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A Brownian motion simulation for the chloride diffusivity of concrete

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HIGHLIGHTS

- A Brownian motion simulation is developed for the chloride diffusivity of concrete.
- The cumulative distribution function for aggregates is derived analytically.
- The validity of the simulation method is verified with experimental results.

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ABSTRACT

The purpose of this paper is to present a Brownian motion simulation for the chloride diffusivity of concrete. According to stereological theory, the probability density function and cumulative distribution function for the circular aggregates in terms of the number of aggregates are derived. By coating each aggregate with an interfacial transition zone (ITZ) layer of equal thickness, concrete is then reduced to a two-phase composite material, composed of a bulk cement paste and equivalent aggregates. The equivalent ITZ thickness and the chloride diffusivity of each equivalent aggregate are formulated in an analytical manner. The Brownian motion simulation is used to compute the chloride diffusivity of concrete. Finally, the validity of the numerical simulation is verified with two sets of experimental results and the effects of the aggregate area fraction, the chloride diffusivity of ITZ, and the ITZ thickness on the chloride diffusivity of concrete are evaluated in a quantitative manner. The paper concludes that the numerical simulation can predict the chloride diffusivity of concrete with an average relative error smaller than 6% for the two selected verification examples.

1. Introduction

In a marine or de-icing salt environment, corrosion of steel bars in concrete has become one of the most fundamental issues of civil engineering. The corrosion process can be generally divided into two distinct phases: initiation stage and propagation stage [1]. In the initiation stage, the presence of chloride ions leads to localized breakdown of the protective oxide film on the steel surface. Once the chloride content on the steel surface exceeds the threshold value for depassivation, steel corrosion is triggered. Therefore, the chloride diffusivity of concrete plays a crucial role in the durability design and assessment of reinforced concrete structures [2].

Over the past decades, extensive experimental and theoretical studies have been conducted to determine the chloride diffusivity of concrete and to correlate it to the details of the microstructure. Using a diffusion test and a migration test, Delagrave et al. [2] measured the chloride diffusivities of three series of mortars with different sand volume contents. It was shown that the presence of aggregates tends to modify the microstructure and the transport properties of mortars. The chloride diffusivity decreases with an increase in aggregate volume fraction. The interfacial transition zone (ITZ) facilitates the movement of chloride ions, but its influence seems to be less significant than that of the increased tortuosity of the matrix created by aggregates. To investigate the effects of the dilution, tortuosity, and ITZ of aggregate on the chloride diffusivity of concrete, a migration test was performed by Yang and Su [3]. They made similar conclusions as Delagrave et al. [2], and proposed a model modified from the Bruggeman theory to evaluate the chloride diffusivity of ITZ. From a non-steady-state diffusion test, Caré [4] further demonstrated that, besides introducing the ITZ, aggregates also modify the pore structure and the transport properties of the bulk cement paste [5]. In the theoretical aspect, various analytical and numerical methods have been developed to predict the chloride diffusivity of concrete. Based on ordered periodic aggregate geometries with the ITZ percolation effect, the

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Nomenclature

a	side length of square simulation element
D_a	chloride diffusivity of aggregate
D_{bcp}	chloride diffusivity of bulk cement paste
D_{con}	chloride diffusivity of concrete
D_{eq}	chloride diffusivity of equivalent aggregate
D_i	chloride diffusivity of ITZ
$D^{(i)}$	chloride diffusivity of phase i (bulk cement paste or equivalent aggregate)
$d_{\min}$	minimum aggregate diameter
$d_{\max}$	maximum aggregate diameter
f_a	aggregate area fraction
f_i	ITZ area fraction
h	ITZ thickness
h_{eq}	equivalent ITZ thickness
$H(x)$	Heaviside step function
M	number of computer simulations
N	number of aggregate size grades
N_a	total number of aggregates
N_V	number of spherical aggregates per unit of aggregate
p_1	probability that a Brownian particle initially at the center of a circle near the interface of two phases hits the circular arc in phase 1 for the first time without hitting the circular arc in phase 2
p_2	probability that a Brownian particle initially at the center of a circle near the interface of two phases hits the circular arc in phase 2 for the first time without hitting the circular arc in phase 1
$p_{2N}(r)$	probability density function for circular aggregates in terms of the number of aggregates
$\bar{p}_{2N}(r)$	modified probability density function for circular aggregates in terms of the number of aggregates
$P_{2N}(r)$	cumulative distribution function for circular aggregates in terms of the number of aggregates
$\bar{P}_{2N}(r)$	modified cumulative distribution function for circular aggregates in terms of the number of aggregates
$p_{3N}(R)$	probability density function for spherical aggregates in terms of the number of aggregates
$p_{3V}(R)$	probability density function for spherical aggregates in terms of the volume of aggregates
P_{Vj}	aggregate volume percent passing the sieve with radius R_j
r	radius of circular aggregates
r_i	radius of constructed circle for a Brownian particle located in phase i (bulk cement paste or equivalent aggregate)
r_j	radius of constructed circle for a Brownian particle located near the interface of two phases
r_s	distance from Brownian particle to the interface of two phases
$\langle r^k \rangle$	kth moment of area about the origin for circular aggregates
R	radius of spherical aggregates
$\langle R \rangle$	average radius of spherical aggregates
R_0	radius of constructed circle for a Brownian particle located in homogeneous concrete
R_j	jth sieve radius
t_1, t_2	coefficients in terms of f_a, $\langle r \rangle$, and $\langle r^2 \rangle$
$\bar{t}(X)$	mean hitting time for a Brownian particle initially at the center of a circle of radius X to hit the circumference for the first time
w/c	water/cement ratio
(x_i, y_i)	circular center of ith aggregate
X_i, Y_i	random variables uniformly distributed on the interval $[0, a]$
α, β	chloride diffusivity reduction factors due to addition of slag and fly ash and increase in curing age, respectively

relationship of chloride diffusivity between the ITZ, bulk cement paste, and mortar was established through the Padé approximation [6]. For concrete with low aggregate volume contents, the chloride diffusivity can be estimated by the analytical approximation proposed by Garboczi and Bentz [7]. Caré and Herve [8] put forward an analytical method for the chloride diffusivity of concrete using an n-layered inclusion-based micromechanical modeling. The validity of this method was verified with experimental data on specimens made of plain cement paste and mortar. To take into account the inhomogeneity of the ITZ, Zheng et al. [9] estimated the local water/cement ratio and hydration degree at the ITZ using Powers' empirical model and developed a transfer matrix method to evaluate the effects of various factors on the chloride diffusivity of concrete. Zheng et al. [10,11] also quantified the effect of aggregate shape on the chloride diffusivity of concrete through numerical and analytical methods. However, these analytical methods belong to effective-medium approximations. They are based on idealized unit cell models and therefore are not exact predictions of the chloride diffusivity of concrete. Although the numerical method has attempted to solve the local governing differential equations for the computer-generated heterogeneous concrete subjected to specified boundary conditions, a sufficiently large number of such random configurations need to be solved to give the effective chloride diffusivity of concrete [12]. Clearly, this wasteful way results in a significant loss of information in going from the local to the average fields [13]. In view of these difficulties, a feasible alternative for evaluating the transport properties of heterogeneous media is Brownian motion simulation. Lee et al. [14] adopted a Pearson random walk, in which the step size is fixed and successive directions are random and uncorrelated, to obtain the trapping rate by inversing the average survival time for the random walkers. Based on the first passage time probability distribution, Zheng and Chiew [15] proposed a Brownian motion simulation for the steady-state trapping rate associated with diffusion-controlled reactions. With the probability distribution, the zig-zag random motion of a diffusing particle can be realized in a single simulation step. To dramatically reduce the computational time, Torquato and Kim [16] combined the Einstein-Smoluchowski equation [17] with the grid method to check for trapping [14]. Kim and Torquato further used the Brownian motion simulation technique for predicting the effective conductivity of n-phase heterogeneous media [12] and of two-phase composites composed of hard spheres [13], penetrable spheres [18], and spheroidal inclusions [19]. Another advantage of the simulation method is that it could provide unambiguous tests on effective-medium approximations and rigorous bounding techniques for well-defined continuum models [12]. Therefore, it is highly necessary to apply the pioneering work to concrete to yield the desired chloride diffusivity.

The purpose of this paper is to develop a Brownian motion simulation for the chloride diffusivity of concrete. In this simulation, the concept of equivalent aggregate is introduced by coating each aggregate with an ITZ layer. With this concept, concrete is modeled as a two-phase composite material, consisting of a bulk cement paste and equivalent aggregates. Finally, the Brownian motion simulation proposed by Kim and Torquato [12,13] is used to