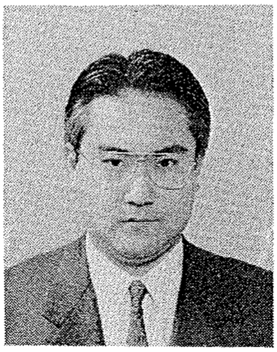
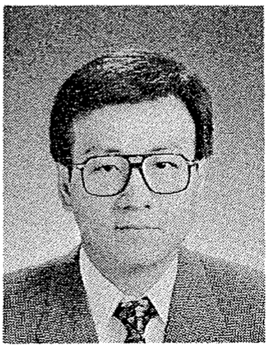
CONCRETE LIBRARY OF JSCE NO. 30, DECEMBER 1997

MULTI-COMPONENT MODEL FOR HYDRATION HEATING OF BLENDED CEMENT WITH BLAST FURNACE SLAG AND FLY ASH

(Translation from Proceedings of JSCE, No. 550/V-33, November 1996)



Toshiharu KISHI



Koichi MAEKAWA

This study proposes a multi-component model for hydration heat of blended cement for the temperature analysis of massive concrete structures. In the temperature analysis, a hydration heat model of cement applicable to any given conditions is required. A multi-component system is adopted in which each mineral compound of cement, blast furnace slag and fly ash is treated as a separate reaction unit and the interdependencies among them are evaluated based on their individual mechanisms. The heat generation rate of each reaction is expressed in two material functions, the reference heat rate at constant temperature and the thermal activity. The degree of reaction of each component is computed step by step with modified Arrhenius' law of chemical reaction. The mutual interactions among mineral compounds of Portland cement and pozzolans are taken into account in terms of the specific free water and the amount of calcium hydroxide assigned as state variables representing the chemical environment of the pore solution. The proposed model has been verified through analyses of the adiabatic and semi-adiabatic temperature rises.

Keywords: *clinker minerals, blast furnace slag, fly ash, hydration heat, multi-component model*

Toshiharu Kishi is a lecturer in the Department of Civil Engineering at the University of Tokyo, Tokyo, Japan. He obtained his D.Eng. from the University of Tokyo in 1996. His research interests include thermal stresses on mass concrete and the evaluation of the temperature rises. He is a member of the JSCE and the JCI.

Koichi Maekawa serves as professor in the Department of Civil Engineering at the University of Tokyo, Tokyo, Japan. He obtained his D.Eng. from the same university in 1985. He specializes in nonlinear mechanics and the constitutive laws of reinforced concrete, the seismic analysis of structures, and concrete thermodynamics. He is a member of the JSCE and the JCI.

1. INTRODUCTION

As admixtures for concrete, various powder materials such as blast furnace slag, fly ash, lime stone powder, expansive agent and so on are used. Blast furnace slag and fly ash are especially useful for massive concrete structures because they function as binders. In the thermal crack inspection at design stage, combinations of powder selection and blending proportion to be examined have a wide scope since various sorts of materials including low heat type Portland cement are used to prevent the occurrence of thermal cracking. Therefore, it is necessary that the hydration heat model covers not only Portland cement but also blended cement with admixtures in order to contribute to the temperature analysis for mass concrete. This is significant for self-compacting high performance concrete [1] which has to more than a certain unit content to maintain self-compactability, so powder selection and blending proportion are examined carefully in the thermal crack inspection [2]. The authors have proposed a multi-component hydration heat model which covers variations in Portland cement types [3,4]. In this model, reactions shown in Portland cement are described in each clinker mineral and interdependencies among them are evaluated separately. That is, the model has a constitution in which reactions in the binder are treated as assemblies of appropriate reaction units and mutual interactions among reactions can be rationally taken into account. This constitution makes it easy to incorporate new components for blended admixtures. The purpose of this study is to extend the scope of applicability of the existing multi-component hydration heat model from Portland to blended cement which includes blast furnace slag and fly ash by incorporating new components.

For blended cement in which several admixtures are used, it is not always rational to treat a whole powder as a single system. When a macroscopic model in which a whole system is treated as a sole powder is considered, the degree of hydration or the accumulated heat is defined as an indicator which represents the degree of reaction for the entire system. In the combination of reactions which have different temperature dependencies, however, the degree of each reaction cannot be identified in terms of the indicator which defines the degree of reaction for the entire system when temperature history differs.

In blended cement, the interdependencies among reactions are more complicated than Portland cement alone and one cannot guarantee the rationality of an assumption that the degree of the entire reaction process can be defined by any single indicator. If the whole system is treated as a single reaction process, the interdependency of reactions in the system is not negligible and more complex modeling might be necessary. Therefore, each reaction of clinker mineral is individually described and then mutual interactions are taken into account in the multi-component hydration heat model in order to account for the wide variety of Portland cements and arbitrary temperature histories. The multi-component hydration heat model [4] in which heat rate is described for each reaction unit and interdependencies are evaluated according to individual mechanisms has greater rationality for blended cement which has more complex interdependencies.

The reactions of blast furnace slag and fly ash in blended cement are dependent on the calcium hydroxide produced by alite and belite in Portland cement [5]. The reaction of admixtures proceeds if calcium hydroxide is sufficiently supplied, and the reaction is inversely restrained due to shortages. In order to express the exothermic process of blended cement, it is essential to evaluate quantitatively both production from alite and belite hydration and consumption by admixture reactions in terms of elapsed time. Thus, it is indispensable to classify reaction of blended cement into appropriate reaction units and describe those heat rates respectively in order to evaluate accurately the interdependency of reactions under arbitrary temperature history. This approach, in which each reaction of clinker mineral or admixture is described respectively, can apply to various sorts of cement with different replacement ratios and arbitrary temperature histories.

In this study, the exothermic reaction processes of blast furnace slag and fly ash are described in terms of the amount of calcium hydroxide produced by hydration and the delaying effect of slag and fly ash on reactions in cement is taken into account. These factors are mutual interactions which take place between the exothermic hydration process of Portland cement and admixtures, and it becomes possible to deal with them rationally by using the multi-component system adopted here.

2. MODELING THE EXOTHERMIC HYDRATION PROCESS OF BLENDED CEMENT

2.1 Basic concept of multi-component hydration heating model and general formula [4]

In the model, hydration of cement is expressed by classification into individual clinker minerals which are regarded as fundamental units of reaction. The heat reactions for alite (C_3S), belite (C_2S), aluminate phase (C_3A) and ferrite phase (C_4AF) were individually described. To extend the scope of the model to blended cement, blast furnace slag and fly ash are regarded as single units of reaction and incorporated into the model as individual components. Slag and fly ash are not classified like Portland cement because a part reacting is only glass phase at normal temperature, which can be regarded as a homogeneous material. However, at this stage, the reaction of slag is assumed to be unaffected by the existence of gypsum [5]. Therefore, heat rate of the entire cement including blending powders is given as the sum of the heat rate of all reactions as follows,

$$\begin{aligned} H &= \sum p_i H_i \\ &= p_{C_3A}(H_{C_3AET} + H_{C_3A}) + p_{C_4AF}(H_{C_4AFET} + H_{C_4AF}) \\ &\quad + p_{C_3S}H_{C_3S} + p_{C_2S}H_{C_2S} + p_{SG}H_{SG} + p_{FA}H_{FA} \end{aligned} \tag{1}$$

Where, i represents each mineral component including blast furnace slag (SG) and fly ash (FA). H and H_i are the heat rates of blended cement as a whole and mineral i per unit weight respectively, p_i is the weight fraction of component i in the binding powder. H_{C_3AET} and H_{C_4AFET} are both heat rates as a result of the formation of ettringite.

The hydration heat rate of blast furnace slag and fly ash are described by two material functions which are the reference heat generation rate expressing heat rate at a constant temperature and the thermal activity indicating temperature dependency of the reaction as well as clinker minerals [4,6]. Here, it is essential that interdependencies among reactions of component are adequately expressed in order to establish modeling of the exothermic hydration process of trinal blended cement. The reactions of slag and fly ash are dependent on the supply of calcium hydroxide produced by cement hydration, which is a stimulant for reactions and consumed by them. To express the above reaction dependency of slag and fly ash to calcium hydroxide, the coefficient λ is introduced. In this study, other factors of mutual interaction, such as free water consumed, are shared by components. Fly ash and organic admixture delay reactions of Portland cement and blast furnace slag are also taken into account. Therefore, the hydration heat rate of each component is generally expressed, with interdependency among the reactions, as follows,

$$H_i = \gamma \cdot \beta_i \cdot \lambda \cdot \mu \cdot s_i \cdot H_{i,T_0}(Q_i) \exp\left\{ -\frac{E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\} \tag{2}$$

$$Q_i \equiv \int H_i dt \tag{3}$$

Where E_i is the activation energy of component i, R is gas constant, $H_{i,T0}$ is the reference heat generation rate of component i at constant temperature T_0 and also the function of accumulated heat Q_i, γ is a coefficient to express delaying effects of fly ash and organic admixture in the initial hydration exothermic process, β_i is a coefficient to express reduction of heat rate due to reduction of free water (precipitation space), λ is a coefficient to express change of heat rate of blast furnace slag and fly ash depending on the amount of calcium hydroxide in the liquid phase, μ is a coefficient to express change of heat rate related to difference of mineral composition of Portland cement, s_i is a coefficient to express change of referential heat rate due to change of fineness of powders. Coefficients, γ, β_i, λ and μ are assumed to give changing ratios when there are no effects from other factors. The minimum coefficient is adopted as the reducing ratio when several coefficients give a value less than 1. Coefficients λ and s_i are newly introduced into the proposed model and $-E_i/R$ is defined as thermal activity.

2.2 Reference heat generation rate of components

The reference heat generation rate H_{i,T_0} at the reference temperature T_0 is set as a material function of each reaction as shown in **Fig. 1**. These rates of clinker minerals are generally set at the mineral compositions of ordinary Portland cement and the reference temperature T_0 was set at 293K. The reference heat rates shown in **Fig. 1**, which were originally determined by a previous study [4], are slightly modified in this study. That is, in the division of hydration exothermic processes of C_3S and C_2S, a boundary between Stage 1 and Stage 2 was shifted from 3% to 1% of the total heat, and one between Stage 2 and Stage 3 was shifted from 20% to 25% for C_3S and to 30% for C_2S. The reference heat generation rates of blast furnace slag and fly ash are assumed to be under conditions where water and calcium hydroxide are sufficiently supplied to their reactions. The reaction rate of fly ash, which is referent heat rate divided by total heat generation, is set much smaller than the slag reaction in the model because a reaction between glass phase in fly ash and Ca^{2+} in the solution is relatively slow and is accelerated after 1 or 3 days from mixing at the normal temperature [5].

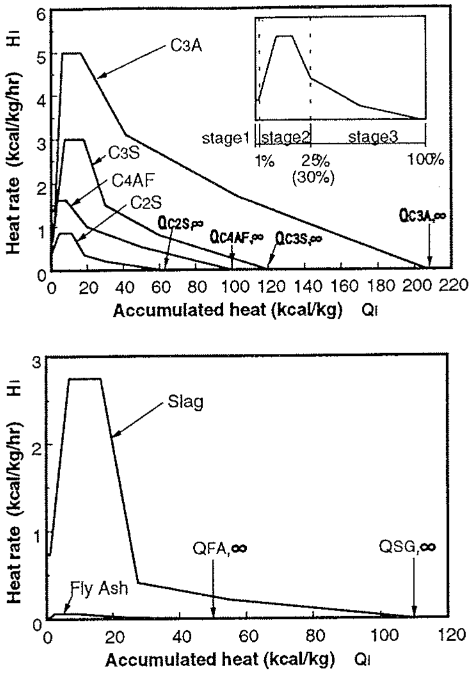


Fig. 1 Reference heat generation rate set for each reaction

In general, it is difficult to derive the reaction heat generation rate of blending admixtures individually from experiment, since it can not continue to react without an activator. Besides, it is well known that heat rate measured under the addition of a reagent is not similar in blended cement since the type of reagent affects the reactivity of admixtures [5]. Thus, the reference heat generation rates of slag and fly ash are set by comparing the analytic to the experimental data as in Suzuki [7]. The total heat generation per unit weight set in the model, which corresponds to 100% reaction ($Q_{i,\infty}$) can also be derived from qualitative observations of reactions besides analytic trials. In the case of blast furnace slag, it is well known that replacement of slag up to 50% hardly changes the ultimate temperature rise of ordinary Portland cement in adiabatic test and gradually raises that of moderate heat Portland cement [8]. Therefore, the total heat generation of slag was assumed to be approximately the same as ordinary cement and slightly greater than moderate heat cement. Then, 110 kcal/kg was assumed for the total heat generation of unit weight blast furnace slag in this study. On the other hand, quantitative information for fly ash reaction is scarce and it is not clear that the reaction of fly ash terminates within the testing period of adiabatic temperature rise. The total heat generation of fly ash in reference heat generation rate was set as a temporal value (50 kcal/kg) in this study.

The proposed model should also be applicable to changes of powder fineness. In general, reaction rate per unit mass proceeds faster with finer particles. Powder fineness is enhanced for early hardening Portland cement with changes of mineral composition rather than ordinary cement for early strength development. In the case of blast furnace slag, wide variations in fineness are also produced. Thus, the material functions assumed in the model can be regarded as corresponding values to certain fineness powders which are used in experiments adopted comparison. Here, it is assumed that the fineness of powder affects only the probability of contact between particles and surrounding water which is the reacting object. In this study only reference heat generation rate is changed according to powder fineness and coefficient s_i represents the change of referential heat rate expressed by means of the Blaine value as an indicator of fineness,

$$s_i = S_i / S_{i0} \tag{4}$$

Where, S_i is Blaine value of component i (cm^2/g), S_{i0} is the reference Blaine value of component i. The reference Blaine value of blast furnace slag and fly ash are certain values of powders used in experiments which were adopted for comparison [6,7]. These are assumed to be 3380, 4330 and 3280 (cm^2/g) from material specifications of experiments. In Stage 2 of C_3S, C_2S and slag, however, the effect of fineness is not taken into account at the current stage (s_i = 1).

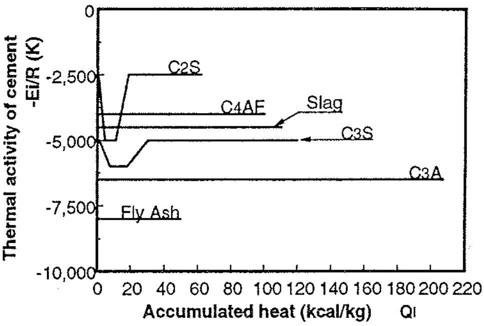


Fig. 2 Thermal activity set for reaction of each component

2.3 Temperature dependency of each reaction

In this study, the thermal activity of each reaction in terms of the accumulated heat is set according to expressions of temperature dependency of minerals developed by Suzuki et al. [6], except we assumed that the thermal activity that may superficially undergo complicated changes for cement on the whole [6] can be rationally explained as accumulation of reactions having individual thermal activity. Then, setting the order of mineral reactivity in C_3A>C_3S> C_4AF>C_2S, constant values ranging from -6500 to -2500(K) were allocated to the thermal activity of each mineral with reference to the thermal activity of cement on the whole derived by Suzuki et al. Thermal activity of each component set in this model is shown in **Fig. 2**. For Stage 2 in the hydration heat process of C_3S and C_2S, a different thermal activity has been set than in other divisions of the hydration process since the effect of precipitation of hydrates from oversaturated ions already dissolved at Stage 1 exerts a prevailing influence rather than that from newly eluded ions in the stage.

The thermal activity of blast furnace slag was given a slightly smaller value, -4500, than the one given to Stage 3 of C_3S which is a major mineral compound in cement because the thermal activity of blended cement with 40% slag replacement showed a slightly smaller value than the entire ordinary Portland cement in a previous study conducted by Suzuki [7]. For analysis, the same value was applied to Stage 2 and Stage 3 of the slag reaction process. For fly ash, it is difficult to assume thermal activity from the measured value of fly ash blended cement since heat generation of the fly ash reaction is much smaller than cement. An appropriate value for thermal activity was assumed for fly ash reaction through an analytical approach. In the analytical reproduction of adiabatic temperature rise of fly ash blended cement, it is difficult to ignore the heat generation of fly ash even if fly ash reaction is not active at the normal temperature. Thus, it is supposed that the fly ash reaction is greatly accelerated at high curing temperatures. That is why a relatively large thermal activity, -8000, was provisionally assumed at the current stage.

2.4 Ettringite formation reaction model by aluminate and ferrite phase with gypsum dihydrate

It was reported that the ultimate temperature rise in the adiabatic test is somewhat affected by initial temperature at casting and the higher temperature rise was observed generally when the casting temperature became lower in experiments conducted by Suzuki et al. [9]. However, the model did not simulate the lower initial temperature with higher ultimate temperature rise and it always results that higher initial temperature leads to higher temperature rise. One possible reason for the initial temperature dependency for ultimate temperature rise is the microstructure formation of hydrate which plays a role as diffusion resistance changes according to temperature history [10]. It is also possible that the heat generation accounted for temperature rise at the initial stage after casting changes because the heat release during casting time from mixing to beginning of measurement is not constant according to casting temperature in adiabatic temperature rise test. In the temperature history of adiabatic temperature rise measured by Suzuki [6], we find the existence of a period in which no temperature rise takes place just after casting at initial temperature 30°C, while at an initial temperature of 10°C, a small temperature rise comes first and subsequent stagnation follows. Temperature history changes slightly according to the initial state because the heat generation before casting changes as a result of the temperature dependency of the reaction. It is possible that when the initial temperature is higher, most heat generation corresponding to the first peak of the exothermic process just after mixing raises initial temperature itself since it almost finishes before casting, while in the case of the lower, a part appears as a slight temperature rise just after the start of temperature measurement. Therefore, to explain how higher initial temperature brings lower ultimate temperature rise, it was considered that heat generation at the initial stage counted as a part of adiabatic temperature rise changes according to initial temperature besides the change of the micropore structure under different temperature histories.

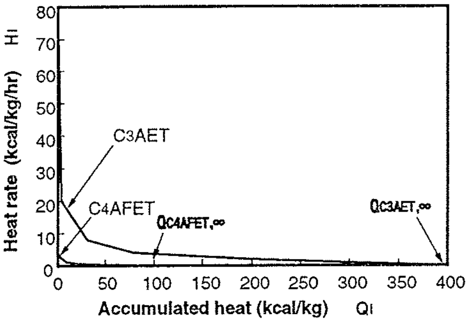


Fig. 3 Reference heat generation rate set for ettringite formation reaction

It is necessary to accurately model the ettringite formation which brings rapid heat generation just after mixing in order to reproduce adequate temperature rise according to the initial temperature. Although the heat generation model of ettringite formation was incorporated in the previous multi-component hydration heating model proposed by the authors, the exothermic process from mixing up to casting was not properly evaluated due to inadequate setting of the reference heat generation rate. The reference heat generation rate is modified and further, it is assumed that the casting time from mixing to beginning of measurement is 0.015 days (around 20 min.) and the heat generation during this period is excluded from the analytical result of the temperature rise. This results from the fact that a part of heat generation after mixing is already included in the initial temperature which is the starting point of computation in this study. Therefore, in all analyses in this study, heat generation after the start of computation up to 0.015 days is not counted in the temperature rise. This means the starting point of the temperature rise is at 0.015 days after hydration starts. The reference heat generation rates modified for reactions to form ettringite by C_3A and C_4AF with gypsum are shown in **Fig. 3**. In the model, hydration heat of interstitial phases expressed by H_{C3A}, H_{C4AF} starts immediately after ettringite formation terminates due to the disappearance of unreacted gypsum.

2.5 Evaluation of interdependency among component reactions

In this study, reactions of minerals are described individually, so their interdependency needs to be separately allowed for. In the multi-component hydration heating model for Portland cement, one possible factor that causes mineral reactions to interact with one another is the amount of water consumed by hydration and shared by constituents as the space in which hydrates can be precipitated [4]. Another fact is then further considered and modeled which is the difference mineral composition causes in the heat rate of each mineral to change in the diffusion control process (Stage 3) of C_3S and C_2S. It was also noted that the temperature of the system on the whole changes with the heat generation of reactions and is a factor affecting interdependency as a common environment that governs each hydration exothermic process.

For treatment of blended cement reactions, the mutual interaction among Portland cement, blast furnace slag and fly ash should be taken into account in the system. Both slag and fly ash are unable to continue their reactions without $Ca(OH)_2$ as an activator which is produced by C_3S and C_2S hydration in cement and are quite different in their reactivity. That is, reactions of both slag and fly ash are dependent on hydration of cement and have a correlation in which $Ca(OH)_2$ is shared in trinal blended cement. Therefore, the interdependency related to $Ca(OH)_2$ should be suitably evaluated for expanding the applicability of the model to blended cement. Further, the retarding effects by organic admixture and fly ash to cement and slag reactions should also be included.

a) Reduction of hydration heat rate by reduction of free water

Free water is one possible source for continuation of hydration and simultaneously implies a space to allow hydrates to precipitate. The reference heat rate set in the proposed model is based on the assumption that hydration proceeds with an ample supply of free water. However, the actual hydration rate is reduced against the reference heat rate at a low water cement ratio since it is impossible to assume that sufficient free water exists around powder particles. In the multi-component hydration heating model it is assumed that the reduction of heat rate due to a shortage of free water results from the reduction of the probability of contact between the reacting surface of particles and free water and coefficient β_i which represents the reduction of heat rate and is simply formulated in terms of both amount of free water and the thickness of internal hydrates layer [4]. The function adopted varies from 0 to 1 and gives the reduction when free water exists sufficiently and hydrates layer is thin. On the other hand, it sharply reduces the heat rate when the amount of free water is reduced and unhydrated particles are covered by thick clusters of hydrates. In this study, the coefficient β_i is modified as Eq.(5) with coefficient s_i which represents the change of reference heat generation rate due to the fineness of powder. This is because the surface area of unit weight particles, which can come in contact with free water also varies according to fineness as well as reference heat rate changes.

$$\beta_i = 1 - \exp\left\{ -r \left\{ \left(\frac{\omega_{free}}{100 \cdot \eta_i^{\nu}} \right) \Big/ s_i^{\frac{1}{2}} \right\}^{s} \right\} \tag{5}$$

where r, s, ν are all material constants common for all minerals. From comparison between the experimental and the analytic results, it was determined that $r = 5.0$, $s = 2.4$ and $\nu = 1.0$. ω_{free} is free water ratio, η_i is the thickness of internal reaction layer of component i. These are defined by the following equations,

$$\omega_{free} = \frac{W_{total} - \sum W_i}{C} \tag{6}$$

$$\eta_i = 1 - \left(1 - \frac{Q_i}{Q_{i,\infty}} \right)^{\frac{1}{3}} \tag{7}$$

where W_{total} is unit water content; W_i is the water consumed and fixed by the reaction of constituents, C is the unit cement content, Q_i is the accumulated heat of component i; and $Q_{i,\infty}$ is final heat generation (**Fig. 1**).

The amount of water bound by each reaction can be arrived at by multiplying the bound water ratio, as obtained from the reaction equation of each mineral, by the degree of reaction computed by the model ($Q_i / Q_{i,\infty}$). The reaction equations used in this model are,

$$\begin{gathered} C_3A + 6H \rightarrow C_3AH_6 \\ C_4AF + 2CH + 10H \rightarrow C_3AH_6 - C_3FH_6 \\ 2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \\ 2C_2S + 4H \rightarrow C_3S_2H_3 + CH \end{gathered} \tag{8}$$

where $C \equiv CaO$, $S \equiv S_iO_2$, $A \equiv Al_2O_3$, $F \equiv Fe_2O_3$, $H \equiv H_2O$, $CH \equiv Ca(OH)_2$. Except for the water chemically combined, which is determined by Eq.(8), the 15% retained water ratio assumed is also incorporated into Eq.(6) for all components, which is the water physically trapped on the surface of the micro-texture.

The reactions of clinker minerals can be assumed to terminate with the arrival of a hydration degree of 100% or the reduction of hydration rate caused by a shortage of free water when only Portland cement is used in the model. In the blended cement case however, the reaction rates of blast furnace slag and fly ash are reduced because of an insufficient supply of $Ca(OH)_2$. Nevertheless, the amount of free water is sufficient. If the shortage of $Ca(OH)_2$ brings the reduction of admixture reactions, free water left in the system can be assumed to fulfill its function in hydration of Portland cement as the reacting object or the space where the hydrates can be precipitated. When the reaction of admixtures are stagnant due to a shortage of $Ca(OH)$, the effect of free water reduction on Portland cement is expressed by modifying Eq.(6) as follows,

$$\omega_{free} = \frac{W_{total} - \sum W_i}{C \cdot (p_{PC} + m_{SG} \cdot p_{SG} + m_{FA} \cdot p_{FA})} \tag{9}$$

$$m_i = \lambda / \beta_i \tag{10}$$

b) Change of heat rate by difference of mineral composition

In the multi-component hydration heating model, we came to the conclusion that the heat rate of each mineral changes with its proportioning in the Portland cement in question, since mineral reactions depend greatly on the composition and then the coefficient μ was introduced. It is not yet clearly understood what causes the heat rate of minerals to change according to constitutive mineral composition. One plausible factor that constitutive mineral composition influences the heat rate is changes of pH as a result of change of $Ca(OH)_2$ concentration in the liquid phase or changes of other ions in the vicinity of the particles. If one focuses on the liquid phase in the vicinity of particles, once the mineral composition of Portland cement changes, the existence probability of C_3S and C_2S adjacent to some cement particles undergoes relative change and a reaction environment as represented by pH changes or various ion's concentration. The issue of reaction dependency among clinker minerals still leaves many facts unidentified, and up to date it is still difficult to make quantitative evaluations of possible causes and their degree of influence. It was therefore decided, for the time being, that the effect of mineral composition on the heat rate is simply expressed by using a C_3S/C_2S ratio that is considered to represent the mineral composition of Portland cement and heat generation characteristics. A function was adopted which gives larger reduction to the heat rate when the constitutive fraction of C_2S is higher and inversely increases the heat rate when C_3S/C_2S ratio is greater than composition of ordinary Portland cement [4]. In this study it is assumed that the above effect is the interdependency between C_3S and C_2S, and then the coefficient μ is not applied to C_3A and C_4AF even though it was applied to all mineral compounds in the previous study. With the extension of scope of model applicability to cover early hardening and special low heat Portland cement, the coefficient μ of the reference heat rate is modified as follows,

$$\mu = 1.4 \cdot \left\{ 1 - \exp\left(-0.48 \cdot \left(\frac{p_{C_3S}}{p_{C_2S}} \right)^{1.4} \right) \right\} + 0.1 \tag{11}$$

The reference heat rates of C_3S and C_2S in stages other than Stage 3 were assumed to be constant regardless of any change of cement mineral compositions (μ=1). This assumption is due to the fact that it is possible to reproduce the initial adiabatic temperature history quite precisely within the range of interest in this study without varying the heat rate in Stage 2 according to the composition and the assumption that the effect of precipitation of ions eluted in the dormant period prevails in Stage 2. Interdependency of mineral reactions due to composition was simply treated in Eq.(11) at the current stage, however, the authors understand the need to further discuss this matter in the future.

c) The evaluation of reaction rate of admixtures dependent on calcium hydroxide produced by Portland cement hydration

Santhikumar studied the interdependency between Portland and blast furnace slag where the hydration heat rates of blended cement at various replacements were measured by conduction calorie-meter [12]. The heat generation rate of blast furnace slag were calculated by extracting the hydration heat rate of Portland cement according to its constitutive ratio from that of blended cement on the assumption that the reaction of Portland cement was not affected by slag reaction. Through his study, it was found that the slag reaction is stable at any replacement of slag in the former term of reaction process where it is considered that $Ca(OH)_2$ was sufficiently supplied and the heat generation of slag was reduced in accordance with the reduction of Portland cement content which indicates the shortage of $Ca(OH)_2$ supply. It is assumed that a similar mechanism to slag reaction exists in the fly ash reaction though quantitative study of fly ash reactions having less reactivity are difficult. Therefore, the evaluation of interdependency in which the amount of $Ca(OH)_2$ is focused on is indispensable in order to evaluate the heat generation process of blast furnace slag and fly ash in blended cement [13].

In trinal blended cement, $Ca(OH)_2$ is simultaneously consumed by blast furnace slag and fly ash. The consumption of $Ca(OH)_2$ should be computed step by step with the production from Portland hydration in the analysis. In this study, it is assumed that the reducing ratio of the reaction rate of admixtures can be expressed by the following equation by means of a quantitative ratio between the amount of $Ca(OH)_2$ left in the system and what is necessary for active reaction of slag and fly ash at that time and which is simply expressed by Eq.(12).

$$\lambda = 1 - \exp\left\{ -2.0 \cdot \left(\frac{F_{CH}}{R_{SGCH} + R_{FACH}} \right)^{5.0} \right\} \tag{12}$$

Where, F_{CH} is the amount of $Ca(OH)_2$ which is produced by hydration of C_3S and C_2S, and not yet consumed by C_4AF reaction, R_{SGCH} and R_{FACH} are the amount of $Ca(OH)_2$ necessary for reactions of slag and fly ash when $Ca(OH)_2$ is in sufficient supply. F_{CH} can be computed from the reaction degree of each component and the ratios of production and consumption of $Ca(OH)_2$ which is given by chemical equations adopted in this study. R_{SGCH} and R_{FACH} are computed by the consumption ratio of $Ca(OH)_2$ by blast furnace slag and fly ash, and their reaction rates when $Ca(OH)_2$ is sufficient.

It is not clear how much $Ca(OH)_2$ is consumed by unit weight of reacted slag and fly ash and also the *Ca/Si* ratio of products changes according to the amount of $Ca(OH)_2$ supplied and the character of admixtures [5]. However, it is assumed in this study that the consumption ratio of $Ca(OH)_2$ is constant through the whole reaction process irrelevant to character of admixture. Their values are determined through the analysis by qualitative observation. The reaction of blast furnace slag is restrained just after contact with water because of the formation of a low penetrable layer on the surface [5]. The supply of OH^- ions from the ambient solution is essential for the continuity of active hydration of slag besides what is eluted from the slag itself. In general, it is assumed that a sufficient supply of $Ca(OH)_2$ can apply to slag reactions up to 60-70% replacement because adiabatic temperature rise barely changes within these replacement ranges. On the other hand, the reaction of fly ash does not proceed without the active stimulation of OH^- ions from outside since the condensation degree of silicate ion is high in the glass [5]. Therefore, $Ca(OH)_2$ consumption when a unit weight of fly ash reacts seems to be much higher than in the slag case. In fact, around 60% or 70% replacement ratio to cement is often adopted in the slag case but fly ash replacement is 30% at most. Thus, the consumption ratios of slag and fly ash reactions are assumed to be 22% and 100% of reacted mass for the analysis. In trinal blended cement, it is assumed that $Ca(OH)_2$ in the liquid phase is almost completely consumed by the slag reaction since it is faster than fly ash.

d) Delaying effect of organic admixture and fly ash on the hydration exothermic process

It is known that the addition of organic admixture delays the start of active heat generation [14]. The reason is that consumption of Ca^{2+} formed by cement hydration in the solution, which results from reaction with organic admixtures, delays the formation of a crystal core of $Ca(OH)_2$ that triggers the start of active hydration heat generation or delays the formation rate of crystals [15]. In the multi-component hydration heating model, the delay due to organic admixture was simply modeled as a first approximation. It is also known that the addition of fly ash to Portland cement delays hydration [5].

Santhikumar measured the hydration heat rate of binary blended cement in various replacements of fly ash and then observed that the exothermic peak corresponding to active hydration of cement is retarded according to increases of fly ash replacement [12]. It was also found that fly ash has a delay effect in the slag reaction as well as cement through the study of the reaction heat rate of binary composite of slag and fly ash with a reagent [12]. If fly ash exists, Ca^{2+} in the liquid phase is adsorbed on the surface of fly ash particles instead of Al^{3+} eluted just after it comes in contact with water. That is why fly ash delays the initial reaction of cement [5]. Thus, it can be assumed that the mechanism of the delay effect for fly ash is similar to that of organic admixture. Hence, the delay effect of fly ash in reactions of Portland cement and blast furnace slag is dealt with in the same way as organic admixtures.

Table 1 Cement mineral composition in adiabatic temperature rise test

	C_3A	C_4AF	C_3S	C_2S	CS2H	Blaine
OPC	10.4	9.4	47.2	27.0	3.9	3380

Unit) Blaine: cm^2/g

Table 2 Concrete mix proportions in adiabatic temperature rise test

	W/C	W	C	S	G	Ad
SG400	39.2	157	400	658	1129	0.25
SG300	49.3	148	300	765	1129	0.25
SG200	78.5	157	200	862	1089	0.25
FA400	39.2	157	400	663	1129	0.25
FA300	49.3	148	300	770	1129	0.25
FA200	78.5	157	200	865	1089	0.25

Note) Ad.: AE water reducing agent,
Unit) W/C: %, W, C, S, G: kg/m^3, Ad: C%

In the multi-component hydration heating model so far, the amount of organic admixture consumed irrelevant to delaying [15] was expressed in terms of the amounts of C_3A, C_4AF and gypsum dihydrate assuming that it is combined by ettringite formation. However, it is assumed in this study that the aforementioned organic admixture corresponds to that adsorbed on the surface of particles immediately after mixing since the delay effect is markedly different between simultaneous addition of water and post-addition [14]. Thus, assuming that a part of the organic admixture is adsorbed on the surface of C_3A, C_4AF, blast furnace slag and fly ash which have an Al composite, the amount of organic admixture consumed regardless of delaying effect is expressed as,

$$\vartheta_{Waste} = \frac{1}{200} \cdot (16 p_{C_3A} \cdot s_{C_3A} + 4 p_{C_4AF} \cdot s_{C_4AF} + p_{SG} \cdot s_{SG} + 5 p_{FA} \cdot s_{FA}) \qquad (13)$$

where, ϑ_{Waste} represents composite of organic admixtures which do not exert a delay effect due to adsorption on the surface of powder particles. Thus, the effective delaying capability ϑ_{ef} may be expressed by the following equation,

$$\vartheta_{SPef} = p_{SP} \cdot \chi_{SP} - \vartheta_{Waste} \qquad (14)$$

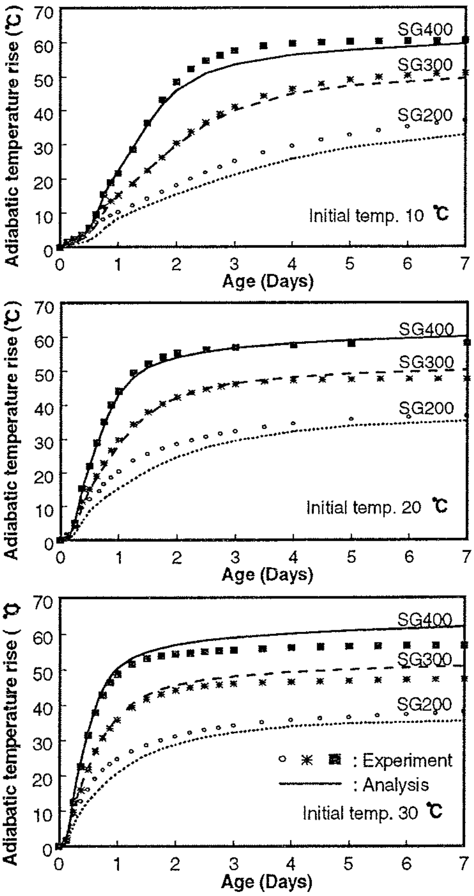
Where, p_{SP} is a dosage of organic admixture expressed as additive ratio to binder ($C\times\%$), χ_{SP} is a coefficient representing the delay effect per unit weight of organic admixture. Thus, $P_{SP} \cdot \chi_{SP}$ represents the total delay effect brought about by added organic admixture. When the adsorption capacity of the components exceeds total capacity of the delay effect by organic admixture, ϑ_{SP} is assumed to be zero. Assuming that the delay effect brought about by fly ash is in proportion to its replacement ratio, it is expressed as,

$$\vartheta_{FAef} = 0.02 p_{FA} \cdot s_{FA} \qquad (15)$$

In this study, C_3S, C_2S and blast furnace slag were adopted as providers of Ca^{2+} against the delaying capability of organic admixture and fly ash. Then, the coefficient γ representing the reduction of the heat rate due to organic admixture and fly ash is expressed in terms of the above effective delaying capability and the amount of components as offset to it, which supply Ca^{2+} as follows,

$$\gamma = \exp\left\{ -\frac{1000(\vartheta_{SPef} + \vartheta_{FAef})}{10 p_{C_3S} \cdot s_{C_3S} + 5 p_{C_2S} \cdot s_{C_2S} + 2.5 p_{SG} \cdot s_{SG}} \right\} \qquad (16)$$

The delaying effects are regarded as an extension of the dormant period and then the delay of reactions are expressed by reducing the heat rate of components concerned in Stage 1 which correspond to the dormant period by means of γ in this model. In the previous model, appropriate weights were given to this coefficient which was defined for each component through sensitivity analysis since each component has a different reaction rate (heat rate / total heat generation) assumed at Stage 1 [4].



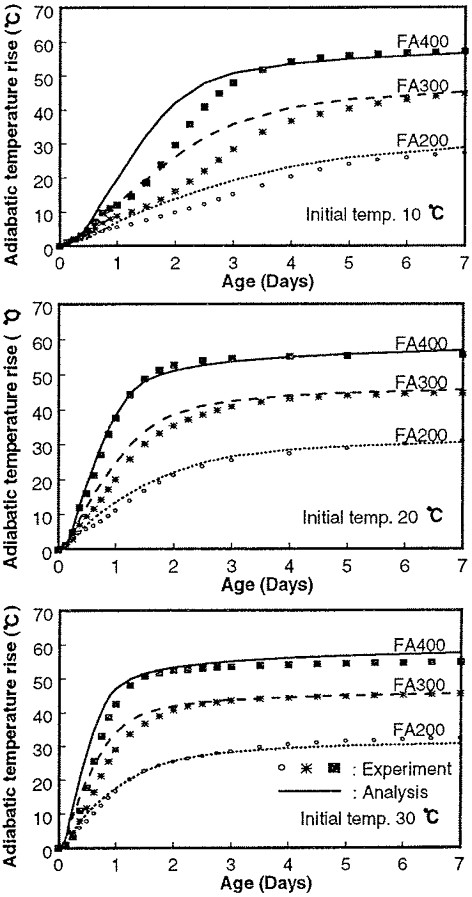


Fig. 4 Analytical result for adiabatic temperature rise history (Blast furnace slag blended cement)

Fig. 5 Analytical result for adiabatic temperature rise history (Fly ash blended cement)

However, since the starting time of active reaction is scattered among components when the delaying effect was so large, it is modified so that each component has the same reaction rate at Stage 1 and the same coefficient must be given each.

3. REVIEW ON ADIABATIC TEMPERATURE RISE OF BINARY BLENDED CEMENT

The adiabatic temperature rise tests of binary blended cement including blast furnace slag or fly ash and ordinary Portland cement as a basis were carried out systematically by Suzuki [7]. Three casting temperatures, 10°C, 20°C and 30°C, and three unit cement contents, 200 kg/m^3, 300 kg/m^3 and 400 kg/m^3, were examined for both slag blended cement and fly ash in the experiment (SG200, SG300, SG400, FA200, FA300, FA400). Mineral compositions of base cement and mix proportions of concrete are shown in **Table 1** and **Table 2**. The delaying capability per unit weight of the delaying type AE water reducing agent $\chi_{SP} = 5.0$ was used in the analyses due to modification of the delaying effect model of admixtures. Time step intervals in all analyses of this study are 0.01 days from beginning of hydration up to 0.3 days, and after that 0.05 days is adopted. The applicability of the multi-component hydration heating model for ordinary and moderate heat Portland cements were reported and for early hardening cement it was also examined (**Fig. 7**). Experimental and analytical results are shown in **Fig. 4** and **Fig. 5**.

The reference heat rate and the thermal activity were assumed so as to reproduce experimental results. The adiabatic temperature rise history was quite accurately reproduced, reflecting temperature dependency of reaction at each casting temperature. But, in case of fly ash blended cement when initial temperature is 10°C, the accuracy of the proposed model is not sufficient since it could not closely reproduce the delaying of heat generation at the latter part of Stage 2. It can be assumed that this disagreement is not caused by the data setting of fly ash characteristic, since heat generation from Portland cement hydration delivers the temperature rise of this part in the analysis. Although ignorance of delaying effects by organic admixture and fly ash at other stages except Stage 1 and combining effects are possible reasons, the temperature dependency of delaying effect should be also investigated. Further, the characteristic of the AE water reducing agent used in experiment needs to be properly modeled. The water consumption ratios of slag and fly ash were assumed to be 30% and 10% respectively through analytical discussion. For unit cement content of 400 kg, reductions in the heat rate and in the adiabatic temperature rise in the terminal period of the reaction was closely reproduced since the effect of a low water cement ratio of 40% on hydration heat rate was considered. The ultimate temperature rises at different initial temperatures was almost the same because the loss of heat generation mainly derived from ettringite formation from mixing to casting was taken into consideration although the experimental results showing a higher initial temperature bring about lower ultimate temperature rise was not accurately reproduced.

Table 3 Cement mineral proportion used in quasi-adiabatic temperature rise tests

	C_3A	C_4AF	C_3S	C_2S	CS2H	Blaine
EPC	9.1	7.9	61.5	13.0	6.5	(4210)
OPC	10.4	7.9	49.9	24.7	4.5	(3380)
MC	2.9	12.5	49.5	28.7	4.1	3240
BC	2.5	13.1	26.3	52.8	4.5	3040
SBC	2	6	16	71	4.3	3480

Note) EPC:Early hardening Portland cement, OPC: Ordinary Portland cement, MC: Moderate-heat Portland cement; BC: Low-heat Portland cement; SBC: Super low-heat Portland cement; CS2H: Gypsum dihydrate, Blane: cm^2/g, ( ): assumed in analysis.

Table 4 Concrete mix proportions used in quasi-adiabatic temperature rise tests

	W/C	W	C	S	G	SP	Initial T.
EPC	31.9	174	545	857	827	$1.5^{*1)}$	23.5°C
OPC	31.6	174	550	857	827	$1.5^{*1)}$	23.5°C
MC	31.5	182	577	828	827	$1.0^{*1)}$	19.5°C
BC	24.3	185	761	722	798	$0.9^{*2)}$	17.5°C
SBC	25.0	187	749	722	798	$0.9^{*2)}$	13.1°C

Note) SP:Superplasticizer, *1): β-naphthalene sulfonate, *2): Polycarbonate

Unit) W/C: %, W, C, S, G: kg/m^3, SP: C%

Table 5 Thermal constants used in analyses

Thermal Conductivity	41 kcal / m/day/K
Heat Trans. Coefficient	18 kcal / m^2/day/K

4. VERIFICATION BY QUASI ADIABATIC TEMPERATURE TESTS

4.1 Experiment outline

To verify the applicability of the proposed hydration heat model and the material functions established for the model, temperature measurements at center points were carried out on concrete blocks completely covered in Styrofoam to a depth of 8 cm in the previous study [4]. In order to examine the wider applicability of the model, the experiments on early hardening and special low heat Portland cements were included. These experiments were conducted in an experimental room where temperature was kept almost constant. The specimen is outlined in **Fig. 6**. The mix proportion for self-compacting concrete was used for all cases. The mineral composition of cement and the mix proportions used are shown in **Table 3** and **Table 4**.

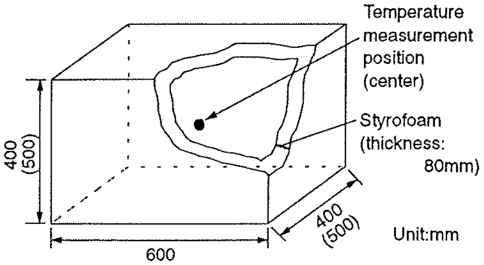
4.2 Temperature analysis by hydration heat model

a) Several types of Portland cement

Temperature analysis was conducted by incorporating the proposed hydration heat model to a non-linear finite element analysis developed by Harada et al. that allows for the coupling of the hydration exothermic process with thermal conduction [16]. The thermal constants used in thermal conductivity analysis are shown in **Table 5**. Superplasticizers used are those based on β-naphthalene sulfonate for early hardening (EPC), ordinary (OPC) and moderate heat (MC) cements and on polycarbonate for low heat belite rich cement (BC) and special low heat (SBC). χ_{SP} was given 1.2 respectively for those admixtures to reproduce the starting time of rapid temperature rise shown in the experiments. The results of the experiment and analysis are shown in **Fig. 7**. The experimental results were relatively close to those produced by the hydration heat model for 5 cement types from early hardening cement (EPC) to special low heat belite rich cement (SBC). In the cases of low heat and special low heat cements however, the peak temperature and the its drop after peak were not satisfactorily modeled. Further investigation needs to be carried out on the effect of the mineral composition on the hydration heat rate, which affects mainly Stage 3.

b) Binary blended cement

For verifying applicability of the proposed model to binary blended cement, quasi-adiabatic temperature rise tests were also conducted. Two mixtures were adopted as blast furnace slag blended cement with 50% replacement of ordinary Portland cement (O5S5) and 40 % replacement of moderate heat Portland cement (M6S4) by blast furnace slag. As fly ash blended cement, one mixture of 30% replacement of ordinary Portland cement (O7F3) by fly ash was used. 100% pure ordinary Portland cement mixture(O10), which is the same to base cement of fly ash blended one was also checked for comparison. The test specimen is same shown in **Fig. 6**, but sizes of O7F3 and O10 cases are slightly larger than the others as indicated by parentheses in the Figure. Mineral compositions of base cements used and mix proportions of concrete are shown in **Table 6** and **Table 7**.



Dimensions in ( ) for O10, O7F3, OSF

Fig. 6 Quasi-adiabatic temperature rise test specimen

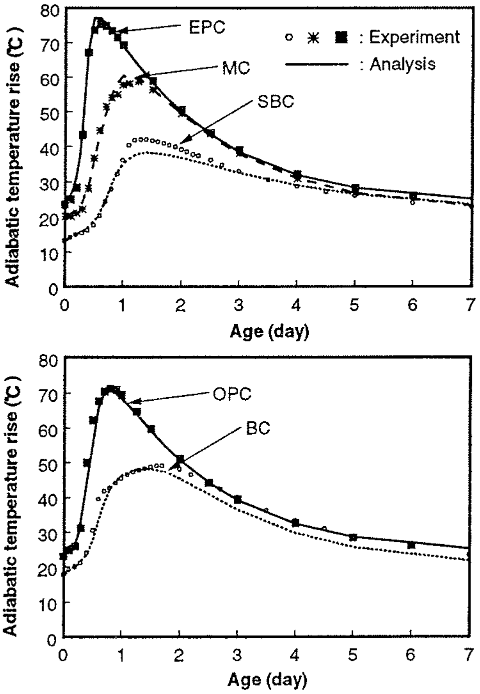


Fig. 7 Analytical results of quasi-adiabatic temperature rise test
(Various types of Portland cement)

The temperature histories including maximum temperature rise are satisfactorily reproduced in both mixtures of O5S5 and M6S4 of blast furnace slag blended cement (**Fig. 8**). For the O5S5 case however, a 0.25 day earlier result was computed. A possible explanation is that the effect of post addition of organic admixture is not taken into account in the proposed model although a part of it was mixed in the way of post addition in the experiment. For fly ash blended cement in O7F3, analytical and experimental results approximately coincide accompanying 100% base cement mixture O10 (**Fig. 9**). However, the decline after peak temperature was predicted faster than the measured data.

c) Trinal blended cement

The quasi-adiabatic temperature rise test of concrete using trinal blended cement with blast furnace slag and fly ash was conducted (OSF, **Fig. 10**). The size of the specimen is noted in parentheses of **Fig. 6**. The mineral composition of base cement and mix proportions are shown in **Table 6** and **Table 7**.

Table 6 Cement mineral proportion used in quasi-adiabatic temperature rise tests

	C_3A	C_4AF	C_3S	C_2S	CS2H	Blaine
O5S5	10.4	7.9	49.9	24.7	4.5	(3380)
M6S4	2.9	12.5	49.5	28.7	4.1	3240
O10	10.3	8.2	53.7	19.8	4.3	(3380)
O7F3	10.3	8.2	53.7	19.8	4.3	(3380)
OSF	10.3	8.2	53.7	19.8	4.3	(3380)

Unit) Blaine: cm^2/g, ( ): assumed in analysis.

Table 7 Concrete mix proportions used in quasi-adiabatic temperature rise tests

	W/C	W	C	S	G	SP	Initial T.
O5S5	32.9	182	553	828	827	$1.1^{*1)}$	20.0°C
M6S4	31.3	180	576	803	827	$1.5^{*2)}$	16.5°C
O10	36.0	180	500	757	902	$0.25^{*3)}$	25.5°C
O7F3	36.0	180	500	731	873	$0.25^{*3)}$	25.5°C
OSF	30.1	160	531	765	879	$1.2^{*1)}$	25.0°C

Note) O5S5: OPC 50% + slag 50%, M6S4: MC60%+slag 40%, O10: OPC 100%, O7F3: OPC 70% + fly ash 30%, OSF: OPC30% + slag28% + fly ash 42%,
*1): β-naphthalene sulfonate, *2): Polycarbonate
*3): AE water reducing agent
Unit) W/C: %, W, C, S, G: kg/m^3, Ad: C%

The beginning point of temperature rise is satisfactorily reproduced because the delaying effects of organic admixture and fly ash are taken into account in the model. However, temperature history after rising is not closely simulated. It was determined that reactions of slag and fly ash were greatly restrained because of a shortage of calcium hydroxide where base cement contained less than 30%. On the other hand, coefficient β_i was moderated for clinker minerals in computation since reactions of slag and fly ash were restrained and free water was mainly assigned to clinkers in spite of low water cement ratio. However, the match between analytic experimental data is not still satisfactory at the decline aspect after peak temperature.

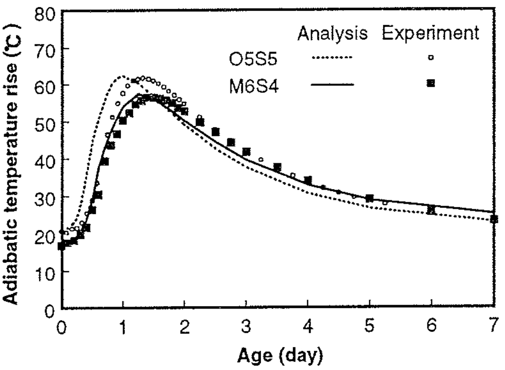


Fig. 8 Analytical results of quasi-adiabatic temperature rise test
(Blast furnace slag blended cement)

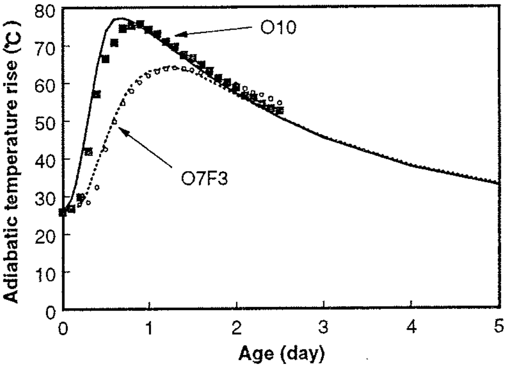


Fig. 9 Analytical results of quasi-adiabatic temperature rise test
(Fly ash blended cement)

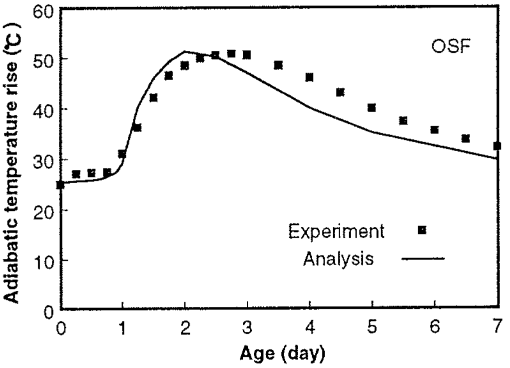


Fig. 10 Analytical results of quasi-adiabatic temperature rise test
(Trinal blended cement)

5. SUMMARY

Based on the multi-component hydration heat model of Portland cement [4] in which the hydration exothermic process is described by dissolving chemical actions shown in Portland cement into minerals, the hydration heat model for blended cement is proposed by incorporating reactions of blast furnace slag and fly ash in the system with consideration of interdependencies among them. The effect of initial temperature on the ultimate temperature rise is discussed by considering heat generation related to reaction before casting. The reactions of blast furnace slag and fly ash are modeled to be dependent on the amount of calcium hydroxide produced by cement hydration. The applicability of the proposed model was verified by analyzing the results of existing adiabatic temperature rise tests and temperature histories of small quasi-adiabatic blocks. A wide scope with sufficient accuracy was found for engineering applications. It is now necessary to work on such issues as improving the precision of the model and verifying the validity of the parameters assumed in setting it up.

REFERENCES

[1] Okamura, H., Maekawa, K. and Ozawa, K.: *High Performance Concrete*, published by Gihodo, 1993. (In Japanese)

[2] Kishi, T., Shimomura, T. and Maekawa, K.: Thermal crack control design of high performance concrete, *Proc. of Concrete 2000*, pp. 447 - 456, Dundee, UK., 1993.

[3] Kishi, T., Ozawa, K. and Maekawa, K: Multi-component model for hydration heat of concrete based on cement mineral compounds, Proc. of JCI, Vol.15, No.1, pp. 1211 - 1216, 1993.

[4] Kishi, T. and Maekawa K.: Multi-component Model for Hydration Heat of Portland Cement, Journal of Materials, Concrete Structures and Pavements, JSCE(Japan Society of Civil Engineers), No. 526/V-29, pp.97-109, 1995. (In Japanese)

[5] Uchikawa, H.: Effect of blending component on hydration and structure formation, Proc. of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Brazil, 1986.

[6] Suzuki, Y., Tsuji, Y., Maekawa, K. and Okamura, H.: Quantification of Hydration-heat Generation Process of Cement in Concrete, Concrete Library of JSCE(Japan Society of Civil Engineers), No. 16, 1990.

[7] Suzuki, Y.: Heat of Hydration Evolution Process of Cement in Concrete and Quantification, Doctoral dissertation submitted to The University of Tokyo, 1990.(In Japanese)

[8] Ito, H. and Fujiki, Y.: About Concrete blended Blast Furnace Slag, Proc. of JSCE Symposium on Application of Blast Furnace Slag to Concrete, pp.37-42, 1987. (In Japanese)

[9] Suzuki, Y., Harada, S., Maekawa, K. and Tsuji, Y.: Evaluation of Adiabatic Temperature Rise of Concrete Measured with The New Testing Apparatus, Concrete Library of JSCE(Japan Society of Civil Engineers), No. 13, 1989.

[10] Moriwake, A., Fukute, T. and Horiguchi, K.: Study on Durability of Massive Concrete, Proc. of JCI, Vol.15, No.1, pp. 859 - 864, 1993. (In Japanese)

[11] Arai, Y.: *Chemistry of Cement Materials*, Dai-nippon Tosho Publishing Co., Ltd., 1984. (In Japanese)

[12] Santhikumar, S.: Temperature dependent Heat generation model for mixed cement concrete with mutual interactions among constituent minerals, The Master thesis submitted to the university of Tokyo, 1993.

[13] Kishi, T., and Maekawa, K.: Thermal and Mechanical Modelling of Young Concrete Based on Hydration Process of Multi-Component Cement Minerals, *Proceedings of the international RILEM symposium on Thermal Cracking in Concrete at Early Ages*, pp.11-18, Munich, Germany, 1994.

[14] Uchikawa, H., Sawaki, D. and Hanehara, S.: Effect of type of organic admixture and addition method on fluidity of fresh cement paste, Proc. of JCI Symposium on High-fluid Concrete, pp.55-62, 1993.(In Japanese)

[15] Uomoto, T. and Ohshita, K.: A fundamental study on Set-retardation of Concrete due to superplasticizer, Concrete Research and Technology(JCI), Vol.5/No.1, pp.119-129, 1994. (In Japanese)

[16] Harada, S., Maekawa, K., Tsuji, Y. and Okamura, H.: Non-linear Coupling Analysis of Heat Conduction and Temperature-dependent Hydration of Cement, Concrete Library of JSCE(Japan Society of Civil Engineers), No. 18, 1991.