Hydration Heat and Autogenous Shrinkage of High-Strength Mass Concrete Containing Phase Change Material

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Abstract
In this study, to reduce the HHV of the high-strength mass concrete at early ages, PCM that could absorb the occurred hydration heat was applied, and the changes of autogenous shrinkage and the relationship between the hydration temperature and autogenous shrinkage were investigated. The addition of the PCM leads to a decrease of the fluidity and an increase of the air content in concrete. The acceleration of the cement hydration process by the PCM leads to an early setting and a higher development of the compressive strength and elastic modulus of concrete at very early ages. The function of PCM could be worked below the original melting point due to the eutectic effect. While the hydration temperature and HHV of high-strength mass concrete can be decreased with the use of the PCM. A close relationship could be found between the hydration temperature and autogenous shrinkage; the higher the HHV, the higher the ASV and the greater the ultimate autogenous shrinkage.

Keywords: phase change material; high-strength mass concrete; hydration heat; autogenous shrinkage

1. Introduction
An essential relationship exists between hydration heat and autogenous shrinkage as it pertains to cement hydration. A relationship between the hydration temperature and autogenous shrinkage has been shown in several studies. Some researchers have reported that the magnitude and the development rate of autogenous shrinkage of the cement paste, mortar and concrete were affected by the history and magnitude of the inner temperature at early ages (Bjøntegaard et al. (1997), Horita et al. (2001), Loukili et al. (2000) and Shima et al. (2006)).

Kim et al. (2008, 2009) aimed for a quantitative analysis of the relationship between the hydration temperature and autogenous shrinkage. They suggested an analysis method regarding the histories of the hydration temperature and autogenous shrinkage. They investigated the relationship between these two factors. They found that there was a close relationship between the hydration temperature and autogenous shrinkage at an early age, especially between the HHV(hydration heating velocity) and the ASV(autogenous shrinking velocity); the higher the HHV, the higher the ASV and the greater the ultimate autogenous shrinkage. In consideration of this result, it can be concluded that the ultimate autogenous shrinkage is affected by the HHV at an early age.

The present study focuses on a reduction of the HHV and a change of autogenous shrinkage of the high-strength mass concrete. The reduction mechanism of the HHV can be divided into three methods. The first involves controlling the total amount of hydration heat by regulating the types of cement, the amount of cement and the replacement of cementitious admixtures. The second is to control the reaction velocity of the hydration using a modified retarder, in this case an encapsulated retarder (Mihashi et al., 2002). The third is to control the hydration heat occurring from cement hydration by applying a heat absorption material, in this case a phase change material (PCM) (Zhang et al., 2003).

For a precise comparison of the reduction of the HHV and the change of autogenous shrinkage, an experiment should be conducted in which the same mixture conditions are used to the extent possible; this is especially true for the binder conditions. Hence, the first method of the aforementioned reduction mechanism is inappropriate if applied to the experiment. However the other two can be applied as an admixture in identical mixture proportions.

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In this study, a PCM was applied to reduce the HHV of the high-strength mass concrete at an early age, and the changes of autogenous shrinkage were investigated. Additionally, the relationship between the hydration temperature and autogenous shrinkage was analyzed.

### 2. Experimental Plan and Methods

#### 2.1 Experimental plan

Table 1. shows the conditions of the specimens in the experiment. The 300×300×300mm specimens were prepared in a semi-adiabatic condition considering the insulation effect of a massive member. To reduce the HHV of the high-strength mass concrete, a PCM was applied at addition ratios of 3% and 5% according to the weight of the cement content.

Tests of the slump-flow, air content, setting time, compressive strength and elastic modulus were carried out to investigate the effect of the PCM on the fundamental properties of the concrete. The compressive strength and the elastic modulus were each measured at age 1, 2, 3, 7, 14, 28 and 56 days. Also, the hydration temperature and deformation were measured.

### 2.2 Mixture proportion and materials

The mixture proportion of concrete is shown in Table 2. The water/cement (W/C) ratio was 20% and the unit weight of the cement was 800kg/m$^3$. Details concerning the types and properties of the materials are shown in Table 3.

In this study, PCM was applied to reduce the HHV of the high-strength mass concrete. Fig.1. shows the basic mechanism of HHV reduction by the PCM. PCMs have the ability to absorb and to release energy in the form of heat at a specific temperature when its state changes. In the building materials field, the PCMs can be applied to store the heat energy, for example the solar energy, and to prevent high hydration temperature peaks in massive concrete (Hunger et al., 2009). Hence, it is possible to reduce the inner temperature of
high-strength mass concrete with a PCM and thus to reduce the HHV. The properties of the PCM are shown in Table 4. Strontium hydroxide hydrate in powder form was used as the PCM in this study.

2.3 Specimen and methods

The schematic of the specimen and test method for the hydration temperature and deformation of concrete is shown in Fig.2. The 300×300×300mm specimen was cast in a mold made with expanded polystyrene board with a thickness of 100mm. To reduce the friction between concrete and the mold, a double layer of PVC film and teflon film were used. The temperature and deformation of the 300×300×300mm specimen were measured continuously without removal of the mold. The inner temperature and deformation of the specimen were measured by thermocouple and embedded gage (KM-100B, Japan) every ten minutes after casting.

To evaluate autogenous shrinkage of the 300×300×300mm semi-adiabatic specimen, the total measured deformation should be corrected for the thermal deformation because the inner temperature greatly increased. So, in this study, total measured deformation was corrected by Eq. (1).

\[ \varepsilon_{\text{auto}} = \varepsilon_{\text{total}} - \varepsilon_{\text{thermal}} \]  

Where, \( \varepsilon_{\text{auto}} \): autogenous shrinkage (\( \times 10^{-6} \))

\( \varepsilon_{\text{total}} \): total measured deformation (\( \times 10^{-6} \))

\( \varepsilon_{\text{thermal}} \): thermal deformation (\( \times 10^{-6} \))

Thermal deformation can be calculated by Eq. (2).

\[ \varepsilon_{\text{thermal}} = \gamma \times \Delta t \]  

Where, \( \gamma \): linear thermal expansion coefficient (TEC) of specimen (\( \times 10^{-6}/^\circ C \))

\( \Delta t \): temperature change (\(^\circ C\))

The thermal expansion coefficient (TEC, \( \gamma \)) of concrete varies according to its mixture proportions and materials, and it should be carefully measured. Moreover, it is difficult to evaluate the TEC of concrete in the early ages since its phase and microstructure change with time. If rise in temperature is sufficiently fast, the measured deformation will be only of thermal origin (Loukili et al., 2000). In this study, \( \Phi 100 \times 200 \)mm cylinder specimen embedded thermocouple and strain gage was cast and immersed in a water bath as shown in Fig.3. The temperature of the water bath was initially about 20\(^\circ C\) and the water bath was heated for 10 minutes. Then the temperature change (\( \Delta t \)) and amount of expansion (\( \Delta \varepsilon \)) in the specimen were measured, and the TEC (\( \Delta \varepsilon/\Delta t \)) of concrete was calculated with age as shown in Fig.4.(a). Based on
the measured TECs with age, TEC history could be calculated by regression (Fig.4.(b)). However, in the case of 300×300×300mm semi-adiabatic specimen, the TEC may change more quickly than that of the Φ100×200mm cylinder specimen due to the high inner temperature (Teramoto and Maruyama, 2008). At this time, the maturity method is very useful. The concept of maturity makes it possible to estimate the degree of advancement of the hydration reactions corresponding to the concrete hardening (Turcry et al. (2002)). Finally the age factor was calculated by using the maturity with the base temperature -10°C and the TEC history was corrected by it (Fig.4.(c)).

2.4 Analysis methods

To analyze numerically early age properties of hydration temperature and autogenous shrinkage, Kim et al. (2008) centered on two sections where the hydration temperature and autogenous shrinkage rapidly increase as shown in Fig.5.; hydration heating section (HHS) and autogenous shrinking section (ASS). And the statistical methods to set HHS and ASS were suggested. HHS and ASS were determined by regression analysis with a determination coefficient of over 0.95 from the datum points. The datum point of HHS was the final point; the point of 80% of maximum temperature rise, and it was determined by analyzing the histories drawn by the adiabatic temperature equation. The datum point of ASS was the bend point (turning point (Horita et al. (2001)), mentioned as bend point in this study). Table 5. shows a summary of the factors used in the analysis.

On the basis of this analysis method, in this study, the early age properties and the relationship of hydration heat and autogenous shrinkage of high strength mass concrete were investigated.

3. Results and Discussion

3.1 Slump-flow, air content and setting time

Although the amount of HRWR used was identical to that of the OPC, the slump-flow of PCM-3 decreased by nearly 14%. The use of HRWR to regulate the
### Table 6. Analysis Results of HHS

| Symbol | Initial point | Final point | Regression equation | HHV ($^\circ$C/hr.) | Temperature rise ($^\circ$C) |
|--------|---------------|-------------|---------------------|---------------------|-----------------------------|
| OPC    | 10.5          | 24.1        | 15.7                | 61.9                | 7.79                        |
|        |               |             | $Y = -63.5 + 7.79X$ |                     | 37.8                        |
| PCM-3  | 7.2           | 21.8        | 14.8                | 55.5                | 4.81                        |
|        |               |             | $Y = -18.8 + 4.81X$ |                     | 33.7                        |
| PCM-5  | 2.0           | 22.0        | 12.3                | 52.9                | 3.12                        |
|        |               |             | $Y = 11.0 + 3.12X$  |                     | 30.9                        |

### Table 7. Measurements of the Temperature Change and the Expansion in $\Phi100 \times 200$mm Cylinder Specimen for TEC Test

| Symbol | Measuring age (hr.) | Temperature change ($\Delta t$, °C) | Expansion ($\Delta \varepsilon$, $\times 10^{-6}$) |
|--------|---------------------|------------------------------------|-----------------------------------------------|
| OPC    | 1.5                 | 5.0                                | 346                                           |
|        | 3.5                 | 3.5                                | 234                                           |
|        | 4.5                 | 4.3                                | 270                                           |
|        | 6                   | 3.9                                | 242                                           |
|        | 7.5                 | 4.0                                | 234                                           |
|        | 9.5                 | 4.3                                | 224                                           |
|        | 11.5                | 9.5                                | 134                                           |
|        | 25                  | 2.8                                | 43                                            |
|        | 27                  | 2.9                                | 34                                            |
|        | 30                  | 3.0                                | 29                                            |
| PCM-3  | 1.3                 | 5.2                                | 325                                           |
|        | 3.3                 | 4.7                                | 174                                           |
|        | 4                   | 3.7                                | 109                                           |
|        | 5.8                 | 4.1                                | 106                                           |
|        | 7.3                 | 4.1                                | 34                                            |
|        | 9.3                 | 9.3                                | 24                                            |
|        | 11.3                | 11.3                               | 25                                            |
|        | 24.8                | 29.3                               | -19.5                                         |
| PCM-5  | 1                   | 4.7                                | 295                                           |
|        | 3                   | 4.4                               | 100                                           |
|        | 4                   | 3.0                               | 40                                            |
|        | 5.5                 | 3.3                               | 43                                            |
|        | 7                   | 4.1                               | 29                                            |
|        | 9                   | 3.8                               | 27                                            |
|        | 11                  | 3.5                               | 24                                            |
|        | 24.5                | 3.2                               | -19.5                                         |
|        | 27                  | 24                                | -19.5                                         |
|        | 30                  | 23                                | -19.5                                         |

**Fig. 9. Temperature Histories of the 300×300×300 and $\Phi100\times200$ Specimens**

**Fig. 10. Maturity Results of the 300×300×300 and $\Phi100\times200$ Specimens**
slump-flow within the target scope increased in PCM-5. This indicates that the fluidity of concrete decreases as more of the PCM is added.

In the results of the air content, although the amount of the AE agent used was identical to that of the OPC, the air content of PCM-3 was 2.5% greater compared to the OPC. The use of the AE agent to maintain the air content range of 3% to 6% decreased in PCM-5. These results show that the addition of PCM leads to a higher air content.

Fig. 6 shows the setting time results. The final setting times of PCM-3 and PCM-5 were 3.7 and 5.5 hours, respectively, both earlier than the OPC. This implies that the addition of the PCM accelerated the cement hydration process. If the temperature exceeds the melting point, the PCM absorbs the heat and its phase changes from a solid state to a liquid state. At that time, the H2O that is bonded chemically with Sr(OH)2 separates from it. The separated H2O is consumed upon the cement hydration. This can lead to the acceleration of cement hydration and to early setting of the concrete.

3.2 Compressive strength and elastic modulus

Fig. 7 shows the development ratio of the compressive strength of the concrete containing the PCM to the corresponding OPC concrete. The compressive strength of the concrete containing the PCM after one day was significantly higher than that after one day with the OPC. However, after two days, the compressive strength of the concrete containing the PCM was similar to the OPC results. The result of the elastic modulus shows the same tendency. The elastic modulus of the concrete containing the PCM after one day was significantly higher than the OPC; however, after two days, the test results were similar. It is likely that the acceleration of the cement hydration process by the PCM led to a higher development of the compressive strength and elastic modulus of concrete at very early ages.

3.3 Hydration temperature

Fig. 8 shows the histories of the hydration temperature. The maximum temperature for the OPC is 72.2°C. The maximum temperatures of PCM-3 and PCM-5 are 64.3°C and 61.2°C, respectively, and these decrease by 10~15% compared to the OPC. These findings can be ascribed the heat absorption effect of the PCM. However, although the melting point of the PCM used in this study was 88°C and the maximum temperatures of the OPC is below the melting point, a phase change most likely occurred and the temperature therefore decreased. This can be explained by the eutectic effect. The melting point shown in Table 4 is the value of the PCM in its pure form. If the PCM mixes with any other chemical compound, the melting point will likely decrease to the point known as the eutectic point. It is probable that the PCM used in this study mixed with many different types of chemicals in the cement, which decreased the melting point to less than 88°C due to the eutectic effect.

Table 6 shows the HHS analysis results. The maximum temperature rise and temperature rise of the HHS decrease as more of the PCM is added. The temperature rise ratio of the HHS ranges between 72 and 75%. The HHV of the OPC was determined to be 7.79°C/hr. The HHV values of PCM-3 and PCM-5 decrease by 38% and 60%, respectively, compared to that of the OPC. This indicates that the hydration temperature and HHV of high-strength mass concrete can be decreased with the use of the PCM.

3.4 Thermal expansion coefficient

At first, the temperature change and amount of expansion were measured through the TEC test. The measuring results are shown in Table 7, and TECs are calculated from them. Based on the measured TECs with age, TEC history could be calculated by regression. However, the 300×300×300mm semi-adiabatic specimen shows a very much higher temperature than the Φ100×200mm cylinder specimen (Fig. 9), so the TEC of the 300×300×300mm semi-adiabatic specimen changes more quickly than that of the Φ100×200mm cylinder specimen. In this study, the maturity concept was used for the temperature correction. Fig. 10 shows maturity results of the 300×300×300 and Φ100×200 specimens. The age factors were calculated and the TECs were corrected by them.

Fig. 11 shows the measured TEC history and the corrected TEC history. The high TEC values observed at the early ages correspond to the time when the water phase dominates (Loukili et al. (2000) and Yang et al. (2005)). The TEC decreases slowly and, approximately 6.8 hours after casting, decreases more rapidly. Finally, it converges to 11.5×10^-6°C nearly 17 hours after casting.

For both of PCM-3 and PCM-5, different TEC values were observed. In contrast to the OPC results, the TEC values of PCM-3 and PCM-5 decrease rapidly after casting and converge to 8.0×10^-6°C and 7.0×10^-6°C at approximately 8.8 and 6.0 hours, respectively.

3.5 Autogenous shrinkage

To separate autogenous shrinkage from the total measured deformation, it is necessary to calculate the thermal deformation using the TEC and hydration temperature history. The thermal deformation is calculated by Eq. (3) as proposed by Loukili et al. (2000).

\[
e_{\text{thermal}}(n) = e_{\text{thermal}}(n-1) + \left[ T(n) - T(n-1) \right] \gamma(n) + \gamma(n-1) \frac{\gamma(n) + \gamma(n-1)}{2}
\]

where, \(e_{\text{thermal}}(n)\): thermal deformation, \(T(n)\): the temperature at time \(n\), \(\gamma(n)\): TEC.

By subtracting the thermal deformation from the total measured deformation, the amount of autogenous shrinkage is calculated.

Fig. 12 shows the total measured deformation, the thermal deformation and autogenous shrinkage. A large difference between the total measured deformation...
and autogenous shrinkage was observed in the OPC. However, for both of PCM-3 and PCM-5, the difference between the total measured deformation and autogenous shrinkage is slight. In the OPC, the TEC of the section where the hydration temperature increases shows a high value. On the other hand, the TEC of the section where the hydration temperature decreases is low. This indicates residual thermal deformation, the difference between the thermal expansion and the thermal shrinkage, in the OPC specimen. But, in the PCM-3 and PCM-5 specimens, the TEC values of the sections where the temperature increases and decreases are similar. This caused only a slight difference between the thermal expansion and shrinkage, as well as between the total measured deformation and autogenous shrinkage.

Autogenous shrinkage at 91 days in the OPC was \(-1425 \times 10^{-6}\). The autogenous shrinkage at 91 days in PCM-3 and PCM-5 decrease by approximately 58% and 65%, respectively, compared to that of the OPC.

Lothenbach et al. (2007) reported that the higher curing temperature lead the precipitation of a denser inner C-S-H, the decrease of the ettringite content and very short needles of the ettringite. The density of PCMs decreases as its phase changes to liquid form and it is thought that hydrates reacted with strontium hydroxide may cause expansion. These phenomena

### Table 7. Analysis Results of ASS

| Symbol | Initial point | Final point | Regression equation | ASV \(\times10^6/\text{hr.}\) | Shrinkage rise \(\times10^6\) | Shrinkage at 91 days \(\times10^6\) |
|--------|---------------|-------------|---------------------|------------------|-----------------|------------------|
| OPC    | 10.7          | -415        | 14.8 -1161          | y=1649-184x      | -184.0          | -746             | -1425            |
| PCM-3  | 16.5          | -250        | 39.7 -408           | y=135-7.48x      | -7.8            | -158             | -595             |
| PCM-5  | 13.5          | -178        | 72.0 -409           | y=172-3.69x      | -3.7            | -231             | -490             |

**Fig.11. Thermal Expansion Coefficient**

**Fig.12. Autogenous Shrinkage**
4. Conclusions
The main conclusions that can be drawn from this study are the following:
1) The addition of the PCM leads a decrease of the fluidity and an increase of the air content in concrete.
2) The acceleration of the cement hydration process by the PCM leads to an early setting, a higher development of the compressive strength and elastic modulus of concrete at very early ages.
3) The TEC values of concrete containing PCM, unlike OPC, decrease rapidly after casting and converge at specific values.
4) The hydration temperature and HHV of high-strength mass concrete can be decreased with the use of the PCM, and autogenous shrinkage of high-strength mass concrete containing PCM is lower than OPC.
5) A close relationship could be found between the hydration temperature and autogenous shrinkage; the higher the HHV, the higher the ASV and the greater the ultimate autogenous shrinkage.

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