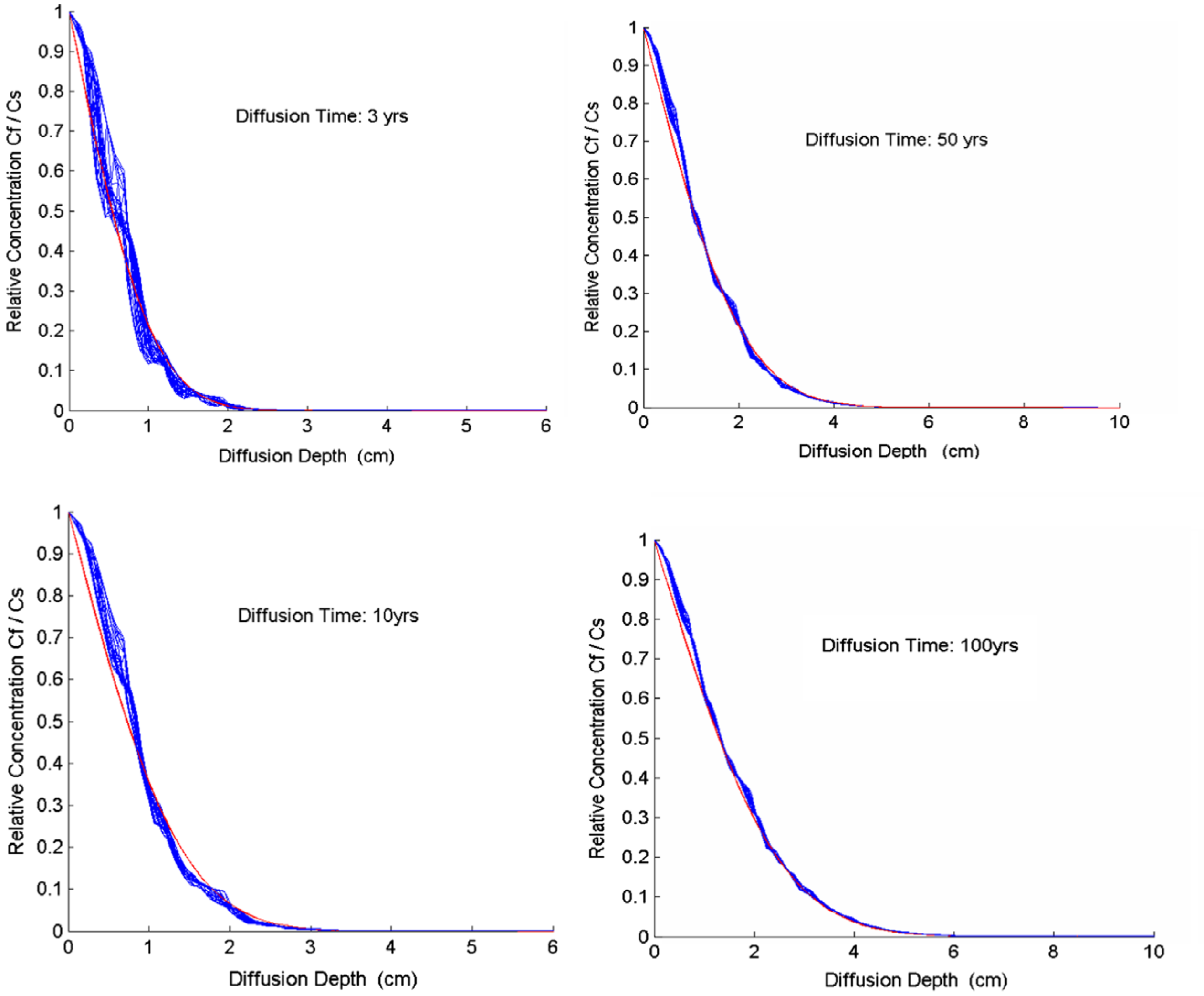

Fig. 7. Chloride concentration profiles for Case 3 (in blue) and Case 4 (in red). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

aggregates and cement pastes were carried out. Nevertheless, to surely clarify the particular conditions that make the chloride diffusion in a real concrete sufficiently approximate to a homogeneous one in a sense of engineering, further study is still needed.

6. Conclusions

Through the simulation of chloride diffusions in a two-dimensional hetero-structured model concrete by using finite element method, the following conclusions can be reached:

(1) In a hetero-structured concrete composed of multiple phases with distinct diffusivities, the chloride diffusion behavior is quite different from that in its derived homogeneous medium. The chloride concentration distribution in the hetero-structured concrete shows a band-like profile instead of a smooth curve for a homogeneous medium, with the band width undulating and narrowing as the diffusion time or diffusion depth increases.

(2) Generally, the chloride diffusion in a hetero-structured concrete appears to lag behind that in its derived homogeneous medium with a single effective diffusion coefficient. This causes an increasing discrepancy in their chloride concentration distributions as the diffusion time is increased.

(3) The chloride binding and time-reducing effect of diffusion coefficient in cement paste may remarkably slow down the chloride diffusion in concretes. Moreover, when these effects are supposed to happen to the homogeneous medium, the chloride concentration difference between the hetero-structured concrete and its homogeneous one can be greatly reduced. This phenomenon can make the hetero-structured concrete behave like a homogeneous medium to some extent.

References

[1] Verbeck GJ. Mechanisms of corrosion in concrete. In: Corrosion of metals in concrete, ACI SP-49, Detroit, Michigan; 1975. p. 21–38.

[2] Garboczi EJ. Permeability, diffusivity and microstructural parameters: a critical review. Cem Concr Res 1990;20(4):591–601.

[3] Neville AM. Chloride attack. In: Properties of concrete. Congman; 1996. p. 563–75.

[4] Andrade C. Calculation of chloride diffusion coefficients in concrete from ionic migration measurement. Cem Concr Res 1993;23(3): 724–42.

[5] Chatterji S. Transportation of ions through cement based materials. Part 1: Fundamental equations and basic measurement techniques. Cem Concr Res 1994;24(5):907–12.

[6] Zhang T, Gjorv OE. Diffusion behavior of chloride ions in concrete. Cem Concr Res 1996;26:907–17.

[7] Johannesson BF. Nonlinear transient phenomena in porous media with special regard to concrete and durability. Adv Cem Based Mater 1997;6:71–5.

[8] Mangat PS, Limbachiya MC. Effect of initial curing on chloride diffusion in concrete repair materials. Cem Concr Res 1999;29: 1475–85.

[9] Liang MT, Wang KL, Liang CH. Service life prediction of reinforced concrete structures. Cem Concr Res 1999;29:1411–8.

[10] Roy DM, Jiang WM, Silsbee MR. Chloride diffusion in ordinary, blended and alkali-activated cement pastes and its relation to other properties. Cem Concr Res 2000;30:1879–84.

[11] Thomas MDA, Bamforth PB. Modeling chloride diffusion in concrete, effect of fly ash and slag. Cem Concr Res 1999;29:487–95.

[12] Martin-Perez B, Pantazopoulou SJ, Thomas MDA. Numerical solution of mass transport equations in concrete structures. Comput Struct 2001;79:1251–64.

[13] Hobbs DW. Aggregate influence on chloride ion diffusion into concrete. Cem Concr Res 1999;29:1995–8.

[14] Care S. Influence of aggregates on chloride diffusion coefficient into mortar. Cem Concr Res 2003;33:1021–8.

[15] Tallen NM. Electrical conductivity in ceramics and glass, Part B. Marcel Dekker Inc.; 1974. p. 628.

[16] Martin-Perez B, Zibara H, Hooton RD, Thomas MDA. A study of the effect of chloride binding on service life predictions. Cem Concr Res 2000;30:1215–23.

[17] Tang L, Nillson LO. Chloride binding capacity and binding isotherms of OPC pastes and mortars. Cem Concr Res 1993;23(2): 247–53.

[18] Allen AJ. Time-resolved in cements, clays and porous rocks. J Appl Cryst 1991;24:624–34.

[19] Yu HF, Sun W, Ma HY. Diffusion equations for chloride ions in concretes under the combined actions of durability factors. J Build Mater 2002;5(3):240–8 (in Chinese).

[20] Yu HF, Sun W, Ma HY. Study on prediction of concrete service life (I) – theoretical model, model's examination and applications, evaluation of influence factors and service life. J Chinese Ceram Soc 2002;30(6):686–701.