

論文 Two-Dimensional Simulation of Cement Hydration

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ABSTRACT: This study was to simulate the hydration process of calcium silicate (C_3S), the main mineral component of Portland cement. The effect on hydration of size distribution of cement particle was clarified in this simulation. Hydration of cement particle is considered to be mainly controlled by two mechanisms: phase – boundary control and diffusion control. This model can be used to predict the degree of hydration, porosity, and other properties of cement-based materials. The study might be a good tool for research related to microstructure, mass transportation, and other properties of cement-based materials.

KEYWORDS: Cement hydration, simulation.

1. INTRODUCTION

A large amount of recent research has been focusing on computer simulation of the microstructure of various materials in order to predict, evaluate, and understand problems related to microstructure, and in order to design a material having desired properties. Cement is the most important material in civil engineering. Many properties of cement-based materials such as permeability, strength, creep, etc. depend on its microstructure. Formation of the microstructure of cement-based material largely depends on the hydration process of cement. When cement is mixed with water, it will react with water to form hydration products. Realistically, cement and its hydration products are really a complicated system to understand. Among the main constituents of cement, C_3S is present in the largest amount compared to the others and easy to understand from the point of view of chemical products. The reaction between C_3S and water forms surface product (C–S–H) and pore product (CH). The surface products include an inner layer, which grows inward from the original boundary, and an outer layer, which deposits on the surface of cement particle itself. In addition, a thin middle layer forms soon after the contact between C_3S and water, this layer gradually disappears after the induction period of hydration process, which is not taken into account in this simulation. The rate of hydration is controlled by the diffusion of chemical species through these product layers. As hydration proceeds, the thickness of the hydration product increases, and consequently, their resistance to diffusion increases as well. This simulation is based on the mathematical hydration model of C_3S , firstly introduced by J.M Pommersheim [2] and cited by researchers [1, 3].

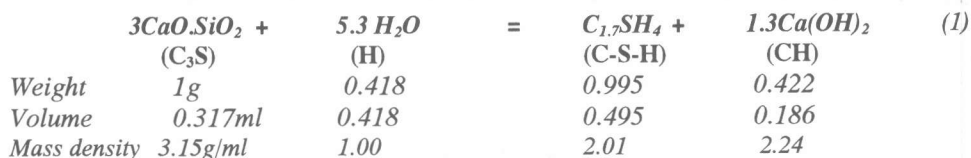
2. FUNDAMENTAL OF HYDRATION MODEL

2.1 PARTICLE KINETICS

It is reported that one unit volume of C_3S , when react with water, will form 1.66 units volume of surface product (C–S–H) and 0.56 units volume of pore product (CH) as show in chemical equation (1):

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The hydration process of a cement particle is controlled by three mechanisms. The first mechanism, which controls the initial reaction until a degree of hydration of 1 – 2% is reached, is nucleation and growth of products. This mechanism is often not taken into account. The second mechanism is the phase – boundary controlled reaction. In this mechanism, the penetration depth of the reaction front (the thickness of the inner product) for a flat reactant surface and for a constant ion concentration in the liquid phase is expressed as follows:

$$dr_{in}(t) = K_1 dt \quad (2)$$

Where: K_1 is the diffusion coefficient.

When hydration proceeds, total thickness of inner and outer products formed around the anhydrate increases. Once that thickness reaches a critical value, control of the reaction gradually passes to the third mechanism, which is controlled by diffusion. Then, the progress of the inner product thickness is obtained as follows:

$$dr_{in}(t) = \frac{K_2 dt}{r_{out} - r_{in}} \quad (3)$$

Where: r_{in} is the radius of the unhydrated C₃S core and r_{out} is the outside radius of the hydrating particle, K_2 is a constant.

It is suggested that the change from the second mechanism (phase-boundary-controlled reaction) to the third mechanism (diffusion control) takes place when the corresponding rates of hydration $\frac{dr_{in}}{dt}$, become equal.

Equalizing the $\frac{dr_{in}(t)}{dt}$ given by equation (2) and (3), we can get:

$$r_{out} - r_{in} = \frac{K_2}{K_1} \quad (4)$$

According to [1], the diffusion coefficient K_1 and $r_{out} - r_{in}$ are 0.086 and 0.4 μm , respectively.

2.2 INTERPARTICLE CONTACT

Equation (1) shows that the total volume of hydration products is larger than that of reactants, consequently, the size of cement particles increases during the hydration process, and some of them come into contact with one another: This is the interparticle contact. This contact resists the transport of ions into and out of the hydration product, which have deposited on the surface of cement particle [3]. In a free, hydrating particle, the transport of ions may occur concentrically (Fig. 1.a). However when interparticle contacts have been formed, concentric transport of ions becomes impossible (Fig. 1.b)

In addition, during the hydration process, the amount of water available for hydration of a cement particle will be reduced due to water consumption used for hydration of the surrounding particles. Therefore, a general factor K , to consider the effects of interparticle contact and available water for hydration, firstly given by Rohling and cited by Navil et al [1], was used in this simulation for each hydrating particle:

$$K_i = \left(1 - \frac{\text{Free surface}}{\text{Total surface}}\right)_i * \left(1 - \frac{v\alpha}{\rho W_o + \alpha}\right) \quad (5)$$

Where: v is the ratio between the volume of the reaction products and that of reactants, ρ is the ratio between the specific mass of tricalcium silicate and that of water, and W_o is the initial water – cement ratio, α is the degree of hydration at the considering time.

Even after coming into contact with other particles, cement particles still continue to react with water, forming hydration products. It means, some particles will become “overlapped” with others. To consider this “overlap”, we use an algorithm as shown in Fig. 2: The overlapping area will be redistributed outside the hydrating particle. When the hydration proceeds, some small particles will be completely overlapped by hydration products of large particles. If it is so, hydration of the “completely overlapped” particles will cease.

2.3 PORE PRODUCT

The volume of the pore product (CH) is calculated based on equation (1). There is some evidence that the pore product (CH in this case) doesn't form randomly in pore space but concentrates near the hydrating cement particle, or on the surface of cement particle [6] and it acts as surface product. The effect of CH on the diffusion is assumed to be equal to that of C-S-H. Further more, it is reported that the size of CH crystals at the beginning is very large compared to the late period of hydration. This may be caused by the fact that there is more space for CH to form at the beginning of hydration. In this model, at a certain number of steps of hydration, a random number is generated to decide the percentage of CH volume to be formed on the surface of the particle itself or in the pore space. In this simulation, the size of the CH particle is reduced

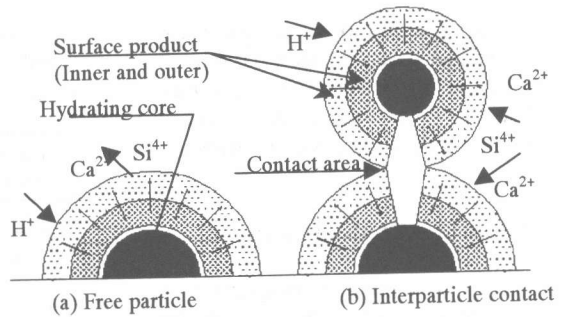


Figure 1. Effect of particle interaction on rate of diffusion.

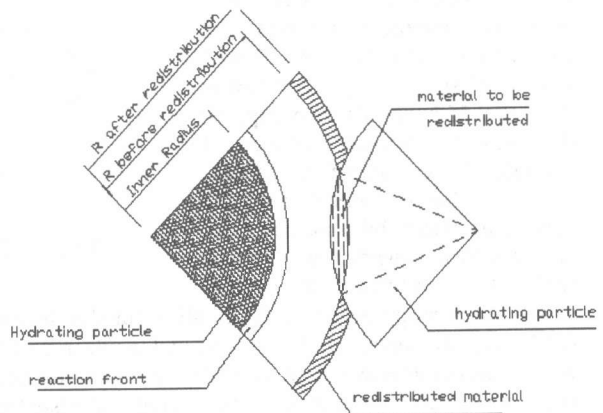


Figure 2. Redistribution of cement hydration product after overlap

when there is no more space for placement of large-sized particle. It may be so under real conditions because hydration products aren't formed unless there is enough space.

3. SIMULATION PROGRAM

A computer program was developed based on the model described above. Firstly, cement particles are distributed randomly from the largest to the smallest one within a fixed area, in accordance with the water-cement ratio and size distribution of cement. The volume (area) of consideration in the simulation is $400 \times 400 \mu\text{m}$. This area is large enough to assure that the result of simulation is independent of the distribution of particles. The hydration process is, then, allowed to proceed step by step; each step is equal to 0.25 hours. At each step, the thickness of surface product of particles is calculated to decide which mechanism will control the next step. Meanwhile, particles are also checked whether it overlaps with other particles. If overlap exists, the overlapping area will be redistributed as mentioned before. At a certain number of steps (20 hours), the porosity of the system and the degree of hydration are calculated and output to file for processing afterwards. Meanwhile, the inner and outer radii of cement particles as well as of pore product are output to a file for a graphical visualization program developed by the authors. (Fig. 4, 5)

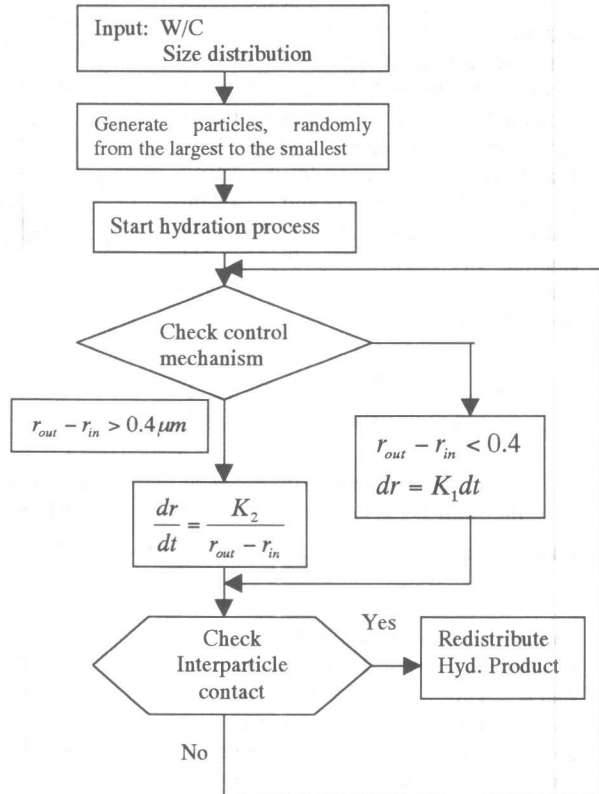


Figure 3. Flow chart of program

Table 1. Three examples used in this simulation

Cement A		Cement B		Cement C	
Size (μm)	Cumulative percentage (%)	Size (μm)	Cumulative percentage (%)	Size (μm)	Cumulative percentage (%)
< 8	16.7	< 8	19.3	< 6	18.4
15	33.3	15	40.9	10	37.9
30	62.6	30	68.7	15	66.3
40	81.5	40	87.6	30	84.8
60	100	60	100	45	100

The examples used were three kinds of cement having different size distributions (Table 1.) The simulation was performed with three values of water – cement ratio 40%, 50% and 60%.

4. RESULTS AND DISCUSSION

Fig. 4 shows the initial distribution of cement particles separated by water, and Fig. 5 shows the result of hydration after 1500 hours (\approx 2 months). These figures give a good visualization of cement hydration: pore space is gradually filled by hydration product.

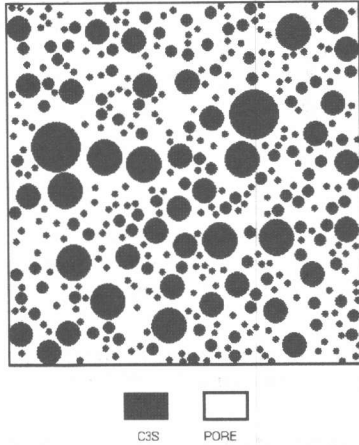


Figure 4. Initial distribution of cement particle (W/C = 50%)

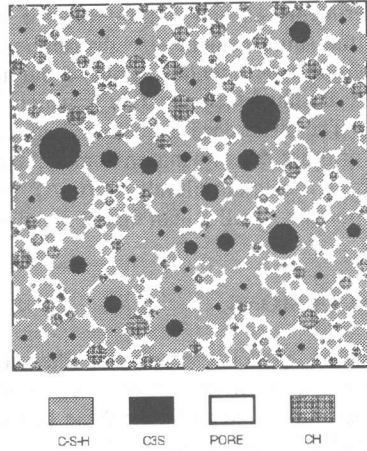


Figure 5. Structure of cement paste after 1500 hours (W/C = 50%)

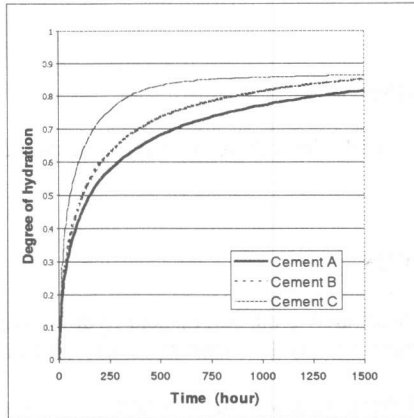


Figure 6. Effect of size distribution on hydration, W/C = 50%

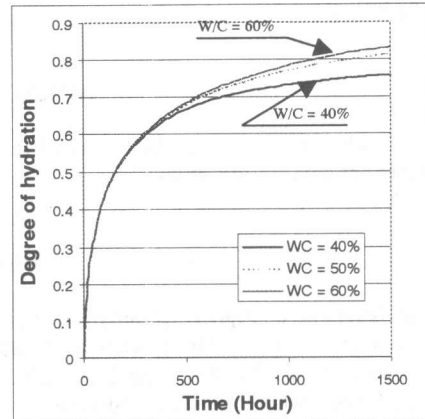


Figure 7. Hydration of cement A with different values of W/C

Fig. 6 indicates that the smaller the size of cement, the higher is the degree of hydration. At the late age of hydration, the degree of hydration depends on the amount of large-sized particles (Fig. 5). For cement C, the rate of hydration was very fast compared to other two cements at the early age. The author believes that large amounts of small particles are the cause of that fast hydration. The simulation was carried out with three values of water-cement ratios for each kind of cement. It is obvious that at the early age of hydration, the water – cement ratio does not affect the rate of hydration (Fig. 7), but after about 300 hours (13 days), the rate of hydration reduces in

accordance with the reduction of W/C value. This is due to less available water and more interparticle contact for small W/C cement paste. It is likely that this model can be used to predict the porosity of ordinary Portland cement at a given time. Fig. 8 shows that the porosity calculated by this simulation almost coincides with that of experiments carried out by [6] for Alite Cement having the same cement size distribution and slightly differs from experimental results of our laboratory for Ordinary Portland Cement (OPC), which includes 60% of C₃S. The difference is believed to be due to the effects of other constituents in cement, such as the fast reaction of tricalcium aluminate (C₃A), resulting in an overall porosity smaller than that of simulation.

5. CONCLUSIONS

This model can predict the effect of size distribution on the hydration of cement and can be used as a simple model to understand the hydration process.

The aim of this study is also to develop, a model of cement hydration as a tool for future research, such as the effect of filler powder, microstructure of concrete, percolation of phases, etc. We are aware that a three-dimensional model can be more relevant to simulate the hydration process of cement, especially when considering the surface area of cement powder as an important influence on hydration.

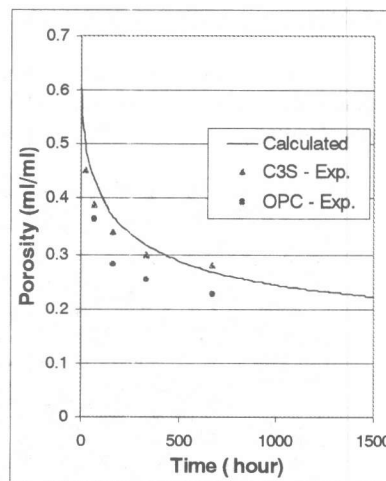


Figure 8. Porosity vs. time of hydration for first cement A, W/C = 50%

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