研 究 速 報

TWO-Dimensional Computer Simulation of Cement Hydration (2)

Effect of Temperature on Hydration Process Cement

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1. INTRODUCTION

Temperature affects the rate of strength development of cement-based material and consequently, the time needed to reach a required strength. Concrete cured at high temperature gains strength very fast but its loss in ultimate strength is usually observed. The increase in early strength at higher temperature is due to the fact that the cement simply hydrates more rapidly, but the decrease in later strength is not easy to explain. In this paper, authors aim at a possible explanation of that decrease in later strength. The two-dimensional simulation was carried out using multi-component, digital-image-based model of cement hydration [2]. Taking into account the effect of temperature on hydration rate, specific density and on chemical composition of hydration product, the inverse effects of temperature on strength and porosity of cement paste were obtained. Gel/space ratio model was found to be suitable for the prediction of strength of cement paste cured at various temperatures.

2. FUNDAMENTAL CONCEPTS

2.1 Digital-image-based model of hydration

This hydration model was put forward by Bentz and Garboczi [1]. Firstly, whole the domain of cement paste is divided into many small pixels; each pixel represents an amount of cement mineral or water. The main concept of this model is the "random walk" algorithm, which is the random movement of pixels and their reactions after colliding with corresponding pixels.

Hydration process is a series of the following processes: Dissolution, diffusion and reaction. For details of the original model and its related works, readers can refer to [1] and [4]. The authors have introduced a simple method of obtaining the starting structure of cement paste instead of using the complicated approach in the original model [4].

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2.2 Effect of temperature on hydration rate of cement

Hydration rates of cement mineral components are accelerated by the increase of temperature. The rate of hydration discussed here is the one of whole cement, not of individual components. It means that the effect of temperature on the rate of hydration is equal for mineral components. The reaction rate can be calculated using Arrhenius's equation:

$$k = K_0 \cdot \exp\left(-E_a / RT\right) \quad \cdots\cdots (1)$$

Where, K_0 is a constant, E_a is apparent activation energy, R is the universal gas constant, T is absolute temperature in degree K.

The equivalent time for hydration at any temperature of interest, T, can be calculated relative to that of reference temperature, T_0 (20°C in this case).

$$t_T = K_T \cdot t_0 \quad \cdots\cdots (2)$$

Where, t_T : time of hydration at temperature T
t_0 : time of hydration at temperature T_o
T_0 : reference temperature
T : considering temperature
K_T : time scale,

$$K_T = Exp\left(-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad \cdots\cdots (3)$$

2.3 Effect of temperature on physical properties and chemical composition of hydration products

Temperature affects not only the reaction rate but also the physical properties of hydration products. Morimoto [1] reported that the increase in curing temperature is accompanied by the increase in specific density of hydration product.

In addition, the amount of Calcium hydroxide in cement paste decreases at higher temperature. It means that a part of calcium oxide is now in the molecular composition of calcium-silicate (C-S-H), the main product of cement paste formed from the reactions of tricalcium-silicate and dicalcium-silicate with water.

Among hydration products, C-S-H is present in the largest amount. Therefore, the increase in specific density of hydration products is mainly attributed to that of C-S-H, which possibly results from:

- The increase of the Ca/ Si ratio of C-S-H
- The reduction in the amount of water in C-S-H.
- The fast deposition at high density of products

In this research, it is assumed that the chemical formula of C-S-H changes from $C_{1.7}SH_4$ to $C_{1.85}SH_4$ when cement hydrates at temperature higher than 40°C. With this assumption, the reactions between tricalsicum-silicate and dicalcium-silicate with water have to be adjusted for hydration at each considering temperature. Below or equal to 40°C, the change in specific density is attributed to the fact that high temperature causes the fast deposit of hydration product at adjacent region of diffusing sources.

From experimental results of Morimoto [3], the following equation was proposed for the relationship between specific density of hydration products and temperature

$$\delta = \delta_0 - B.e^{\left(-(x-x_0)/t\right)} \quad \cdots\cdots (4)$$

Where, δ is the specific density of hydration product, $\delta_0 = 2.31$ (T< 100°C), x is the temperature of consideration. B, x_0 and t are constants: B = 0.1663, $x_0 = 20$, t = 8.815

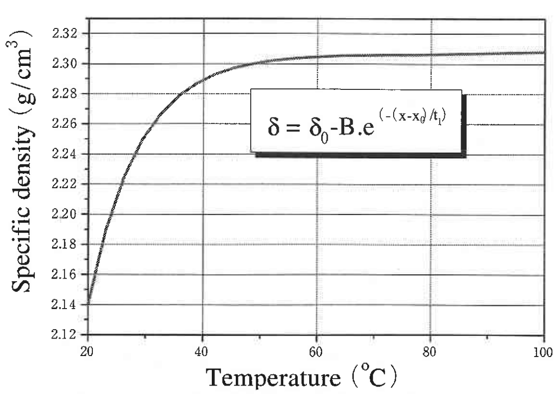

Fig . 1 Proposed relationship between specific density of hydration product and temperture

The specific density of pore products such as $Ca(OH)_2$ is considered to be immutable at different temperature.

In order to consider the effect of temperature on hydration process, the following works have to be done:

- Determining the reaction rate at considering temperature
- Adjusting the specific density of hydration products
- Adjusting the chemical equilibrium of hydration equations of C_2S and C_3S.

3. EXAMPLE OF CALCULATION

Calculations were carried out for hydration at temperatures of 20, 40 and 60°C. Hydration equations of silicate phases at 60°C are adjusted as follows:

Reactions of C_3S and water:

$3CaO.SiO_2$ +	$5.15H_2O$ =	$C_{1.85}SH_4$ +	$1.15Ca(OH)_2$ ··· (5)
(C_3S)	(H)	(C-S-H)	(CH)
3.21g/ml	1.00	2.30	2.24
71.13ml	92.7	102.54	38.031

Reaction of C_2S and water:

$2CaO.SiO_2$ +	$4.15H_2O$ =	$C_{1.85}SH_4$ +	$0.15Ca(OH)_2$ ···· (6)
(C_2S)	(H)	(C-S-H)	(CH)
3.28g/ml	1.00	2.30	2.24
52.52 ml	74.7	102.54	4.9605

Similarly, it is possible to consider the volumetric equilibrium of hydration at any temperature of interest while the rate of hydration is calculated relative to temperature.

Figure 2 exhibits that the reaction of cement under high curing temperature proceeds very fast and quickly reaches the maximum hydration ratio. The ultimate degree of hydration is slightly higher in case of high temperature. This is due mainly due to the reduction in the volume of hydration products and, as a result, there is more space for the later formation of other products.

Along with the fast hydration at the early age, the porosity of cement paste under high temperature reduces very fast and soon reaches the critical value while the porosity of cement paste cured at normal temperature still decreases steadily when hydration proceeds (Fig. 3). The inverse effect of temperature on porosity at about 30 days suggests that there may be a similar effect on the strength of cement paste because the inherent close relationship between the two quantities.

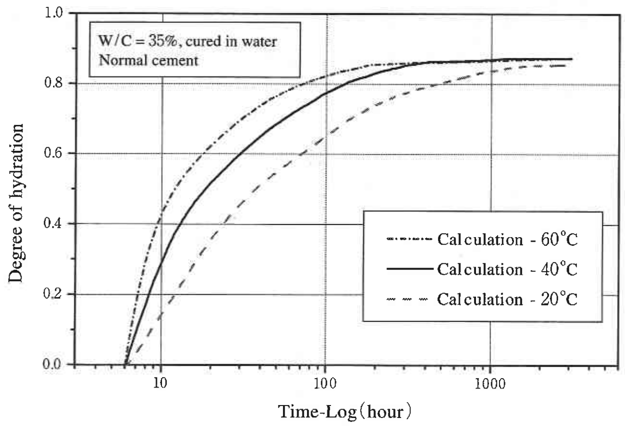

Fig. 2　Degree of hvdration at different temperatures other products.

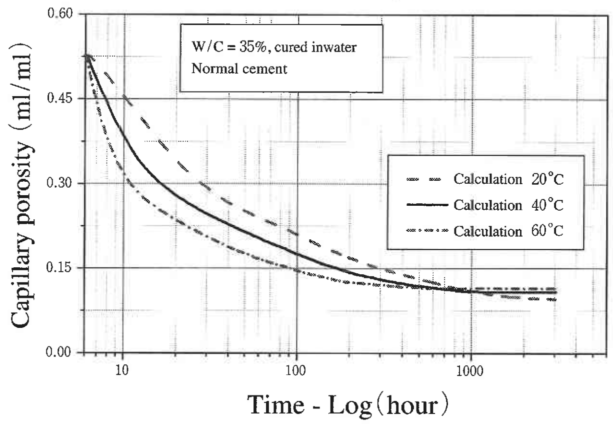

Fig. 3　Porositv of cement at different temperatures

4. STRENGTH PREDICTION

In this research, strength of cement paste was predicted using the gel/space ratio - based model proposed by Powers and Brownyard[2]. The gel/space ratio, X, is the ratio of the solid products of hydration to the space available for these hydration products, In other words, the gel/space ratio is a representation of the capillary porosity of the paste in terms of its measurable parameters.

The modified gel space ratio of cement paste cured at normal temperature is:

$$X = \frac{(0.68/K)\alpha}{(1-0.68/K)\alpha + W/C} \quad \cdots\cdots (7)$$

Where,

- K is the ratio of specific density of hydration product at considering temperature to that at normal temperature.
- α is the degree of hydration.
- W/C is the initial water-cement ratio.

Then, at normal temperature, (20°C), the gel/space ratio is:

$$X = \frac{0.68\alpha}{0.32\alpha + W/C} \quad \cdots\cdots (8)$$

Similarly, at 40°C, the gel/space ratio is

$$X = \frac{0.63\alpha}{0.37\alpha + W/C} \quad \cdots\cdots (9)$$

The relationship between compressive strength and the gel/space ratio is expressed as follow:

$$\sigma_c = A\, X^n \quad \cdots\cdots (10)$$

Where, A is a constant representing the intrinsic strength of the cement gel (i.e., the strength at a gel/space ratio of 1.0), n is a constant having values in the range 2.6 to 3.0

The 3-day compressive strengths of cylinder specimens were used to determine the intrinsic strength A at each temperature while n is selected of 3 in advance (Equation 10). To compare the calculated results with experiment ones, 5cm x 10cm cylinder specimens were cured in 20°C, 40°C and 60°C hot water after 6 hours from mixing time.

Cement paste cured at high temperature gains strength very fast at the early age but gradually reaches critical value while cement paste cured at normal temperature still develops strength at a remarkable rate. From the calculated result, the inverse effect was seen at about 30 days of hydration (crossing point in Figure 4). Experimental results in the case of 60°C curing also shows a reduction in the ultimate strength of cement paste compared to the normal temperature case.

The reduction in ultimate strength cannot be attributed solely to

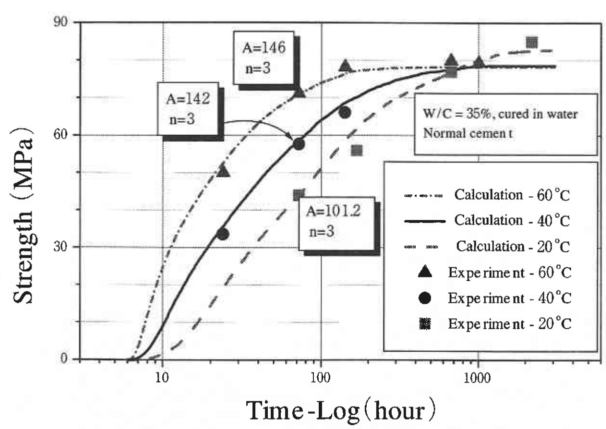

Fig. 4　Strength of cement paste at different tempertures

the increase in porosity at higher temperature, but other factors such as the effect of pore size should be taken into account. Another effect that should not be neglected is the non-uniform distribution of hydration products at high temperature. In addition, hydration products tend to form large crystal at high temperature resulting in the reduction in total surface area and therefore bringing in the reduction in ultimate strength.

4. CONCLUSIONS

- The inverse effect of temperature on the porosity and the strength development of cement paste was obtained from simulation; the calculated results coincide well with that of experiment.
- The gel/space ratio model was found to be suitable for prediction of strength of cement paste cured at different temperatures. This prediction may help reduce the time needed for examine the compressive strength if cement paste is cured at high temperature.
- This research was performed for the case of constant temperature; more works are necessary for the case of inconstant temperature.

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5. PREFERENCES

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