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A model for predicting the specific heat capacity of fly-ash concrete

Pongsak Choktaweekarn[a,*], **Warangkana Saengsoy**[b], **Somnuk Tangtermsirikul**[b]

[a] School of Civil Engineering and Technology, Sirindhorn International Institute of Technology, Thammasat University, Thailand

[b] Construction and Maintenance Technology Research Centre, Sirindhorn International Institute of Technology, Thammasat University, Thailand

[*]Corresponding author, e-mail: pongsak@siit.tu.ac.th

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ABSTRACT: This study is aimed at investigating the specific heat of fly-ash concrete. The experiments were conducted to obtain the specific heat of fly-ash cement pastes and mortars. Mortars were prepared by varying the sand type and content. It was found that the specific heat decreases as the amount of free water content decreases. The replacement of cement by fly ash resulted in high specific heat at young age but it tends to decrease in the long term due to the pozzolanic reaction. Mortars had lower specific heat than cement pastes. We propose a model for predicting the specific heat of concrete as a function of time, material, and mix proportion. The model, which was verified with various experimental results, simulated the trend of specific heat quite well.

KEYWORDS: hydration, free water content, thermal properties, mass concrete

INTRODUCTION

Thermal stress of concrete due to heat of hydration causes thermal cracking in mass concrete structures. In order to avoid this, designers must be able to obtain a realistic temperature distribution in the mass concrete especially at early age. The accuracy of the temperature prediction model depends on many factors, of which the specific heat and thermal conductivity are the most important. These thermal properties change with age (degree of hydration), amount and type of aggregate, temperature, and water content[1,2]. Specific heat or heat capacity of concrete is an important parameter for computing the temperature distribution in mass concrete. Neville[3] stated that specific heat considerably increases with an increase in moisture content of concrete. Brown and Javaid[4] reported that the specific heat of normal strength concrete varied from 1130.4 to 879.2 J/(kg K) at the ages from 6 h to 7 days, respectively. Schutter and Taerwe[5] measured the specific heat of hardening cement paste samples made with blast furnace slag cement and found that the specific heat decreases linearly with the degree of hydration. Xu and Chung[6] reported that adding sand decreases the specific heat of mortars with and without silica fume by 11% and 13%, respectively.

In mass concrete, fly ash is used to replace cement and hence reduce the heat from the hydration reaction, thus preventing thermal cracking. In order to predict the temperature of mass concrete, the specific heat of fly-ash concrete must be accurately obtained. Many studies on the specific heat of concrete have been conducted and equations for predicting the specific heat of concrete have been proposed[5,7]. It was found that all of the proposed equations predict a decrease of the specific heat during hardening but the effect of fly ash has not been included. Some researchers[8,9] have found that the specific heat of concrete c at age t could be obtained from

$$c(t) = m_\mathrm{g} c_\mathrm{g} + m_\mathrm{s} c_\mathrm{s} + m_\mathrm{p} c_\mathrm{p}(t) \tag{1}$$

where c_i and m_i are the specific heat and mass fractions of component i, and g, s, and p denote coarse aggregate, sand, and paste, respectively. Note that the effect of fly ash has not been included in the model.

During the reaction process, the specific heat changes with respect to time. The amount of free water in concrete decreases with the increase in the degree of reaction. As the specific heat of water is the highest among all ingredients of concrete, the specific heat of concrete decreases rapidly at the early stage of reaction when there is a rapid decrease of the amount of free water. The constant specific heat values of matured concrete have been traditionally used in the analysis of thermal cracking problems[10,11]. However, this is not realistic, especially during very early age where the specific heat varies significantly. As a result, this study proposes a model for predicting the specific heat of fly-ash concrete as a function of time, material, and mix proportion. The objective is to adopt the proposed model for simulating thermal cracking of mass concrete.

MATERIALS AND METHODS

Mix proportion and materials

Ordinary Portland cement and lignite fly ash were used as cementitious materials. In the case of paste, various values of water to binder ratio by mass (w) and fly ash to binder ratio by mass (r) were used. We denote a mixture with w of 0.25 and r of 0.30 by w25r3. For mortar, w and r were fixed at 0.4 and 0. Two different types of fine aggregate (natural river sand and crushed limestone sand) were used in this study. Several values of natural river sand to binder ratio by mass (s) and crushed limestone sand to binder ratio by mass (g) were used. We denote a mixture with w of 0.4 and s of 1 by w40s1. Pastes and mortars were tested at 7 and 28 days of age. Some mixtures of cement, fly-ash pastes, and mortars (w25r5, w40s1, w40s3 and w40g3) were also tested at 1 and 3 days of age to investigate the specific heat at early age.

Specimen preparation and test procedure

All samples were cast in PVC pipes (diameter 2.5 cm, length 5.0 cm). After casting, the specimens were covered with aluminium foil in order to prevent the loss of moisture. After one day, the pipes were removed and all specimens were firmly wrapped in aluminium foil in order to prevent the evaporation of water and to simulate the physical condition of the specimens inside the mass concrete (no moisture loss or gain). The seams of the aluminium foil were sealed by using an adhesive to prevent the leakage of water into the specimens during testing. The specimens were tested without removing the wrapped aluminium foil. The specimens were kept in the room temperature (28 ± 2 °C) and in seal-curing condition.

Two specimens were cast for each mixture and a thermocouple was installed either at the centre, or at mid-height but near the side face (0.5 cm from the surface of the specimens) of each. This location takes into account the non-uniform temperature that might occur within the specimen during the test. However, the test revealed later that the differences can be neglected. The specific heat, obtained from the tests, was then the average value obtained from the two specimens.

A test method to determine of the specific heat of hardened cement paste has been proposed[5] and our method was based on this. The specimens were submerged in hot water in an insulated container. The heat supplied to the specimens was obtained from the hot water. The temperature of the hot water and the specimens were simultaneously recorded every 30 seconds by using a data logger. The measurement was repeated 3 times for each pair of specimens and the average value was used. The specific heat was calculated from

$$c_{\mathrm{sp}} = \frac{M_{\mathrm{w}} c_{\mathrm{w}} (\Delta T_{\mathrm{w}} - \Delta T_{\mathrm{loss}}) - M_{\mathrm{f}} c_{\mathrm{f}} \Delta T_{\mathrm{f}}}{M_{\mathrm{sp}} \Delta T_{\mathrm{sp}}} \tag{2}$$

where M_i is the mass of component i, and w, sp, and f refer to the water, aluminium foil, and specimen, respectively. ΔT_{w} is the temperature reduction of water, ΔT_{sp}, ΔT_{f} are the temperature increase of specimen and aluminium foil, and ΔT_{loss} is the temperature reduction of water due to loss of heat to the environment. Due to the very low heat capacity of the aluminium foil (very thin and small mass), the effect of the aluminium foil can be neglected in the calculation of specific heat of the specimens.

The tests were conducted at 25 ± 1 °C. In order to measure ΔT_{loss}, the system with water only was used to record the temperature change of the water due to loss into the environment. The temperature was recorded by using a data logger at an interval of 30 s. This calibration was done 3 times and the average value was calculated.

Specific heat model

By using the same principle as shown in (1), we propose using the following equations for estimating the value of specific heat of pastes, mortars and concrete:

$$\begin{aligned} c(t) = m_{\mathrm{g}} c_{\mathrm{g}} + m_{\mathrm{s}} c_{\mathrm{s}} + m_{\mathrm{fw}}(t) c_{\mathrm{w}} + m_{\mathrm{uc}}(t) c_{\mathrm{c}} \\ + m_{\mathrm{ufa}}(t) c_{\mathrm{fa}} + m_{\mathrm{hp}}(t) c_{\mathrm{hp}} \end{aligned} \tag{3}$$

where fw, uc, ufa, and hp denote free water, unhydrated cement, non-reacted fly ash, and the products of hydration and pozzolanic reactions, respectively. The hydrated products consist of hydrated cement, reacted fly ash, water consumed by hydration, and pozzolanic reactions. Their mass fraction relation can be determined from

$$\begin{aligned} m_{\mathrm{hp}}(t) = 1 - m_{\mathrm{g}} - m_{\mathrm{s}} - m_{\mathrm{fw}}(t) - m_{\mathrm{uc}}(t) \\ - m_{\mathrm{ufa}}(t) \end{aligned} \tag{4}$$

$$m_{\mathrm{uc}}(t) = (1 - \alpha_{\mathrm{hy}}(t)) m_{\mathrm{c}}(0) \tag{5}$$

$$m_{\mathrm{ufa}}(t) = (1 - \alpha_{\mathrm{poz}}(t)) m_{\mathrm{fa}}(0) \tag{6}$$

$$m_{\mathrm{fw}}(t) = m_{\mathrm{w}}(0) - m_{\mathrm{whp}}(t) - m_{\mathrm{wgel}}(t) \tag{7}$$

where wgel and whp denote gel water in paste and water consumed by hydration and pozzolanic reactions, α_{hy} and α_{poz} are the average degree of hydration of cement and the degree of pozzolanic reaction of fly ash, respectively. The time of mixing is $t = 0$. The effect of air was not considered in this model. The mass fraction of free water is defined as the mass fraction of water excluding water consumed by the hydration and pozzolanic reaction.

As the reaction proceeds, the amount of free water in concrete decreases and there is an increase in the amount of the reaction products as concrete turns from a fresh state to plastic and then hardened states. Hence the specific heat of concrete decreases with time. As coarse and fine aggregates are inert materials, their mass fractions and specific heat remain constant throughout the reaction period. At the same time, the volume of non-reacted cementitious materials (the cement and fly ash) and free water decreases and the amount of reacted product increases. The details of free water determination are adopted from Tangtermsirikul et al[12].

The average degree of hydration of cement is defined as the mass-averaged degree of hydration of four major oxide compounds in cement, whereas the degree of pozzolanic reaction of fly ash is defined as the mass fraction of already reacted fly ash to total fly ash. The four major oxide compounds in cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF)[3]. The average degree of hydration and degree of pozzolanic reaction depends on the water to cement ratio, concrete temperature, and age[13,14]. Examples of average degree of hydration of cement pastes and the degree of pozzolanic reaction of cement pastes with fly ash are shown in Figs. 1 and 2.

The values of the specific heat of cement, fly ash, water, quartz sand, and limestone used in the analysis were 753.62, 711.76, 4186.8, 795.49, and 837.36 J/(kg K), respectively[7,15–17]. By using these values and (3), the specific heat of hydration and pozzolanic products was derived by using the method of regression analysis from the test results of specific heat of the tested pastes. The specific heat of the hydrated and pozzolanic products was found to be about 419 J/(kg K). By using (3) and the specific heat of the concrete ingredients, the specific heat of the tested pastes and mortars were computed.

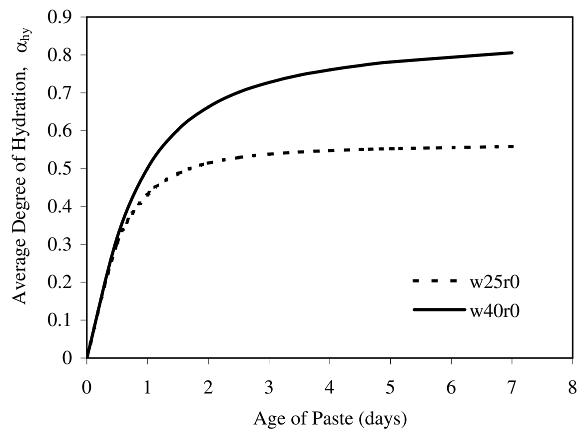

Fig. 1 Average degree of hydration of cement pastes with $w = 0.25$ and 0.40 at 28 °C (from Ref. 13).

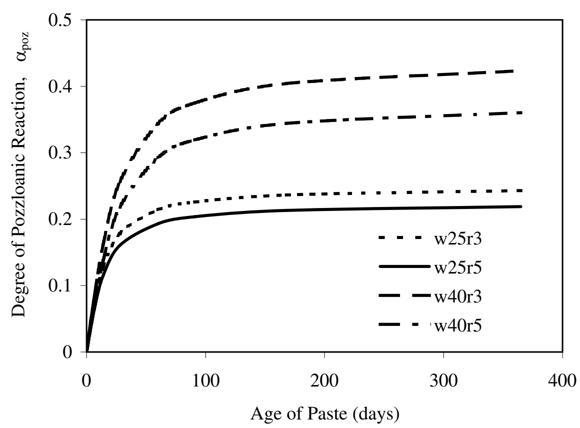

Fig. 2 Degree of pozzolanic reaction of cement-fly ash pastes with $r = 0.30$ and 0.50, and $w = 0.25$ and 0.40 at 30 °C (from Ref. 14).

RESULTS AND DISCUSSION

Effect of age

Of the ingredients, water has the highest specific heat. From the experimental results, it was found that the specific heat of pastes and mortars decreased with a decrease in the amount of free water. As the reaction proceeds, the amount of free water in paste decreases with an increase in the amount of hydrated products so that the specific heat of pastes and mortars decreases with age (Figs. 3 and 4). Many researchers have found that the increase in water content tended to increase the specific heat of concrete[3,7,8,17].

Effect of constituents

The effect of water to binder ratio is shown in Fig. 3a. Pastes with lower water content ($w = 0.25$) have

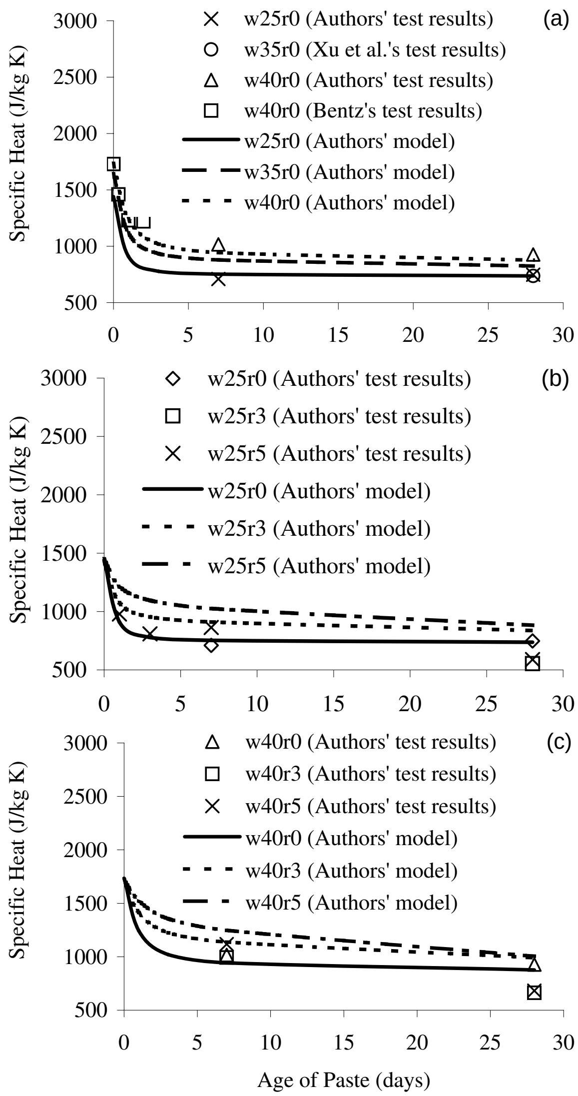

Fig. 3 Comparison between predicted and authors' and other researchers' test results of specific heat (a) cement pastes with $w = 0.25$, 0.35 and 0.40, (b) cement-fly ash pastes with $r = 0$, 0.3 and 0.5, and $w = 0.25$, (c) cement-fly ash pastes with $r = 0$, 0.3 and 0.5, and $w = 0.40$.

lower specific heat than those with higher water content ($w = 0.40$). The specific heat of water is much higher than that of cement, so lower w gives lower specific heat.

The effect of fly-ash content is shown in Figs. 3b and 3c. Specific heat of pastes with fly ash at young age is higher than that of cement paste but continues decreasing in a long term when compared to that of the cement paste. This is because the replacement of cement by fly ash causes relatively higher free (non-reacted) water content of mixtures at early age

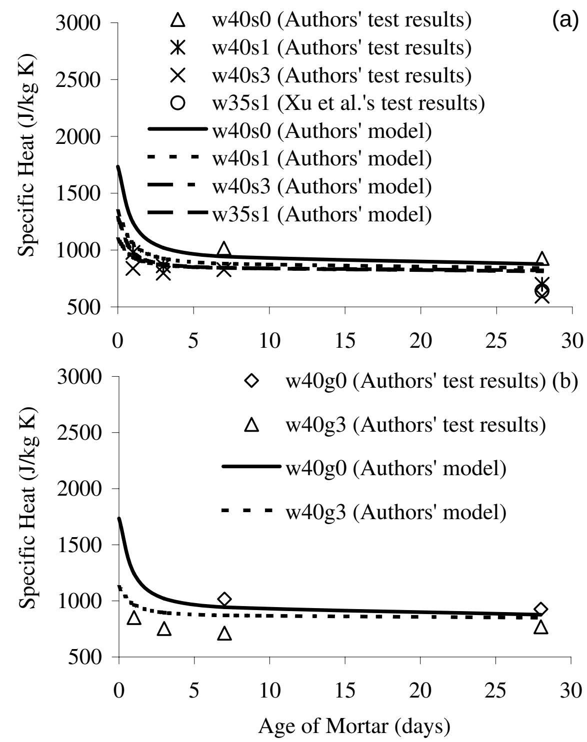

Fig. 4 Comparisons between predicted and authors' and Xu et al's test results of mortar (a) river sand mortars with $s = 0$, 1 and 3, and $w = 0.40$ and $s = 1$, and $w = 0.35$, (b) crushed limestone sand mortars with $g = 0$ and 3, and $w = 0.40$.

but tends to decrease at longer age due to pozzolanic reaction[12]. As the results, the specific heat of fly-ash cement paste has similar time-dependent tendency as the pozzolanic reaction. The higher specific heat of paste with fly ash at young age indicates that using fly ash to replace cement is beneficial to reduce the temperature of mass concrete and the generation of heat.

Fig. 4 shows the effect of content of river sand and crushed limestone sand on specific heat of mortars. The specific heat of cement paste is higher than that of the mortars because of its higher amount of free water content. Moreover, both river sand and crushed limestone sand have lower specific heat than water, so the specific heat of mortars are lower than that of the cement paste and the mixtures with higher aggregate content give smaller specific heat, consistent with previous experimental results[6].

Verification of specific heat model

It can be seen that the specific heat model is nearly quantitatively satisfactory in predicting the specific

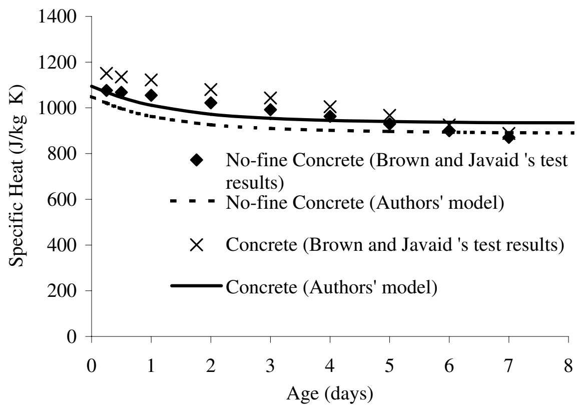

Fig. 5 Comparisons between predicted and Brown and Javaid's test results specific heat of no-fine concrete and concrete.

heat of the tested pastes and mortars (Figs. 3 and 4). The model shows that the pastes with higher free water content have higher specific heat than those with lower free water content (Fig. 3a). The model also shows that the specific heat of pastes with fly ash has a tendency to continue decreasing in long term when compared to that of the cement paste (Figs. 3b and 3c). The model is able to predict the lower values of specific heat of mortars relative to that of the cement paste (Fig. 4). The proposed model also agreed with test results from other researchers. As shown in Fig. 5, the model was compared with the test results obtained by Brown and Javaid[4] in which no-fine concrete and concrete were prepared and tested at the age of 0.25, 0.5, 1, 2, 3, 4, 5, 6, and 7 days. The mix proportions can be obtained from Ref. 4. The model was also verified with the test results obtained by Xu and Chung[6] (Figs. 3a and 4a), in which cement paste and mortar were tested at 28 days. The w was 0.35 for cement paste and mortar. The s was 1.0 for mortar. The model was compared with the test results conducted by Bentz[7] in which cement paste ($w = 0.4$) was prepared and tested at various ages (Fig. 3a). It was found that the proposed model can simulate the trend of specific heat of tests quite well.

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