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論 文

[1206] Multi-Component Model for Hydration Heat of Concrete Based on Cement Mineral Compounds

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1. INTRODUCTION

Thermally induced crack at early age of concrete is of great interest to engineers involved in durability design and construction of massive structures. Here, it is crucial to accurately predict the thermal expansion associated with temperature rise in structures of young concrete. As a source of temperature rise, the hydration heat of cement in concrete has to be modeled for thermal crack control in the scheme of durability design [1]. Lately, High Performance Concrete, that is, super fluidized and durable concrete being placed into forms without vibrating works, was innovated [2,3]. This paper aims at the rational predictive method for heat generation of cement in concrete covering High Performance Concrete with small amount of water and wide variety of powders.

For making thermal crack control possible in the durability design stage, the heat generation corresponding to the specified mix proportion has to be predicted without any temperature rise test. For meeting the required versatility, we have to take into account the following characteristics of High Performance Concrete. Owing to the super-fluidity without segregation [3], lower amount of water is specified in general and larger content of powders (cement, pozzolans and rock mineral powders) is essential. The retarded rate of hydration due to lower water content will occur unlike conventional concrete. Furthermore, the model required has to be applicable to ordinary Portland cement (OPC) as well as moderate heat Portland cement (MHPC) and their mixture with pozzolans. In this case, different ratio of constituent minerals of clinker has to be rationally modeled.

In meeting the engineering challenge mentioned above, this paper proposes the multi-component model of cement hydration heat based on Arrhenius's law of chemical reaction. The nonlinear coupling of heat generation under lower water content with thermal conduction in structures are also undertaken.

2. MULTI-COMPONENT MODEL OF CEMENT HYDRATION HEAT

Cement consists of several clinker minerals with different hydration processes. The proposed model is built on the multi-component concept of mineral assembly of cement. The thermodynamic energy conservation must be satisfied in time and space domains as,

$$(\rho c)\frac{\partial T}{\partial t} = -div\vec{J} + H \qquad (1)$$

$$div\vec{J} = -k \cdot \nabla T$$

where, k = mean thermal conductivity of concrete, ρc = heat capacity of concrete by $kcal/{}^{\circ}K/m^3$, and H is defined as the heat generation rate by $kcal/hr/m^3$, T = temperature by K°.

It is well known that the cement content affects the hydration process of cement in concrete under rather thermally isolated condition because of the high temperature dependency of hydration process. For requirement of versatility, the cement and water contents should be rationally involved in the model as a parameter related to the mix proportion. The concrete based heat generation rate denoted by H can be further idealized as,

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$$H = C\overline{H} \tag{2}$$

where, C = cement content (kg/m^3), $\overline{H}$ = specific heat rate of cement ($kcal/kg/hr$).

Suzuki et al.[4] reported that the Arrhenius's law can be extended to the composite with different chemical reactions of clinker minerals. In the model, cement in concrete is regarded as a single fictitious material having the averaged heat rate and variable mean activation energy uniquely specified in terms of the accumulated heat of cement. However, particular activation and rate of hydration have to be defined according to the sort of cement, because the heat generation, in fact, arises from each clinker mineral. As a matter of fact, the sort of cement or mineral compound should be modified when we find problems in view of thermal crack control design.

It is clear that within the frame of durability design, the adaptable model should fit in any combination of clinker minerals, and that the specific heat rate as a whole consists of mineral based heat rates. The authors take up four chemical compounds (aluminate C_3A, alite C_3S, belite C_2S, ferite C_4AF) and five patterns of chemical reactions for Portland cement as,

$$\begin{aligned} \overline{H} &= p_{mono}\overline{H}_{mono} + p_{C_3A}\overline{H}_{C_3A} + p_{C_3S}\overline{H}_{C_3S} \\ &\quad + p_{C_2S}\overline{H}_{C_2S} + p_{C_4AF}\overline{H}_{C_4AF} \end{aligned} \tag{3}$$

$$p_{mono} + p_{C_3A} + p_{C_3S} + p_{C_2S} + p_{C_4AF}p_{else} = 1$$

where, p_i = mass ratio of i-component, $\overline{H}_i$ = specific heat rate of i-component. Subscript '*mono*' represents the transformation of ettringite to the mono-sulfate.

The heat generation when the calcium sulfo-aluminate (ettringite) is produced from aluminate with gypsum is assumed negligible in the structures but considered when transformation to mono-sulfate proceeds, since the former reaction is thought to mostly terminate before casting of concrete. According to the Arrhenius's law [4,5], the temperature dependent rate of reaction yields,

$$\overline{H}_i = \overline{H}_{i,T_o} \exp\left\{-\frac{E_i}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right\} \tag{4}$$

where, E_i = activation energy of i-component hydration, R = gas constant and $\overline{H}_{i,To}$ = referential heat rate when temperature is T_o (= 293°K).

The activation energy represents the barrier identical to each chemical reaction for advancing further reaction. The referential heat rate of each reaction embodies the probability of molecular collision with which the hydration is evolved. Since the events of collision will be dependent on the amounts of free water, the thickness of cluster made by already hydrated product and unhydrated chemical compound, we propose,

$$\overline{H}_{i,To} = \beta_i \cdot F_i(\overline{Q}_i) \tag{5}$$

$$\overline{Q}_i \equiv \int \overline{H}_i$$

where, the function F represents the events occurrence of i-component in terms of accumulated heat as the indicator of hydration level.

The parameter β_i indicates the reduction of hydration rate with respect to the increasing thickness of cluster made of already hydrated product and the decreasing free water during hydration as,

$$\beta_i = 1 - \exp\left\{-r \cdot \left(\frac{\omega_{free}}{100 \cdot \eta_i}\right)^s\right\} \tag{6}$$

where, the constants $<r,s>$ are material parameters, parameters η_i and ω_{free} = non-dimensional indicators for the thickness of cluster around the unhydrated compound and free water which can be consumed by further reaction. According to mass conservation, these values are idealized as,

$$\omega_{free} = \frac{W_{total} - W_{mono} - W_{C_3A} - W_{C_3S} - W_{C_4AF}}{C} \tag{7}$$

$$\eta_i = 1 - \left(1 - \frac{\overline{Q}_i}{\overline{Q}_{i,\infty}}\right)^{\frac{1}{3}} \tag{8}$$

where, the values of W_{total} and W_i = total water content at mixture and updated consumed water by each component, and $\overline{Q}_{i,\infty}$ means the final heat generation identical to the following hydration process.

In this model, the consumed water in Eq.(7) is computed [10] through Eq.(9) when we know the accumulated heat and the final specific heat of each process. Total water content is assumed constant. This implies that the pore water transport caused by the hydration and drying is neglected.

$$\begin{array}{ll}
CaSO_4 \cdot H_2 + C_3A + 10H \rightarrow C_3A \cdot CaSO_4 \cdot H_{12} & C \equiv C_aO \\
C_3A + 6H \rightarrow C_3AH_6 & A \equiv Al_2O_3 \\
2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH & H \equiv H_2O \\
C_4AF + 2CH + 10H \rightarrow C_3AH_6 - C_3FH_6 & F \equiv Fe_2O_3 \\
2C_2S + 4H \rightarrow C_3S_2H_3 + CH & S \equiv SiO_2
\end{array} \tag{9}$$

By simultaneously solving Eq.(1)-Eq.(9), we obtain the temperature distribution in time domain. The cement and water contents are quantitative parameters as concrete mixture. The weight ratio of each mineral with different activation and specified rates of hydration are also qualitative parameters related to the sort of cement used in concrete. Since Eq.(1) is nonlinear with respect to the temperature, nonlinear iterative computation by discretized finite element was conducted [6].

3. EXPERIMENTAL VERIFICATION

The material constants and referential heat rate of each clinker are shown in Figure 1 and Table 1. These values are related to the quality of powders. Regarding the quantity of High Performance Concrete, two mixtures are adopted for verification as shown in Table 2. The larger amount of cement and low water to cement ratio are noticeable as for characteristics of super fluidity.

Two mixtures were cast in the forms surrounded by the polymer foam as shown in Figure 2, and the temperature at the center was measured. The experimental and analytical results as shown in Figure 2 fairly coincide with each other. Temperature rise and corresponding volumetric expansion are affected approximately 10 degree (K) owing to the different mineral components. In fact, the cement contents in these mixtures are closely the same. The mixed cement with pozzolans can be idealized with the same manner [9].

The adiabatic temperature rise test results [8] and predictions for OPC and MHPC are also shown in Figure 2. It is important to recognize that aluminate is computed to react at the beginning of entire hydration process and the hydration of belite is oppositely retarded. Furthermore, due to the lower water to cement ratio, some belite which no longer hydrates still remains in the mixture 5 days after casting. The free water concept incorporated with the heat rate model is vital on this matter.

When the water content does not get critical, the final temperature rise becomes proportional to the cement content. But, the hydration pattern in time domain under adiabatic condition is not similar [4] since the temperature dependent nonlinearity is incorporated. In fact, the adiabatic temperature rise condition derives from Eq.(1) and Eq.(2) by assuming zero of the mass flux term as,

$$\overline{Q} = \frac{\rho c}{C} \cdot \Delta T \tag{10}$$

where, ΔT = temperature rise as $T - T_{init}$ and T_{init} is defined as initial temperature when concrete is cast.

By amalgamating Eq.(10) and Eq.(2), we have,

$$(\rho c)\frac{d(\Delta T)}{dt} = C \cdot \overline{H}\left(\frac{\rho c}{C} \cdot \frac{d(\Delta T)}{dt}, \Delta T + T_{init}\right) \tag{11}$$

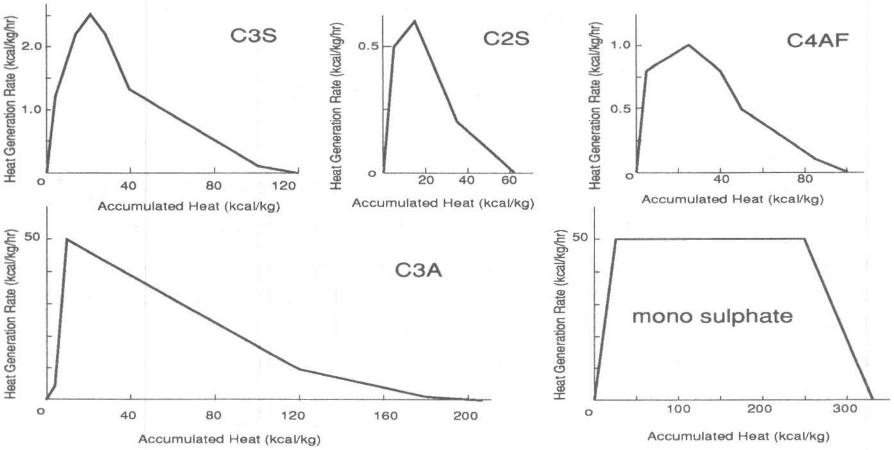

Figure 1 Idealized referential heat rate function

Table 1 Material constants and clinker components used in analysis.

Clinker	E/R $(kcal^{\circ}K/kg \cdot hr)$	$\overline{Q}_{i,\infty}$ $(kcal/kg)$	r	s	OPC (weight %)	MHPC (weight %)
Aluminate	6500	207	2.0	2.5	10	4
Alite	6000	120	2.0	2.5	47	44
Belite	3000	62	2.0	2.5	27	34
Ferite	3000	100	2.0	2.5	9	12
Gypsum	-	-	-	-	4	4
Ettringite	6000	330	2.0	2.5	-	-

Table 2 Mix proportion of OPC and MHPC cement concrete.

Test ID	Water (kg/m^3)	Cement (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Air (%)	Admixture
MHPC	174	550	857	827	3	1.5% of C
OPC	182	557	828	827	3	1.5% of C

Eq.(11) is the governing differential equation on temperature rise with respect to time. Mathematically speaking, it is not possible to exactly define the unique function H because of the multi-component expression in Eq.(3). As far as OPC is concerned, however, Suzuki [4] experimentally examined the presence of the averaged referential heat rate denoted by H no matter what proportion of components is specified. It is recognized that the solution of ΔT depends on the cement content and initial temperature. It is emphatic that the mix proportion of concrete is rationally taken into account and only the quality of cementitious powder is to be specified in the thermal control design.

4. ACCUMULATED HEAT AND MATURITY

The volumetric strain caused by the temperature rise is the chief ingredient of thermal stress induced to massive concrete. The hardening and drying shrinkage evolved by the water transition and transport also activates the free volumetric change. It is required for the control of cracks to solve the followings in both time and space domains. Here, it is crucial to precisely appraise the stiffness under the transient condition in which the cement evolves hydration heat and mechanical strength.

The so called maturity has been used for prediction of strength development. As a matter of fact, the concept of maturity is implicitly incorporated in the system. If we could assume sufficient free water in the mixture, the value of β in Eq.(5) approximately gets unity. Then, we have,

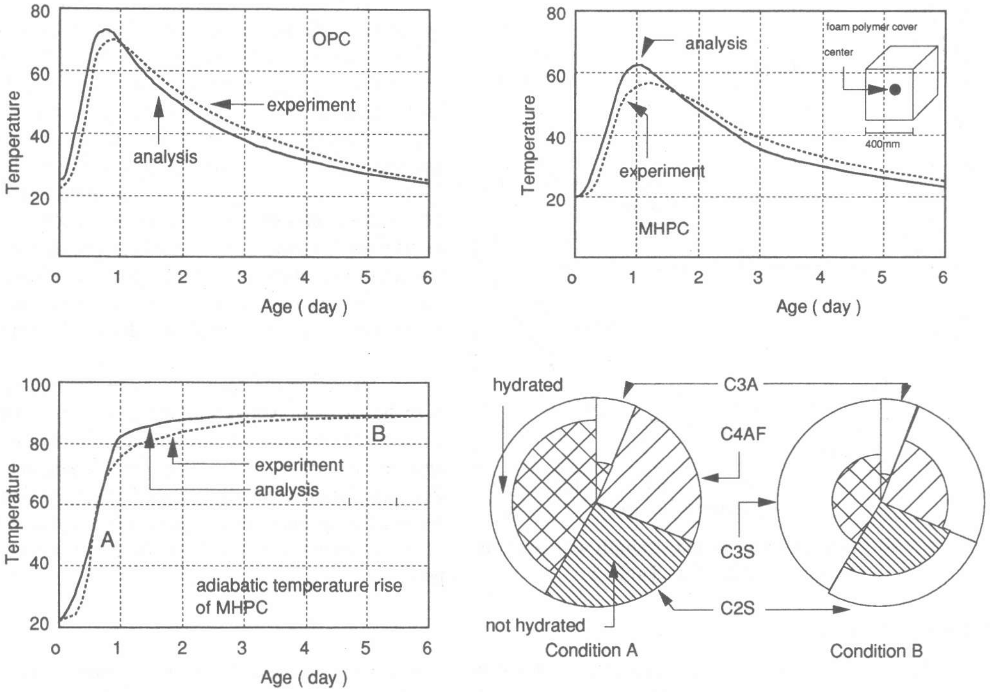

Figure 2 Experimental and analytical temperature rise of high performance concrete.
(OPC and MHPC concrete, quasi and full adiabatic temperature conditions)

$$Z(\overline{Q}_i) \equiv \int \frac{d\overline{Q}_i}{F_i(\overline{Q}_i)} = \int \exp\left\{-\frac{E_i}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right\} dt \equiv M_i \tag{12}$$

Since the right term of Eq.(12) can be defined as maturity of each mineral compound, Eq.(12) yields the one-to-one relation of the accumulated heat and the maturity as,

$$\overline{Q}_i = Z^{-1}(M_i) \tag{13}$$

It means that the accumulated heat of single component of clinker is mathematically equivalent to the maturity. But, it must be recognized that the maturity has to be defined in each component of clinker mineral. As the activation energy is not common among the constituents listed in Table 1, it is not possible to derive the averaged cement maturity exactly from the governing equation. Therefore, the authors take up the averaged entire hydration level as the alternate of maturity for estimating mechanics of young concrete. The level is expressed by the total accumulated heat of all cement components normalized by the final generation of heat. If the activation energy could be equal, the hydration level becomes equivalent to the maturity indeed.

The relation of the stiffness and the compressive strength with the accumulated heat generation of concrete is shown in Figure 3. The accumulated heat is the computed one by integrating Eq.(5) with respect to time under the temperature history. Compared with the maturity model proposed in the past, clear bi-linear relation is seen. This feature is advantageous in line with the simple formulation and enhanced computation.

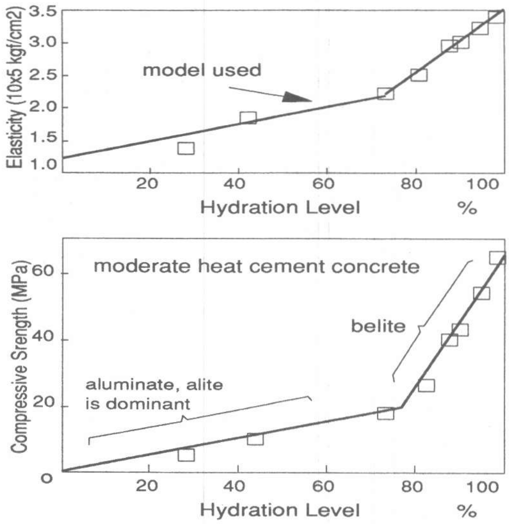

Figure 3 Relation of stiffness and strength with accumulated heat. : MHPC in Table 2.

As shown in Figure 2 and Figure 3, the hydration of aluminate and alite is dominant at earlier age of concrete. In this region, the rate of development for strength and stiffness is small no matter how much the total hydration proceeds up to 75% of the final heat generation. But, when hydration of belite starts to be active, the sharp gradient is seen in Figure 3 on the stiffness versus the accumulated heat to which belite chiefly contributes. As reported, the belite mainly serves as the ingredient to enhance the strength development in the long range. Furthermore, the reaction of belite is effective on the improvement of mechanical soundness of concrete.

The modeling for multi-component can deal with the interaction of hydration among each mineral components through Eq.(6) and Eq.(7). From the engineering view point, lately, the interaction of Pozzolans with Portland cement is being investigated for improving the multi-component concept in terms of the concentration of calcium hydro oxide in the pore water.

5. CONCLUSIONS

The unified hydration heat model of cement in concrete mixes was proposed for a future frame of assuring required functions and durability of structures based on vibration free high performance concrete of super fluidity. The cement clinkers are classified into four minerals with which five patterns of hydration are embodyed. The coupling of free water and temperature, which indicate the thermodynamic environment of cement in concrete, with the hydration rate was taken into account. The hydration model was also experimentally verified. Though plenty of items have to be clarified for crack control design, the structural discussion on the thermal crack risk was made under some simplified conditions. Finally, this research was financially supported by Ministry of Education through Grant-in-Aid for Scientific Research No.04555114.

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