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An adaptive approach for the chloride diffusivity of cement-based materials

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Abstract. Adaptive schemes are constructed in this paper for modeling the effective chloride diffusion coefficient of cement-based materials (paste and concrete). Based on the polarization approximations for the effective conductivity of isotropic multicomponent materials, we develop some fitting procedures to include more information about the materials, to improve the accuracy of the scheme. The variable reference parameter of the approximation involves a few free scalars, which are determined through the available numerical or experimental values of the macroscopic chloride diffusion coefficient of cement paste or concrete at some volume proportions of the component materials. The various factors that affect the chloride diffusivity of cement-based material (porous material structure, uncertainty of value of the chloride diffusion coefficient in water-saturated pore spaces, etc.) may be accounted to make the predictions more accurate. Illustrations of applications are provided in a number of examples to show the usefulness of the approach.

Keywords: polarization approximation; effective chloride diffusivity; concrete; cement paste; reference parameter

1. Introduction

A widely recognized observation is that the chloride ingress phenomenon is one of the major durability problems in reinforced concrete structures. To date, some accurate service life models such as Life 365 or DuraCrete (Ehlen *et al*. 2009, EuRam III 2000) are available to optimize sustainable performance of a concrete structure in its intended environment. Chlorides entering concrete can be separated into two parts: bound chlorides which are trapped by the solid skeleton, and free chlorides which diffuse freely through the concrete. The governing equation of diffusion processes for saturated cement-based materials involves two material parameters: the chloride binding capacity and the chloride diffusivity (Xi and Bazant 1999). In the steady state condition applied in this study, we are interested only in the chloride diffusivity. Further, for the time/depth dependent diffusion model, the chloride binding capacity plays an important part and has been studied in some theoretical and experimental researches (Hirao *et al*. 2005, Martın-Pérez *et al*. 2000, Carrara *et al*. 2016, Torquato and Pham 2004, Pham and Torquato 2005).

Over several decades, determining the chloride diffusion coefficient has become a stimulating subject for numerous theoretical (Pivonka *et al*. 2004, Caré and Hervé 2004, Zheng and Zhou 2008, Yoon 2009, Zheng *et al*. 2010, Dridi 2013, Zheng and Zhou 2013, Ma *et al*. 2015, Hu *et al*. 2017) and experimental (Page *et al*. 1981, Yu and Page 1991, Tang and Nilsson 1993, MacDonald and Northwood 1995, Ngala *et al*. 1995, Ngala and Page 1997, Yang and Su 2002, Park *et al*. 2012) studies because it is an important parameter to estimate the initiation period of corrosion. This period is the time that chloride from free surface diffuses through cover concrete and reaches a critical threshold value at steel bars. Because of the multi-scale characteristic of cement-based materials (Constantinides and Ulm 2004), some theoretical analyses in the framework of homogenization approach have been developed to predict the chloride diffusion coefficient depending on material properties. The cement-paste structure is described as the porous composite material (Pivonka *et al*. 2004, Zheng and Zhou 2008, Zheng *et al*. 2010, Yang and Su 2002). While the n-phase model (Christensen and Lo 1979, Hervé and Zaoui 1990, Hervé and Zaoui 1993) originated from the Hashin's composite sphere assemblage method is usually used to model mortar or concrete structure with coated inclusions composed by aggregate and interfacial transition zone (ITZ) embedded in the matrix of bulk cement paste (Caré and Hervé 2004, Dridi 2013, Sun *et al*. 2011, Liu *et al*. 2016, Tu *et al*. 2018). Besides the advantages of describing the physical phenomena exactly, multi-scale approximations also have drawbacks which result from the lack of detailed information relating to porous material structure, size, and shape of aggregate and ITZ, and the uncertain value of chloride diffusion coefficient in water-saturated porous spaces.

In order to maximize use of the multi-scale approach and overcome the challenges cited above: we propose a strategy. Firstly, based on the framework of variational approach (Hashin and Shtrikman 1962, Le and Pham 1991, Pham 1996, 2011, Pham *et al*. 2013), a simple polarization approximation was constructed for the effective diffusivity of isotropic multicomponent materials. The approximation contains a reference parameter that should be determined

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from available information about a given composite. The effective medium approximation constructed from Eshelby-type micromechanical models (Mori and Tanaka 1973, Christensen 1979, Phan-Thien and Pham 2000, Pham 2008, Markov *et al*. 2012) is rewritten to clarify the physical characteristics of the reference parameter. Secondly, adaptive schemes applied to polarization approximations are proposed to account for more information about a composite to make more accurate estimates of the effective diffusivity. In the following sections, the free parameters will be calibrated based on available results derived from experimental and numerical references related to the chloride diffusivity of cement-based materials. Examples will be provided and analyzed to illustrate how to calibrate these parameters.

2. Theoretical homogenization framework

We start with a simple porous medium configuration Ω_0 in which the pore space is saturated by a liquid composed of different chemical species (e.g., chloride ion, carbon dioxide, sulfate ...). In order to provide a unique approach to the entire chloride-induced reinforcement corrosion process, we don't take into account the coupling of chemical species and chloride diffusion. The diffusion of chloride at the microscopic scale is described by Fick's law, which establishes a correlation between the diffusive flux j and the gradient of the solute concentration, in dilute case (Dormieux *et al*. 2006)

$$j = -D_0 \underline{grad}_z \rho, \tag{1}$$

where D_0 the diffusion coefficient which refers to the diffusion of chloride ions through the solvent at a certain point $\underline{z}$. In the dilute situation as noted above, the diffusion coefficient is independent of the morphology of pore space and we consider that it is constant. The link between the average diffusive flux $\underline{J}$ and the average concentration gradient $\underline{H}$ becomes

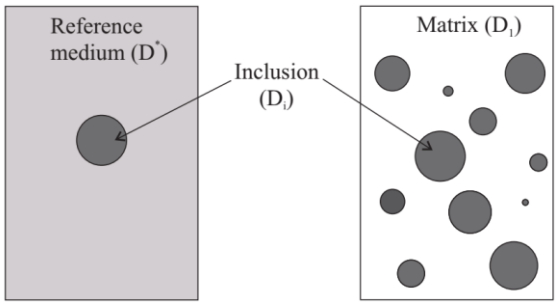
$$\begin{aligned} \underline{J} &= <\underline{j}>_{\Omega_0} = \frac{1}{\int_{\Omega_0} d\Omega} \int_{\Omega_0} \underline{j} dz = -\mathbf{D} \cdot <\underline{grad}_z \rho> \\ &= -\mathbf{D} \cdot \underline{H} = -v\mathbf{T} D_0 \cdot \underline{H}. \end{aligned} \tag{2}$$

$\boldsymbol{D}, \boldsymbol{T}, v$ are respectively recognized as the homogenized diffusion tensor, tortuosity tensor and porosity. In the isotropic case

$$\mathbf{D} = D\mathbf{1} = \frac{vD_0}{T}\mathbf{1}. \tag{3}$$

T is referred to as the tortuosity factor, an intrinsic parameter of the pore space and $\mathbf{1}$ is the second-order identity tensor.

The general linear problem for a multiphase material consists of n different inclusion phases of homogenized diffusivity tensor $\boldsymbol{D_i}$ ($\boldsymbol{D_i} = D_i\mathbf{1}$ in the isotropic case) and volume fraction v_i ($i = 1..n$). For simplicity, we assume the contacts between the component materials are perfect; the solid phase is undeformable, and the solvent velocity is negligible (no advection) in steady-state conditions.



(a) (b)

Fig. 1 (a) localization problem; (b) average problem

In Pham and Nguyen (2015), they studied the heat conduction problem when Fourier's law satisfied. The polarization approximations for the effective conductivity (Eq. (17) in Pham and Nguyen 2015) are constructed using variational approach. Due to the same mathematical structure between Fick's law for mass diffusion and Fourier's law for heat conduction, the polarization approximation (PA) for the effective diffusivity D^{eff} of the composite described above in general d-dimensional space has the particular form in the isotropic case

$$D^{eff} = \left(\sum_{i=1}^{n} \frac{v_i}{D_i + D_*} \right)^{-1} - D_*. \tag{4}$$

where the reference parameter D_* should be determined from a reference dilute solution result, or reference effective diffusivities of the composite.

Alternatively, the formula (4) is obtained from the homogenization approach based on the Eshelby-type model. Effective diffusivity is normally calculated in two successive problems: localization problem in which we look for the dilute solution result of an inclusion (D_i) embedded in infinite reference matrix (D_*) (Fig. 1 (a)), and an average problem in which some schemes are used to take average values form n dilute solutions in real configuration (Fig. 1 (b)). Some classical approaches are obtained depending on the theoretical values of D_* in d-dimensional space ($d = 2; 3$) as follow (see more in (Dormieux *et al*. 2006))

$$D_* = \begin{cases} (d-1)D^{MT} & : \text{Mori - Tanaka scheme}, \\ (d-1)D^{eff} & : \text{self - consistent scheme}, \\ (d-1)\max\{D_i\} & : \text{upper Hashin - Shtrikman bound}, \\ (d-1)\min\{D_i\} & : \text{upper Hashin - Shtrikman bound}. \end{cases} \tag{5}$$

where D^{MT} is diffusion coefficient of matrix in the case of spherical or circular inclusion composite.

So, the classical homogenization schemes can be obtained by adequately choosing the properties of the reference D_*. Due to the dependence of D_* on homogenization schemes, the results obtained by the classical homogenization schemes are very different.

3. Adaptive schemes for the determination of reference parameter

Like the other classical homogenization schemes, if D_* in (4) is calculated from the dilute solution problem; the polarization approximation may diverge significantly from the observed effective diffusivity at high volume proportions of the inhomogeneities. So, we propose that the variable reference parameter D_* that depends on the volume proportions of the components. The adaptive schemes using variable reference parameters include more information about a particular mixture, if possible, get better estimations for the effective diffusion coefficient over the range of components' volume proportions of interest.

In order to simplify the process of determining the reference parameter, and support the application of this approach in engineering which will be described in the next sections, we shall restrict ourselves to two-component composite materials with the volume proportions and diffusivities of the matrix and inclusion components being v_1, D_1 and v_2, D_2, respectively. In the more general cases of multiphase composite, formulae become more complex, while the procedure is similar. For two-component materials, the variable reference parameter D_* is defined as follows

$$D_* = D_1\left(\alpha + \beta v_2^{\gamma}\right) \tag{6}$$

where 3 dimensionless parameters α, β, γ shall be found from available reference information of composite materials that shall be done subsequently. The estimate is called a multipoint adaptive polarization approximation (MPA) for chloride diffusivity. It's necessary to note that the variable reference parameter D_* depended on α, β, γ in (6) should be a simple, monotonous function of the components' volume proportions, and should lie within the limits $\min\{D_i\} \le D_* \le \max\{D_i\}$ for the approximation to obey Hashin-Shtrikman bounds.

As a distinction from other homogenization approximations, including the Mori-Tanaka, self-consistent, differential and some others adaptive homogenization schemes proposed recently (Nguyen *et al*. 2016, Nguyen *et al*. 2016, Tran *et al*. 2018), which have been derived from the field equations using the inhomogeneities' dilute solution reference, the present adaptive polarization approximation has been constructed from the minimum energy principles. The approximation contains reference parameters that should be determined from the inhomogeneities' dilute solution result for a matrix composite, and/or from available experimental or/and numerical value of the macroscopic diffusivity of the composite at certain finite-volume-proportion point of the component materials. Once the appropriate reference parameter had been chosen, the approximation should obey Hashin-Shtrikman bounds over all the ranges of volume proportions of the component materials while the other effective medium approximation schemes may not. Furthermore the polarization approximations for the effective diffusivity of the composite constructed from the minimum energy principles in general *d*-dimensional space are valid for any ellipsoidal shape of inclusions while it is not able to capture size distribution effect.

Firstly, if we have three numerical or/and experimental data points from the relationship effective diffusivity - volume proportion (D^a, v_{2a}), (D^b, v_{2b}), (D^c, v_{2c}), using formula (4), we obtain the respective values of the reference parameter $D_* = D_*^a, D_*^b, D_*^c$

$$\begin{cases} D^a = \left(v_1/(D_1 + D_*^a) + v_{2a}/(D_2 + D_*^a)\right)^{-1} - D_*^a \\ D^b = \left(v_1/(D_1 + D_*^b) + v_{2b}/(D_2 + D_*^b)\right)^{-1} - D_*^b \\ D^c = \left(v_1/(D_1 + D_*^c) + v_{2c}/(D_2 + D_*^c)\right)^{-1} - D_*^c \end{cases} \tag{7}$$

Replacing D_*^a, D_*^b, D_*^c from (7) in (6) one obtains an unique equation for γ

$$\frac{v_{2a}^{\gamma} - v_{2b}^{\gamma}}{v_{2a}^{\gamma} - v_{2c}^{\gamma}} = \frac{D_*^a - D_*^b}{D_*^a - D_*^c} \tag{8}$$

and two explicit expressions for β and α

$$\beta = \frac{D_*^a - D_*^b}{D_1(v_{2a}^{\gamma} - v_{2b}^{\gamma})},\ \alpha = D_*^a / D_1 - \beta v_{2a}^{\gamma}. \tag{9}$$

The three-point adaptive polarization approximation (MPA3) has the particular expression

$$D^{eff} = \left(\sum_{i=1}^{2} \frac{v_i}{D_i + D_*}\right)^{-1} - D_*, \quad D_* = D_1\left(\alpha + \beta v_2^{\gamma}\right) \tag{10}$$

with γ, β, α from (8), (9).

If we have only two numerical or/and experimental data points (D^a, v_{2a}), (D^b, v_{2b}), we need fix any of the three free parameters α, β, γ. For the reason that α can be determined from the analytical dilute solution result (see below). When α is fixed, one obtains two explicit expressions for γ and β

$$\gamma = \ln \frac{D_*^a / D_1 - \alpha}{D_*^b / D_1 - \alpha} / \ln(v_{2a} / v_{2b}), \tag{11}$$

and

$$\beta = \frac{D_*^a / D_1 - \alpha}{v_{2a}^{\gamma}}. \tag{12}$$

The two-point adaptive polarization approximation from (4), (6), (11) and (12) is referred as MPA2.

If only one reference point is available, we first fix α. For simplicity and to respect the condition $\gamma > 0$, γ should be selected, then we obtain the remaining parameter β from (12). The present approximation is called MPA1. Additionally, with only one measured data (D^a, v_{2a}), the reference parameter D_* can be calculated directly from (4) as follows

$$D_*^1 = \frac{D^a(v_{1a}D_2 + v_{2a}D_1) - D_1D_2}{v_{1a}D_1 + v_{2a}D_2 - D^a}. \tag{13}$$

The polarization approximation using one reference at the finite volume proportions of the component materials (PA1) is

$$D^{eff} = \left(\sum_{i=1}^{2} \frac{v_i}{D_i + D_*^1}\right)^{-1} - D_*^1. \tag{14}$$

Furthermore, if the dilute solution result for the inhomogeneities suspended in an infinite matrix is available (Torquato 2002)

$$D^{eff} = D_1 + v_2(D_2 - D_1)F(D_1, D_2) \quad (15)$$

where $F(D_1, D_2)$ are inclusion-function, which depend on the inhomogeneity's geometry. Equalizing (4) and (15) at $v_2 \ll 1$, one can find explicitly

$$D_*^0 = \frac{F(D_1, D_2)D_2 - D_1}{1 - F(D_1, D_2)}. \quad (16)$$

In the case of isotropically-distributed ellipsoidal inclusions, explicit expression of inclusion-function $F(D_1, D_2)$ are depends only on the three aspect ratios, and are solved explicitly from Eshelby's problem that can be find in some well-known micro-mechanical handbooks (Mura 1982, Torquato 2002). The approximation

$$D^{eff} = \left(\sum_{i=1}^{2} \frac{v_i}{D_i + D_*^0} \right)^{-1} - D_*^0. \quad (17)$$

with D_*^0 from (16) is called the polarization approximation using dilute solution reference (denoted as PA0). Equalizing (16) and (6) at $v_2 \ll 1$, one can find the explicit expression of α

$$\alpha = \frac{F(D_1, D_2)D_2 - D_1}{(1 - F(D_1, D_2))D_1}. \quad (18)$$

Putting α from (18) in (11) and (12), we have the two-point (or one-point if we fix γ and use only (12)) adaptive polarization approximation with dilute solution. The approximations are referred respectively as MPA02 and MPA01.

In the specific case of spherical inclusions, we have the simple expression of $\alpha = 2$. $D_*^0 = 2D_1$ from (14) and D^{MT} from (5) are identical then PA0 coincides with the Maxwell and Mori-Tanaka approximations and one of the HS bounds.

4. The effective diffusivity in cement paste

The cement paste structure is a composite material with porous matrix and solid inclusions. While the diffusivity of solid inclusion (D_2) is considered as zero, the value of chloride diffusivity in a porous matrix (D_1) is a question to debate. Pivonka (Pivonka *et al*. 2004) indicated that, if $D_1 = 1610 \times 10^{-12} m^2/s$ corresponds to the salt diffusivity of NaCl in a pure solution system, experimental data are largely overestimated by the differential effective medium approach (Lemarchand 2001, Dormieux and Lemarchand 2001). Pivonka *et al*. propose a correlation value of $D_1 = 107 \times 10^{-12} m^2/s$, that takes into account the constriction effects of the narrow pore space, and is accepted by some successive authors (Zheng and Zhou 2008, Zheng *et al*. 2010, Liu *et al*. 2012). Similarly, Stora (Stora *et al*. 2008) and Ma (Ma *et al*. 2015) adopted $D_1 = 200 \times 10^{-12} m^2/s$ while $2030 \times 10^{-12} m^2/s$ is the selected value in the model of (Sun *et al*. 2011).

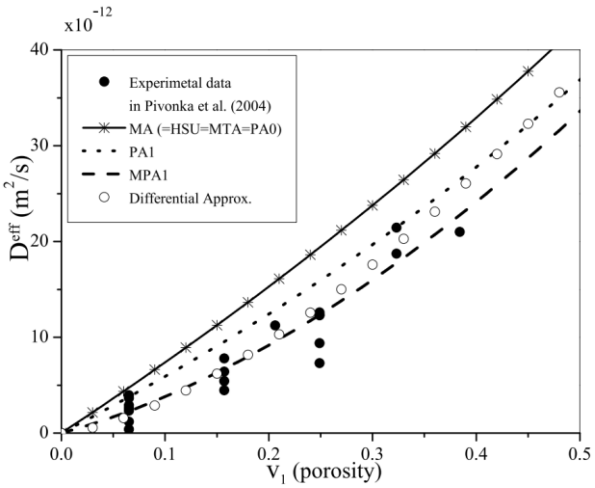


Fig. 2 Experimental data for chloride diffusivity of cement paste in Pivonka *et al*. (2004), compared with analytical solutions: Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation MTA) and PA0; PA1; MPA1; differential approximation

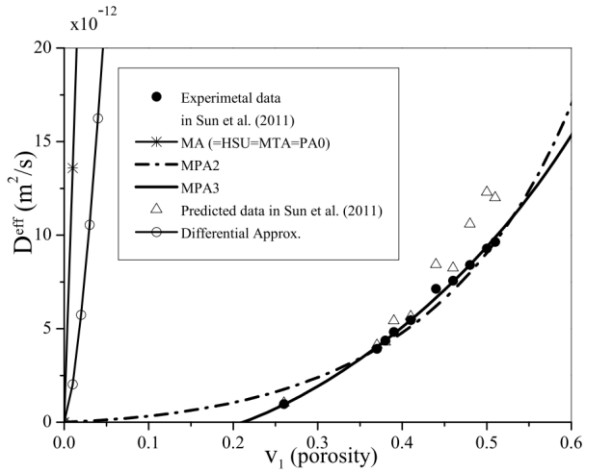


Fig. 3 Experimental data for chloride diffusivity of cement paste in Sun *et al*. (2011), compared with analytical solutions: Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation (MTA) and PA0; MPA2; MPA3; the results of Sun *et al*. (2011); differential approximation

Firstly, the proposed methods are compared with the experimental data combined in (Pivonka *et al*. 2004). Graphics of Maxwell approximation (MA) that coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation for spherical inclusions (MTA) and PA0, PA1, MPA1 are plotted in Fig. 2. The parameters of models, as D_1, D_2, reference points, α, β, γ, used in Fig. 2 and other examples (Figs. 3-7 and 10) will be presented in Table 1. Pivonka used the classical differential effective medium approach to propose $D_1 = 107 \times 10^{-12} m^2/s$ which is presented in Fig. 2, and takes the form

$$D^{DA} = D_1 v_1^{3/2}. \quad (19)$$

Fig. 3 illustrates the flexibility of our approach, and

Table 1 The values of the model parameters (chloride diffusivity coefficient is in unit of $10^{-12}m^2/s$; the values in Fig. 10 are dimensionless)

Figure	Model	D_1	D_2	Reference point						Parameter		
				v_{2a}	D^a	v_{2b}	D^b	v_{2c}	D^c	α	β	γ
Fig. 2	PA1	107	0	0.323	21.46	-	-	-	-	-	-	-
	MPA1			0.249	12.35	-	-	-	-	1	-0.62	2
Fig. 3	MPA2	2030	0	0.37	3.92	0.51	9.64	4	-4	0.0013	0.37	3.92
	MPA3			0.38	4.37	0.41	5.46	0.48	8.41	0.005	-0.016	4.49
Fig. 4	MPA3	107	0	0.23	1.11	0.37	2.66	0.56	20.75	-0.008	0.008	-4.1
	MPA3M			0.295	1.11	0.37	2.66	0.56	20.75	0.005	11.1	-8.93
Fig. 5,6	MPA01	107	0	0.313	1.96	-	-	-	-	2	-2	0.06
	MPA02			0.29	2.06	0.49	8.87	-	-	2	-2	0.087
	MPA3			0.18	0.597	0.36	2.61	0.489	8.87	0.02	0.0024	-5.3
	MPA3M			0.18	0.597	0.36	2.61	0.489	8.87	0.02	13.48	-10
Fig. 7	MPA01	2.03	0	0.3	1.487	-	-	-	-	2	-11.1	0.2
	MPA02			0.1	0.83	0.4	1.367	-	-	2	-2.57	-0.86
Fig. 10	MPA01	1	0.43	0.5	0.688	-	-	-	-	2	2.94	4

compares the results obtained by some approximations and the experimental data of Sun *et al*. (Sun *et al*. 2011). The value of $D_1 = 2030 \times 10^{-12}m^2/s$, which differs from that of the above example by a factor of 19. Experimental values are largely overestimated by PA0 and the differential approximation. However, with just two reference points, MPA2 is better than the complex analytical model proposed by Sun. MPA3 shows even better agreement with the same experimental data for a slightly higher volume factor value.

In Fig. 4, we are interested in comparing our models with the calibrated model proposed by Zheng and Zhou (2008) and the experimental results of (Page *et al*. 1981, Yu and Page 1991, MacDonald and Northwood 1995). Fig. 4 shows that MPA3 agrees with the experimental results. However, γ=-4.1 violates the condition $\gamma > 0$ that caused the situation that D^{eff} may not be determined when v_2 approaches unity. To overcome this difficulty, a small modified version of MPA3 called MPA3M is proposed as follow

$$D_* = D_1\left(\alpha + \beta e^{\gamma v_2}\right) \tag{20}$$

Eqs. (8), (9) are replaced by

$$\frac{e^{v_{2a}\gamma} - e^{v_{2b}\gamma}}{e^{v_{2a}\gamma} - e^{v_{2c}\gamma}} = \frac{D_*^a - D_*^b}{D_*^a - D_*^c} \tag{21}$$

and

$$\beta = \frac{D_*^a - D_*^b}{D_1(e^{v_{2a}\gamma} - e^{v_{2b}\gamma})},\ \alpha = D_*^a / D_1 - \beta e^{v_{2a}\gamma}. \tag{22}$$

The coincidences between the two multi-point polarization approximations MPA3 and MPA3M in the domain of experimental data are observed in Fig. 4.

For the last example concerning the diffusivity of cement paste, some numerical reference points from literature were selected. In (Ma *et al*. 2015), the transport properties of cement paste are modeled through a two-scale random walk simulation. The numerical results at low porosity permit us to use the approximations with dilute

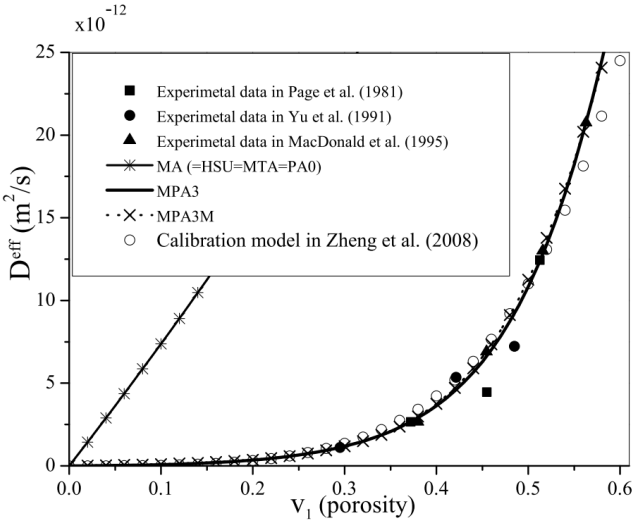


Fig. 4 Experimental data for chloride diffusivity of cement paste in Page *et al*. (1981),Yu *et al*. (1991), MacDonald *et al*. (1995), compared with analytical solutions: Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation (MTA) and PA0; MPA3; MPA3M; calibration model in Zheng *et al*. (2008)

solution reference (MPA01, MPA02). By combining Eqs. (3) and (4), the tortuosity factor of cement paste structure is estimated by ours adaptive polarization approximations using some numerical information (see Table 5 in Ma *et al*. 2015). The results are presented in Fig. 5 with $D_1 = 107 \times 10^{-12}m^2/s$. Using (3), the effective diffusivities are calculated and plotted in Fig. 6. In Figs. 5, 6, some experimental data violate the bound. Note that the adaptive polarization approximations are constructed depend on reference points, if reference points do not respect Hashin-Shtrikman bound, the curves are not guaranteed to be so valid. The numerical and analytical results are concordant with the seven independent sets of experimental data presented above (three in Zheng and Zhou 2008) and four in Sun *et al*. 2011). This agreement is an interesting one.

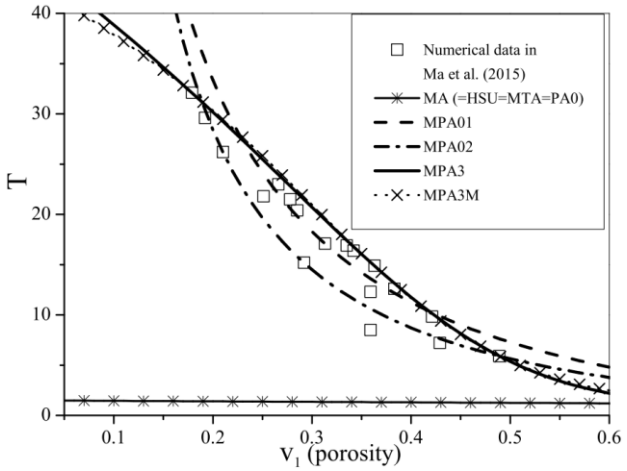


Fig. 5 Computed diffusion turtorsity of cement paste in Ma *et al*. (2015), compared with analytical solutions: Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), MoriTanaka approximation (MTA) and PA0; MPA01; MPA02; MPA3; MPA3M

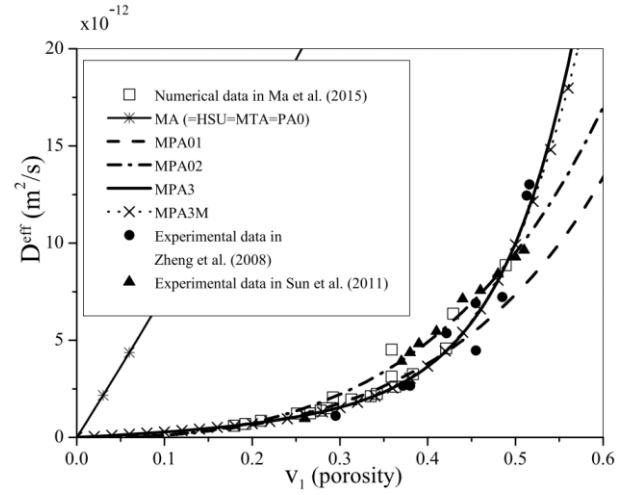


Fig. 6 Computed chloride diffusivity of cement paste in Ma *et al*. (2015), experimental data for chloride diffusivity of cement paste in Sun *et al*. (2011) and in Zheng *et al*. (2008), compared with analytical solutions: Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation (MTA) and PA0; MPA01; MPA02; MPA3; MPA3M

5. The effective diffusivity in cement paste

Mortar and concrete are complex, heterogeneous, composite materials which are usually considered three-phase materials: the bulk cement paste (matrix), the aggregate (inclusion) and the layer around the aggregate called the ITZ (coated shell).

Firstly, we consider a simple situation in which the ITZ is not taken into account. The material is compounded of a bulk cement paste ($D_1 = 2.03 \times 10^{-12} m^2/s$) and rigid inclusions ($D_2 = 0$). Based on this configuration, PA0 and the differential approximation are compared with experimental result of (Yang and Su 2002) in Fig. 7.

In order to verify the above result, and propose some

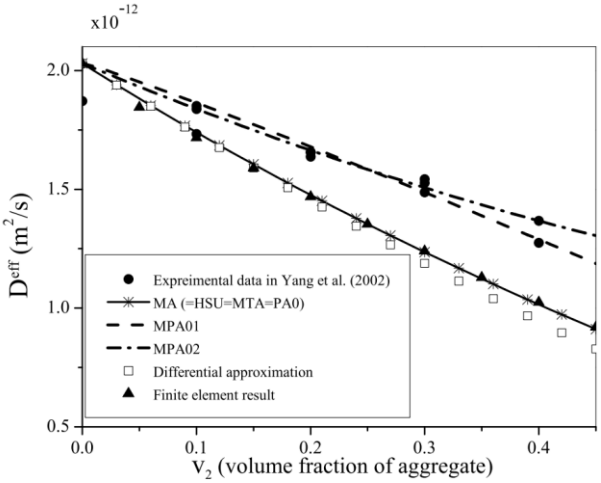


Fig. 7 Experimental data for chloride diffusivity of mortar in Yang *et al*. (2002), compared with analytical and numerical solutions (the case of non ITZ effect): Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation(MTA) and PA0; MPA01; MPA02; differential approximation; finite element result

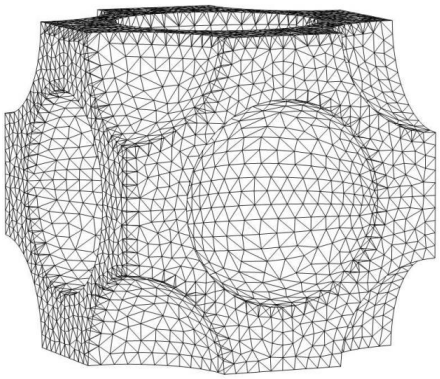


Fig. 8 A periodic elementary cell (face-centered cubic)

numerical reference points, we make finite element calculations for a number of periodic suspensions of spheres in three dimensions. The mortar and concrete structure in these particular situations are periodic and defined by an elementary cell which is similar to the case of face-centered cubic symmetry shown in Fig. 8. The numerical results are obtained within the framework of the periodic homogenization technique established in the literature that permits us to determine the effective diffusivity from the solution over the domain of an elementary cell. The open source finite element code (CASTEM) was utilized for numerical calculations (CEA 2011). Fig. 7 demonstrates that the finite element results and PA0 are quite close, up to the high packing of the spheres (aggregate), even though the component properties differ largely.

The results show that the analytical and numerical curves are not in agreement with the experimental data (Fig. 7). Moreover, the experimental points violate the HS upper bound. It is significant that we cannot use the simple configuration (non-ITZ) to model this effect.

In Fig. 7, the adaptive polarization approximations with

Table 2 ITZ properties for different thickness (dimensionless values)

ITZ thickness	v^I/v^A	D^I/D_1	v'_1	v'_2	D_1	D^I	D^A	D^{ei}
20 μm	0.27	2.83	0.212598425	0.787401575	1	2.83	0	0.431694915
40 μm	0.65	1.76	0.393939394	0.606060606	1	1.76	0	0.532093023
50 μm	0.9	1.55	0.473684211	0.526315789	1	1.55	0	0.58125

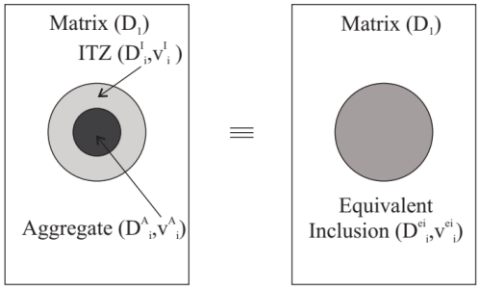


Fig. 9 Equivalent-inclusion approach

dilute solution MPA01, MPA02 are also constructed based on the experimental reference points of Yang *et al*. As the experimental reference points violate HSB, the MPA01, MPA02 curves are not guaranteed to be obey HSB.

Secondly, the configuration with ITZ is examined. The model called "equivalent-inclusion approach" proposed recently by Pham and Tran (Pham and Tran 2014, Tran *et al*. 2015) enable us to use the adaptive method proposed above for the three phase materials as a concrete structure. The model permits us to replace coated spherical inclusions (ITZ and aggregate) in d dimensions (d=2, 3) by equivalent-inclusions having properties as follow (Fig. 9)

$$D_i^{ei} = \left(\frac{v'_1}{D_i^I + (d-1)D_i^I} + \frac{v'_2}{D_i^A + (d-1)D_i^I} \right)^{-1} - D_i^I, \quad (23)$$

$$v_i^{ei} = v_i^I + v_i^A, \quad v'_1 = \frac{v_i^I}{v_i^I + v_i^A}, \quad v'_2 = \frac{v_i^A}{v_i^I + v_i^A}, \quad (24)$$

where D_i^{ei}, $v_i^{ei}, D_i^I, v_i^I, D_i^A, v_i^A$ are respectively diffusivity and volume factor of the equivalent-inclusion, ITZ, and aggregate of the "ith" phase. Equations (23) and (4) are combined to propose a simple approach to model the effective diffusivity of the concrete structure.

Based on some experimental observations, Yang *et al*. (Yang and Su 2002) described some properties of the ITZ dependent on the thickness (h). Using equation (23), the properties of the equivalent-inclusion are calculated (see Table 2). The finite element results (the face-centered cubic case) are obtained for three different values of thickness of ITZ and compared with experimental data in Fig. 10. Using a numerical reference point in the case of h = *20*μm, MPA01 is calculated and presented together with PA0, and the result of the model of Yang in Fig. 10, which show good agreement between the results of the present study and those proposed in the literature.

It is necessary to note that, for illustration, we used the numerical computations for concrete considering a periodic arrangement of spherical aggregates that is far from reality. Complex numerical simulations are expected to be considered "good reference" results.

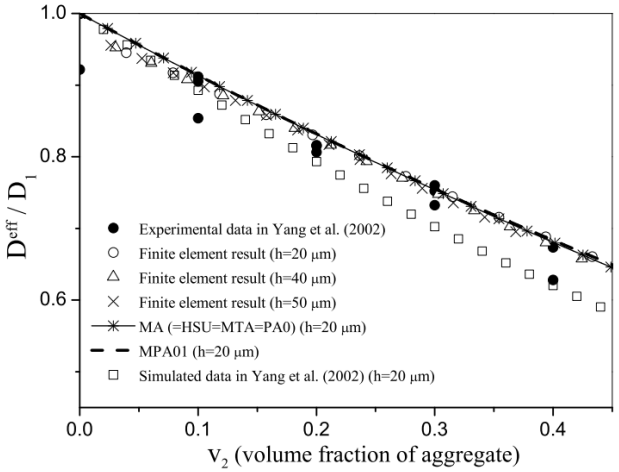


Fig. 10 Dimensionless experimental data for chloride diffusivity of mortar in Yang *et al*. (2002), compared with analytical and numerical solutions (the case of ITZ effect): Maxwell approximation (MA) coincide with upper Hashin-Shtrikman bound (HSU), Mori-Tanaka approximation (MTA) and PA0; MPA01; model of Yang *et al*. (2002); finite element result

6. Conclusions

Based on the available analytical results in the framework of micromechanics, some "optimal" polarization approximations have been constructed for the effective chloride diffusivity of isotropic cement-based materials. The reference parameters are determined from the inhomogeneities' dilute solution result for a matrix composite, and/or from available numerical or experimental values of the macroscopic diffusivity of the composite at certain finite volume proportions of the component materials. In regard to engineering applications, this paper focuses on two-component materials and proposes the variable reference parameter $D*$ as a monotonous function of the volume proportion of a component, which depends on 3 dimensionless free parameters α; β; γ. Some applications are made to present the transport properties of cement paste or concrete. The following conclusions can be drawn from this study:

- A simple model for engineering applications is proposed through combination of the equivalent inclusion approach, and "adaptive" polarization approximations to evaluate the transport properties of three-phase material such as mortar or concrete.
- The agreement between the numerical solution and seven independent sets of experimental data with the analytical model (Fig. 6) show that the MPA3M in Fig. 6 is a good reference for further applications.
- Finite element results show that (Fig. 10), if we accept the relationship between the thickness and diffusivity of

ITZ proposed by Yang *et al*. (Yang and Su 2002), the effective diffusivity of mortar structure is almost independent from the ITZ size.

• Developments of the approximations to the cases of anisotropic particle distribution, more complex porous material structure and those involving the effect of aggregate size distribution on the chloride diffusivity are interesting subjects for the further studies.

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