

The simulation of hydration of Portland cement blended with chemical inert filler

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ABSTRACT

The addition of chemical inert filler in blended cement, such as limestone or chemical inert silica fume, will produce a physical effect on cement hydration. Due to the high surface area of inert filler in the mixtures, it provides sites for the nucleation and growth of hydration products, thus improving the hydration rate of cement compounds and consequently increasing the strength at early age. This paper proposes a model of hydration of Portland cement blended with chemical inert filler. This model considers the influence of water to cement ratio, cement particle size, cement composition and addition of chemical inert filler on hydration. The heat evolution, degree of hydration and porosity are obtained as accompanied results in hydration process. The prediction results agree well with experiment results.

1. Introcution

The mineral admixture, such as silica fume, fly ash and blast furnace slag, is widely used in construction site. As reported in reference [1-4], there exist three effects of mineral admixtures on hydration, i.e. dilution effect, physical effect and chemical effect (pozzolanic effect). The dilution effect is a consequence of the replacement of cement by the same quantity of a mineral powder. The increase in the amount of mineral admixture involves a decrease in the amount of cement and consequently an increase in water/cement ratio. As far as cement hydration is concerned, the physical effect is heterogeneous nucleation effect. Heterogeneous nucleation is a physical process leading to a chemical activation of the hydration of cement and is related to the nucleation of hydrates on foreign mineral particles. Since heterogeneous nucleation leads to an enhancement of cement hydration, its effect at a given time is an increase in the compressive strength. This physical effect depends essentially on the fineness and the amount of the powders used. Chemical effect (pozzolanic effect) is noticed after periods of a few days (e.g., silica fume) to several months (some fly ash or natural pozzolans), depending principally on the amount and solubility of amorphous silica in the material.

In reference [5-7], based on thermogravimetric analysis(TGA), the derivative thermogravimetric analysis(DTA) and BSE image analysis, it was found that the mass of limestone powder does not change even at hydration age of 28 days and limestone powder can be treated as inert in the mixture at the micro level. So that the influences of limestone filler on cement hydration are dilution effect and heterogeneous nucleation effect. The addition of limestone filler improves the hydration rate of cement compounds and consequently increasing the strength at early age. To predict early-age properties of concrete containing limestone filler in construction site, it is necessary to quantitatively evaluate hydration rate. This paper proposes a model of hydration of Portland cement blended with chemical inert filler. This model considers the influence of water to cement ratio, cement particle size, cement composition and addition of chemical inert filler on hydration. The heat evolution, degree of hydration and porosity are obtained as accompanied results in hydration process. The prediction results agree well with experiment results.

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2. Modeling of Portland cement hydration

2.1 Hydration model

The hydration model is expressed as a single equation composed of four rate coefficients. These coefficients determine the rate of formation and destruction of the initial impermeable layer, the activated chemical reaction process, and the following relevant, diffusion-controlled process. The model cement particle is assumed to be a sphere having an initial surface film composed of hydration products. External water diffuses through this layer, reacts with fresh cement, and then the newly formed hydration products diffuse outward. The process is considered to be mass transfer controlled so that the rate of water diffusion determines the hydration rate and is expressed as follows:

$$\frac{d\alpha}{dt} = \frac{3C_{w_0}}{(v + w_{ag})r_0\rho} \frac{1}{\left(\frac{1}{k_d} - \frac{r_0}{D_e}\right) + \frac{r_0}{D_e}(1-\alpha)^{-1} + \frac{1}{k_r}(1-\alpha)^{-2}} \quad (1)$$

where α denotes the hydration degree of the mineral component in given cement particles, v is the stoichiometric ratio by the mass of water to mineral component, w_{ag} is the physically bound water that is equal to 13% of the weight of reacted cement, ρ is the density of the anhydrate cement mineral component, k_d is the reaction coefficient in a dormant period, r_0 is the radius of anhydrate cement particles, D_e is the effective diffusion coefficient of water in the hydration product for each mineral component, and k_r is the coefficient of reaction rate for each mineral component. The influence of temperature on the reaction rate can be considered by the Arrhenius law [8].

Whereas, k_d is assumed to be a function of degree of hydration during initial reaction period and it is expressed as following equation (2):

$$k_d = \frac{B}{\alpha^{1.5}} + C\alpha^3 \quad (2)$$

The effective diffusion coefficient of water is affected by the tortuosity of the gel pores as well as the radius of gel pores in the hydrate. This phenomenon can be expressed as a function of degree of hydration and is described by equation (3):

$$De = De_0 \ln\left(\frac{1}{\alpha}\right) \quad (3)$$

2.2 Water withdraw mechanism

The illustration of water withdraw mechanism is shown in figure 1. During the hydration period, at a certain time point after the initial setting time, due to the increasing interconnection among cement particles, the contact area between cement particle and surrounding water will be decreased. As a result, the slower hydration rate will be achieved. On the other hand the available space for packing of cement hydration products will be decreased because the volume of hydration products volume is 2.2 times bigger than the volume of the original cement. As proposed by Park [8] and Breugel [9], the water presenting in the paste can be classified into evaporable and non-evaporable fractions. The former is the capillary water and the gel water that resides partially within the hydration product. The non-evaporable water is defined as the bound water which has chemically reacted with cement. During hydration process, only the capillary water contributes to further hydration. With the increasing of gel-space ratio, the capillary water will be consumed and the relative hydration rate will be decreased. By considering these two points, the modifications of equation (1) can be expressed as equation (4):

$$\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt} * \left(\frac{freesurface}{totalsurface}\right) * \frac{w_0 - 0.38 * C_{e_0} * \alpha}{w_0} \quad (4)$$

In equation (5), the item $\left(\frac{\text{freesurface}}{\text{totalsurface}}\right)$ is the ratio between the free surface area (the area which contact with water) and the total surface area. w_0 is water content and C_{e_0} is cement content in mixing proportion. The item $\frac{w_0 - 0.38 * C_{e_0} * \alpha}{w_0}$ considers the decreasing of available space for packing of cement hydration products.

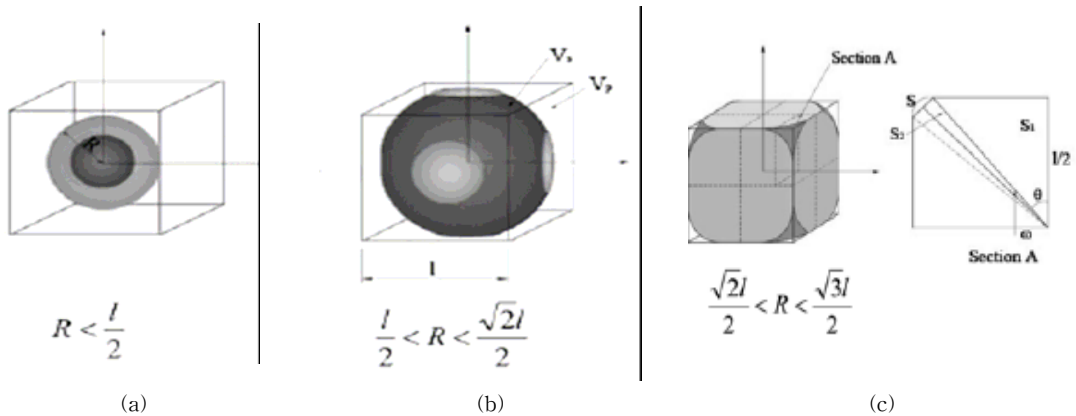


Fig. 1 illustration of water withdraw mechanism

3. Modeling of hydration of Portland cement blended with chemical inert filler

In this part, the experimental results in reference [5] are used to verify the proposed model. The mixing proportions and experimental results of heat evolution rate are shown in table 1 and figure 2, respectively. As shown in figure 2, it is obvious that the heat evolution rate of cement is accelerated due to addition of limestone. This acceleration can be attributed to dilution effect and physical effect (acceleration of heterogeneous nucleation of cement hydration). Based on regression of heat evolution, the parameters of B, C, De and kr of Portland cement blended with chemical inert filler can be obtained. The comparison between simulation results and experimental results is shown in figure 3. As shown in figure 3, the prediction results, including heat evolution and porosity, generally agree well with experimental results.

4. Conclusion

The proposed simulation method in this paper can consider both dilution effect and the acceleration of heterogeneous nucleation during hydration of cement blended with chemical inert filler. The heat evolution, degree of hydration and porosity are obtained as accompanied results in hydration process. The prediction results agree well with experimental results.

Acknowledgement

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Table 1 Mix proportions of the cement paste (kg/m³)

	TC	SCC01	SCC02
Portland cement I 52.5	350	400	400
Water	165	165	192
Limestone powder		200	300
Glenium 51 (liter/m ³)		3.2	2.7
Total powder content	350	600	700
Water/powder ratio	0.48	0.27	0.27
Water/cement ratio	0.48	0.41	0.48

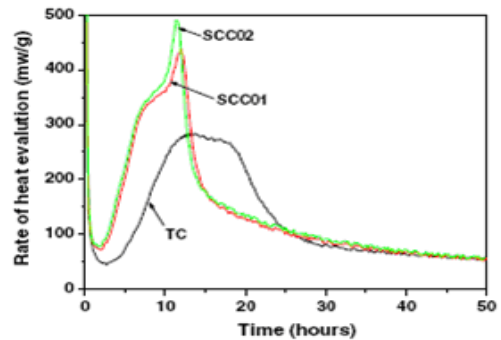


Figure 2. experimental result of heat evolution rate

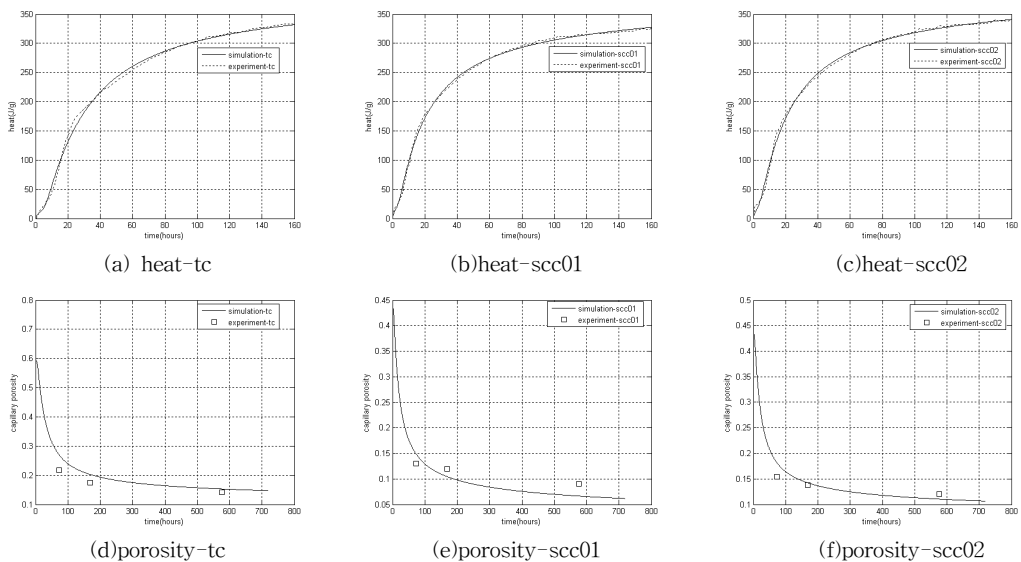


Figure 3 the comparison between simulation results and experimental results

References

- 1.P.Lawrence et al. Mineral admixtures in mortars effect of inert materials on short-term hydration, Cement and Concrete research, (2003)1939-1947
2. Philippe Lawrence, Martin Cyr, Erick Ringot, Mineral admixtures in mortars effect pf type, amount and fineness of fine constitutes on compressive strength, Cement and Cconcrete Research(2005)1092-1105
3. Martin Cyr, Philippe Lawrence, Erick Ringot, Mineral admixtures in mortars quantification of the physical effects of inert materials on short-term hydration, Cement and Concrete Research(2005)719-730
- 4.Martin Cyr, Philippe Lawrence, Erick Ringot, Efficiency of mineral admixtures in mortars: quantification of the physical and chemical effects of fine admixtures in relation with compressive strength, Cement and Concrete Research(2006)264-277