Hydration Heat Modeling for Cement with Limestone Powder

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Summary

The filler effect of limestone powder on hydration heat of Portland cement was successfully implemented into the multi-component hydration heat model. The ratio between total surface areas of limestone powder and Portland cement is adopted as an indicator to express the filler effect since the surface of limestone powder particles is thought to play roll as precipitation site for cement hydrates. The applicability of the proposed model was verified with temperature measurements carried out at center points on concrete blocks covered by quasi-insulator.

1. Introduction

Self-compacting high performance concrete requires high powder content and low water-powder ratio to maintain high segregation resistance. However, in case of mass concrete structure the high content of binder brings shortcomings in viewpoint of prevention of thermal cracking since it yields large amount of heat of hydration. Thus, it is recommended to reduce unit cement content to mitigate temperature rise. Usually, the low water-binder ratio yields high strength. Then, it is possible to replace a part of binder by inert material like limestone powder with maintaining low water-powder ratio that is, physically, a crucial condition for self-compactability. Further, limestone powder has a preferable feature to improve flowability of self-compacting concrete with small dosage of superplasticizer. Therefore, the use of limestone powder has been recently increased as inert admixtures for self-compacting concrete.

On the other hand, the modeling of hydration process of cement including blending admixtures is required to predict temperature history of mass concrete for thermal crack analysis, and further to pursue property change of concrete with time in the scheme of life span simulation of concrete structures [1]. Here, the effect of limestone powder on hydration process of cement should be taken into account to achieve wider applicability of modeling, since it is well known that the existence of limestone powder promotes hydration process of cement. It can be said that the multi-component hydration heat model proposed to evaluate exothermic process of cement hydration at arbitrary temperature has proper frame to take into account the interdependence of reactions among powder materials, since the hydration process of cement is described by dissolving into minerals [2]. In this study, therefore it is attempted to implement the filler effect of limestone powder on hydration heat of Portland cement into that hydration heat model.
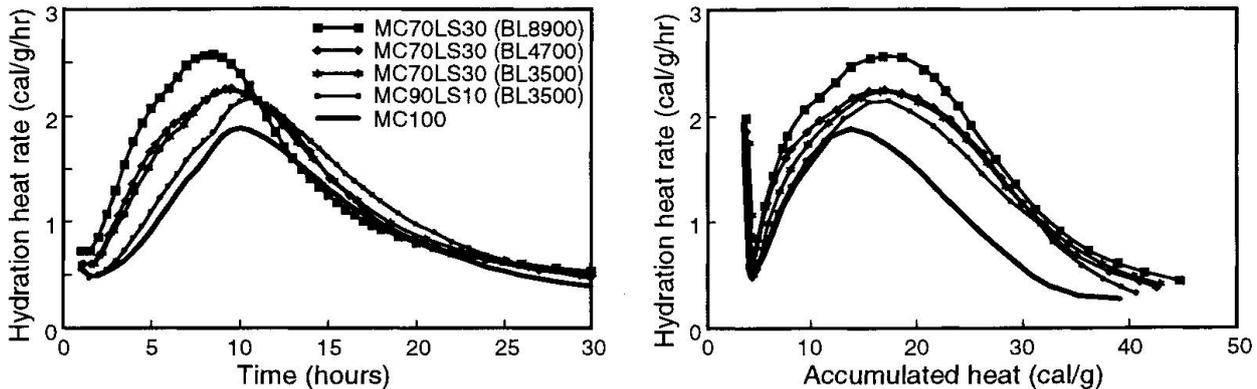
Fig.1 Accelerated hydration heat of cement in terms of time and accumulated heat [5]

2. Physical effect of inert powders on hydration heat process of cement

It is known that the strength of concrete and hydration process of cement is affected by addition of inert powder materials. Yamazaki quantitatively reported through well arranged series of experiments that mineral fines, which even does not have pozzolanic reactivity, physically promotes strength of concrete by increasing the degree of hydration of cement [3]. It was explained as promotion mechanism that inert powder materials could provide additional precipitation site for hydrates, which is an adjacent part of surface area being in contact with cement particle, by getting into flocculation of cement particles. Recently attention is paid towards the use of limestone powder and the related researches were conducted in terms of hydration heat process of cement with conduction calorimeter. Then, it was reported that cement hydration is accelerated according to amount and fineness of limestone powder especially at the second peak in the hydration heat process, which is mainly corresponding to active hydration of alite [4]. However, it is still hardly discussed how cement hydration is affected in viewpoint of controlling factors for reaction rate. Since the quantitative effects of inert powder to the rate controlling factors are not apparent, it was attempted to compare the hydration heat processes accelerated by limestone powder in terms of accumulated heat as shown in Fig.1 [5]. The legends in Fig.1 indicate weight fractions of moderate heat Portland cement and limestone powder with Blaine value of limestone powder shown in a parenthesis in the mixture of cement paste. Here, the relationship between the acceleration effect and division of hydration heat process could be discussed in viewpoint of same degree of hydration. Then it was found that the acceleration is remarkable at around and just after the second peak, where rate of hydration is thought mainly governed by diffusion mechanism at the hydrates formed around unreacted cement particles. Further, it was pointed out that the diffusion resistance at the layer of hydrates should be mitigated since the surface of limestone powder shares some part of them and consequently decreases loads for cement particles.

To adopt an appropriate indicator that can express the effect of inert powder on cement hydration it is necessary to know how the surface of inert powders contribute to precipitation of cement hydrates. Here, it is appreciated that Goto et. al. have directly observed by Scanning Electro Microscope (SEM) that hydrates were similarly formed on overall surfaces of both particles of alite and limestone powder in their mixture [6]. Based on this observation it is thought that the outer layer of hydrates could be precipitated from eluted ion phase at any locations even away from cement particles, and all surface areas of particles can contribute as precipitation site from the beginning of hydration. Further, they found in hydration heat of alite mixed with limestone powder that the linear relationship exists between the heat rate at the second peak and the total surface area of powder particles, those both are normalized by unit weight or volume of alite
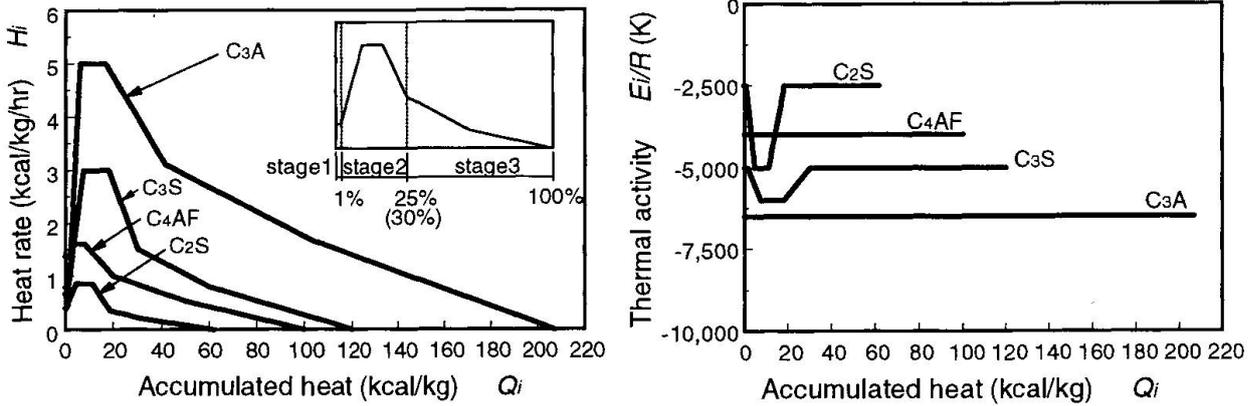
Fig.2 Reference heat rate and thermal activity of each mineral compound [7]

included [6]. These results indicate that the total surface area of powder particles normalized by some factors related to cement included, such as volume, weight or surface area, is suitable as an indicator to express the acceleration effect to hydration heat rate of unit weight of cement.

3. Implementation of the effect of limestone powder to hydration heat model

3.1 Multi-component hydration heat model [2]

In the model, hydration of cement is expressed by hydration of 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. The heat rate of cement is given as the sum of the heat rate of all reactions as follows,

$$H = \sum p_i H_i = p_{C_3A}(H_{C_3AET} + H_{C_3A}) + p_{C_4AF}(H_{C_4AFET} + H_{C_4AF}) + p_{C_3S}H_{C_3S} + p_{C_2S}H_{C_2S} \qquad (1)$$

Where, i represents each mineral component. H and H_i are the heat rates per unit weight of cement as a whole and mineral i, respectively, p_i is the weight fraction of mineral i. H_{C_3AET} and H_{C_4AFET} are both heat rates as a result of the formation of ettringite.

The hydration heat rate of clinker minerals are described by two material functions shown in Fig.2, which are the reference heat generation rate at a constant temperature and the thermal activity indicating temperature dependence of the reaction [7]. The hydration heat rate of each component is generally expressed, with interdependence among the reactions, as follows,

$$H_i = \beta_i \cdot \mu \cdot s_i \cdot H_{i,T_0}(Q_i) \exp\left\{-\frac{E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\}, \qquad Q_i \equiv \int H_i dt \qquad (2)$$

Where E_i is the activation energy of component i, R is gas constant, H_{i,T_0} is the reference heat rate of component i at constant temperature T_0 and also the function of accumulated heat Q_i, β_i is a coefficient to express reduction of heat rate due to shortage of free water (free space), μ is a coefficient to express change of heat rate related to difference of mineral composition of cement, s_i is a coefficient to express change of reference heat rate due to fineness of cement.

3.2 Implementation of physical effect of limestone powder

In Fig.1 it must be seen that the hydration heat rates around the second peaks, which are represented as Stage 2 in Fig.2, show approximately similar figures in terms of the accumulated
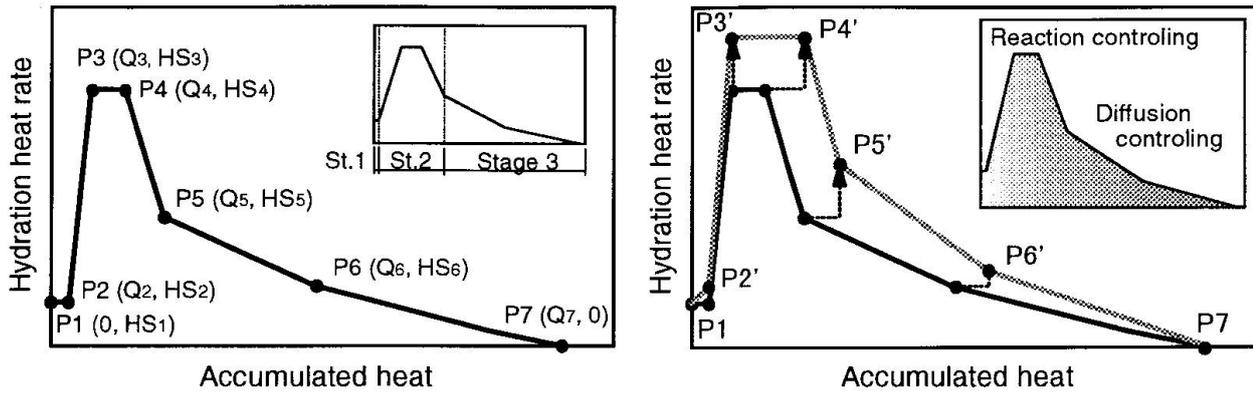
Fig.3 Schematic representation of physical effect model for limestone powder

heat, although they return to stagnated rate simultaneously in time domain. This indicates that not only the hydration heat rate at same degree of hydration but also the regions of respective stages, which are reaction and diffusion controlling ones, are affected due to the physical effect of limestone powder. In the exothermic process around second peak, the heat generation, which must accompany precipitation of hydrates, is thought to be attributable to two sources of ions eluted. One is a group of ions that were already eluted during the dormant period and stored at over-saturation, and the other is new elution of ions accompanied by simultaneous precipitation at that moment [2]. Hence, if the diffusion resistance at the layer of hydrates is mitigated, ions that can additionally elute during Stage 2 are thought to be increased, and consequently the region of the stage expands accordingly. In the model, therefore, the change of regions of stages due to physical effect of limestone powder should be expressed, besides acceleration of hydration heat rate that is supposed to be corresponding to precipitation rate of hydrates.

Fig.3 shows schematic representation of modeling for physical effect of limestone powder on cement hydration. As shown in Fig.2, the reference heat rate is graphically expressed as multi-linear function to represent complicated process. To express acceleration of the hydration heat process the coordinates of points in the function are shifted by the following relationships.

For P2 and P3: $\quad Q'_{ij} = Q_{ij}, \quad HS'_{ij} = HS_{ij} \cdot (1 + k_{H1} r_s)$

For P4 and P5: $\quad Q'_{ij} = Q_{i\,max} - ((Q_{i\,max} - Q_{ij})/(1 + k_Q r_s)), \quad HS'_{ij} = HS_{ij} \cdot (1 + k_{H2} r_s)$ $\qquad$ (3)

For P6: $\qquad\quad Q'_{ij} = Q_{i\,max} - ((Q_{i\,max} - Q_{ij})/(1 + k_Q r_s)), \quad HS'_{ij} = HS_{ij} \cdot (1 + k_{H3} r_s)$

$$r_s = (P_{LS} \cdot B_{LS})/(P_{PC} \cdot B_{PC})$$

Where, j: point number in reference heat rate function, Q_{ij} and HS_{ij}: the accumulated heat and heat rate of point j of i component, $Q_{i\,max}$: the maximum heat generation of i component, P_{LS}, P_{PC} and B_{LS}, B_{PC}: weight fractions and unit weight surface areas of limestone powder and Portland cement. r_s is the ratio of surface areas between limestone powder and cement, which is adopted as the indicator to express the acceleration effect of limestone powder in this study. To represent the degree of contribution by limestone powder certain coefficients, those are k_{H1}, k_{H2}, k_{H3}, k_Q, are multiplied to r_s. Through the analyses shown later they are set as 0.3, 0.3, 0.1, 0.05, respectively. Tentatively, this model is equally applied to all four components of clinker minerals.

4. Verification for scheme of filler effect modeling

To verify the proposed scheme of model and set appropriate parameters, temperature measurements at center points were carried out on concrete blocks covered in styrene foam and

Table 1 Mineral composition of cement

	C3A	C4AF	C3S	C2S	CS2H	Blaine
Cement	11.0	10.4	53.9	18.8	5.83	3350

Note) CS2H: Gypsum dihydrate

Unit) Blaine value: cm^2/g

Table 3 Initial and ambient temperatures

	OPC	LS15	LS30	LS40	LS55	LS70
Initial T.	30	30	28	28	28	28
Ambient T.	23	23	23	23	23	28

Unit) Temperature: °C

Table 2 Mix proportions of concrete

	W/P	W	C	LS	S	G	SP
OPC	30.3	171	565	-	820	915	1.0
LS15	31.3	173	480	74	820	915	0.8
LS30	32.7	177	396	146	820	915	0.7
LS40	32.6	172	311	218	820	916	0.7
LS55	32.6	168	226	291	820	916	0.7
LS70	32.0	165	155	362	820	915	0.7

Note) W/P: Water powder ratio in weight, C:
Ordinary Portland cement, LS: Limestone
powder (Blaine: 5650), SP: Superplasticizer

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

plywood formwork having depths of 30 and 15 mm, respectively. The specimen is outlined in Fig.4. Five different replacement ratios by limestone powder were tested. The mineral composition of cement and mix proportions of concrete are shown in Table 1 and Table 2, respectively. The initial and ambient temperatures are shown in Table 3. Thermal conductivity and heat transfer coefficient are assumed to be 41 kcal/m/day/°K and 35 kcal/m²/day/°K, respectively.

Fig.5 shows comparison between the results of experiment and analysis. The analytical results by original model, in which no acceleration effect was considered, are also shown. It is seen that the proposed model can appropriately represent the acceleration effect of limestone powder on hydration heat of cement at arbitrary replacement ratio.
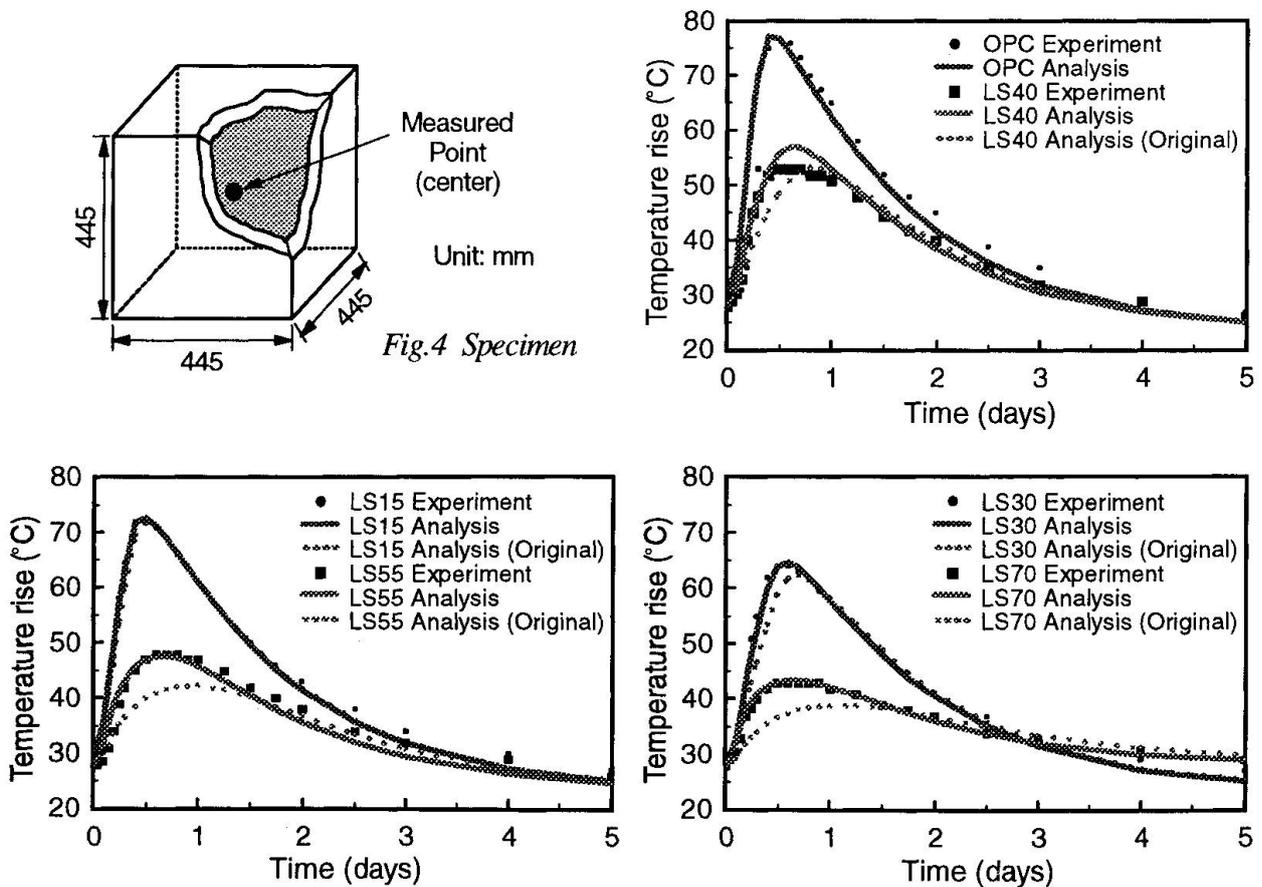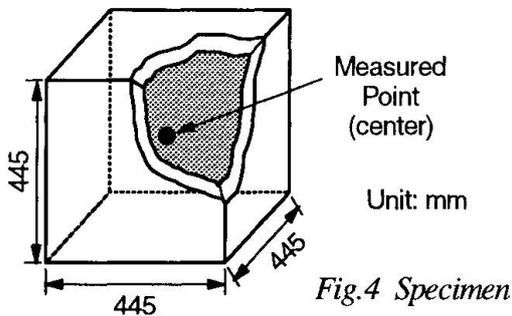

Fig.4 Specimen

Fig.5 Comparison between analysis and experiment

5. Conclusion

The model for physical effect of limestone powder on hydration heat of cement is successfully implemented into the multi-component hydration heat model. The ratio between total surface areas of cement and limestone powder, which are represented by weight fraction multiplied by Blaine value of them, is adopted as the indicator to express the contribution of limestone powder as precipitation site for cement hydrates. Based on review of previous researches, it was found that the change of regions having different rate controlling factors should be taken into account besides the acceleration of hydration heat rate at same degree of hydration. At and around second peak in the hydration heat process of cement, it is thought that the additional elution of ions can increase since diffusion resistance at the layer of hydrates is mitigated due to sharing by limestone powder. Then, both the acceleration of hydration heat rate and the change of ranges so called reaction control and diffusion control stages are expressed in the model. The applicability of the proposed model was verified with temperature histories at the center of small concrete blocks. A wide scope with sufficient accuracy was found in the engineering point of view.

The acceleration effect of limestone powder is thought as a physical effect on hydration of cement. Although the physical effect of limestone powder, that is inert material, is modeled in this study the similar effect would appear even when another inert or low reactivity powders are mixed. In case of blending cement mixed with pozzolanic admixtures, this effect would become apparent at higher replacement since pozzolanic reactions tend to stagnate due to their reaction dependence on cement one. In the multi-component hydration heat model for blending cement, this physical effect of blending powders is not taken into account at all so far [7]. Thus, it is required to rationalize modeling for hydration heat of blending cement by extending and incorporating the physical effect model of powder admixtures proposed in this study.

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