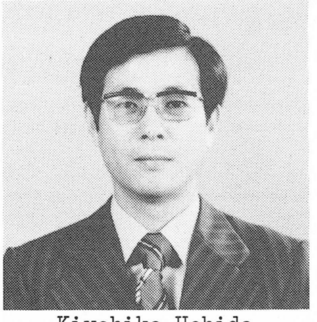
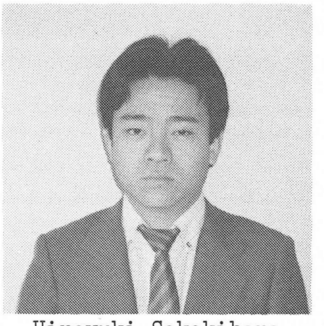
CONCRETE LIBRARY OF JSCE NO.9. JUNE 1987

FORMULATION OF THE HEAT LIBERATION RATE OF CEMENT AND PREDICTION METHOD OF TEMPERATURE RISE BASED ON CUMULATIVE HEAT LIBERATION

(Reprint from Concrete Journal, Vol. 24, No. 4, 1986)





Kiyohiko Uchida   Hiroyuki Sakakibara

SYNOPSIS

In this paper, the rate of heat liberation of cement was formulated and a new prediction method for temperature rise in concrete was established. It was found that cumulative heat liberation of cement is an effective parameter for uniquely expressing the hydrated state of cement and the activation energy of cement hydration can be expressed as a function of cumulative heat liberation and the rate of heat liberation at any temperature determined. A method of predicting temperature rise of concrete was proposed based on rate of heat liberation at any temperature of cement expressed by cumulative heat liberation. By this method, temperature prediction were made of adiabatic conditions such as in mass concrete and good results were obtained.

K. Uchida is working as a senior research scientist of basic research section at Cement/Concrete Technical Development Center, Sumitomo Cement Co.,ltd., Chiba, Japan. He received M.S.(1972) from Kyoto University. His fields of interest are kinetics, hydration reaction of cement, chemical and physical property of concrete. He is a member of JCI, the Ceramic Society of Japan, the Society of Polymer Science of Japan and the Society of Chemical Engineers, Japan.

H. Sakakibara is a research engineer at Cement/Concrete Technical Development Center, Sumitomo Cement Co.,ltd., Chiba, Japan. His research interests include problems concerning hydration reaction of cement, durability and pore structure of concrete. He is a member of JCI.

---

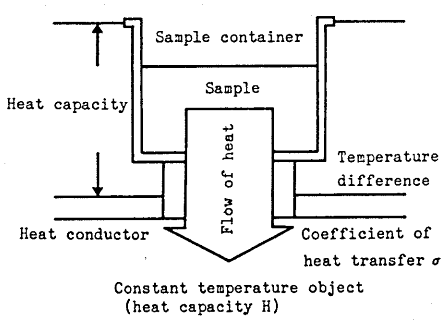
1. INTRODUCTION

Prediction of temperature rise of concrete is presently being done by various methods in order to analyze thermal stresses of concrete. Factors that determine temperature rise of concrete are of diverse kinds such as type and content of cement, kind of aggregate, and variation in outside air temperature[1][2][3]. In spite of the fact that temperature rise of concrete is due to heat of hydration of cement, in almost all cases, it is determined based only on the results of adiabatic temperature rise tests. To take mass concrete as an example, when the center portion which can be considered to be close to an adiabatic condition and the surface portion where radiation of heat is great are compared, the respective temperatures are different. Accordingly, it is conceivable that the states of progress of hydration and the rates of heat liberation will differ. In this way, in case of making temperature predictions for non-adiabatic portions of concrete or under special conditions such as when performing pipe cooling, it will be insufficient to have only the results of adiabatic temperature rise tests, and it is necessary for analyses to be made from the hydration reaction of cement itself.

Therefore, the authors carried out formulation of the rate of heat liberation through measurements of the rate of heat liberation of cement under various constant temperatures and proposed a method of predicting temperature rises of concretes having all kinds of temperature paths.

2. HEAT OF HYDRATION OF CEMENT

The most effective method by which continuous measurements can be made is measurement of rate of heat liberation by conduction microcalorimeter (hereafter abbreviated as "calorimeter")[4]. The basic diagram of the device's principle is shown in Fig. 1. The entire tank is maintained at constant temperature, and the variations in heat of hydration (calorific value released to the outside from the reaction vessel) can be directly measured continuously from immediately after injection of water. The authors used this device for measurement of "heat of hydration at constant temperature."



With cumulative liberation per unit length of time as q

$$q = H \cdot d(\Delta T) \cdot dt + \sigma \Delta T$$

Integrating the above equation, total cumulative heat liberation Q will be

$$Q = \int_0^{+\infty} g\,dt = H[\Delta T]_0^{+\infty} + \sigma \int_0^{+\infty} \Delta T\,dt$$

ΔT will be 0 at $t \leqq 0$ and $t = +\infty$, and can be expressed by

$$Q = \sigma \int_0^{+\infty} \Delta T\,dt$$

Fig. 1 Principle of conduction microcalorimeter.

Fig. 2 shows the rate of heat liberation curves of 6 kinds of cement commercially available. The conditions for hydration were temperature of 20°C and water-cement ratio of 0.65. The rate of heat liberation curve of cement is very complex in this way and differs greatly according to the variety of cement. Further, the rate of heat liberation varies greatly according to quality and quantity of admixture added as with blended cements such as portland blast-furnace slag cement and portland fly ash cement[5]. Besides this, many factors such as fineness and particle-size distribution of cement have large effects on the rate of heat liberation of cement.

The rate of heat liberation curves under various temperatures are shown in Fig. 3 for ordinary portland cement. It can be seen that the shape of the rate of heat liberation curve differs greatly depending on the temperature of the system. The early-age heat liberation peak is "larger" the higher the temperature of the system regardless of variety of cement, while moreover, the time in which the peak appears" shifts to the short-term side", while contrastedly, on the long-term side, a trend is seen for heat liberation to be rapidly decreased.

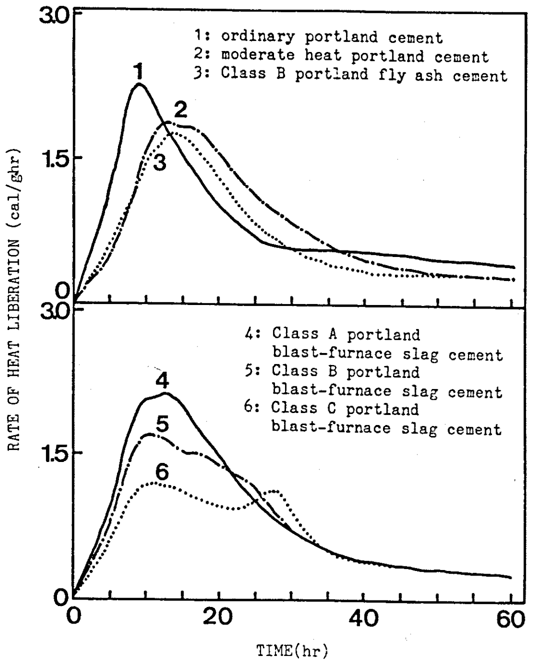


Fig. 2 Rate of heat liberation curves of commercially available cements.

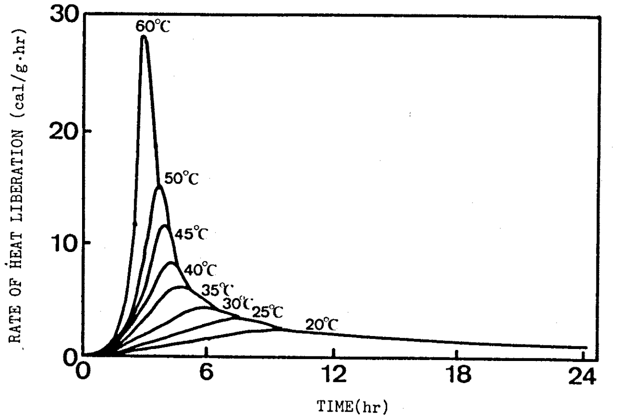


Fig. 3 Temperature dependence of rate of heat liberation of ordinary portland cement (with numbers in figure representing measurement temperatures).

3. HYDRATION AND CUMULATIVE HEAT LIBERATION OF CEMENT

There have been many findings with regard to variations in the hydrated state of cement under constant conditions, especially, under conditions of constant temperature[6][7]. However, with a system such as mass concrete in which temperature changes with time, and moreover, the cause of the change is the heat of hydration of cement, the situation is completely different from what have been found under constant temperatures. Because of this, it is necessary to set up a different parameter to take the place of hydration time and express the hydrated state of cement by it. Furthermore, whatever the temperature hysteresis of the cement, this parameter must be capable of uniquely expressing the hydrated state of the cement at any time.

3.1 Cumulative heat liberation as parameter

The hydration reaction of cement is very complex and it is difficult to express it by a simple numerical equation, but the hydration reaction will be considered here simply as "cement + water = hydrate + Q (heat of hydration)".
In chemical reactions in general, reaction rate is expressed as a function of reaction ratio, and the reaction heat is considered as being proportional to reaction ratio. In effect, the reaction rate is expressed as a function of the reaction heat. When this is replaced by the hydration of cement, the cumulative heat liberation, which is considered to be the parameter expressing the degree to which hydration of the cement had progressed at that time and the degree of the subsequent rate of heat liberation. When a certain cement has been mixed with identical mix proportions but made to hydrate at different temperatures, the period of time in which a given cumulative heat liberation is attained will be shorter the higher the temperature, but it can be considered that the hydrated states of cement at the time the given cumulative heat liberation is attained will be equal.

Therefore, ordinary portland cement pastes were cured at different temperatures and at the times that identical cumulative heat liberation were attained, hydration arresting and D-drying treatment (vacuum drying) were done, and the hydration ratio of alite in the cement was calculated by the X-ray diffraction method. Also, the amount of bonding water was measured by heat-weight analysis. As a result, it was shown that although samples of identical cumulative heat liberation had different hydration times, hydration ratios and bonding water quantities indicated very similar trends, and it was recognized that cumulative heat liberation is effective as a parameter uniquely expressing the hydrated state of cement[8].

3.2 Cumulative heat liberation model

Fig. 4 shows cumulative heat liberation expressed by models. It is assumed there is a cement with cumulative heat liberation at constant temperatures of 20, 30, and 40°C, and the temperature of the system accompanying progress of hydration varies in steps from 20°C to 40°C. The cumulative heat liberation while the temperature of the system is 20°C coincides with OA. In the case temperature rises to 30°C at time t_A, and this temperature is maintained until t_B, AB which is obtained by shifting parallel to Point A, the heat liberation after Point D for 30°C, which is the same cumulative heat liberation as Point A, may be considered as the cumulative heat liberation of this section.

Further, the section of 40°C (t_B-t_C) is BC with FG for 40°C shifted similarly, and in effect, it can be considered that OABC is the cumulative heat liberation curve of this system. Since actual temperature variation is continuous, the rate of heat liberation must be obtained from an optional cumulative heat liberation and temperature.

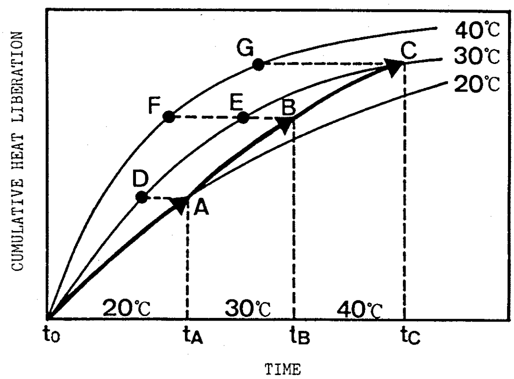


Fig. 4 Model diagram of cumulative heat liberation.

3.3 Rate of Hydration of Cement

With cumulative heat liberation at absolute temperature T and time t as H_T, and with rate of heat liberation as h_T (= dH_T/dt), h_T may be expressed by a function $f(H_T)$ such the following:

$$h_T = k_T f(H_T) \qquad (1)$$

where, rate constant of hydration kT may be expressed as follows by the equation of S. Arrhenius.

$$k_T = A\exp(-E/_{RT}) \qquad (2)$$

provided, however, that A is frequency factor, E is activation energy, and R is gas constant.
From Eq. (1) and (2)

$$h_T = A\exp(-E/_{RT})f(H_T) \qquad (3)$$

When in Eq. (3) cumulative heat liberation H_{To} is the same as H_T at reference temperature To,

$$h_{To} = A\exp(-E/_{RTo})f(H_{To}) \qquad (4)$$

and the rate ratio of heat liberation for temperature T in relation to reference temperature To at the same cumulative heat liberation will be

$$h_T/h_{To} = \exp(-E/_R)(1/_T - 1/_{To}) \qquad (5)$$

3.4 Rate of Heat Liberation Based on Cumulative Heat Liberation

Fig. 5 shows the rates of heat liberation of ordinary portland cement plotted in relation to cumulative heat liberation. Even though temperaures are different, the heat liberation patterns and peak locations show very similar trends. However, the following may be said when ordinary portland cement is taken as the example. Taking the measured temperature 25°C as the reference temperature in Fig. 3 and plotting the rate ratios of heat liberation of other temperatures in relation to the reference temperature, the results will be as shown in Fig. 6. It can be seen that a shape with a peak at around 35 cal/g becomes more pronounced the higher the temperature. In other words, the higher the temperature the more difficult will it be to represent from beginning to end of the reaction by the average value of rate ratio of heat liberation as reported by the authors in a separate paper[8].

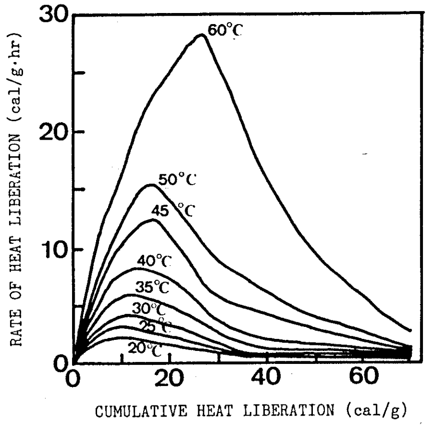


Fig. 5 Relation between cumulative heat liberation and rate of heat liberation of ordinary portland cement.

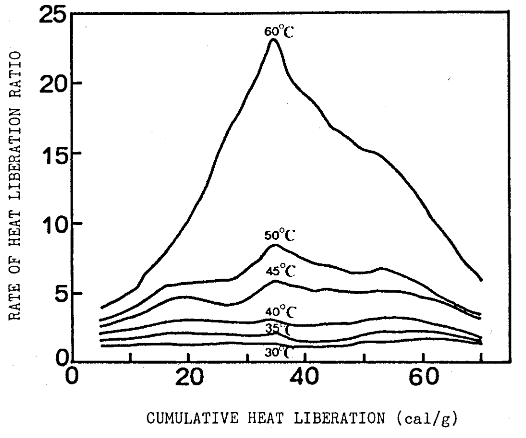


Fig.6 Relation between cumulative heat liberation and rate ratio of heat liberation (reference temperature 25°C)

Therefore, the authors divided the cumulative heat liberation into sections of every 10 cal/g, took the logarithm of the average ratio of the rate of heat liberation to the reference rate of heat liberation, for every section at each temperature and carried out Arrhenius plotting for 1/T as shown in Fig. 7. A good correlation is seen for each section. The inclination ($-E/_R$) of the straight line in each section plotted according to representative cumulative heat liberation is shown in Fig. 8. It is clearly seen that the apparent activation energy varies according to cumulative heat liberation as stated by Copeland and Kantro[9].

Generally speaking, the activation energy of a chemical reaction does not vary according to reaction ratio. However, it is thought the apparent activation energy of cement varies according to cumulative heat liberation in the way because cement is a mixture of several kinds of minerals. If the function of this is taken as $g(H_T)$, the $-E/_R$ in Eq. (5) may be expressed by $g(H_T)$, and will result:

$$\ln(h_T/h_{T_o}) = g(H_T) \qquad (6)$$

In this paper, this was cubically regressed and $g(H_T)$ was approximated in the form of Eq. (7).

$$g(H_T) = aH_T + bH_T + cH_T + d \qquad (7)$$

where, a, b, c, and d are constants.

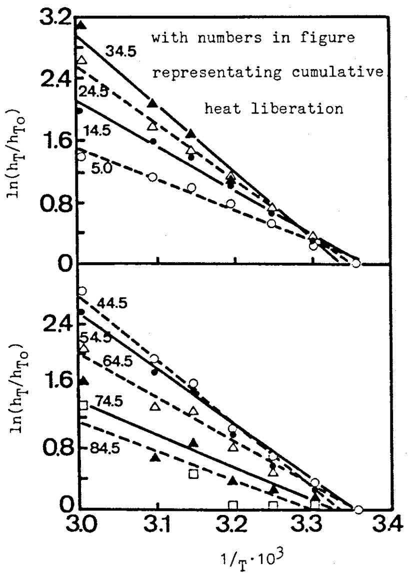


Fig. 7 Arrhenius plotting according section.

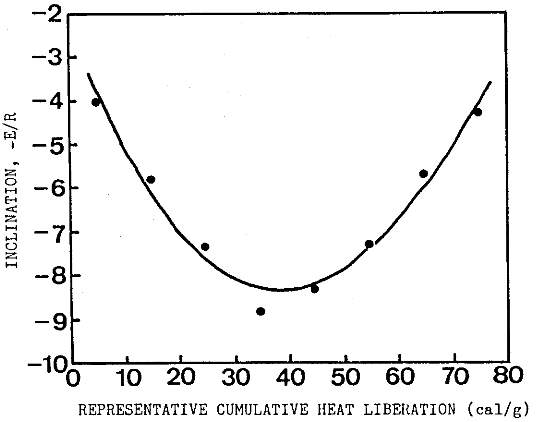


Fig. 8 Relation between representative cumulative heat liberation and inclination.

4. PREDICTION OF TEMPERATURE RISE

In order to predict the temperature rise of actual mortar or concrete by the method described in the foregoing, the value of $g(H_T)$ must be established measuring beforehand the rate of heat liberation of the cement to be used at two or more temperature levels including the reference temperature. When a chemical admixture is to be used, it will be necessary to make the measurements adding that admixture since the rate of heat liberation will vary depending on retarding component, accelerating component, etc. The specific heats of the cement and aggregates to be used must also be measured.

The prediction is made by diving the time elapsed into unit periods of time, determining the cumulative heat liberation and temperature after the next unit period of time based on the cumulative heat liberation and temperature at certain time, and repeating this process. The flow of prediction calculations within a unit period of time is shown in Fig. 9.

The rate of heat liberation h_T at cumulative heat liberation H_T and temperature T_1 is obtained by Eq. (6), and after elapse of the unit length of time, heat liberated of H_T was released, and the cumulative heat liberation became $H_{T2}(=H_{T1}+ H_{T2})$. Further, specific heat is estimated by Eq. (10), and the temperature T_2 after elaspe of the unit length of time is obtained from H_{T2}. Temperature is predicted by repeating the above process. And in case there is irregularity in the heat as at the surface portion of mass concrete, prediction is made correcting H_T at the part of * in Fig. 9.

Accordingly, the temperature at which prediction is started, that is, the temperature as mixed itself is an important parameter deciding the subsequent rate of heat liberation and has a great influence on the prediction. In general, during the several minutes in which concrete is mixed, there is contact moisture pressure of cement and the rapid heat liberation 4 to 5 cal/g of C_3A and CaO, and because of this, the temperature rises slightly after mixing compared with before introduction of water. Further, there is frictional heat of apparatus and aggregates so that it is difficult to accurately predict this temperature difference. Therefore, it was decided that the temperature at which prediction is started is to be the temperature as mixed, and the cumulative heat liberation at this time was taken as 5 cal/g.

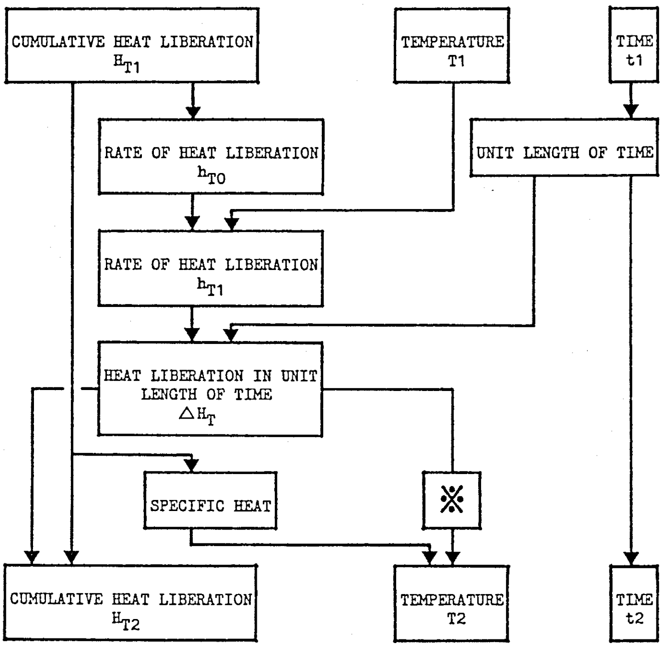


Fig. 9 Flow chart of temperature prediction.

5. COMPARISONS WITH ACTUAL MEASUREMENTS

The prediction is made by dividing the time elapsed into unit periods of time, determining the cumulative heat liberation and temperature after the next unit period of time based on the cumulative heat liberation and temperature at a certain time, and repeating this process. Temperature rises of actual mortar and concrete were predicted based on the method described in the foregoing. The mix proportions were as follow; the mortar contained 352kg/m^3 cement, 266kg/m^3 water, 1525kg/m^3 sand and 0.106kg/m^3 air-entrained agent, and the concrete contained 212kg/m^3 cement, 158kg/m^3 water, 812kg/m^3 sand, 1118kg/m^3 aggregate and 0.424kg/m^3 air-entrained agent.

Mass blocks of 2-m cubes (volume 8 m^3) covered on all sides by foamed polystyrene insulation material 20 cm in thickness were placed with mortar and concrete of these mix proportions, and the temperatures at various mass sections were measured immediately after placement. Furthermore, adiabatic temperature rises of mortar and concrete of the same mix proportions as mentioned above were measured using an improved water-circulation type adiabatic temperature testing apparatus[6].

For making predictions, rates of heat liberation were measured by calorimeter at temperatures of 20°C and 40°C on the cement used in the mortar and concrete. Arrhenius plotting was done by section based on the results, and the variations in -E/R in relation to cumulative amount of heat evolution were plotted and regression was done by cubical curve. The four coefficients of its function $g(H_T)$ are given in Table 1.

Table 1. Coefficients of function $g(H_T)$ used in predictions.

	a	b	c	d
Mortar	4.616E-2	-5.148	1.623E+2	-6.319E+3
Concrete	2.588E-2	-1.293	-1.040E+2	-2.649E+3

In Fig. 10, the results of predicting temperature rise using the prediction method proposed in this study for mortar and concrete and the results of adiabatic temperature rise tests[10] are shown respectively. The adiabatic temperature rise testing apparatus used in these experiments are performance of which had been ascertained by Suzuki et al[10]. through comparisons with mass blocks. The appropriateness of the prediction method under adiabatic conditions was examined in these experiments. As shown in the figure, the initial temperature reached was approximately 3℃ lower with mortar of high cement content and approximately 3°C higher with concrete, while the ultimate temperatures reached were roughly the same regardless of cement content to show good correspondence.

Fig. 11 show the variations in the temperatures at the centers of the 2-m cube (8-m^3 volume) mass blocks and the results of predictions by this method. This takes into account the additions and deductions of heat and verifies that it becomes unifiedly possible for concrete temperature to be predicted for temperature paths of all kinds. Although actually covered with insulation material over the entire surface, heat had escaped after all from the mass block, and temperature at the center began to decline from the third day. Regarding comparisons with predicted results, although there are parts which are lower than the measured values, it can be seen that correspondence is good. Good correspondence is also indicated in case of concrete with comparatively small temperature rise.

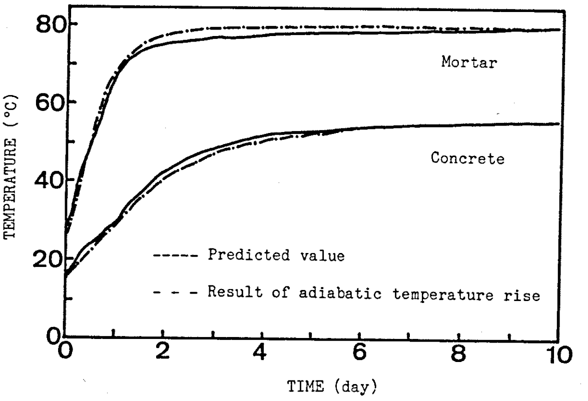


Fig. 10 Predicted values of adiabatic temperature rises of mortar and concrete and results of adiabatic temperature rise tests.

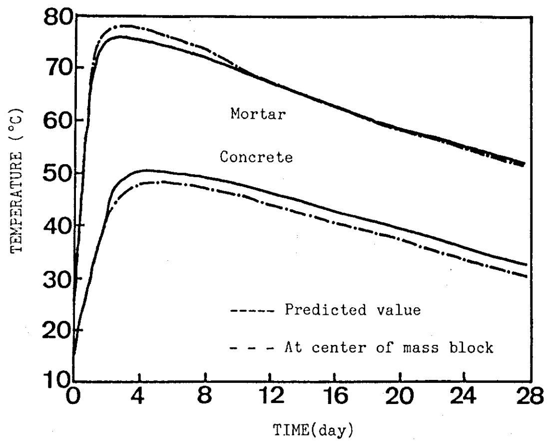


Fig. 11 Predicted and measured values of temperature at center of mass block.

6. Conclusions

The study described in this paper consisted of an attempt for formulation of the rate of heat liberation of cement at any temperature from the results of measurements by conduction calorimeter under various constant temperatures. The results may be recapitulated as follows;

(1) As a result of measuring hydration ratio of cements under different temperatures, the cumulative heat liberation are of equal values if the hydration ratios of the cement are the same, and it was found that cumulative heat liberation is an effective parameter for uniquely expressing the hydrated state of cement.

(2) By dividing cumulative heat liberation into sections of 10 cal/g and assuming that the rate of heat liberation in that section conforms to Arrhenius' equation concerning temperature dependence of chemical reaction, the activation energy at that section was determined from the ratio of rates of heat liberation at the reference temperature and any temperature. As a result, the activation energy of hydration reaction can be expressed as a function of cumulative heat liberation and the rate of heat liberation at any temperature determined.

(3) A method of predicting temperature rise of concrete was proposed based on rate of heat liberation and specific heat of cement paste at any temperature of expressed by cumulative heat liberation.

(4) Temperature predictions were made of adiabatic conditions such as in mass concrete by the method of temperature prediction proposed and good results were obtained. This verifies the appropriateness in an adiabatic condition of the method of prediction proposed based on the rate of heat liberation under a constant temperature where heat liberation is not accumulated at all.

(5) On predicting the temperatures of mass blocks of mortar and concrete from which there was actual release of heat by the proposed method of predicting temperature, good correspondence was indicated and the appropriateness of this prediction method in a non-adiabatic condition was shown.

According to the foregoing, since the prediction method here is based on the

rate of heat liberation of cement obtained under a constant temperature, it is possible for transfer of heat to be incorporated simply into the prediction method to make possible a unified explanation of prediction of temperature rise at a non-adiabatic portion which had been impossible with the conventional method that had been based only on amount of adiabatic temperature rise.
It is intended for further studies to be made on prediction of temperatures in structures subject greatly to influences of outside air temperature and structures under special conditions such as performance of pipe cooling.

ACKNOWLEDGMENTS

The authors are indebted to Professor Hajime Okamura of the University of Tokyo, Associate Professor Yukikazu Tsuji of Gunma University, and Associate Professor Koichi Maekawa of the University of Tokyo for their valuable advice and guidance in carrying out this study for which the sincerest gratitude is hereby expressed.

REFERENCES

(1)Report of the Subcommittee for Research on Thermal Stress of Mass Concrete, Concrete Journal, Vol. 21, No. 8, 1983 (in Japanese).
(2)Y. Nojiri, "Method of Calculating Temperature of Concrete after Placement", Concrete Journal, Vol. 5, No.8, 1967 (in Japanese).
(3)R. Tsukayama, "Estimating Adiabatic Temperature Rise of Concrete", Cement Association of Japan Review of the 26th General Meeting Technical Session, Vol. 30, 1972, p. 408 (in Japanese).
(4)K. Minegishi and M. Daimon, "Hydration Mechanism of Cement According to Calorimeter", Ceramics, Vol. 5, 1976, p. 11 (in Japanese).
(5)R. Kondo, H. Shimizu, and S. Yamauchi, "Trial Manufacture of Self-conduction Calorimeter and Study on Hydration of Slag Cements", J. of the Ceramic Assoc. of Japan, Vol. 68, No. 5, 1960, p. 119 (in Japanese).
(6)D. L. Kantro, S. Brunauer, and C. H. Weise, J. Phys. Chem., Vol. 66, 1962, p. 1804.
(7)R. Kondo and M. Kodama, "Considerations of Rate of Heat of Hydration Reaction", CAJ Review of the 21st General Meeting Technical Session, Vol. 21, 1967, pp.77 (in Japanese).
(8)Y. Saito, H. Sakakibara, and K. Uchida, "Heat of Hydration of Cement and Temperature Rise", CAJ Review of the 38th General Meeting Technical Session, Vol. 38, 1984, p.68 (in Japanese).
(9)The Chemistry of Cements, Vol. I, Academic Press, London and New york, 1964, edited by H. F. W. Taylor. See Chapter 8 by L. E. Copeland and D. L. Kantro.
(10)Y. Suzuki, S. Harada, and K. Maekawa, and Y. Tsuji, "Applicability of Adiabatic Temperature Test Results in Thermal Analysis", Proc. of 7th Annual Concrete Engineering Lecture Meeting, Japan Concrete Institute, 1985, p. 25 (in Japanese).