Development of Multi-Components Model of Cement Hydration

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Abstract.

This paper presents a numerical model which can predict degree of hydration of cement mineral component, such as C_3S, C_2S, C_3A, C_4AF and microstructure of hydrating cement as a function of water to cement ratio, cement particle size distribution, cement mineral components and temperature. In this model cement particles are parked randomly in cell space and hydration process is described using a multi-component integrated kinetic model. The simulation result of degree of hydration of cement mineral component agrees well with experiment result. The content of cement hydration product, such as CSH and CH can be obtained as an accompanied result during hydration process. By introducing of equal-area projection method, water withdrawl mechanism and contact area among cement particles can be considered in detail. By using proposed method, pore size distribution of hydrating cement is predicted.

Keywords: integrated kinetic model, multi-component, cement hydration, microstructure

1. Introduction

When cement particles are mixed with water, they react with water and produce a solid with micropore of various sizes. The properties of cement paste such as strength, permeability, creep and drying shrinkage are controlled by this process. Hydration process is the backbone for the understanding of the evolution of cementitious material properties. In few decades ago, some numerical models have been built to simulate cement hydration process.

Bentz and Grboczi[1][2]proposed the three-dimensional digital image based simulation model. In their model a digital image of cement paste sample is subdivided into elements which are represented by pixels with a volume of $1um^3$. Van Breugel[3][4] and Koenders[5]explained the hydration process as a function of particle size distribution, the chemical composition of cement, water to cement ratio and the reaction temperature. Ducom model[6][7] is built by Maekawa et al. and can be regarded as a multi-scale model connecting cement-based material with reinforced concrete structure. The hydration part in Ducom focused on the simulation of heat evolution process of cement. Tomosawa[8][9] simulated hydration process using a single kinetic expression. Based on his unreacted core model which is limited to the case where cement

particle is immersed in an infinite pool of water, Hyun[10],Park[11,12], Maruyama and Noguchi[13,14] made some improvement considering such as water to cement ratio, cement particle size distribution, mineral component, and temperature.

Besides considering physical aspect of cement hydration, some researchers tried to consider chemical aspect of that. Papadakis[16] built a chemical kinetic model to simulate hydration process of cement mineral component, including C_3S, C_2S, C_3A, C_4AF. M.M.Y. Delmi[17] made some improvement of Papadakis's model by considering coupled evolution between hydration and porosity. Based on basic hydration mechanism of Hymostruc and chemical reaction equation in reference [16], Sujano[15] made a monosized hydration model considering cement components, such as C_3S, C_2S, C_3A, C_4AF. The degree of hydration of cement was obtained as a weighted average of mineral components. By similar method, most recently Maruyama[13] made a multi-component hydration model to predict degree of hydration of cement mineral component.

In this paper a multi-component integrated kinetic model which considers both physical aspect and chemical aspect is built. In physical aspect, the cement particles with different size are parked randomly in the representative cell volume. Based on Tomosawa's hydration model, the degree of hydration of cement mineral components is modeled. Based on equal area projection method, the water withdrawlmechanism among cement particles is considered in detail. The development of microstructure can be obtained as an accompanied product of physical aspect. In chemical aspect, as a trial method, based on the chemical reaction formulas, simulation focused on degree of hydration of cement components, including C_3S, C_2S, C_3A and C_4AF. The content of hydration product, such as $C_3S_2H_3$ and $Ca(OH)_2$ can be obtained based on degree of hydration of cement components. The development of compressive strength of cement paste, in physical aspect, has many relation with gel/space ratio or contact area among cement particles[4]and in chemical aspect has many relation with the amount of $C_3S_2H_3$[18]. As both two aspects are considered, this hydration model has a strong potential to predict the development of compressive strength of cement paste. As the amount of $Ca(OH)_2$ be predicted, this hydration model has a potential to simulate pozzolanic reaction process of cement paste.

2. Modeling of Hydration Reaction

2.1 Hydration Mechanism

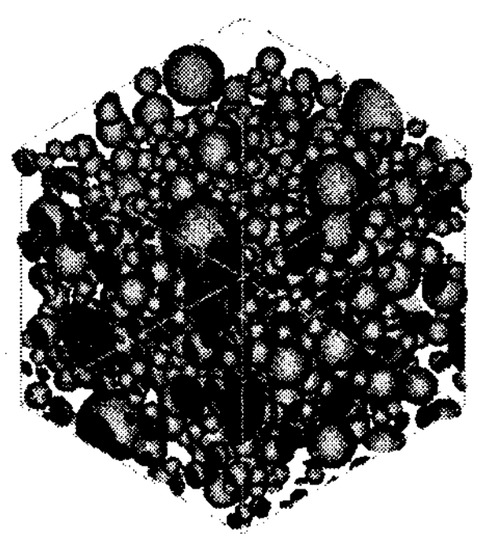

Fig. 1 cement particles at mixing time(cement particles are parked randomly and Separately)

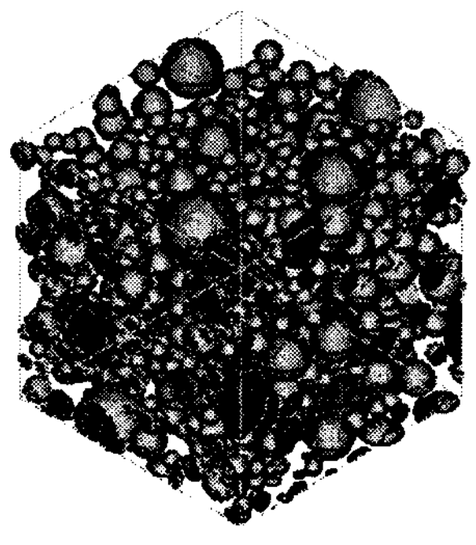

Fig. 2 cement particles at hydration degree equals 0.3

In this model, as proposed in Navi's paper, cement particles are parked randomly and separately in representative cell space (100*100*100um) at mixing time, as shown in figure 1. With hydration process going on, cement particles will expansion outward and intersect each other and form a matrix with micropore of different size (shown in figure 2).

Cement particle size distribution will make a big difference in the cement hydration process. The degree of hydration of total cement paste should account for the different degree of hydration of each particle. In the proposed model, it is assumed that the cement particle distribution can be expressed with the Rosin-Ramler Function (Equation 1).

$$G(x)=100(1-e^{-bx^n}) \tag{1}$$

Where $G(x)$ percentby mass passing the sieve with diameter x(%)

x=character particle size (um)

b,n constant

The basic hydration equationof each mineral composition in cement particles can be described as following equation (2), which is originally built by Tomosawa to describe hydration process of single cement particle:

$$\frac{d\alpha_i^j}{dt}=\frac{3C_{w\infty}}{(v_i+w_{ag})r_0^j\rho_i}\frac{1}{(\frac{1}{k_d}-\frac{r_0^j}{D_{ei}})+\frac{r_0^j}{D_{ei}}(1-\alpha_i^j)^{\frac{-1}{3}}+\frac{1}{k_{ri}}(1-\alpha_i^j)^{\frac{-2}{3}}} \tag{2}$$

Where α_i^j denotes degree of hydration of mineral component in a given cement particle. Subscript i, denotes mineral component, such as C_3S,C_2S,C_3A and C_4AF, superscript j denotes cement particle number, v_i: stoichiometric ratio by mass of water to mineral component, and can be determined by chemical reaction listed in Table 1. w_{ag}: physically bound water, equal to 15% of the weight of reacted cement ρ_i: density of unhydrated cement mineral component k_d: reaction coefficient in dormant period. r_0^j: radius of unhydrated cement particle. D_{ei}: effective diffusion coefficient of water in the hydration product of each mineral component. k_{ri}: coefficient of reaction rate of each mineral component. The temperature influenceon reaction rate can be considered by Arrhenius law[9].

Table 1 chemical reaction of cement component

Chemical reaction	v_i
$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$ (1)	0.236
$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$ (2)	0.209
$C_3A + C\bar{S}H_2 + 10H \rightarrow C_4A\bar{S}H_{12}$ (3)	0.666
$C_3A + CH + 12H \rightarrow C_4AH_{13}$ (4)	0.799
$C_4AF + 2CH + 2C\bar{S}H_2 + 18H \rightarrow C_8AF\bar{S}_2H_{24}$ (5)	0.667
$C_4AF + 4CH + 22H \rightarrow C_8AFH_{26}$ (6)	0.814

2.2 Microstructural Model

When cement is mixed with water, the hydration of each mineral component goes step by step based on process described in previous section. Given a certain cement particle, hydration degree can be obtained from weighted average of components, as shown in figure 3. The degree of hydration of global cement paste can be calculated as following :

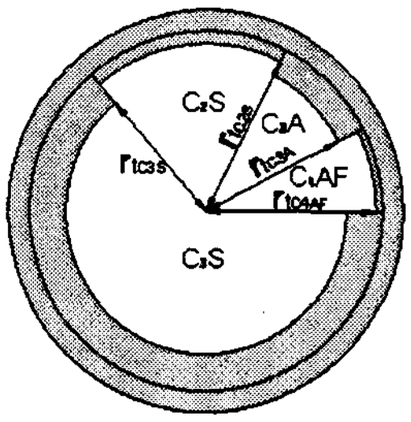

Fig. 3.1 hydration degree of cement components

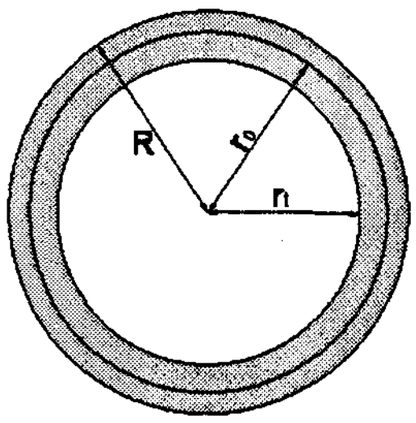

Fig. 3.2 the weighted average hydration degree

$$\alpha = \frac{\sum_{j=1}^{j=n}\sum_{i=1}^{i=4} \alpha_i^j g_i g_j}{\sum_{j=1}^{j=n}\sum_{i=1}^{i=4} g_i g_j} \quad (3)$$

Where α_i^j is denotes degree of hydration of mineral component in a given cement particle, g_i is weight fractionof mineral component, g_j is weight fraction of each cement particle and n is total amount of cement particles in cell space. As shown in equation 3, the global degree of hydration of cement is a weighted average of mineral component and cement particles. The porosity of hydrating cement paste equals that cell volume minuses solid paste volume, as shown in equation 4.

$$poro = \frac{V_{cell} - V_{solid}}{V_{cell}} \quad (4)$$

2.3 Water Withdrawl Mechanism

During hydration process, to take into account water withdrawl influence on the rate of

hydration,the concept of cement particle cluster [4] is adopted. The cement particle cluster is defined as a collection of cement particles which can be connected by a continuous path. By applying a burning algorithm [1], at each time step, the cement particle clusters can be found in detail. Given a certain cement particle, once the cluster which includes this certain particle is detected, the water withdrawl coefficient equals to the ratio between cluster's free surface and summation of surface area of cement particles included in cluster.
The modified hydration rate can be written as following:

$$\left(\frac{d\alpha^j}{dt}\right)' = \frac{d\alpha^j}{dt} * \left(\frac{CL_{freesurface}}{CL_{totalsurface}}\right)^j \tag{5}$$

Where j denotes cement particle number. $CL_{freesurface}$ is free surface area of the cluster which includes calculated cement particles and $CL_{totalsurface}$ is summation of surface area of cement particles included in cluster.

3. Simulation Result and Discussions

3.1 Degree of Hydration and Hydration Product

The experiment result (from reference 13) about degree of hydration of ordinary Portland cement and belite rich Portland cement with water to cement ratio 0.5 and 0.35 is adopted. As shown in Figure 4, the simulation result fits well with experimental result.

According to chemical reaction listed in Table1, when degree of hydration of cement mineral component is confirmed, the content of hydration product can be determined and the calculation equations can be described as following :

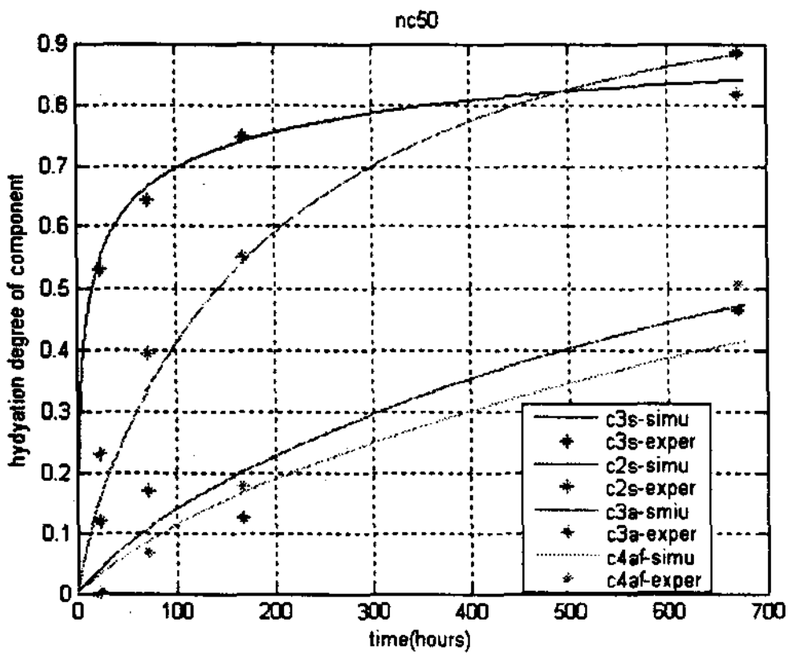

Fig. 4.1 comparison of experiment and simulation result of degree of hydration of mineral component: OPC, w/c=0.5

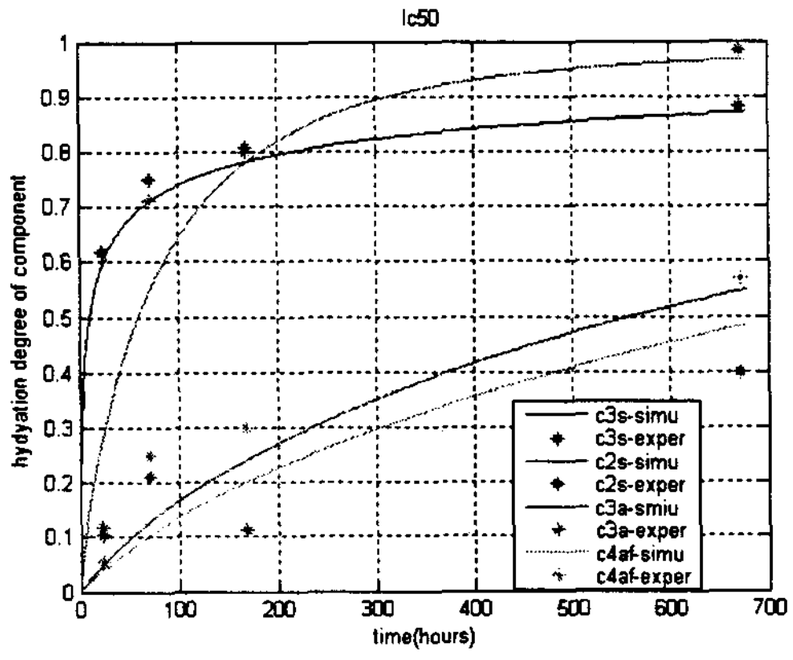

Fig. 4.2 comparison of experiment and simulation result of degree of hydration of mineral component : BPC, w/c=0.5

$$CSH=0.75*\alpha_{C3S}*g_{C3S}+0.99*\alpha_{C2S}*g_{C2S} \quad (6)$$

$$CH=0.486*\alpha_{C3S}*g_{C3S}+0.21*\alpha_{C2S}*g_{C2S}-0.61*\alpha_{C4AF}*g_{C4AF} \left(\text{when } \alpha_{C3A} \le \frac{1.57*g_{gypusm}}{g_{C3A}}\right) \quad (7\text{-}1)$$

$$CH=0.486*\alpha_{C3S}*g_{C3S}+0.21*\alpha_{C2S}*g_{C2S}-0.61*\alpha_{C4AF}*g_{C4AF}-0.273*\alpha_{C3A}*g_{C3A}$$

$$\left(\text{when } \alpha_{C3A} \ge \frac{1.57*g_{gypusm}}{g_{C3A}}\right) \quad (7\text{-}2)$$

Where CSH denotes $C_3S_2H_3$, CH denotes $Ca(OH)_2$

$\alpha_{C3S}, \alpha_{C2S}, \alpha_{C3A}, \alpha_{C4AF}$ denotes degree of hydration of mineral component

$g_{C3S}, g_{C2S}, g_{C3A}, g_{C4AF}$ denotes weight composition of each mineral component.

3.2 Microstructure

In thishydration model, cement particles is parked randomly in cell space with periodic boundary condition. Two kinds of cement, C1 and C2, are designed for simulation. As presented in Table 2, C2 contains more small particles and has bigger surface area than C1. Due to the increasing of small particles composition, the included cement particles in cell space are significantly increased, from 2110 in C1 to 6220 in C2.

Based on the hydration model, the weighted degree of hydration of C1 and C2 is calculated and shown in Figure 5. Because cement particleswith smaller size have higher hydration rate than bigger ones, given a certain time, the degree of hydration of C2 is a little bigger than that of C1.

By aforementioned systematic point sampling method [1]and equal area projection method [20], the pore wall area (free surface area) and pore volume during hydration process can be obtained. As suggested in reference 5, the hydraulic radius, R_H, can be defined by equation 8 as following :

$$R_H = \frac{V_{por}}{A_{por}} \quad (8)$$

Where V_{por} is pore volume and A_{por} is pore wall area.

Table 2 cumulative weight distribution of cement (water to cement ratio 0.5, edge length=100um)

C1		C2	
Radius(um)	CWD	Radius(um)	CWD
2.875	0.30	1.75	0.19
4.125	0.39	2.875	0.30
5.5	0.49	4.125	0.39
7.125	0.60	5.5	0.49
9	0.70	7.125	0.60
11.375	0.80	9	0.70
14.5	0.90	11.375	0.80
19.375	1.00	14.5	0.90
Total number: 2110 Surface area: 1806.6cm^2/g		19.375	1.00
		Total number: 6220 Surface area: 2216.9cm^2/g	

Based on pore volume and pore wall area, the hydraulic area is calculated and shown in Figure 6. Owing to the increasing of small size cement particles, given a certain time, the hydraulic radius of C2 is much smaller than that of C1. It reflects that the capillary pore of C2 is much finer than that of C1. As suggested in reference 5, the capillary pore size distribution of cement paste can be described as equation 9.

$$V_{por} = a \ln\left(\frac{\phi}{\phi_0}\right) \tag{9}$$

Where a is pore structure constant and ϕ_0 =0.002um.

Assuming that the hydraulic radius represented the weighted pore radius for the hardening paste, the pore constant "a" can be determined from this hydration model. From the hydraulic radius R_H and the pore volume V_{por}, the pore structure constant "a" can be calculated ($\phi = 2R_H$) and shown in Figure 7.

As shown in this figure, with hydration process going on, the pore structure constant differ slightly and levels off to a constant value. The pore constant value of C2 is bigger than that of C1. It means that microstructure of C2 is much finer than that of C1.

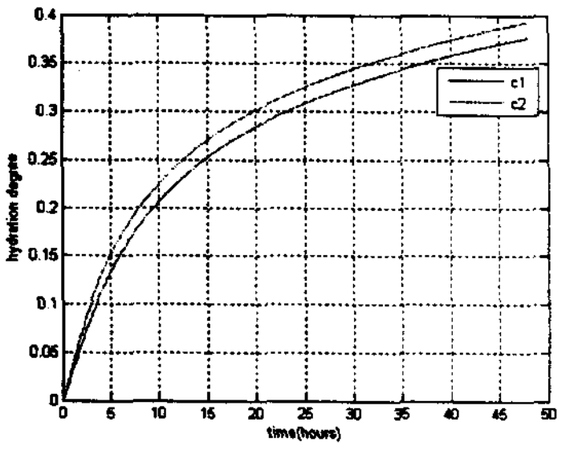

Fig. 5 hydration degree versus time

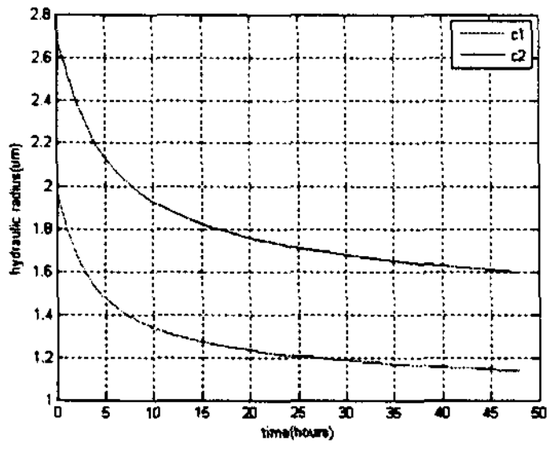

Fig. 6 hydraulic radius versus time

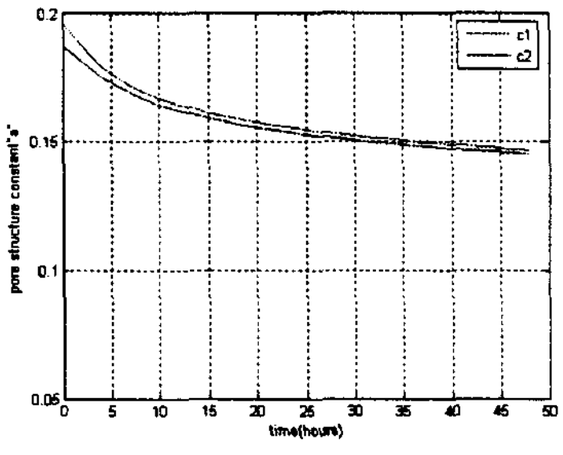

Fig. 7 pore structure constant versus time

4. Conclusion

A multi-component integrated kinetic model, which considers water to cement ratio, cement particle size distribution, curing temperature and cement mineral component, is built. In hydration aspect, based on the multi-component integrated hydration model, the degree of hydration of cement mineralcomponent, such as C_3S, C_2S, C_3A, C_4AF is predicted and agrees well with experiment result. The content of cement hydration product, such as CSH and CH can be obtained as an accompanied result during hydration process. In microstructure aspect, based on systematic point sampling method andequal-area projection method, the contact area among cement particles and pore size distribution are predicted.

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