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Development of a New Adiabatic Calorimeter for Quality Control of Cement

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Abstract

As the use of industrial waste as a raw material for the production of cement is expanded, it will become increasingly important to control the adiabatic temperature rise of cement. The evaluation of adiabatic temperature rise in concrete is not adequate for daily quality control because it requires considerable labor. In order to establish a convenient method for evaluating adiabatic temperature rise using only about 30ml of mortar sample, we produced an experimental adiabatic calorimeter. This paper investigates the accuracy and the applicability of this equipment. In addition, the adiabatic temperature rises of cement samples with different C_3A content were investigated for future utilization of industrial waste. Values of adiabatic temperature rise measured using this equipment were found to correspond to those obtained using existing equipment, with correction for the heat capacity of the sample container. Clear differences in adiabatic temperature rise were observed among mortar samples with different blending conditions. Changes in adiabatic temperature rise were negligible even when the aluminate phase content of the studied cement was increased from 9 mass% to 12 mass%. These results suggest that quality control of cement and preparatory experiments could be practiced reasonably by using this adiabatic calorimeter.

1. Introduction

In recent years, the cement industry has promoted the use of industrial waste and byproducts as raw materials. In this instance, one of the most important factors is to accurately determine quality variations in cement (Trezza and Scian 2000, 2005; Sakai and Daimon 2006). Quality control of the fluidity (Maruya *et al.* 2003, 2007) and thermal properties of cement are increasingly important, especially given that the interstitial phase content and minor components in cement clinker can change.

The thermal properties (heat release) of cement are generally determined by measuring the heat of solution. However, this method cannot be used to estimate the temperature rise of concrete in an adiabatic state. In an actual concrete structure, the thermal stress resulting from temperature rise can cause cracking at early ages. Thus, it is important to quantify the adiabatic temperature rise of concrete to prevent thermal cracking of the concrete (Kuroiwa *et al.* 2007), and it would appear that this property needs to be assessed by a routine laboratory

test of cement.

In fact, the evaluation of adiabatic temperature rise in concrete is not adequate for daily quality control because it requires considerable labor. There is a method of predicting adiabatic temperature rise based on data sets for both the heat capacity of materials and the hydration heat of cement paste, which can be measured using a conduction calorimeter with a different curing temperature (Saito *et al.* 1984; Uchida *et al.* 1986; De Schutter 1995, 1999; Poppe and De Schutter 2006). However, this method is not readily applicable to daily quality tests because it is cumbersome and requires a long time for measurement. Thus, a method of evaluating the adiabatic temperature rise of concrete based on the quality control of cement is far from well established.

Based on the above discussion, we produced an experimental adiabatic calorimeter to be used for small mortar samples in order to establish a convenient method for evaluating adiabatic temperature rise. This paper examines the accuracy and applicability of this equipment, the latter being verified by comparing results for mortars to those typically achieved in general concrete. In addition, the adiabatic temperature rise characteristics of cement samples with different C_3A content were investigated for future utilization of industrial waste.

2. Experimental

2.1 Outline of equipment

Figure 1 depicts the prototype equipment. This equipment uses a 30 ml sample in a film case, used as a sample container. The adiabatic state can be controlled by adjusting the temperature of the air surrounding the adiabatic container to follow that of the sample. The fewer

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Fig. 1 Prototype adiabatic calorimeter.

the samples, the harder it is to maintain exact adiabatic control. This equipment includes a temperature-control circuit that combines a zener diode and a supersensitive direct amplifier and has a maximum control sensitivity of $5 \times 10^{-3} \text{ }^{\circ}\text{C}$.

Four copper-constantan thermocouples are used for local temperature measurement. The adiabatic container is made from aluminum, and the insulating material surrounding the film case is polyurethane. It is also possible to process the insulating material and increase the size of the sample container.

After connecting the equipment to the data logger and to a constant-voltage power supply used for feeding Joule heat, we proceeded as described below.

2.2 Materials

Table 1 presents the types of cement samples and aggregate used in this study. The equipment performance was evaluated using mainly the mortar of ordinary Portland cement. For fine aggregate, standard siliceous sand specified by Japanese industrial standards (JIS R 5201-1997) was used. In some experiments, standard sand with particles of less than $150 \text{ }\mu\text{m}$ removed or commercial silica sand with particle sizes of 0.2 to 1.7 mm was used to examine the effect of the type and size of siliceous sand on the adiabatic temperature rise characteristics.

Clinker samples were prepared using industrial materials including limestone, silica stone, coal ash, blast-furnace slag, and ferrous slag. Clinkers were sintered in an electric furnace for 30 min at a maximum temperature of 1550°C and then removed from the furnace at a temperature of 1350°C . A control sample with interstitial phase content of about 18% (determined by Bogue's equation), high C_3A samples, and high C_4AF samples were synthesized. **Table 2** lists the mineral composition of the clinker samples. These samples were ground using a ball mill until the Blaine specific surface area became $320 \pm 5 \text{ m}^2/\text{kg}$. Cement samples were prepared by adding gypsum and hemihydrate to clinker and adjusting the SO_3 content to 2%. For all cements, the hemihydrate content in the calcium sulfate was set to 50%.

Table 1 Types of cement samples and aggregate.

Material	Type
Cement	Ordinary Portland cement
	Early-strength cement
	Moderate-heat cement
	Synthesized cement
Fine aggregate	Standard sand (JIS R 5201)
Water	Ion-exchanged water

Table 2 Mineral composition of synthesized clinker.

Sample		Mineral composition (by Bogue's eq., mass%)				
		C_3S	C_2S	C_3A	C_4AF	Interstitial phase
Control	A9F9	59.2	19.6	9.4	9.0	18.4
High C_3A	A12F9	56.6	19.4	12.1	9.1	21.2
	A15F9	57.9	15.5	15.2	8.6	23.8
High C_4AF	A9F12	59.7	16.5	9.1	11.8	21.0
	A9F14	58.2	15.4	9.1	14.4	23.5

2.3 Tests on adiabaticity

The adiabaticity and responsiveness of the equipment was tested prior to examining the mortar by checking the adiabatic temperature rise when Joule heat was supplied electrically. An aluminum block ($\phi 25 \text{ mm} \times h 30 \text{ mm}$) wrapped in manganin wire ($70 \text{ }\Omega$ resistance) was set in the film case, and a voltage of 1.0, 1.3, 1.6, or 2.0 V was applied for 24 hours. The center temperature of the aluminum block was then measured.

2.4 Preparation of mortar

The adiabatic temperature rise of mortar was measured using prototype equipment and also by using an existing adiabatic calorimeter (SAC-120, made by Tokyo Riko Corp., Ltd.; sample volume, 500 ml). The existing equipment used a 500 ml polyethylene container as the sample container, and a stainless-steel Dewar vessel as an insulating container. The water-cement ratio by mass (W/C) of the mortar was fixed at 0.5. The sand-cement ratio by mass (S/C) was set to within a range such that it could be sufficiently mixed, 2 to 5. In the experiments on the prototype equipment, the mortar was prepared by hand mixing because the volume of samples was small. After mixing cement and water for 2 min, sand was added into the mixture and then stirred for 3 min. In the experiments on existing equipment, the mortar was prepared using a Hobart mixer (Model N-50, made by Hobart Inc.; capacity of bowl, 5 liters; mixing speed, 285 rpm) with a mixing time of 150 s. In each case, mortar

was prepared in a thermostatic chamber set to $20 \pm 1^\circ\text{C}$. After mixing, the mortar sample was set into the sample container, and thermocouples were inserted for measuring and controlling the temperature. Silicon grease was applied around the insertion sites to prevent water dissipation. When the amount of sample is small, a negligible evaporation of water has a significant influence on temperature rise because the heat of evaporation of water is quite high (40.7kJ/mol).

2.5 Evaluation of temperature rise

After placing the insulating container, which contained the sample container, into the equipment set to 20°C preliminarily, the adiabatic temperature rise of the mortar sample was measured. The measurement was conducted over two days in such a way that the temperature rise had slowed significantly. The mass changes before and after measurements were confirmed to check for leaks of water vapor.

3. Results and discussion

3.1 Adiabaticity of equipment

The changes in the center temperature of the aluminum block with time when the supply voltage is changed are shown in Fig. 2. It was confirmed that the temperature climbed when Joule heat was supplied and decreased slightly with time after its cessation. This result indicates that the equipment was slightly short of adiabaticity. It would appear that the reduction in temperature is sufficiently small compared to the temperature rise so as to not matter in daily quality control, which requires short-term measurements. However, the measurement error may increase with longer measurement periods. Therefore, we decided to correct the data to take the heat loss into consideration.

Previous studies (Ohtomo *et al.* 2002; Miyazawa *et al.* 2004) reported a method for predicting the temperature rise under a complete adiabatic state based on the result of a semi-adiabatic test. In this method, a coefficient of heat loss must be calculated by comparing the results between a complete adiabatic test and a semi-adiabatic test. However, the prototype equipment used in this study cannot conduct both tests. Therefore, we calculated the coefficient of heat loss by applying the temperature data after the supply voltage has stopped (Fig. 2) to Newton's cooling equation, expressed as follows:

$$\frac{dT}{dt} = -k \cdot (T - T_0) \quad (1)$$

$$\ln(T - T_0) = -k \cdot t + c \quad (2)$$

$$T = A \cdot \exp(-k \cdot t) + T_0 \quad (3)$$

where T = sample temperature [$^\circ\text{C}$], T_0 = ambient temperature [$^\circ\text{C}$], t = time [h], k = coefficient of heat loss [h^{-1}], and A , c = constant.

Equation (3) demonstrates that the ambient temperature T_0 equals T when t is infinite, so T_0 was set to room temperature (20°C). Equation (2) indicates that the coefficient k can be obtained from the slope of a line in the $t - \ln(T - T_0)$ plot. The relationships between t and $\ln(T - T_0)$ for the different supply voltages are given in Fig. 3. Each plot could be fitted to a linear equation and the slopes are approximately equal. The value for k was determined to be $0.0013 (\text{h}^{-1})$ using the average of these values.

Next, the observational data were corrected by calculating the amount of reduction in temperature per unit time from Eq. (1). An example of changes in temperature after correction is provided in Fig. 4. The amended data present the ideal output under completely adiabatic conditions. The results indicate that this equipment can estimate the adiabatic temperature rise by correcting for the

Fig. 2 Temperature change of aluminum block.

Fig. 3 Relationships between t and $\ln(T - T_0)$.

reduction in temperature. **Figure 5** presents the relationship between supply heat and the temperature rise of an aluminum block in reference to the amended data. It was confirmed that the two had a linear relationship, and that this calorimeter had the ability to evaluate the temperature rise with high accuracy.

Also, considering the heat balance, the relationship between the two can be described as:

$$H = (C_s + C_c) \cdot Q(t) \quad (4)$$

where H = supply heat [J], C_s = heat capacity of sample [J/°C], C_c = heat capacity of container [J/°C], and $Q(t)$ = temperature rise [°C].

The heat capacity of container C_c was determined to be 36.3 J/°C from both Eq. (4) and the slope of the regression line in **Fig. 5** when the heat capacity of the aluminum block was substituted for C_s . This value is considered to include the heat capacity of the film case and part of the heat capacity of the insulating material (polyurethane). This value is sufficiently large compared to the heat capacity of the mortar sample, estimated to be about 80 J/°C.

Fig. 4 Temperature change after correction.

Fig. 6 Adiabatic temperature rise curve of mortar sample.

3.2 Examination of the conditions for quality control

The adiabatic temperature rise curve for a mortar sample of ordinary Portland cement prepared with S/C=3, measured using prototype equipment, is seen in **Fig. 6**. The data is corrected by heat loss as described above. **Figure 6** includes a regression curve, expressed as (Japan Society of Civil Engineers, 2002):

$$Q(t) = Q_{\infty} \{1 - \exp(-rt)\} \quad (5)$$

where Q_{∞} = ultimate temperature rise [°C], and r = rate coefficient of temperature rise.

The adiabatic temperature rise curve obtained from prototype equipment could be approximately described by Eq. (5). It was confirmed that its graphical form was similar to that of general concrete.

The relationship between the sand-cement ratio of mortar and the ultimate temperature rise is given in **Fig. 7** for both the prototype equipment and existing equipment. The ultimate temperature rise measured using the prototype equipment was less than that of the existing equipment, but the relationship between S/C and Q_{∞} for

Fig. 5 Relationship between supply heat and temperature rise.

Fig. 7 Relationship between sand-cement mass ratio and ultimate adiabatic temperature rise.

each set of equipment exhibits the same tendency. The reason why the temperature rise observed on the prototype equipment became smaller was that the effect of the heat capacity of the container was large. We corrected the data for the prototype equipment by assigning the heat-capacity values of the sample, C_s , and of the container, C_c , to the following equation and comparing Q_∞ for each set of equipment.

$$Q_\infty' = \frac{1 + C_{c_proto} / C_{s_proto}}{1 + C_{c_exist} / C_{s_exist}} Q_\infty \quad (6)$$

In Eq. (6), C_{s_proto} and C_{s_exist} were calculated from the specific heat and mix proportion of each material. The relationship between the corrected value for the prototype equipment and the measured value for the existing equipment is shown in Fig. 8. The two were in accordance with each other.

In this prototype equipment, the adiabatic temperature rise became small because of the effect of the heat capacity of the sample container, which could substitute for coarse aggregate. Thus, it can provide the same temperature history as general concrete to the mortar sample, even when the S/C of the sample is small. For example, in the case of ordinary Portland cement, the S/C of the mortar sample must be set in the range of 2.5 to 3.0, in order to evaluate the adiabatic temperature rise corresponding to general concrete prepared at a temperature of 20°C (Fig. 6). Similarly, this method is thought to be applicable to all cement, including other Portland cement or blended cement, unless the samples show a drastic exothermal reaction. However, there is concern that segregation may occur as the S/C of mortar is decreased below 2.5. It is necessary to clarify the acceptable S/C range in this regard.

The adiabatic temperature rise curves of mortar samples prepared from standard sand with particles smaller than 150 µm removed or commercial silica sand, with W/C and S/C fixed at 0.5 and 3.0, are shown in Fig. 9. The curve had the same shape as that of the sample prepared with regular standard sand for either sample. This indicates that the influence of the type of sand on the adiabatic temperature rise was small within the range of testing.

Figure 10 illustrates an example of assessment of reproducibility. This figure indicates that the variation in observed data is small. We were able to confirm similar reproducibility with other samples.

3.3 Applicability of the method

The adiabatic temperature rise curves for mortar samples with S/C=2.5 and 3.0, for various types of cement, are given in Fig. 11. Early-strength cement exhibited the largest adiabatic temperature rise, with ordinary Portland cement in second place, followed by moderate-heat cement. Clear differences were observed among the mortar samples with different types of cement, and these differences showed the same tendencies as those seen in

general concrete data. The relationship between mortar data and concrete data should be examined in a future study.

The adiabatic temperature rise curves for mortar samples of high C₃A cement and high C₄AF cement, prepared with S/C=2.5, are shown in Figs. 12 and 13.

Fig. 8 Comparison of ultimate adiabatic temperature rises.

Fig. 9 Effects of type of sand on adiabatic temperature rise.

Fig. 10 Assessment of measurement reproducibility.

The change in the adiabatic temperature rise with increasing interstitial phase content differed between high C_3A cement and high C_4AF cement. When the C_3A content was increased, the temperature rise of the samples was equal to that of a control sample until 0.6 days. However, after that, the temperature rise increased depending on the C_3A content. In particular, with a sample containing C_3A of 15 mass%, the temperature rise over a period of one day reached the same level as the control sample obtained over a period of three days, and the ultimate temperature rise occurred rapidly. In contrast,

when the C_4AF content was increased, the temperature rise of the samples after 0.6 days increased with increasing C_4AF content, but the differences among samples were small.

It was confirmed that changes in the adiabatic temperature rise were negligible even when the C_3A content of the cement was increased from 9 mass% to 12 mass%, or when the C_4AF content of the cement was increased from 9 mass% to 14 mass%. These results suggest that it is possible to control the quality of cement if the interstitial phase composition is controlled. It is difficult to predict these results from the heat of dissolution. Therefore, we should evaluate the temperature rise of cement by using an adiabatic calorimeter and clarify the hydration of cement materials under adiabatic curing in future work. This will aid the development of a prediction method for properties such as strength (Jinnai *et al.* 2007).

4. Conclusions

In order to establish a convenient method for evaluating adiabatic temperature rise using only about 30ml of mortar sample, we produced an experimental adiabatic calorimeter. The main findings in this study are as follows.

- (1) This equipment needed some improvement in its heat-insulating properties, but that this could be corrected by a coefficient of heat loss.
- (2) By using this equipment, the temperature history of mortar prepared with sand-cement ratios from 2 to 3 exhibited the same level as that of general concrete.
- (3) Values of adiabatic temperature rise measured using this equipment were found to correspond to those obtained using existing equipment, by correction of the heat capacity of the sample container.
- (4) This method clearly detected differences in temperature rise among commercial cements.
- (5) For the cements examined in this study, changes in adiabatic temperature rise were negligible even when the C_3A content of the cement was increased

Fig. 11 Effects of type of cement on adiabatic temperature rise.

Fig. 12 Effect of C_3A content in cement on adiabatic temperature rise.

Fig. 13 Effect of C_4AF content in cement on adiabatic temperature rise.

from 9 mass% to 12 mass%, or when the C_4AF content of the cement was increased from 9 mass% to 14 mass%.

References

- De Schutter, G. and Taerwe, L. (1995). "General hydration model for Portland cement and blast furnace slag cement." *Cement and Concrete Research*, 25(3), 593-604.
- De Schutter, G. (1999). "Hydration and temperature development of concrete made with blast-furnace slag cement." *Cement and Concrete Research*, 29, 143-149.
- Japan Society of Civil Engineers (2002). "Standard specifications for concrete structures-2002, materials and construction." (in Japanese)
- Jinnai, H., Kuroiwa, S., Watanabe, S. and Namiki, S. (2007). "Adiabatic curing method for estimating 91-day strength in structure with 150MPa concrete." *Journal of Advanced Concrete Technology*, 5(2), 161-170.
- Kuroiwa, S., Inoue, Y., Fujioka, K. and William, A. (2007). "Performance confirmation tests on C100 concrete in Dubai, UAE." *Journal of Advanced Concrete Technology*, 5(2), 171-180.
- Maruya, E., Osaki, M., Sakai, E. and Daimon, M. (2003). "Influence of C_3A and calcium sulfate on the fluidity of cement increasing interstitial phase." *Cement Science and Concrete Technology*, 57, 38-44. (in Japanese)
- Maruya, E., Osaki, M. and Igarashi, H. (2007). "Relationship between composition of cement increased interstitial phase content and the fluidity of fresh cement paste." *12th international congress on the chemistry of cement, Montreal*, T6-04.5
- Miyazawa, S., Ohsawa, T., Hiroshima, A. and Koibuchi, K. (2004). "Autogenous shrinkage and adiabatic temperature rise of Portland blast-furnace slag cement." *Cement Science and Concrete Technology*, 58, 154-159. (in Japanese)
- Ohtomo, T., Abe, K., Sato, K. and Sasaki, R. (2002). "Study on the mechanism and estimation method of thermal cracking of steel-pipe concrete composite pier structure." *Concrete Research and Technology*, 13(3), 91-103. (in Japanese)
- Poppe, A. -M. and De Schutter, G. (2006). "Analytical hydration model for filler rich binders in self-compacting concrete." *Journal of Advanced Concrete Technology*, 4(2), 259-266.
- Saito, Y., Sakakibara, H. and Uchida, K. (1984). "Heat liberation and temperature rise of cement in the hydration." *CAJ Review of the 38th General Meeting*, 60-63.
- Sakai, E. and Daimon, M. (2006). "Technical strategy of cement industry in recycling system of wastes." *Bulletin of the Ceramic Society of Japan*, 41(2), 94-99. (in Japanese)
- Trezza, M. A. and Scian, A. N. (2000). "Burning wastes as an industrial resource. Their effect on Portland cement clinker." *Cement and Concrete Research*, 30, 137-144.
- Trezza, M. A. and Scian, A. N. (2005). "Waste fuels: their effect on Portland cement clinker." *Cement and Concrete Research*, 35, 438-444.
- Uchida, K., Sakakibara, H. and Saito, Y. (1986). "Formation of rate of heat liberation and prediction of temperature rise based on heat of hydration." *Concrete Journal*, 24(4), 105-113. (in Japanese)