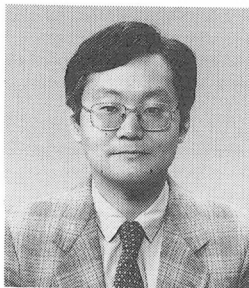
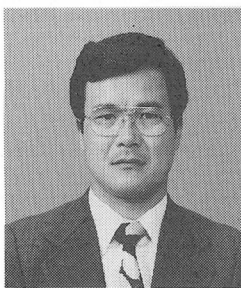


QUANTIFICATION OF HYDRATION-HEAT GENERATION PROCESS OF
CEMENT IN CONCRETE

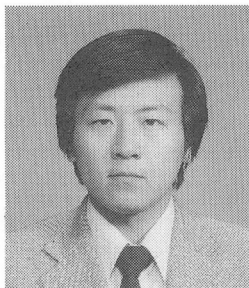
(Reprint from Transaction of JCSE, No.414, February 1990)



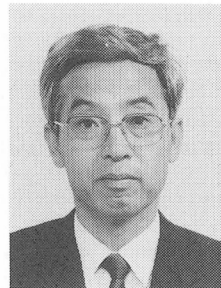
Yasunori SUZUKI



Yukikazu TSUJI



Kouichi MAEKAWA



Hajime OKAMURA

SYNOPSIS

This study is conducted for the purpose of creating a quantification technique of the hydration-heat generation process dependent on the temperature of cement in concrete and provides a general approach for deriving a hydration-heat generation model capable of conforming with any temperature hysteresis. The authors show that by using adiabatic temperature rise curves of concretes with different pouring temperatures, a more generalized hydration-heat generation model could be given for cement in concrete even when a conduction type microcalori-meter is not used. For cements in paste and concrete, it is shown quantitatively that the hydration-heat generation rate differs greatly at the early age because of the difference in dispersion properties of cement particles.

Y.Suzuki is a senior research engineer at the Cement/Concrete Technical Development Center of Sumitomo Cement Co.,Ltd., Chiba, Japan. His research interests include problems concerning thermal stress in mass concrete.

Y.Tsuji is a prof. in the Dept. of Civil Eng. at Gunma Univ., Gunma, Japan. He received his Doctor of Eng. Degree from the Univ. of Tokyo in 1974. His research interests include behavior of reinforced concrete structures, chemically prestressed concrete, and properties of fresh concrete.

K.Maekawa is an associate prof. in the Dept. of Civil Eng. at the Univ. of Tokyo, Tokyo, Japan. He received his Doctor of Eng. Degree from the Univ. of Tokyo in 1985. His research interests include constitutive models for concrete, structure analysis of RC and the development of high performance concrete.

H.Okamura is a prof. in the Dept. of Civil Eng. at the Univ. of Tokyo, Tokyo, Japan. His research interests include fatigue and shear of RC members, durability design of RC structures and application of FEM to RC.

1. INTRODUCTION

Improvement in the accuracy of thermal stress analysis in concrete structures is of great importance from the viewpoint of enhancing the durability of concrete structures which have become more massive. Among the factors affecting most sensitively the analysis results of the thermal stress, those which we should discuss first of all are the temperature rise and the temperature distribution in the concrete accompanying the cement hydration-heat generation.

According to the conventional method, the temperature rise in concrete structure is numerically analyzed under assumption that heat generates uniformly at all places, though actually the hydration-heat generation in concrete is produced in a specific adiabatic environment. However, the temperature hysteresis the concrete undergoes actually changes with its position in the structure. In the case of a relatively small structure, there exist some places where the hydration-heat generation process is largely different, because of heat radiation, from that in the adiabatic state. Therefore, if we assume that the hydration heat which is confirmed from an adiabatic temperature rise test, generates uniformly all over the sections, the calculation value of heat generation tends to be calculated higher than the actual one[1].

On the other hand, an attempt to predict the hydration-heat generation process by establishing a hydration model of cement has been pursued[2],[3]. The approach based upon a hydration reaction model of cement can be appreciated as an excellent method, because it enables one to predict the hydration-heat generation rate for any temperature hysteresis. The adiabatic temperature rise, from its nature, should be given as a particular solution from a generalized heat generation governing equation. Using a synthesized method, approach starting from a hydration reaction model of cement, the author et al. consider it possible to predict the hydration-heat generation rate of different positions in the concrete structure under the various temperature hysteresis.

In the conventional cement hydration reaction models, reaction parameters such as activation energy are determined on the basis of a cement paste test using, for example, a conduction type microcalori-meter. These can be used as a hydration reaction model for cement paste. But, on the next step, we proceed to apply these models to concrete structures. Consider that, paste and concrete can be thought to be different in dispersion of cement particles, because their mixtures of cement powder are different in efficiency from one another[4]. In other words, the cement hydration reaction per specific weight may not be the same for paste and concrete. If the cement dispersion varies along with the mix proportion in terms of the cement content per unit volume of concrete (specific cement weight) and water cement ratio, we cannot apply the conventional cement-hydration model as it is to the heat-generation model of concrete.

This paper, first, considers application of the conventional hydration reaction model as a hydration-heat generation model of concrete, and secondly, proposes a method of quantitatively determining the hydration-heat generation process in specific weight taking into consideration its dependency on the temperature hysteresis. Therefore, the purpose of this study is to evaluate the hydration-heat generation rate reflecting the difference in dispersion of cement particles due to the presence of aggregates. As mentioned above, if the hydration-heat generations are compared in terms of specific weight, they may differ from each other according to the difference in concrete mix proportion : here, this problem is quantitatively studied.

2. HYDRATION-HEAT GENERATION RATE AND ITS GOVERNING EQUATIONS

In the temperature analysis of concrete we have to solve, in terms of time and space, the thermal conductivity equation (Eq.(1)). In this equation, the hydration-heat generation rate H per specific volume must be given as a material function, which should be effective at any place in the concrete structure.

$$c\rho \frac{dT}{dt} = \lambda \nabla^2 T + H \quad (1)$$

where c , ρ and λ are specific heat, density and heat conductivity respectively, and T and t are temperature and time.

In the conventional system, the concrete hydration-heat generation rate H is given by the following equation, using the adiabatic temperature rise $\Delta T_{ad}(t)$.

$$H(t) = \frac{d[c\rho \Delta T_{ad}(t)]}{dt} \quad (2)$$

It should be noted that H is calculated as a function of time only. In other words, it is assumed implicitly that over all the analysis range, the hydration reaction proceeds as being equivalent to the adiabatic temperature rise. Near the center of the concrete structure of a large section, it can be expected that hydration heat occurs as corresponding to that in an adiabatic state. However, for the concrete located near the structure surface or the concrete susceptible to cooling because of its position has hydration restrained, it is impossible to expect the same heat generation as shown in Eq.(2). The concrete, when it exists at the position which is susceptible to external heat, may hydrate further, and its hydration-heat generation rate may be higher than that given by Eq.(2) in the material of earlier age. Consequently, when modeling the hydration-heat generation process analytically and considering the hydration-heat generation rate H which varies along with position in the analysis field, the author is convinced that the best way is to follow up the overall hydration-heat generation process at all of the points, and to solve it in combination with the heat conductivity Eq.(1) in order to achieve improvement in accuracy of temperature analysis.

Uchida et al. have demonstrated, using the test results on heat generation of the cement paste at a certain temperature, that the hydration-heat generation rate \underline{H} per specific weight can be expressed by the self-dependent differential equation (Eq.(3)) [3],[5].

$$\begin{aligned} H &= C^* \underline{H} \\ \underline{H} &= \underline{H}_\infty(Q) \exp \left(-\frac{E(Q)}{RT} \right) \\ Q &= \int \underline{H} dt \end{aligned} \quad (3)$$

Where C^* : specific cement weight

R : gas constant

E : activation energy

Q : integrated calorific value of cement per specific weight

and E is given as a function of Q [3]. And \underline{H}_∞ corresponds to the hydration-heat generation rate when T is infinite.

The Eq.(3) means that the hydration-heat generation rate may be given by the temperature and the hydration degree. Uchida et al. kept the cement paste at a

certain temperature by means of a conduction type microcalori-meter, and quantitatively determined H_{∞} and E as function of Q by measuring the hydration-heat generation rate at such a temperature[3].

3. APPLICABILITY OF THE HYDRATION-HEAT GENERATION MODEL ON THE BASIS OF THE CEMENT PASTE

In the past studies on the hydration reaction, H_{∞} , material function and E in the Eq.(3) have been identified based upon the cement paste experiment. Fig. 1 shows an example in which the adiabatic temperature rise was assumed by numerically integrating Eq.(3), according to the Uchida et al's method[3]. The adiabatic temperature rise, which is estimated based on the hydration-heat generation rate of cement paste represents comparatively well the general trend of the change of the measured values with time. As understood in the case of 350 kg/m³ in specific cement weight, the heat generation in terms of pouring temperature is approximately predicted as calculated. However, with a larger water cement ratio, the calculation value is considerably lower than the actual value and with a smaller water cement ratio, the calculation value is considerably higher than the actual value, so from the viewpoint of a quantitative analysis, it is hardly possible to say that sufficient accuracy in terms of engineering is ensured by this method.

Eq.(3) is demonstrated to be effective for cement paste, and is able to give a qualitatively appropriate value, even if the equation, as it is, is calculated as a function of material, that is, cement in the concrete. Accordingly, Eq.(3) itself can be considered to be free of its inherent fault, and the difference between the measurement value and the calculation is attributable to the fact that the material functions obtained by a cement paste test differ from those of the cement in concrete. Fig.1 shows also that if the mix proportion differs even with the same cement, the difference between measurement and calculation does not vary uniformly; this indicates that the material functions in Eq.(3) may be influenced by the mix proportion as well.

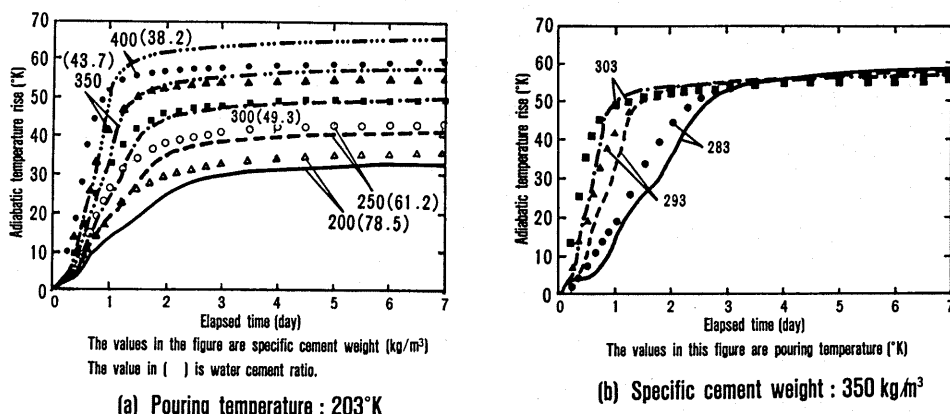


Fig. 1 Estimation of adiabatic temperature rise based on a hydration-heat generation in cement paste

4. HYDRATION-HEAT GENERATION PROCESS OF THE IN-CONCRETE CEMENT

When the material functions H and E are obtained experimentally in Eq.(3) representing the hydration-heat generation process of cement in concrete, there are three methods as follows:

(1) Taking a certain amount of cement paste from the concrete, the material functions in Eq.(3) are determined by means of a conduction type microcalorimeter.

(2) Developing a conduction type microcalorimeter which is capable of keeping a concrete specimen at a temperature, a hydration-heat generation model is created in the same way as in the case of the cement paste.

(3) By using the adiabatic temperature-rise measurement apparatus, the hydration-heat generation model is identified for the in-concrete cement.

The method (1) involves difficulties in taking cement paste from concrete and in weighing cement accurately. Concerning the method (2), it is not practicable, since a conduction type microcalorimeter currently available on the market, which is capable of measuring hydration-heat generation rate under a certain temperature, can treat extremely small amount of specimen because of its measuring mechanism restricted.

The author et al. have made every possible effort to improve accuracy in the adiabatic temperature rise test of concrete[6],[7]. For this purpose, we have decided to adopt a new method derived from Uchida et al's approach [3] which can be considered as a most promising method to determine quantitatively the cement hydration-heat generation rate. That is, this method, not considering the hydration-heat generation rate H as a function of time, intends to establish a general rule which is able to explain the relationship of three parameters such as hydration-heat generation rate H , integrated calorific value Q and absolute temperature T , making effective use of the adiabatic temperature rise measurement apparatus whose measurement accuracy has been already well demonstrated. Test data of a hydration-heat generation model is detailed in the Reference [6].

4.1 Calculation of the integrated calorific value and the hydration-heat generation rate

As shown in Fig.2 and Eq.(4), in principle, it is possible to follow how the integrated calorific value Q and hydration-heat generation rate H of cement per specific weight change with the time, first multiplying by the average heat capacity of each adiabatic rise ΔT_{ad} and the adiabatic temperature rise curve differentiated by the time and then dividing its product by the specific cement weight.

$$\begin{aligned} Q &= c \rho \Delta T_{ad} / C^* \\ H &= dQ/dt = \frac{c \rho}{C^*} \cdot \frac{d\Delta T_{ad}}{dt} \end{aligned} \quad (4)$$

where c : concrete specific heat

ρ : density

ΔT_{ad} : adiabatic temperature rise

C^* : specific cement weight and

$T = T_0 + \Delta T_{ad}$. where T_0 is pouring temperature

The rate of the adiabatic temperature rise $d\Delta T_{ad}/dt$ is expressed as gradient of

the obtained adiabatic temperature rise curve. In the case of obtaining the gradient of the measured curve, however, it may be, in many cases, influenced sensitively by a variation of measurement data, this requiring carefulness for its treatment[8].

As shown in Fig.2, in the event of determining gradient $d\Delta T_{ad}/dt$ of the adiabatic temperature rise curve at certain time and temperature (t, T) , first of all, it is necessary to obtain a quadratic curve passing through two points of temperature of $T \pm \beta$ and the object point (t, T) , and we assume that the gradient at T corresponds to the hydration-heat generation rate. When the value β is too small, the hydration-heat generation rate may be influenced largely by measurement error. When the value β is too large, the accuracy of the calculated hydration-heat generation rate may decrease. Because of this, selection of the value β depends upon experiment accuracy. Fig.3 shows the curves of hydration-heat generation rate curve when the value β varies in a range of 0.1°K to 3.0°K . If the value β is in the range of 0.5°K to 2°K , it is known that the calculated value \underline{H} of the hydration-heat generation rate changes in about $\pm 1\%$ at maximum. Therefore, for this study, the hydration-heat generation rate is calculated with $\beta = 1.5^\circ\text{K}$.

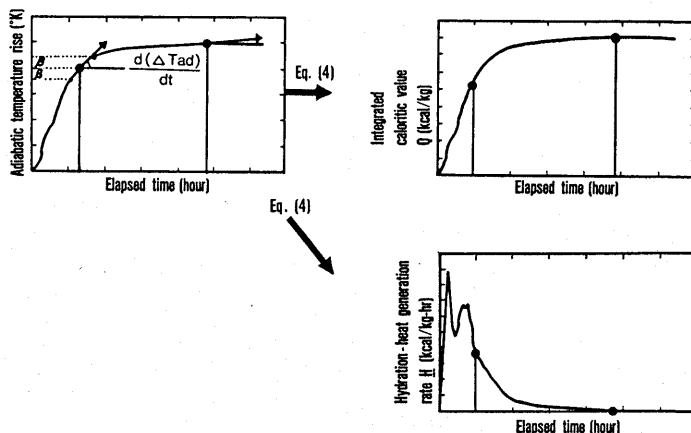


Fig. 2 Method of obtaining the integrated calorific value and hydration-heat generation rate from adiabatic temperature rise

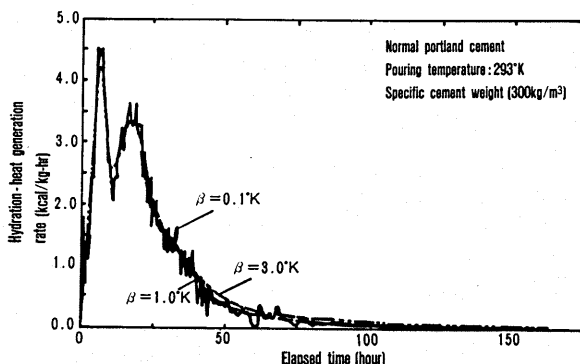


Fig. 3 Smoothing of hydration-heat generation rate

4.2 Temperature-dependency of the hydration-heat generation rate

Through an adiabatic temperature rise test which is conducted on the concrete to be studied, much data on (H, Q, T) is collected at each of various elapsed times. However, the integrated calorific value Q , governing variable which may exert influence on the hydration-heat generation rate, is not independent of the absolute temperature, their relationship can be expressed by the following equation as a linear combination: $Q = c\rho(T - T_0)/C^*$. It is impossible, to obtain separately the influence of T on \underline{H} at the same integrated calorific value Q (which indicates indirectly the hydration degree). Therefore, we adopted the adiabatic temperature rise, changing the pouring temperature T but using the

concrete of the same mix proportion and the same fabrication procedure. Consequently, as shown in Fig.4, this allows us to plot the hydration-heat generation rate \dot{H} against the integrated calorific value Q which is deemed as the hydration level, at each pouring temperature; it is possible as well to study the temperature-dependency of the hydration-heat generation rate \dot{H} at each integrated calorific value. Quantification of the hydration-heat generation process of cement in concrete by implementing the adiabatic temperature rise test with variable pouring temperature, even at the actual stage, is thought of as a reasonable experimental method of concrete.

Fig.5 shows the relationship between the absolute temperature T and the hydration-heat generation rate \dot{H} of the cement in concrete of 250 kg/m³ in specific cement weight at each integrated calorific value Q representing the hydration level. This relationship is derived from the concrete-adiabatic temperature rise tests at pouring temperatures of 283°K, 293°K and 303°K. As for cement paste, it is known that it follows the linear relation expressed by the Eq.(5) with logarithm of \dot{H} and reciprocal of the absolute temperature, that is, Arrhenius rule. Of course, taking the logarithm of both sides in the basic Eq.(3) of this paper, we obtain the Eq.(5). Then, in Fig.5 also, we rearranged the measurement data, using the reciprocal $1/T$ of the absolute temperature as well as the logarithm \dot{H} of the hydration-heat generation rate.

$$\log \dot{H} = \log \dot{H}_0(Q) - \frac{E(Q)}{R} \left[\frac{1}{T} \right] \quad (5)$$

From Fig.5, we can understand that in the case of the in-concrete cement, $\log \dot{H}$ and $1/T$ are in the linear combination :the Arrhenius rule is effective for any integrated calorific value. The gradients given in Fig.5 correspond to the activation energy E of the Eq.(5) which is divided by the gas constant, being called hereinafter cement thermal activity. Fig.5 shows that the thermal activity $-E/R$ of the in-concrete cement is not constant, but varies with the integrated calorific value Q . This phenomenon is already identified by Uchida et al[3], for the cement paste. Using the adiabatic temperature rise curves at n-

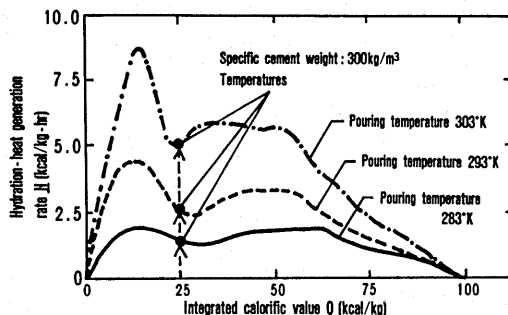


Fig. 4 Integrated calorific value vs. hydration-heat generation rate

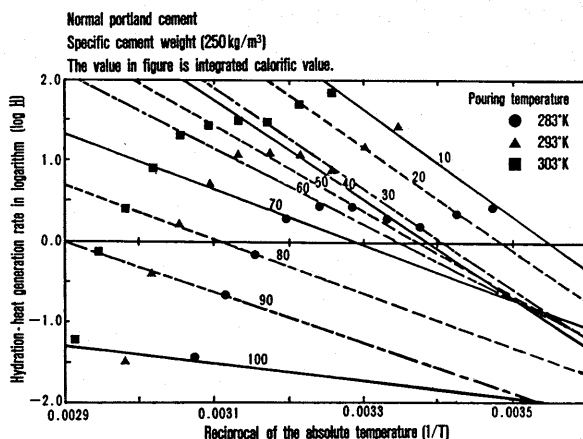


Fig. 5 Absolute temperature vs. concrete hydration-heat generation rate

different pouring temperatures, n-Arrhenius plots can be obtained against each integrated calorific value Q . The thermal activity $-E/R$ of cement is obtained using the method of least squares.

The relationship between the integrated calorific value Q and the thermal activity $-E/R$ is shown in Fig.6. The thermal activity $-E/R$ of cement is a gradient in terms of the temperature, of H which is obtained from the gradient of the temperature measured values. Consequently, considering that even a small error in the experiment may become serious, the irregular fluctuation in Fig.6 is deemed admissible. Variation of the thermal activity along with hydration level may be attributable to the fact that the cement is a compound of minerals of different kinds.

As shown above, if there are at least two adiabatic temperature rise curves of different pouring temperatures, it is possible to quantify the thermal activity $-E/R$ of the cement in concrete.

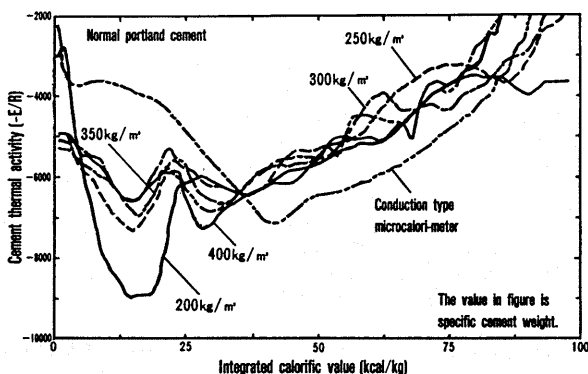


Fig. 6 Integrated calorific value vs. cement thermal Activity ($-E/R$)

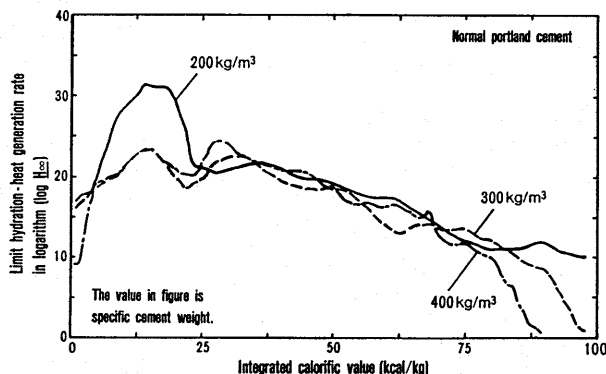


Fig. 7 Integrated calorific value vs. limit hydration-heat generation rate (Log.)

4.3 Quantitative evaluation of temperature-dependent hydration-heat generation rate

The gradient of the graph of the logarithm of hydration-heat generation rate $\log H$ vs. the reciprocal of absolute temperature $1/T$ corresponds to the thermal activity of cement $-E/R$. The value where the graph intersects the ordinate represents the logarithm of limit hydration-heat generation rate $\log H_{\infty}$, when the absolute temperature is infinite. The logarithm of limit hydration-heat generation rate is plotted against the integrated calorific value in Fig.7. The thermal activity of cement $-E/R$ and limit hydration-heat generation rate H_{∞} are quantitatively determined in relation to any integrated calorific value Q as shown in Figs. 6 and 7 respectively. This enables prediction of the hydration-heat generation rate for an arbitrary hysteresis by using the Eq.(3).

Supposing the temperature be constant ($T=T_s$), the corresponding hydration-heat generation rate $H(T_s, Q)$ can be readily obtained by the Eq.(6) derived from the Eq.(3) and material functions of Figs. 6 and 7.

$$\underline{H}(T_s, Q) = \underline{H}_\infty(Q) \exp \left(-\frac{E(Q)}{RT_s} \right) \quad (6)$$

The limit hydration-heat generation rate $\underline{H}_\infty(Q)$ quantified by the Eq.(3) and Fig. 7 is a non-realistic value with the temperature T being infinite. On the other hand, using $\underline{H}(T_s, Q)$ of the Eq.(6) representing a realistic hydration range of cement, it is possible to rewrite the Eq.(3). Eliminating $\underline{H}_\infty(Q)$ from the Eq.(6) and Eq.(3), we obtain

$$\underline{H} = \underline{H}(T, Q) = \underline{H}(T_s, Q) \exp \left[-\frac{E(Q)}{R} \left(\frac{1}{T} - \frac{1}{T_s} \right) \right] \quad (7)$$

where T_s is an arbitrary temperature. Indeed, when T_s is infinite, the Eq.(7) coincides with Eq.(3), that is to say, $\underline{H}(\infty, Q) = \underline{H}_\infty(Q)$.

In numerical analysis, it is necessary to determine two material functions $-E(Q)/R$ and $\underline{H}(T_s, Q)$ in terms of Q . For approximation function of the thermal activity of cement $-E(Q)/R$, a cubic curve of integrated calorific value Q , proposed by Uchida et al.[3] was used in this study. As for functional approximation of the reference hydration-heat generation rate $\underline{H}(T_s, Q)$, there is no restriction to the determination of reference temperature T_s . Hence, if $\underline{H}(T_s, Q)$ is given as accurately as possible in terms of Q for any temperature, then the phenomenon expressed by the Eq.(7) remains unvaried. Thus, it is convenient to select a temperature such that $\underline{H}(T_s, Q)$ is substituted with small errors by a simple function. Fig. 8 shows the hydration-heat generation rate, $\underline{H}(T_s, Q)$, with a constant temperature T_s , computed by the Eq.(6). In this study, with T_s of 293 °K, a spline interpolation function was applied to data quantitatively determined from the adiabatic temperature rise test of concrete and the calculation of the Eq.(7) was conducted.

5. EFFECT OF MIX PROPORTION AND MIXING PRACTICE UPON THE HYDRATION-HEAT GENERATION RATE

5.1 Difference of material functions between cement paste and concrete

In Fig.6 showing the thermal activity of the in-concrete cement, a thermal activity curve of cement paste (water cement ratio being 0.75) obtained through measurement by a conduction type microcalori-meter is plotted also. Both curves are convex downward. Compared with the curve of cement in concrete, the curve of cement paste shows a significantly smaller activity in the early stage of hydration where the integrated calorific value is of a small level, whereas, the activity is greater in a later stage of hydration where the integrated calorific value is larger.

The curves in Fig. 8 respectively show the relationship between hydration-heat generation rate and integrated calorific value at 293°K, 313°K and 333 °K for cement in concrete and cement paste. These curves reveal that, at any temperature range, the hydration-heat generation rate in concrete is larger than measurements by a condition type microcalori-meter of the cement paste. Besides, with the increase of temperature, i.e., 313°K, 333°K, the hydration-heat generation rate of cement in concrete at early stage of hydration is several times the experimental values of cement paste. However, at the stage where about two-thirds of the total heat generation has been completed, there is no difference between the rates of cement in concrete and paste, and it is concluded that, in both cases, almost the same amount of heat generation is liberated till the end of hydration.

As supposed initially, the hydration-heat generation process of the cement in concrete is quantitatively different from that of the cement in paste. This can be attributable to the difference in dispersion system of cement particles. Compared with the cement in paste, the cement particles in concrete, due to the presence of aggregates of various sizes and difference in mixing practice, are more uniformly and stably dispersed in the aqueous medium. Hence the cement particles have a greater possibility of coming into contact with water particles. During initial hydration, cement minerals such as aluminate and silicate are sufficiently hydrated. This is the reason why the cement in concrete liberates, at early stages, greater amount of hydration heat. At later stages, however, where hydration has evolved further and the cement particles in both cases, i.e., concrete and paste are covered with hydrates, the difference in the dispersion state due to mixing effect becomes smaller.

5.2 Influence of mix proportions of concrete

Fig.6 includes also the thermal activity curves for different mix proportions of concrete with different specific cement weight. When the specific cement weight is 200 kg/m^3 and the water cement ratio is large, i.e., 80%, the thermal activity of cement at the initial hydration stage is much larger than that of other mix proportions. This can be explained by the fact that, as the water cement ratio is greater, that is, there is

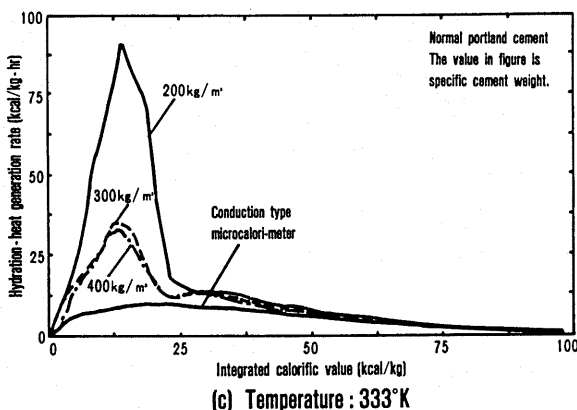
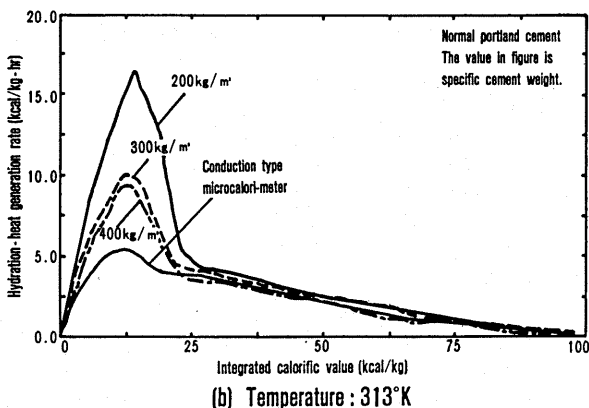
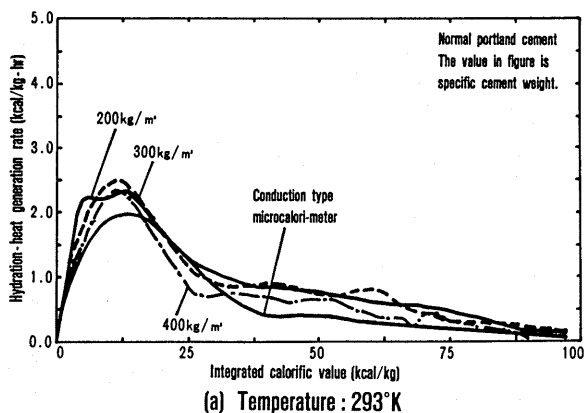


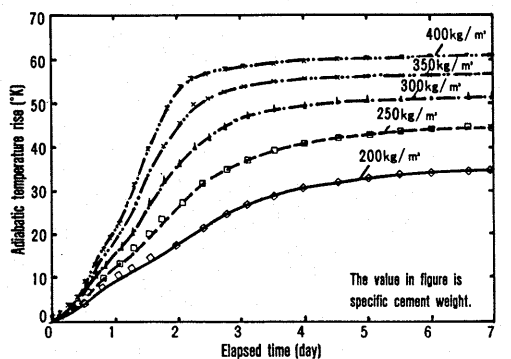
Fig. 8 Integrated calorific value vs. hydration-heat generation rate under a certain temperature

sufficient water for hydration, cement particles are hydrated faster even at an elevated temperature range. But, with other mixes whose water cement ratio is less than 60%, no remarkable difference is found in thermal activity of cement.

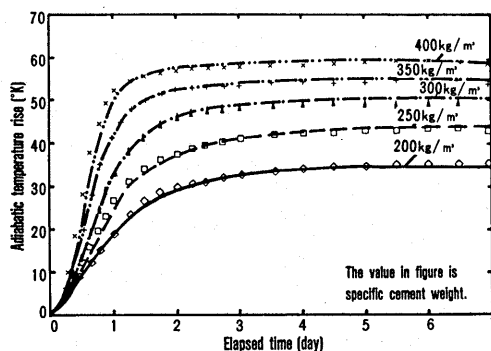
From Fig.8 indicating the relationship between hydration-heat generation rate and integrated calorific value, it is demonstrated that the hydration-heat generation rate varies with the mix proportion. In the same manner as the thermal activity, the mix with low specific cement weight and 80% of water cement ratio presents a significantly higher hydration-heat generation rate at the early stage of hydration than the other mixes. Conversely, the mixes with larger specific cement weight and smaller water cement ratio exhibit smaller hydration-heat generation rates in the range of large integrated calorific value Q , i.e., at later stage of hydration, and its total heat generation at the end of hydration also becomes smaller. This tendency can be explained by the fact that, in the mixes with large specific cement weight and low water cement ratio, cement particles are poorly dispersed. With the concrete also, though not so remarkable as with the paste, it is demonstrated that the hydration-heat generation rate varies with the mix proportion.

6. ACCURACY OF THE HYDRATION-HEAT GENERATION RATE OF CONCRETE

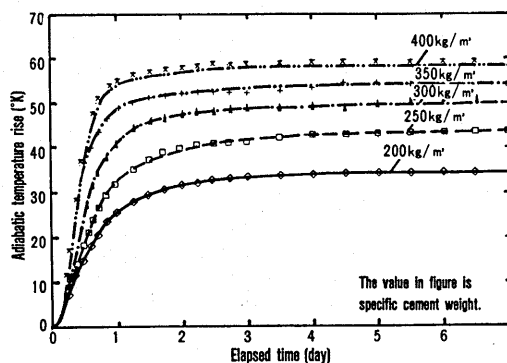
The Eq.(3) and Eq.(7) are generalized equations for any thermal hysteresis. Hence, the adiabatic temperature rise $\Delta T_{ad}(t)$ for an arbitrary pouring temperature, T_0 , is governed by the Eq.(3) or converted Eq.(7) representing the hydration process as well as by the Eq.(4) expressing the adiabatic condition. Eliminating the parameter Q from the Eq.(7) and Eq.(4), a differential equation of first order in terms of the adiabatic temperature rise $\Delta T_{ad}(t)$ is obtained. This Eq.(8) is a generalized governing equation for the adiabatic temperature rise



(a) Pouring temperature : 283°K



(b) Pouring temperature : 293°K



(c) Pouring temperature : 303°K

Fig. 9 Estimation of adiabatic temperature rise

ΔT_{ad} in terms of an arbitrary pouring temperature T_0 .

$$c\rho \frac{d(\Delta T_{ad})}{dt} = C^* \times F(\Delta T_{ad}, T_0)$$

$$F(\Delta T_{ad}, T_0) = \underline{H}(T_s, c\rho \Delta T_{ad}/C^*) \times \exp \left[-\frac{E(c\rho \Delta T_{ad}/C^*)}{R} \left(\frac{1}{T_0 + \Delta T_{ad}} - \frac{1}{T_s} \right) \right] \quad (8)$$

where the initial condition is set as $\Delta T_{ad}(0) = 0$.

The material functions of the hydration-heat generation model were obtained through the adiabatic temperature rise test of concrete. Therefore, the adiabatic temperature rise must be accurately predicted by solving the Eq.(8) for the time t . For the purpose of evaluating the accuracy of the generalized prediction formula of hydration-heat generation rate, numerical integration of Eq.(8) was conducted to calculate the adiabatic temperature rise. The results are shown with the experimental temperature curves in Fig. 9. As the hydration-heat generation process varies with the mix proportion, material functions appropriate for each mix, i.e., a particular thermal activity of cement $-E/R$ and a particular reference hydration-heat generation rate \underline{H} are used in the calculation. The graphs reveal that the deviation between the experimental and analytical values is within 1°K to 2°K for all the concretes of various mix proportions and pouring temperatures, over the whole range from the initial stage to the end of hydration. Hence the governing equation has been proved to have a high accuracy in the adiabatic condition.

To verify the applicability of the generalized hydration-heat generation rate equation, it is necessary to study also temperature hysteresis not in the adiabatic condition. For example, a good verification method is to measure experimentally, at a temperature kept constant, the heat generation in the concrete mass itself. For the present, there is no available means to measure the temperature rise in concrete, keeping uniform its concrete temperature. So, the verification should depend upon the measurement of a concrete structure. As the temperature varies with the location in concrete, it is necessary, in such verification, to follow up the hydration-heat generation process at every point in concrete and to obtain corresponding solutions of Eq.(8) which constitutes a simultaneous system with the thermal conductivity equation (Eq.(1)). The authors are planning to study further the applicability of the model described here.

7. CONCLUSIONS

The investigation is intended to evaluate quantitatively, based on the adiabatic temperature rise, the activation energy of cement in concrete and limit hydration-heat generation rate, and to present a hydration-heat generation model applicable to the temperature analysis of concrete structure undergoing any thermal hysteresis. The results of the investigation has revealed the following.

(1) The adiabatic temperature rise of concrete $\Delta T_{ad}(t)$ and the temperature rise rate obtained by differentiation of the adiabatic temperature rise curves in terms of t are respectively multiplied by the average heat capacity of concrete and divided by the cement content per unit volume of concrete to obtain the quantity of integrated calorific value Q and hydration-heat generation rate \underline{H} per specific weight of cement. Between Q and \underline{H} and the absolute temperature T , the relationship expressed by the Eq.(3) is established. It has been known that this equation holds for the cement paste at a constant temperature[3].

(2) A method was presented here to compute the material functions in the Eq.(3), i.e., thermal activity of cement $-E/R$ and the limit hydration-heat generation rate H^* , in terms of the adiabatic temperature rise obtained from an experiment using concrete specimens of the same mix proportion, prepared by the same process, placed at two or more temperature levels T_0 .

(3) The thermal activity $-E/R$ and the hydration-heat generation rate H^* are the material functions in the governing equation of hydration-heat generation process. The values of $-E/R$ and H^* with cement paste are largely different from those with concrete. Hence, for the hydration-heat generation model of cement in concrete, the material functions quantified by the technique described in (2) are to be used.

(4) The values of the material functions in the Eq.(3) for the cement paste are significantly different from those for the concrete. Besides, the values vary among concrete specimens depending upon the mix proportion and mixing efficiency. This can be explained by the fact that, in dispersion state of cement particles, there is a difference between cement paste and concrete, and that, between concrete specimens, the dispersion state varies with the mix proportion and mixing practice.

(5) The adiabatic temperature rise is evaluated by numerical integration, for each mix proportion, of the generalized equation of concrete adiabatic temperature rise expressed in the Eq.(8). The curves thus obtained agree well with the measured values. This proves the high accuracy of the Eq.(8). In the scope of the present investigation, it was impossible to establish a correspondence between respective concrete mix proportions and material function values of hydration-heat generation model.

Acknowledgment

The authors are grateful to Mr. Norio Yokota, Kiyohiko Uchida, Shusuke Harada, Toshiyuki Sato, Hiroyuki Sakakibara, Kohji Horiguchi, Tohru Chohsokabe at Sumitomo Cement Co., Ltd. for support and advice for this work.

References

- [1] Suzuki. Y., Harada. S., Maekawa. K., Tsuji. Y., "Applicability of Adiabatic Temperature Rise for Estimating Temperature Rise in Concrete Structures", Transactions of the Japan Concrete Institute, Vol.7, pp.49-56, 1985
- [2] Kondo. R., Daimon. M., Akiba. T., "On the Cement Hydration Using Conduction Calorimeter", Review of the 22nd General Meeting of the CAJ, pp.55-58, 1968
- [3] Uchida. K., Sakakibara. H., "Formulation of the Heat Liberation Rate of Cement and Prediction Method of Temperature Rise based on Cumulative Heat Liberation", Concrete Library of JCSE, No.9, pp.85-95, 1987
- [4] Endoh. Y., Maekawa. K., Ozawa. K., "Relationship between Water Retaining Ability of Paste and It's Dispersion", Proceedings of the JCI, Vol.10, No.2, pp.315-320, 1988 (in Japanese)
- [5] Investigation Committee of Durability Design Study (Maekawa. K.), "A State of the Arts Report on Prediction and Design for Service Life of Concrete Structures", Proceedings of JCI Symposium on Prediction and Design for Service Life of Concrete Structures, pp.102-105, 1988 (in Japanese)
- [6] Suzuki. Y., Harada. S., Maekawa. K., Tsuji. Y., "Evaluation of Adiabatic Temperature Rise of Concrete measured with the New Testing Apparatus", Concrete Library of JSCE, No.13, pp.71-84, 1989
- [7] Suzuki. Y., Harada. S., Maekawa. K., Yukikazu. T., "Method for Evaluating Performance of Testing Apparatus for Adiabatic Temperature Rise of Concrete",

Concrete Library of JSCE, No.14, pp.151-162, 1989

[8] Shima. H., Chou. L., Okamura. H., "Bond-Slip-Strain Relationship of Deformed Bars embedded in Massive Concrete", Concrete Library of JSCE, No.12, pp.79-94, 1987