MICROSTRUCTURAL MODELING OF HEATED PORTLAND CEMENT PASTE

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Abstract

When Portland cement paste is exposed to high temperature, a complex chemical transformation takes place. Calcium hydrate silicate (C-S-H) starts to dehydrate at about 105 °C, and Calcium hydroxide dehydrates at about 430 °C. Along with the chemical reactions, the hydration products (C-S-H and CH) shrink, while the volume of unhydrated clinker almost keeps the same. Due to the strain mismatch in microstructure, micro cracking might occur. These chemical reactions lead to the irreversible change of microstructure of Portland cement paste, which can affect the mechanical properties and transport properties.

In this study, a microstructural model is proposed to simulate the microstructural change of Portland cement paste at high temperature. The physiochemical transformation in cement paste is characterized first. The dehydration kinetics of cement paste, the volume change of hydration products and the microstructure change are formulated. Then the lattice model is performed to simulate the micro cracking and microstructure change. Finally, in order to verify the simulation model, the simulated microstructure of heated Portland cement paste is compared with the microstructure obtained by experiments.

Key words: microstructure, simulation, Portland cement paste, high temperature, dehydration, Lattice model

1. INTRODUCTION

At high temperature, the hydration products of Portland cement paste dehydrate. Calcium hydrate silicate (C-S-H) and Calcium hydroxide start to dehydrate at about 105 °C and 430 °C respectively. Along with temperature rising, the C-S-H is partly transformed into \( \beta-C_2S \), and calcium hydroxide is transformed into lime (CaO) finally [2]. These phase transformation lead to the volume change of hydration products. Meanwhile, the unhydrated clinker expands due to thermal dilation, which is surrounded by hydration products. This caused the strain mismatch and micro cracking of cement paste. Furthermore, the micro cracking and the microstructure change influences the meso properties of cement paste, such as elastic modulus,
strength and gas permeability. The schematic mechanism of microstructure change of cement paste due to dehydration is present in Fig. 1.

Figure 1: The dehydration induced microstructure change of cement paste

In the past decade, the microstructure of hardening cement paste was simulated [3]. However, the dehydration induced microstructure change is hardly studied and simulated. In this paper, the Lattice model is performed to simulate the microstructure change of Portland cement paste at high temperature.

2. SIMULATION METHOD
Zhang [1] proposed a method to simulate the microstructure change of Portland cement paste due to dehydration. This simulation method is performed by three steps:
- Determination of the dehydration degree of C-S-H and CH.
- Determination of the volume change of C-S-H and CH due to dehydration.
- Simulation of microstructure change due to dehydration.

2.1 Dehydration
The Friedman model [4] was used for kinetics of nth-order reaction in this study.

\[ f(\alpha) = (1 - \alpha)^n \]  

where \( n \) is the reaction order, \( \alpha \) is the reaction degree. Arrhenius equation is used to describe the influence of temperature.

\[ K(T) = A_0 \exp\left(-\frac{E_a}{RT}\right) \]  

where \( A_0 \), the pre-exponential factor and \( E_a \), the activation energy are referred to as the Arrhenius parameters. Given attention to the reaction order and temperature, the kinetics of dehydration of each phase can generally be expressed as following equation:

\[ \frac{d\alpha}{dt} = K(T) f(\alpha) \]  

By integrating of equation (3), the dehydration degree of C-S-H and CH under arbitrary temperature program can be characterized as equation (4) (5).

\[ \alpha_{\text{CSH}} = \int_0^t \frac{d\alpha_{\text{CSH}}}{dt} dt = \int_0^t (1 - \alpha_{\text{CSH}})^n A_{0,\text{CSH}} \exp\left(-\frac{E_{a,\text{CSH}}}{RT}\right) dt \]  

\[ \alpha_{\text{CH}} = \int_0^t \frac{d\alpha_{\text{CH}}}{dt} dt = \int_0^t (1 - \alpha_{\text{CH}})^n A_{0,\text{CH}} \exp\left(-\frac{E_{a,\text{CH}}}{RT}\right) dt \]  

All above kinetics parameters \( (A_{0,\text{CH}}, E_{a,\text{CH}}, A_{0,\text{CS-H}} \text{ and } E_{a,\text{C-S-H}}) \), together with \( W_{\text{C-S-H}} \) and \( W_{\text{CH}} \), can be determined by experiment [5].

2.2 Volume change of hydration products
The relationship between the C-S-H volume and dehydration degree was separated into two stages in term of the following two reactions [6]:
C-S-H is an amorphous phase, which is a mixture of imperfect tobermorite and jennite. Therefore, the relationship between the C-S-H volume and dehydration degree was simplified into bilinear relationship. Each segment could be determined in the following methods.

**Stage I: dehydration degree from 0% to 80%**

Based on the globules model of C-S-H [7, 8], the volume of C-S-H is comprised by the dense globules particles and inter particles space. The packing density of globules particle was 75% in this study [7, 8]. It was assumed that volume change at this stage is caused by the shrinkage of globules particles, and that inter particles space keeps the same.

In the globules model, the atomic structure of the dense globules particles is similar with tobermorite. $11\bar{A}$ tobermorite is transformed into $9\bar{A}$ tobermorite at high temperature [9]. Merlino etc. [6] studied the atomic structure of both two tobermorite. The detail atomic structure of tobermorite is listed in Table 1. It can be calculated that the unit cell volume of $9\bar{A}$ tobermorite is about 82% of t of $11\bar{A}$ tobermorite. Therefore, it is assumed that the globules particle reduces by 18% in volume when dehydration degree is 80%. The total volume change of C-S-H was characterized by the following formula:

$$V\% = 100\% - 75\% \times 18\% \times \frac{\alpha}{80\%}, \quad \alpha \in [0\%, 80\%]$$

**Stage II: dehydration degree from 80% to 100%**

In this stage, the volume change of C-S-H is mainly caused by crystallization. The XRD/Reitveld measurement [10] showed that around 27% amorphous C-S-H was transformed into crystalline $\beta C₂S$. The molar volume of C-S-H and $\beta C₂S$ was list in Table 2. It was assumed that the recrystallization degree is linear with the dehydration degree in this stage. The volume change of C-S-H in this stage was expressed by the following:

$$V\% = V\%_{\alpha=80\%} - V\%_{\alpha=80\%} \times 27\% \times \frac{102 \times V\%_{\alpha=80\%} - 52}{102 \times V\%_{\alpha=80\%} - 20} \times \frac{\alpha - 80\%}{80\% - 20\%}, \quad \alpha \in [80\%, 100\%]$$

If one substitutes 80% with $\alpha$ in Equation 13, the $V\%_{\alpha=80\%}$ equals 86.5%. Then the formula 14 was simplified as:

$$V\% = 86.5\% - 9.59\% \times \frac{\alpha - 80\%}{9\%}, \quad \alpha \in [80\%, 100\%]$$

Table 1: The atomic structure of tobermorite at different hydration degree

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Cell Volume ($Å^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tobermorite 11Å</td>
<td>11.274</td>
<td>7.3439</td>
<td>11.468</td>
<td>949.4945</td>
</tr>
<tr>
<td>Tobermorite 9Å</td>
<td>11.156</td>
<td>7.303</td>
<td>9.566</td>
<td>779.3637</td>
</tr>
</tbody>
</table>

Table 2: The atomic structure of tobermorite at different hydration degree

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density (mg/m³)</th>
<th>Molar volume (cm³/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-H (Dry)</td>
<td>2.12</td>
<td>108</td>
<td>[6]</td>
</tr>
<tr>
<td>$\beta C₂S$</td>
<td>3.28</td>
<td>52</td>
<td>[6]</td>
</tr>
</tbody>
</table>
2.3 Simulation of micro cracking

The strains caused by thermal dilation and chemical reaction were analyzed in the micromechanics study. Taking different phenomena into account, the total strain in cement paste can be divided into three parts:

\[ \begin{align*}
\sigma(x) &= E(x)\varepsilon_e(x) = E(x)(\varepsilon(x) - \varepsilon_T(x) - \varepsilon_d(x)) \\
\varepsilon(x) &= \frac{1}{2}(u(x)\nabla + \nabla u(x)) \\
\nabla \cdot \sigma &= 0
\end{align*} \]

where \( x \) is the location, \( \sigma \) is the stress field, \( E \) is the stiffness sensor of different phases, \( u \) is the displacement field, \( \varepsilon_e \) is the elastic strain, \( \varepsilon_T \) is the thermal dilation, \( \varepsilon_d \) is the dehydration induced strain. These typical mechanics equations together with boundary condition can be solved with by numerical method.

The above equations (11-13) presented the derivation on micro elastic response on the representative volume element (RVE) under given temperature. The micro-cracking takes place while the local stress reaches the failure criteria. The failed element cannot contribute to the global stiffness any more, which leads to the meso nonlinearity of the RVE. In this case, the local damage becomes an evolution problem. Then the linear system equations are showed as the following

\[ [K(\sigma)]\{r\} = \{f\} \]

The global stiffness matrix \([K(\sigma)]\) depends on the local stress path. The failure criteria followed maximum principal stress theory:

\[ \sigma_{\text{Prin}} > \sigma_{\text{Max}} \]  

Introduce a state variable \( \eta \) to characterize the state of each element:

\[ \eta = \begin{cases} 
1, & \text{the element is intact} \\
0, & \text{the element is damaged} 
\end{cases} \]

If the local stress of each element reaches the maximum principal stress theory, the \( \eta \) is marked as zero. Therefore the global stiffness matrix reads:

\[ [K]\{r\} = \sum \eta_k[T][k_e][T]^T \]

The damage state vector of the whole RVE \( \eta \) depends on micro stress field and strength of each phase, which can be numerical calculated by numerical method.

The nonlinear response of microstructure to the volume change of C-S-H should be analyzed by numerical method. In this study, the fracture analysis was carried out by Lattice model. The lattice model is a numerical method to simulate the fracture process of continues matrix [reference]. In the lattice model, the continuous solid is schematized as a network of two node beams. After determination of boundary condition and external force, the displacements of nodes are calculated. By removing in each loading step the beam elements with highest stress over strength ratio, fracture is simulated. The basic assumption is that the beam elements have a linear elastic behaviour up to failure, and fail in a purely brittle manner. The fracture criterion of each beam is described as:

\[ \sigma_{\text{eff}} = \beta \cdot \left( \frac{N}{A} \pm \alpha \cdot \frac{(|M_k|/A)_{\text{max}}}{A} \right) \leq f_{\text{t,k}} \]
where $N$ is the normal force acting in the beam element, $M_I$ and $M_J$ are the bending moments in two nodes. $\alpha$ is a factor that regulates the amount of bending taken into account. $\beta$ is a scale factor.

4. VALIDATION

In order to validate the simulation model, the microstructure simulated by this model is compared with the observed microstructure by scanning electron microscope (SEM). The initial microstructure of Portland cement paste is built up by HYMOSTRUC3D [reference], which is a microstructural model of the hydration of cement. In the hydration simulation, the water/cement ratio was 0.5, and the curing time was 28 days, which corresponded to the experiments. By mapping the sphere cement particles into digital 3D voxel, the microstructure simulated by HYMOSTRUC3D is transformed into 3D voxel-based structure. The RVE is a cube with side length 100 $\mu$m. The generation of 3D beam in lattice model from voxel-based structure is followed by the following steps (Fig. 2):

- Generating a 3D node with 6 free degrees in the centre of each voxel.
- Generating a 3D beam by connecting two neighbour nodes.
- The length of beam was the side length of voxel.
- The cross section of beam is square with the same side length of voxel.

![Figure 2: The beam generation from voxel and its cross section properties](image1)

The heating program in the dehydration simulation is shown in Fig. 3. The specimens are heated to target temperature 800 °C with heating rate 100°C/min, and then keep at isothermal condition for 6 hours.

In order to compare the simulation results with experiment results, the cement paste samples were prepared as the same material in the simulation. The heating program of sample was also as the same as simulation (Fig. 3). The heated cement paste sample were cooled down to room temperature and observed by SEM at a magnification of 500×.
In Fig. 4, both simulated microstructure and observed microstructure are showed. In the specimen before heating, the unhydrated clinker is surrounded by C-S-H. When the microstructure is heated up to 800 °C, the micro cracking is observed in both simulated results and the SEM image (Fig. 4). It is observed that the simulated microstructure agrees very well with the experiment results.

Figure 3: The heating program in the simulation of microstructure change due to dehydration

To quantitatively compare the simulated results with experiments, the porosity is determined. In the simulated voxel based microstructure, the pore voxel is counted, and the
Porosity is determined by the ratio of amount of the pore voxel over the amount of the all voxel. In experiment, the porosity is determined by applying the histogram of the gray level of the SEM image [11]. The porosity of cement paste before and after heating, is compared and showed in Fig. 5. After heating, the porosity of cement paste increases. The porosity obtained by simulation agrees with that determined by experiment.

Figure 5: The comparison of simulated porosity and measured porosity

5. CONCLUSIONS

- The microstructure simulation of heated Portland cement paste is proposed. The model consists of dehydration kinetics, volume change of C-S-H due to dehydration, and the microstructure response to the volume change of C-S-H. The kinetics of dehydration is characterized by Arrhenius equation. The volume change of C-S-H is analyzed by using globules model [7, 8] and the atomic structure of nature C-S-H. The lattice method is utilized as the numerical method for nonlinear fracture analysis.
- The microstructure of cement paste that heated up to 800 ℃ is simulated. In the simulated microstructure, the micro crack is found in the C-S-H, which agrees with the SEM image. The simulated porosity is very closed to the measured porosity. By comparing simulation results with experiment results, it is found that the simulation method [1] can simulate the microstructure change due to dehydration accurately.

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