Fractal Modeling of Pore Structure and Ionic Diffusivity for Cement Paste

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1. Introduction

Ionic (i.e., chloride ion) diffusivity is one of the critical parameters in service life design of cement based composites for coastal infrastructures [1]. In recent years, much attention has been drawn to the direct assessment of ionic diffusivity on a basis of pore structure which could be obtained from experiment or modeling [2]. However, a practical challenge still exists as a result of the intrinsic complexity of cement based composites. In particular, the pore size distribution may range from nanometer (C-S-H gel pore) to micrometer (capillary pore) of several orders [3]. The multiscale approach is therefore an option, which deals with C-S-H gel and capillary pore in terms of the packing of basic globules and hydration products, respectively [4, 5]. Nevertheless, as it has to assign a large number of parameters and assumptions, the multiscale approach often leads to substantial disadvantages in efficiency and viability. More robust approaches would be beneficial to describe the complex pore structure as well as ionic diffusivity for cement based composites.

The fractal characters have been recognized among natural and artificial porous materials such as limes, soils, rocks, and ceramics [6–10]. In essence, fractal describes a natural phenomenon or object that exhibits similar pattern at different scales [11]. Usually, if one-dimensional length of fractal is magnified, the occupied space of fractal is then magnified by a noninteger power. This power is called the fractal dimension. For a fractal phenomenon or object, the character of similarity at different scales facilitates property characterization.

In an early work, Winslow reported the fractal nature of internal surface for cement paste [12]. Thereafter, the fractal characters in cement paste have been discussed a lot during past decades [13–20]. It was revealed that three types of fractal might be present in cement paste, that is, the pore mass fractal, the pore surface fractal, and the solid mass fractal [21]. Based on the fractal geometry theory, the complex pore structure in cement paste could be modeled via simple iterations, as done in literatures [9, 10, 17, 21]. Moreover, the fractal geometry theory was able to account for various transport properties for porous materials such as permeability [22, 23] and electrical or thermal conductivity [24–28]. In this regard, the fractal modeling shows a great potential to well describe the complex pore structure as well as ionic diffusivity for cement based composites.

In this paper, pore structure in cement paste is modeled by means of the recently proposed solid mass fractal model [21]. Moreover, an enhanced Maxwell homogenization method that incorporates the solid mass fractal model is proposed to determine the associated ionic diffusivity.
Experiments are performed to validate the modeling, that is, mercury intrusion porosimetry (MIP) and rapid chloride migration (RCM).

2. Solid Mass Fractal Model

As shown in Figure 1, for the solid mass fractal to model porous medium, the generator refers to two distinct phases, that is, the pore phase and the iterating phase. At the initial step, a blank region with linear length $L$ is defined in $E$-dimension Euclidean space which can further be divided into $N$ identical subregions. Let $n$ be the number of subregions in each dimension such that $N = n^E$. Moreover, let $w$ and $b$, respectively, be the proportion and number of iterating phase in the generator such that $b = wN$. Upon successive iterations, the pattern of generator is repeated for the iterating phase at different scales. The generated pore structure can be analyzed as follows.

**Step 1.** The number of iterating phase and pore phase with the size $a_1 = L/n$ reads $wN$ and $(1 - w)N$, respectively.

**Step 2.** The number of iterating phase and pore phase with the size $a_2 = L/n^2$ reads $(wN)^2$ and $(1 - w)wN^2$, respectively.

**Step i.** The number of iterating phase and pore phase with the size $a_i = L/n^i$ reads $(wN)^i$ and $(1 - w)N^i w^{i-1}$, respectively.

For the generated porous medium, the solid fraction or density $\chi$ is defined as the ratio of solid volume to the total volume that

$$\chi = \frac{V_{\text{tot}} - V}{V_{\text{tot}}},$$

where $V_{\text{tot}}$ is the total volume and $V$ is the resultant volume of pore phase. As a result, the solid fraction at Step 1 of iteration holds that $\chi_1 = w$. If a constant $D = \log(Nw)/\log(n)$ is defined, the solid fraction $\chi_i$ can then be rewritten as follows with respect to $a_i = L/n^i$ and $N = n^E$:

$$\chi_i = \left(\frac{a_i}{L}\right)^{E-D}.$$  \hfill (2)

Equation (2) suggests that the generated porous medium is a solid mass fractal with the dimension of $D$. In a log-log diagram, the linearity shall be detected for the solid fraction $\chi_i$ against the pore size $a_i$. In addition, the pore size distribution in terms of $f$ versus $a_i$, that is, the cumulative porosity $f$ that counts from the large to the small pores, can be expressed as follows:

$$f \geq a = 1 - \chi_i = 1 - \left(\frac{a}{L}\right)^{E-D}.$$  \hfill (3)

3. Modeling of Pore Structure

The MIP test was performed to validate the solid mass fractal model [29]. Figure 2 shows the pore size distribution of cement paste with water cement (w/c) of 0.4 and age of 28 days, which was cured at the condition of 95\% ± 10\% relative humidity and 20\°C ± 1\°C temperature. For the solid fractal mass model, solid fraction is plotted against pore diameter in the log-log diagram, as shown in Figure 3. It can be noted that the sound piecewise linearity exists. Moreover, the slope of linearity varies within two pore ranges. Let $d_{\text{low}}$ and $d_{\text{upp}}$ be the lower and upper limit of pore diameter, and let $d_{\text{thr}}$ be the threshold of pore diameter for the two pore ranges. The values of $d_{\text{low}}, d_{\text{thr}},$ and $d_{\text{upp}}$ can be determined as $d_{\text{low}} = 0.004 \mu m$, $d_{\text{thr}} = 0.1 \mu m$, and $d_{\text{upp}} = 2 \mu m$. In other words, the two pore ranges, that is, the large and the small pore range, are located as $d_{\text{upp}} \sim d_{\text{thr}}$ and $d_{\text{thr}} \sim d_{\text{low}}$, that is, $2 \sim 0.1 \mu m$ and $0.1 \sim 0.004 \mu m$. The large pore range corresponds to capillary pores, while the small pore range corresponds to C-S-H gel pores.

With the determined pore ranges ($d_{\text{upp}} \sim d_{\text{thr}}, d_{\text{thr}} \sim d_{\text{low}}$), the least square method is then applied to fit the associated slopes ($k_{\text{upp}} = 0.0206, k_{\text{low}} = 0.0607$) as well as
the fractal dimensions \((D_{\text{upp}} = 2.9794, D_{\text{low}} = 2.9393)\) since \(D_{\text{upp}} = E - k_{\text{upp}}, D_{\text{low}} = E - k_{\text{low}}\), and \(E = 3\). Meanwhile, it is possible to specify the partial porosity of large and small pore range \((f_{\text{upp}} = 0.0746, f_{\text{low}} = 0.1497)\) with the total porosity \(f\) holding that \(f = f_{\text{upp}} + f_{\text{low}}\). In rough comparison, the fractal dimension of small pore range is smaller than that of large pore range, that is, \(D_{\text{low}} < D_{\text{upp}}\). The partial porosity of small pore range is larger than that of large pore range, that is, \(f_{\text{low}} > f_{\text{upp}}\). The fractal modeling of pore structure in cement paste refers to two specific structures, that is, two fractal generators for the large and the small pore range.

For the large pore range, let two integers \(i_{\text{upp}}\) and \(n_{\text{upp}}\) be the step of iterations and the number of subregions such that \(i_{\text{upp}} = \log(d_{\text{upp}}/d_{\text{thr}})/\log(n_{\text{upp}})\). The solid mass fractal model requires \(n_{\text{upp}} \geq 2, i_{\text{upp}} \geq 2, \) and \(n_{\text{upp}} \cdot D_{\text{upp}} \geq 1\). In this paper, the symbol \(^{\wedge}\) denotes the power operator. Without complicated mathematical analysis, it leads to \(n_{\text{upp}} = 4\) and \(i_{\text{upp}} = 3\). The value of \(w_{\text{upp}}\) is obtained via \(\log(w_{\text{upp}}) = (D_{\text{upp}} - 3) \cdot \log(n_{\text{upp}})\). The number of iterating phase \(h_{\text{upp}}\) holds that \(h_{\text{upp}} = w_{\text{upp}} \cdot (n_{\text{upp}})^{3}\). The intrinsic porosity of generated pore structure \(f_{\text{upp}}^{\ast}\), holds that \(f_{\text{upp}}^{\ast} = 1 - [h_{\text{upp}}/(n_{\text{upp}})^{3}]^{\wedge} i_{\text{upp}}\). Details of analysis for the example are shown as follows:

The large pore range: \(n_{\text{upp}} = 4, i_{\text{upp}} = 3\)

The proportion of iterating phase: \(w_{\text{upp}} = n_{\text{upp}} \cdot (D_{\text{upp}} - 3) = 4^{\wedge}(-0.0206) = 0.9718\)

The number of iterating phases: \(h_{\text{upp}} = w_{\text{upp}} \cdot (n_{\text{upp}})^{3} = 0.9718 \cdot 4^{3} = 62\)

The intrinsic porosity: \(f_{\text{upp}}^{\ast} = 1 - [h_{\text{upp}}/(n_{\text{upp}})^{3}]^{\wedge} i_{\text{upp}} = 1 - 0.0909\)

For the small pore range, let two integers \(i_{\text{low}}\) and \(n_{\text{low}}\) be the step of iterations and the number of subregions, which holds that \(i_{\text{low}} = \log(d_{\text{thr}}/d_{\text{low}})/\log(n_{\text{low}})\). The solid mass fractal model requires \(n_{\text{low}} \geq 2, i_{\text{low}} \geq 2, \) and \(n_{\text{low}} \cdot D_{\text{low}} \geq 1\). It leads to \(n_{\text{low}} = 3\) and \(i_{\text{low}} = 3\). The value of \(w_{\text{low}}\) is obtained via \(\log(w_{\text{low}}) = (D_{\text{low}} - 3) \cdot \log(n_{\text{low}})\). The number of iterating phase \(h_{\text{low}}\) holds that \(h_{\text{low}} = w_{\text{low}} \cdot (n_{\text{low}})^{3}\). The intrinsic porosity of generated pore structure \(f_{\text{low}}^{\ast}\), holds that \(f_{\text{low}}^{\ast} = 1 - [h_{\text{low}}/(n_{\text{low}})^{3}]^{\wedge} i_{\text{low}}\). Details of analysis for the example are shown as follows:

The small pore range: \(n_{\text{low}} = 3, i_{\text{low}} = 3\)

The proportion of iterating phase: \(w_{\text{low}} = n_{\text{low}} \cdot (D_{\text{low}} - 3) = 3^{\wedge}(-0.0607) = 0.9355\)

The number of iterating phases: \(h_{\text{low}} = w_{\text{low}} \cdot (n_{\text{low}})^{3} = 0.9355 \cdot 3^{3} = 25\)

The intrinsic porosity: \(f_{\text{low}}^{\ast} = 1 - [h_{\text{low}}/(n_{\text{low}})^{3}]^{\wedge} i_{\text{low}} = 1 - (25/27)^{3} = 0.2062\)

The build-up of pore structure in cement paste follows from the large to the small pore range. In particular, after \(i_{\text{upp}}\) steps of iteration to generate the large pore range, the size and number of iterating phase is \(d_{\text{thr}}\) and \((b_{\text{upp}})^{\wedge} i_{\text{upp}}\), respectively. Note that during the process to generate the small pore range, not all the iterating phases with size of \(d_{\text{thr}}\) are to be further iterated but a proportion of \(\gamma\) \((\gamma \leq 1)\). In other words, the \(1 - \gamma\) proportion of iterating phases with size of \(d_{\text{thr}}\) shall not be performed with further iterations. With respect to the chemical composition of cement paste, such \(\gamma\) and \(1 - \gamma\) proportion of iterating phases are introduced as C-S-H gel and solid phases, respectively. The solid phases may be anhydrous cement, calcium hydroxide crystal, Aft, and gypsum. It is necessary to determine \(\gamma\) to fulfill the build-up of pore structure in cement paste. Herewith, consider the total porosity \(f\) satisfying \(f = f_{\text{upp}} + f_{\text{low}} \cdot \gamma \cdot (w_{\text{upp}})^{\wedge} i_{\text{upp}}\). Then, \(f = 0.2243, f_{\text{upp}} = 0.0909, f_{\text{low}} = 0.2062, w_{\text{upp}} = 0.9718\), and \(i_{\text{upp}} = 3\) lead to \(\gamma = 0.7115\). Figure 4 shows one realization of modeled pore structure in cement paste. In particular, it refers to two specific structures, that is, the capillary structure and the C-S-H gel structure. The capillary structure of large pore range consists of three phases, that is, the (capillary) pore phase, the solid phase (anhydrous cement, calcium hydroxide crystal, Aft, and gypsum), and the C-S-H gel phase. The C-S-H gel structure of small pore range consists of two phases, that
Figure 4: Realization of pore structure in cement paste (a) C-S-H gel structure \( n_{\text{low}} = 3, i_{\text{low}} = 3, b_{\text{low}} = 25 \) with element size of 0.004\( \mu \text{m} \); (b) capillary structure of cement paste \( n_{\text{upp}} = 4, i_{\text{upp}} = 3, b_{\text{upp}} = 62, \gamma = 0.7115 \) with element size of 0.1\( \mu \text{m} \). Black denotes the pore phase, white denotes the solid phase, and gray denotes the C-S-H gel phase.

is, the (gel) pore phase and the solid phase (molecule layers within C-S-H gel). The pore size distribution can be written in terms of the piecewise form:

\[
\begin{align*}
\text{for } d > d_{\text{thr}}, & \quad d = d_{\text{upp}}/(n_{\text{upp}}^\wedge j), f(\geq d) = 1 - w_{\text{upp}}^\wedge j, \\
\text{for } d \leq d_{\text{thr}}, & \quad d = d_{\text{thr}}/(n_{\text{low}}^\wedge j), f(\geq d) = (1 - w_{\text{upp}}^\wedge i_{\text{upp}}) \cdot (1 - w_{\text{low}}^\wedge j) \cdot (w_{\text{upp}}^\wedge i_{\text{upp}}), \quad j = 1, \ldots, i_{\text{low}}.
\end{align*}
\]

In particular, for example, it holds that

\[
\begin{align*}
\text{for } d > 0.1\mu\text{m}, & \quad d = d_{\text{upp}}/(4^\wedge j), f(\geq d) = 1 - (62/64)^\wedge j, \quad j = 1, 2, 3; \\
\text{for } d \leq 0.1\mu\text{m}, & \quad d = d_{\text{thr}}/(3^\wedge j), f(\geq d) = 1 - (25/27)^\wedge j \cdot (62/64)^\wedge 3, \quad j = 1, 2, 3.
\end{align*}
\]

4. Enhanced Maxwell Homogenization Method

The calculation of effective properties of heterogeneous materials that contain inclusions of diverse shape and/or properties withstands a long history. Numerous homogenization schemes have been developed so far [30–32]. Among them, the Maxwell homogenization method is probably the oldest and also most famous one [33]. It considers heterogeneous materials with unknown effective ionic diffusivity \( D_{\text{eff}} \) consisting of bulk phase with ionic diffusivity \( D_B \) and inclusion phase with ionic diffusivity \( D_I \). Mathematically, the Maxwell homogenization method can be described as follows:

\[
D_{\text{eff}} = \frac{D_I + 2D_B + 2(D_I - D_B)c}{D_I + 2D_B - (D_I - D_B)c} D_B,
\]

(4)

where \( c \) is the volume fraction of inclusions.

An enhanced Maxwell homogenization method is proposed that incorporates the solid mass fractal model to calculate ionic diffusivity of cement paste. In particular, cement paste is viewed as the composite material consisting of two phases. One refers to the low-diffusivity C-S-H gel structure being bulk. The other refers to the high-diffusivity capillary structure being inclusions. The treatment of two distinct phases was also applied in the general effective media theory [34–36]. For bulk (C-S-H gel structure) and inclusion (capillary structure), the associated ionic diffusivity can be approximated in a power form of intrinsic porosity [37, 38]:

\[
\begin{align*}
D_B & = \gamma D_1 (f_{\text{low}}^*)^{\delta_1}, \\
D_I & = D_2 (f_{\text{upp}}^*)^{\delta_2},
\end{align*}
\]

(5)

where \( D_1 \) and \( D_2 \) are constants, that is, ionic diffusivities in water corresponding to C-S-H gel and capillary structures. \( \delta_1 \) and \( \delta_2 \) are the cementation exponent in Archie’s law for C-S-H gel and capillary structures. Other parameters, that is, \( f_{\text{upp}}^*, f_{\text{low}}^* \), and \( \gamma \) are defined in the solid mass fractal model. In addition, the volume fraction of inclusions is derived from

\[
c = \frac{f_{\text{upp}}}{f_{\text{upp}} + f_{\text{low}}}.
\]

(6)

As presented above, the Maxwell homogenization method is enhanced with critical parameters determined from the solid mass fractal model and Archie’s law. Then, the enhanced Maxwell homogenization method can be applied to predict effective ionic diffusivity of cement paste.

5. Rapid Chloride Migration Test

The RCM test was performed to measure ionic (chloride) diffusivity of cement paste [39, 40]. Cement paste samples
of 50 mm in thickness and 100 mm in diameter were prepared. Samples were then subjected to the vacuum saturation treatment. The saturated samples were treated to be surface-dry. Three samples of replicates were tested at the same time. Power sources with constant voltage outputs (adjustable in the range of 0 ∼ 80 V, accuracy of 0.05 V) were applied. The catholyte and anolyte were 10% NaCl solution and 0.3 M NaOH solution, respectively. The electrolytes were refreshed after each series of tests. After the migration test, the samples were split and sprayed with a 0.1 M AgNO₃ solution in order to determine the penetration depth of chlorides. The non-steady-state migration coefficient $D_{RCM}$, that is, ionic (chloride) diffusivity, was calculated according to the NT Build 492 as follows:

$$D_{RCM} = \frac{0.0239 (273 + T) l}{(U - 2) t_d} x_d \left( \frac{273 + T}{U - 2} \right)^{0.0238},$$

where $D_{RCM}$ is the non-steady-state migration coefficient, $\times 10^{-12}$ m²/s; $U$ is absolute value of the applied voltage, V; $T$ is average value of the initial and final temperatures in the anolyte solution, °C; $l$ is thickness of the specimen, mm; $x_d$ is average value of the penetration depth, mm; and $t_d$ is the test duration, h.

6. Results and Discussions

Cement pastes with w/c ratios of 0.4, 0.5, and 0.6 were compared, as shown in Figure 5. All samples were cured at the same condition (28 days, 95% ± 10% relative humidity, 20°C ± 1°C temperature). Figure 6 shows the parametric analysis with respect to the solid mass fractal model. Results are summarized in Tables 1 and 2. Table 1 suggests that as w/c ratio increases, the partial porosities $(f_{upp}, f_{low})$ increase, while the fractal dimensions $(D_{upp}, D_{low})$ decrease. Table 2 suggests that some parameters, that is, $n_{low}, i_{low}, n_{upp}$, and $i_{upp}$, do not change with w/c ratio, while some parameters, that is, $b_{upp}, b_{low}$, and $\gamma$, do. That means the three parameters $(b_{upp}, b_{low}, \gamma)$ are critical to characterize the effect of w/c ratio on geometry of capillary and C-S-H gel structure. Figure 7 shows the comparison of modeled and measured pore size distributions of cement pastes.

With the enhanced Maxwell homogenization method, ionic diffusivity of cement paste can be obtained. The parameters listed in Tables 1 and 2 are used, that is, $(f_{upp}, f_{low})$ and $(n_{low}, i_{low}, n_{upp}, i_{upp}, b_{upp}, b_{low}, \gamma)$. Besides, values of the parameters $(D_1, D_2, \delta_1, \delta_2)$ are suggested in Table 3. In
Figure 7: Modeled and measured pore size distribution of cement pastes with varying w/c ratios.

Table 4: Parameters measured in RCM test of cement pastes.

<table>
<thead>
<tr>
<th>w/c ratio</th>
<th>( T ) (°C)</th>
<th>( U ) (V)</th>
<th>( t_d ) (hour)</th>
<th>( l ) (mm)</th>
<th>( x_d ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>26.0</td>
<td>25</td>
<td>24</td>
<td>49.6</td>
<td>18.7</td>
</tr>
<tr>
<td>0.5</td>
<td>25.1</td>
<td>15</td>
<td>24</td>
<td>49.8</td>
<td>18.9</td>
</tr>
<tr>
<td>0.6</td>
<td>23.5</td>
<td>15</td>
<td>24</td>
<td>50.2</td>
<td>29.5</td>
</tr>
</tbody>
</table>

For the RCM test, the measured parameters are listed in Table 4, which leads to an easy calculation of the non-steady-state migration coefficient \( D_{RCM} \). As shown in Figure 8, results of the fractal modeling (\( D_{eff} \)) agree well with those obtained from experiment (\( D_{RCM} \)). In this regard, the present fractal modeling provides an optional description of pore structure as well as ionic diffusivity for cement paste.

7. Concluding Remarks

In this paper, modeling of pore structure as well as ionic diffusivity for cement paste is performed based on the fractal geometry theory. The solid mass fractal model is applied to model pore structure, and an enhanced Maxwell homogenization method that incorporates the solid mass fractal model is proposed to calculate the associated ionic diffusivity. Some general conclusions are drawn as follows:

1. The solid mass fractal model well describes pore structure in cement paste in terms of two pore ranges, that is, the large (capillary) and the small (C-S-H gel) pore range. The fractal generator varies with the pore range.

2. The enhanced Maxwell homogenization method considers cement paste consisting of low-diffusivity C-S-H gel structure and high-diffusivity capillary structure. Archie’s law is applicable to approximate ionic diffusivity for C-S-H gel and capillary structures.

Nomenclature

- \( L \): Linear length of modeling space
- \( E \): Dimension of Euclidean space
- \( N \): Total number of identical subregions
- \( n \): Number of identical subregions in one dimension
- \( w \): Proportion of iterating phase in generator
- \( b \): Number of iterating phases in generator
- \( i \): Step of iteration
- \( a_i \): Size of iterating phase
- \( \chi \): Solid fraction or density
- \( V_{tot} \): Total volume of porous medium
- \( V \): Volume of pore phase
- \( D \): Fractal dimension
- \( f \): Cumulative porosity \( f \) that counts from large to small pore
- \( d \): Equivalent pore diameter
- \( d_{low}, d_{thr}, d_{upp} \): Lower, threshold, and upper limit of equivalent pore diameter
- \( k_{upp}, k_{low} \): Slope of large and small pore range
- \( D_{upp}, D_{low} \): Fractal dimension of large and small pore range
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\( f_{\text{upp}}, f_{\text{low}} \): Partial porosity of large and small pore range

\( i_{\text{upp}}, i_{\text{low}} \): Step of iteration to generate large and small pore range

\( n_{\text{upp}}, n_{\text{low}} \): One-dimension number of subregions for large and small pore range

\( w_{\text{upp}}, w_{\text{low}} \): Proportion of iterating phase in generator for large and small pore range

\( b_{\text{upp}}, b_{\text{low}} \): Number of iterating phases in generator for large and small pore range

\( f'_{\text{upp}}, f'_{\text{low}} \): Intrinsic porosity of large and small pore range

\( y \): Proportion of iterating phase being C-S-H gel

\( D_{\text{eff}} \): Effective ionic diffusivity of porous medium

\( D_B, D_I \): Ionic diffusivity of bulk and inclusion phase

\( c \): Volume fraction of inclusions

\( D_1, D_2 \): Ionic diffusivity in water corresponding to gel and capillary pore

\( \delta \): Cementation exponent in Archie's law

\( D_{\text{RCM}} \): Non-steady-state migration coefficient

\( U \): Absolute value of the applied voltage

\( T \): Average value of the initial and final temperatures in anolyte solution

\( l \): Thickness of the specimen

\( x_d \): Average value of the penetration depth

\( t_d \): Test duration.

Competing Interests

The authors declare that they have no competing interests.

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