MATHEMATICAL MODELING OF CEMENT HYDRATION PROCESS 
AND MICROSTRUCTURE DEVELOPMENT

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Abstract

In this research, a mathematical model of cement hydration process and microstructural development was developed. A cubic hydration cell, which is composed by unreacted cement particles, hydration products and free water, is presented to describe the microstructural development of cement particles. The kinetics of cement hydration are given as the driving force of the model. Although the cement particle size distribution is introduced in the model, the specially designed hydration cell can still keep its individual properties. The mathematical model can present the cement hydration process more detailed in such a simple way. The comparison between numerical and experimental results proves that the newly developed model is quite effective and potentially useful for predicting the hydration and microstructure of cement paste.

1. INTRODUCTION

Once cement particles are in contact with water, a set of chemical and physical interactions will occur immediately. In microscopic point of view, cement particles undergo a series of transformation as dissolution, diffusion, deposition and connection. Macroscopically, the cement paste system is converted from a suspension into a dense solid. Undoubtedly, the properties of the final solid, especially the strength and durability, are inherently controlled by the microstructural formation during cement hydration. In recent years, the application of high strength and high performance concrete has emphasized the importance of knowing the early age physical properties during the hardening process. A better understanding and presentation of the cement hydration process, especially with mathematical method, has drawn the interests around the world.

The research on the cement hydration with mathematical model can be traced back to the modeling of the hydration of C₃S [1]. Because the cement hydration model based on hydration kinetics can take an insight into the influence intrinsic factors (the state and microstructure of reactants) and extrinsic factors (activators) to the hydration rate and reaction direction in macro-level. Then a large number of methods and models have been developed [2-4]. In the last 20 years, due to the rapid increase in theoretical research and computer
technology, investigation on cement hydration with mathematical method has gain a considerable progress. In 1991, Bentz and Garboczi [5] gave a three-dimensional digital-image-based simulation model of cement hydration based on the investigation of the effects of water-to-cement ratio, degree of hydration, and the substitution of inert and pozzolanic mineral admixtures for cement. In 1995, van Breugel [6-7] established a model, called HYMOSTRUC, to predict the hydration curves as a function of the particle size distribution and chemical composition of the cement, the water/cement ratio and the actual reaction temperature. Stroeven [8], in 1999, simulated the cement hydration with the application of the software package of particulate system and the structural evolution, SPACE. Both HYMOSTRUC and SPACE analyzed the cement hydration process with the consideration of the difference of cement particles size. Since cement particle size distribution increased the complexity of the model two simplified methods were given. In 2000, Dabic and Krstulovic [9-10] achieved a mathematical method in modeling of cement hydration process in macro-level. Some researchers developed models with uniform cement particle size and distribution in 2D [11] and 3D [12]. The work of Dabic and Krstulovic focused on the presentation of the transition conditions of cement hydration process within the hydration kinetics. But it lost the micro explanations of the cement hydration process. The neglect of particle size distribution will lead to inapposite control of hydration rate in the model. So the balance of the complexity and the accuracy of the mathematical modeling of cement hydration is still a challenge for the researchers.

In this research, a microstructural model of cement particles is presented to describe the cement hydration procedure. To simplify the hydration process, the whole hydration is analyzed in a series of sub-steps. In each step, the hydration degree, as well as the size of the hydration cell, is calculated as a function of the inner diameter of the unreacted cement particles, while the calculated hydration degree is also a key parameter to evaluate the reduction of inner diameter of the next step. The minimum energy consumption law is introduced to determine the controlling process during hydration. The reduction of inner diameter of the cement particles is calculated from the extended hydration kinetic equations which derived under the assumption that the basic kinetic parameters have a linear relationship with the cement compositions. The influences of the reduction of free water, the reduction of the interfacial area of contact between the free water and the hydration products on the reduction of inner diameter and particles distribution are also taken into consideration. The whole calculation is programmed with mathematical tool MATLAB and a comparison between the numerical analysis of model and test results in experiment is conducted.

2. CEMENT HYDRATION MODEL

The basis of development of a cement hydration is defined relative to the hydration degree \( \alpha \) which can be expressed by released heat at time \( t \), \( Q(t) \), and the ultimate heat that cement can release \( Q_{\text{max}} \).

\[
\alpha(t) = \frac{Q(t)}{Q_{\text{max}}} \tag{1}
\]

where \( Q(t) \) is the heat released by age \( t \); \( Q_{\text{max}} \) is the ultimate heat that cement can release which can be calculated with cement composition: \( C_S(500 \, J/g) \), \( C_S(260 \, J/g) \), \( C_A(866 \, J/g) \), \( C_AF(420 \, J/g) \), \( Mgo(850 \, J/g) \), free \( CaO(1168 \, J/g) \), \( SO_3(624 \, J/g) \) [13].
2.1 Unit cell

In this research, the cement paste is assumed to be composed of the cement particles and the water around them. To simplify this model, all the particles dispersed in the water don’t contact with each other. Furthermore, there is no materials exchange between any unit cells even the water solution. As shown in Fig. 1, each particle and corresponding water is formulated geometrically in terms of a cubic cell in which the entire hydration process is carried out. Because the hydration of the cement particles represents the macro hydration process of the concrete, so the cube can be named as unit cell in this investigation.

![Unit cell of cement hydration](image)

(a) Unit cell of single cement particle  (b) Unit cells of cement particles

Figure 1 Unit cell of cement hydration

It can be concluded from geometry that, at the initial step, the side length of the unit cell $L_{R,0}$ and the radius of the cement particle $R$ are related by following equation.

$$L_{R,0} = \left[\frac{4\pi}{3} (\rho_{cw} W_0 + 1)\right]^{\frac{1}{3}} R$$

(2)

where $\rho_{cw}$ is specific gravity of cement particle, $W_0$ is water to cement ratio.

2.2 Microstructural hydration model

The chemical reaction between cement and water produces a gel product. It is clear that the hydration of cement particle starts from the surface of the particles that contact with water. Then some hydration products, named as the inner hydration products, grow inward to the reacted cement, and the other hydration products, named as the outer hydration products, grow outward on the surface of the particles to fill the space of the reacted water. Based on Breugel [6,7], the microstructural model of hydrated cement particle can be shown in Fig. 2. The schematic presentation of the growth of the hydration products during hydration process is shown in Fig. 3 and Fig. 4.
2.3 Geometrical parameters

The geometrical parameter $R_{in,i}$, named as the inner radius, represents the radius of unreacted cement particle, while the outer radius, $R_{out,i}$, represents the outer boundary of the
hydration products growing on the cement particle. It should be emphasized that \( R_{R,0} \) in the subscript expression means the initial radius of cement particle.

Based on the microstructural model of cement particle, the geometrical parameters at hydration step \( i \) can be calculated by following relationships.

### 2.3.1 Inner radius \( R_{\text{in},R,i} \)

At a certain hydration step, i.e., step \( i \), the change of the radius of cement particle is \( dR_{R,i} \). The inner radius at this step can be given as:

\[
R_{\text{in},R,i} = R_{\text{in},R,i-1} - dR_{R,i} 
\]

### 2.3.2 Outer radius \( R_{\text{out},R,i} \)

The change of the reacted cement volume at step \( i \) \( dV_{\text{in},R,i} \) is:

\[
dV_{\text{in},R,i} = \frac{4\pi}{3}(R_{\text{in},R,i-1}^3 - R_{\text{in},R,i}^3) 
\]

Then the change of the outer hydration products volume \( dV_{\text{out},R,i} \) is:

\[
dV_{\text{out},R,i} = (v_1 - 1)dV_{\text{in},R,i} 
\]

where \( v_1 \) is the volume ratio of hydration products to the reacted cement, which is taken as 2.2 [6]. The outer radius \( R_{\text{out},R,i} \) can be expressed as:

\[
R_{\text{out},R,i} = R_{\text{out},R,i-1} + dV_{\text{out},R,i} / S_{w,R,i-1} 
\]

where \( S_{w,R,i} \) is the surface area of a cement particle that contacts with water at step \( i \).

### 2.3.3 Side length of unit cell \( L_{R,i} \)

The water withdrawal during the hydration process will cause the decrease of the unit cell volume. So the side length of unit cell is not a constant in the model.

1) when \( L_{R,i-1} < 2R_{\text{out},R,i-1} \)

When \( L_{R,i-1} < 2R_{\text{out},R,i-1} \), the neighbored cement particles are not in contact with each other. The side length of unit cell decreases with the consumption of the free water. So the volume change of the unit cell \( dV_{L,R,i} \) is attributed to water withdrawal and the growth of the outer hydration products, which can be given as:

\[
dV_{L,R,i} = (v_2\rho_{cw} - v_1)dV_{\text{in},R,i} 
\]

where \( v_2 \) is the ratio of the reacted water to the reacted cement which is taken as 0.4 [6]. So the side length of unit cell \( L_{R,i} \) is:

\[
L_{R,i} = (L_{R,i-1}^3 - dV_{L,R,i})^{1/3} 
\]

2) when \( L_{R,i-1} > 2R_{\text{out},R,i-1} \)
When \( L_{R,i-1} < 2R_{\text{out},R,i-1} \), the neighbored particles will be in contact with each other. Then the hydration products will grow on the surface of the particles in contact with free water. And the side length of unit cell \( L_{R,i} \) will have no change.

\[
L_{R,i} = L_{R,i-1}
\]  

(9)

### 2.3.4. Surface area of the cement particle in contact with water \( S_{w,R,i} \)

Due to the increase of \( R_{\text{out},R,i} \), the contacted area of neighbored particles will extend and \( S_{w,R,i} \) will change correspondingly.

1) when \( L_{R,i} \leq 2R_{\text{out},R,i} \)

When \( L_{R,i} \leq 2R_{\text{out},R,i} \), the area of cement particle is in contact with water at step \( i \) is:

\[
S_{w,R,i} = 4\pi R_{\text{out},R,i}^2
\]  

(10)

2) when \( L_{R,i} < 2R_{\text{out},R,i} < \sqrt{2}L_{R,i} \)

Once the diameter of outer hydration products \( 2R_{\text{out},R,i} \) exceeds \( L_{R,i} \), the neighbored particles are in contact with each other. Then \( S_{w,R,i} \) is:

\[
S_{w,R,i} = 6\pi R_{\text{out},R,i}L_{R,i} - 8\pi R_{\text{out},R,i}^2
\]  

(11)

3) when \( \sqrt{2}L_{R,i} \leq 2R_{\text{out},R,i} < \sqrt{3}L_{R,i} \)

When \( 2R_{\text{out},R,i} \) is larger than the diagonal of the cross section of the unit cell, all the six surface of the unit cell will link with others. Then \( S_{w,R,i} \) is:

\[
S_{w,R,i} = 6\pi R_{\text{out},R,i}L_{R,i} - 8\pi R_{\text{out},R,i}^2 + 12\pi R_{\text{out},R,i}^3 \left[ R_{\text{out},R,i}^2 - L_{R,i}^2 / 2 - 6\pi R_{\text{out},R,i} \arccos(L_{R,i} / (\sqrt{2}R_{\text{out},R,i})) \right]
\]  

(12)

### 2.3.5. Hydration degree of single cement particle \( \alpha_{R,i} \)

Derived from Eq.1, the hydration degree of single cement particle with initial radius \( R \) at step \( i \) \( \alpha_{R,i} \) is given as:

\[
\alpha_{R,i} = Q_{R,i} / Q_{\text{max}} = 1 - R_{\text{in},R,i}^3 / R^3
\]  

(13)

Once the change of the radius of cement particle is determined, the hydration degree of the cement particle at step \( i \) can be calculated with Eq.13.

### 2.4. Microstructural expressions of cement hydration kinetics

The whole cement hydration process is always divided into three simultaneous subprocesses: nucleation and crystal growth (NG), interactions at phase boundaries (I) and diffusion (D). The hydration model is derived under the assumption that only one sub-process controls the hydration rate[14]. The hydration kinetic equations give the macro representation of the cement hydration process, while they can not be applied to the microstructural model directly. In this research, the inner radius change of a cement particle during the nucleation and growth process, interaction process and diffusion process at step \( i \) are defined as follows, respectively:
where $dR_{NG,R,i}$, $dR_{I,R,i}$, $dR_{D,R,i}$ are the inner radius change during the nucleation and growth process, interaction process and diffusion process at step $i$ respectively; $K_{NG}$, $K_I$, $K_D$ are the reaction rate constant of the nucleation and growth process, interaction process and diffusion process; $dt$ is the time change; $n$ is the exponent describing geometrical crystal growth; $d$ is the depth of the inner hydration products at step $i$ and $D_i = R - R_{in,R,i}$; $\lambda$ is the control index, when $K_I/K_D > 2D$, $\lambda = 0$; $K_I/K_D < 2D$, $\lambda = 1$.

Cement hydration is a complex process with the combination of nucleation and growth, interaction and diffusion reactions happening at the same time. In this research, it is assumed that the hydration of single cement particle is governed by one of the three hydration reactions at a certain time and all the mineral components in the cement particle have the same hydration degree. According to the least potential energy theory, the governing hydration reaction must have the least drop of the inner energy. So the hydration degree change during time $dt$ can be given as:

$$ \frac{d\alpha}{dt} = \min\left( \frac{d\alpha}{dt}_{NG}, \frac{d\alpha}{dt}_{I}, \frac{d\alpha}{dt}_{D} \right) $$

Then the inner radius change in theory at step $i$ $dR_{R,i}^{theory}$ can be expressed as:

$$ dR_{R,i}^{theory} = \min(dR_{NG,R,i}, dR_{I,R,i}, dR_{D,R,i}) $$

$dR_{R,i}^{theory}$ here is the inner radius change carried out from the hydration kinetic equations. In fact, during cement hydration process, the assumption of free water and the shrinkage of the contact area between cement particle and free water will have notable influence on $dR_{R,i}^{theory}$. The environment temperature and unreacted cement particle affect the hydration process. So several coefficients are applied in representation of the inner radius change of cement particle at step $i$:

$$ dR_{R,i} = \eta_1(W_{w,R,i-1})\eta_2(S_{w,R,i-1})\eta_3(V_{w,R,i-1})\eta_4(\theta_i)\eta_5(\alpha_{R,i-1})dR_{R,i}^{theory} $$

Where

$\eta_1(W_{w,R,i})$-influence coefficient of free water at step $i$. $\eta_1(W_{w,R,i}) = W_{w,R,i}/W_w$, where $W_{w,R,i}$ is the free water in the unit cell at step $i$, $W_{w,R,i} = W_{w,R,i-1} - dW_{w,R,i}$, $W_w$ is the initial free water by weight in the unit cell, $W_w = 4\pi r_c W_0/3$.

$\eta_2(S_{w,R,i})$-influence coefficient of contact area between cement particle and free water at step i, $\eta_2(S_{w,R,i}) = S_{w,R,i}/4\pi R_{out,R,i}^2$.

$\eta_3(V_{w,R,i})$-influence coefficient of free water volume at step i. $\eta_3(V_{w,R,i}) = V_{w,R,i}/V_{space,R,i}$, where $V_{w,R,i}$ is free water volume in the unit cell at step i, $V_{w,R,i} = V_{w,R,i-1} - dV_{w,R,i}$, $V_{space,R,i}$ is the pore volume at step i, $V_{space,R,i} = L_{R,i}^3 - V_{in,R,0} - (v-1)\alpha_{R,i}V_{in,R,0}$.
\( \eta_{4}(\theta_{0}) \)-influence coefficient of environment temperature calculated with Arrhenius function. 
\[ \eta_{4}(\theta_{0}) = \exp\left[ \frac{E_{a}}{R_{a} \left( \frac{1}{293} - \frac{1}{\theta_{0} + 273} \right)} \right], \]
where \( R_{a} \) is the universal gas constant taken as 8.31 J/molK; \( E_{a} \) is the apparent activation energy, when \( \theta_{0} \geq 20^\circ C \), \( E_{a} = 33.500 \) J/mol, \( \theta_{0} < 20^\circ C \), \( E_{a} = 33.500 + 1470(20 - \theta_{0}) \) J/mol.

\( \eta_{5}(a_{R,i}) \)-influence coefficient of hydration degree, \( \eta_{5}(a_{R,i}) = (1 - a_{R,i})^{3} \) [15].

### 2.5 Kinetic parameters and particle size distribution

In this research, the cement particle is analyzed as an undivided unit and the kinetic parameters have linear relationship with the clinker mineral composition of cement.

\[ K_{K} = \sum k_{K,c} \cdot w_{c} \]  

(20)

where \( K_{K} \) represents the reaction rate constant, \( n, K_{NG}, K_{b}, K_{D} \); \( w_{c} \) is the mineral composition \( c \) of cement (in %), \( C_{3}S\% \), \( C_{2}S\% \), \( C_{3}A+C_{4}AF\% \); \( k_{K,c} \), as shown in Table 1, is the weight value of mineral composition on the kinetic parameters inducted from the research results of Yan [16].

<table>
<thead>
<tr>
<th>( w_{c} )</th>
<th>( n )</th>
<th>( K_{NG} )</th>
<th>( K_{b} )</th>
<th>( K_{D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{3}S )</td>
<td>0.017871</td>
<td>0.000308</td>
<td>0.000188</td>
<td>0.000011</td>
</tr>
<tr>
<td>( C_{2}S )</td>
<td>0.015729</td>
<td>0.001142</td>
<td>0.0000146</td>
<td>0.00016351</td>
</tr>
<tr>
<td>( C_{3}A+C_{4}AF )</td>
<td>0.021707</td>
<td>0.000702</td>
<td>0.0000707</td>
<td>0.00000786</td>
</tr>
</tbody>
</table>

Table 1 \( k_{K,c} \) of reaction rate constant

The cement particle size distribution will be introduced in analyzing the hydration of cement system. For the particle size distribution of the cement, the differential expression of well-known Rosin-Ramler distribution is adopted:

\[ g(x) = abx^{-k} \exp(-ax^{b}) \]

(21)

where \( g(x) \) means the mass of the cement particles with the initial diameter \( x \); \( a \) and \( b \) are the material constants.

### 2.6 Hydration degree of cement system

It was pointed out by Fu [17] that the cement particles with the diameter above 80 \( \mu m \) have no activity but filling effect during hydration process. Due to the independence of each hydration unit cell, the hydration degree of the whole cement system at step \( i \) \( \alpha_{i} \) can be calculated as the sum of \( \alpha_{R,i} \) of each cell. And the equation can be given as:

\[ \alpha_{i} = \sum_{2R=1}^{80} g(2R) \cdot \alpha_{R,i} \]  

(22)

The flow chart of the cement hydration degree calculation is shown as Fig. 5.
Figure 5 Flow chart of cement hydration degree calculation

The whole computation can be easily programmed by means of mathematical software such as MATLAB. And all the parameters and variables in the model can be monitored during the calculation. Potential application on prediction of the porosity and mechanical properties of cement paste during early age hydration can be drawn with the model.

3. APPLICATION

The experiment results obtained from the research of van Breugel [7] (Fig.6) and de Schutter [18] (Fig.7) are applied in testing the model. Fig. 6 gives the influence of the initial temperature and water/cement ratio on the development of hydration degree. The hydration heat release with age of the cement CEM I 52.5 is shown as Fig.7. It can be concluded from Fig.5 and Fig.6 that the cement hydration model established in this research has good agreement with the experiment results.
4. CONCLUSIONS

Based on the hydration kinetics and microstructural development of cement particles, a mathematical model was developed. With the specially designed unit cell and the introduction of cement particle size distribution, the mathematical model can keep a good balance between simplicity and accurate. To test the validity of the model, predictions from the model for the cement hydration degree at different initial temperature and water/cement ratio, also the heat release were compared with experiment data. The results from the model were in good agreement with the experimental results. The developed model can be applied to predict the properties of fresh and hardened concrete. This research will afford reliable support to the design, construction and management of mass concrete structures in theory and practice.

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