

# Two — Dimensional Computer Simulation of Cement Hydration (1)

## The Effect of Size Distribution and Water-Cement Ratio

### コンピュータによるセメントの水和反応シミュレーション (1)

#### —水セメント比とセメント粒子の粒度分布の影響—

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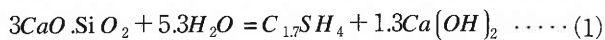
### 1. INTRODUCTION

Cement is the most important material in civil engineering. Many properties of cement-based material such as permeability, strength, etc. depend on its microstructure. Formation of microstructure of cement-based material is largely depends on the hydration process of cement. Among main constituents of cement, C<sub>3</sub>S is the one that has largest amounts compared to the other and easy to understand in the point of views of chemical product. Reaction between C<sub>3</sub>S and water will form two kinds of product: surface product (C-S-H), which deposits in situ (inner product) or on the surface of cement particle itself (outer product) and pore product (CH) which deposits in the pore space of cement paste. The basics for the kinetics of a hydrating C<sub>3</sub>S particle are three layers of product: inner, middle and outer. The rate of hydration is controlled by the diffusion of chemical species through these product layers. As hydration proceeds, the thickness of hydration product increases, consequently, their resistance to diffusion will increase as well. This simulation is based on the mathematical hydration model of C3S, firstly introduced by<sup>2)</sup> and cited by researchers<sup>1,3)</sup>.

### 2. HYDRATION MODEL

#### 2.1 PARTICLE KINETICS

It is reported that one unit volume of C3S, when reacts with water, will form 1.66 unit volume of surface product (C-S-H) and 0.56 unit volume of pore product (CH) as show in chemical equation (1):



	(C <sub>3</sub> S)	(H)	(C-S-H)	(CH)
Weight 1g		0.418	0.995	0.422
Volume 0.317ml		0.418	0.495	0.186

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 follow:

$$dr_n(t) = K_1 dt \dots\dots\dots (2)$$

When hydration proceeds, total thickness of inner and outer products formed around the anhydrous increase. Once that thickness reaches a critical value, control of the reaction gradually

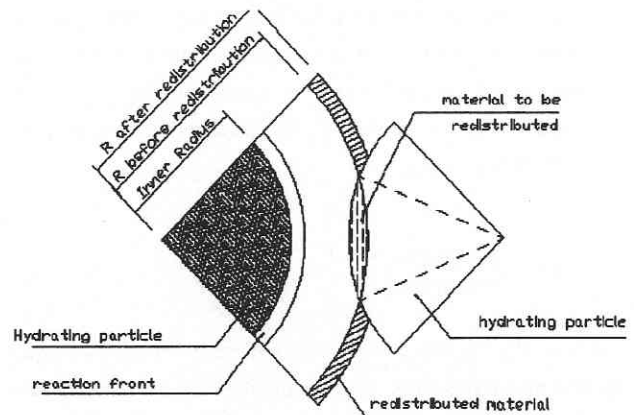


Fig. 1. Redistribution of cement hydration product

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passes to the third mechanism, which is controlled by diffusion. Then, the progress of the inner product thickness is obtained as follows:

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

Where:  $r_{in}$  is the radius of the unhydrated  $C_3S$  core and  $r_{out}$  is the outside radius of 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) take places when the corresponding rates of hydration  $\frac{dr_{in}}{dt}$ , become equal.

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

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

According to<sup>1)</sup>, the diffusion coefficient  $K_1$  and  $r_{out} - r_{in}$  are 0.086 and 0.4  $\mu$ m respectively.

2.2 INTERPARTICLE CONTACT

Equation (1) shows that the total volume of hydration products is larger than that of reactants, consequently, size of cement particles increases during hydration process and some of them will 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<sup>3)</sup>. In a free, hydrating particle, the transport of ions may occur concentrically. However when interparticle contacts have been formed, concentric transport of ions becomes impossible

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 surrounding particle. 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<sup>1)</sup>, was used in this simulation for each hydrating particle:

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

Where:  $v$  is the ratio between the volume of the reaction products and that of reactants,  $\rho$  is the ratio between the specific mass of tricalcium silicate and that of water, and  $W_o$  is the initial water-cement ratio.

Even after coming into contact with other particles, cement particle still continue to react with water, forming hydration product. It means, some particles will become “overlapped” with others. To consider this “overlap”, we use an algorithm as shown in Fig. 1: The overlap area will be redistributed outside the hydrating particle. Hydration will cease if particle is completely overlapped.

2.3 PORE PRODUCT

Volume of pore product (CH) is calculated based on equation (1). There are some evidences that pore product doesn't form randomly in pore space but concentrates near the hydrating cement particle, or on the surface of cement particle<sup>6)</sup> 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 crystal at the beginning is very large compared to the late period of hydration. This may be caused by the evidence that there are 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 percentage of CH volume to be formed on the surface particle itself or in the pore space

3. SIMULATION PROGRAM

A computer program was developed based on model described above. Firstly, cement particles are distributed randomly from the largest to the smallest one within a fixed area (400 × 400  $\mu$ m), in accordance with water-cement ratio and size distribution of cement. The hydration process is, then, allowed to proceed step by step; each step is equal to 0.25 hour. At each step, particles are checked the thickness of surface product to decide which mechanism will control the next step and whether overlap exists with other particles. At a certain number of steps (20 hours), the porosity of system and the degree of hydration are calculated and output to file for processing afterward. The radii of cement particles and that of pore product are output to file at desired times for visualization process as shown in figures 2 and 3. Simulation was run with three value of water-cement ratio 40%, 50% and 60% for three kinds of cement having different size distributions (Table 1., Where CM is cumulative percentage)

4. RESULTS AND DISCUSSIONS

Fig. 2 shows the initial distribution of cement particles separated by water, and Fig. 3 shows the result of hydration after 1500 hours ( 2 months). Figure. 4 indicates that the smaller the size of cement, the higher is the degree of hydration. At the late age of hydration, degree of hydration mainly depends on large cement

Table 1. Three examples in this simulation

Cement A		Cement B		Cement C	
Size	CM	Size	CM	Size	CM
<8 mc	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

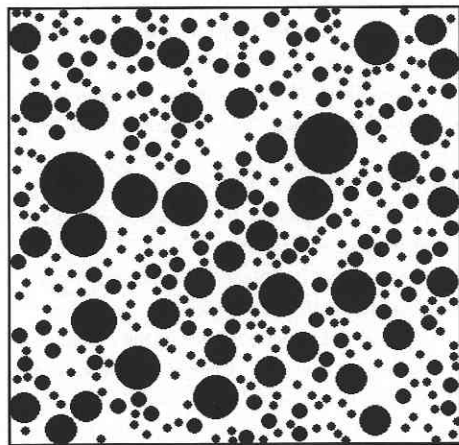


Fig. 2. Initial distribution of cement particles W/C = 50%

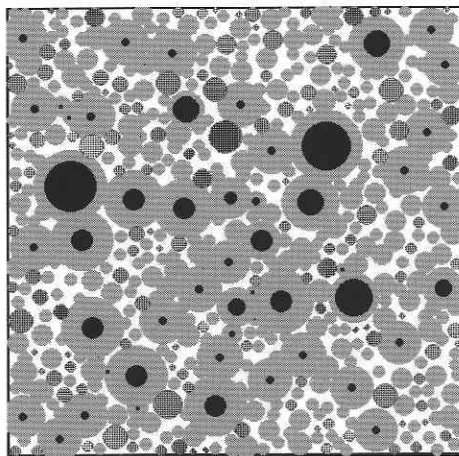


Fig. 3. Structure of cement paste after 1500 hours W/C = 50%

particles (Fig. 3). For cement A, rate of hydration was very fast compared to other two cements at the early age. The authors believe that large amount of small particles is the cause of that fast

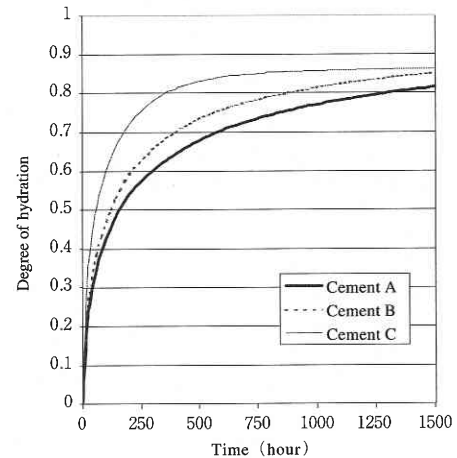


Fig. 4. Effect of size distribution on hydration, W/C = 50%

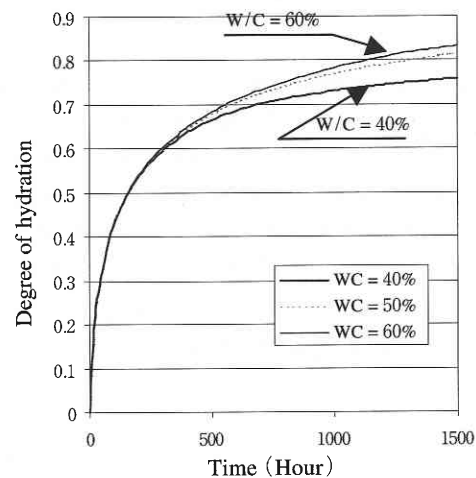


Fig. 5. Hydration of cement A with different values of W/C

hydration. It is obvious that at the early age of hydration, water-cement ratio does not affect the rate of hydration (Fig. 5), but after about 300 hours (13 days), the rate of hydration reduces in accordance with the reduction of W/C value. It is due to less available water and more interparticle contact for small W/C cement paste. Fig. 5 shows that the porosity calculated by this simulation almost coincides with that of experiments carried out by<sup>6)</sup> for Alite Cement having the same cement size distribution and slightly differs from experimental result of our laboratory for Ordinary Portland Cement (OPC), which includes 60% of C3S. The difference is believed due to effects of other constituents in cement, such as the fast reaction of tricalcium aluminate ( $C_3A$ ), resulting in the overall porosity smaller than that of simulation.

### 5. CONCLUSIONS

This model can predict the effect of size distribution on the

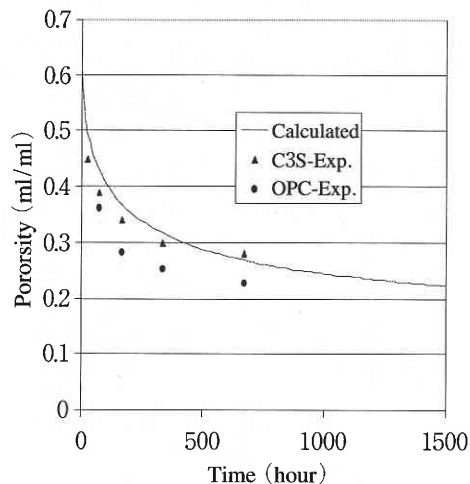


Fig. 6. Porosity vs. time of hydration for cement A, W/C = 50%

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 hydration process of cement, especially to consider surface area of cement powder as an important identity of hydration.

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