Chapter 5
Model of Specific heat of Concrete

5.1 General

Specific heat or heat capacity of concrete is an important parameter for computing temperature distribution in mass concrete. During the reaction process specific heat changes with respect to time. The amount of free water in concrete decreases with an increase in the degree of reaction. As shown in Table 5.1, specific heat of water is the highest among all ingredients of concrete. Specific heat of concrete is considered to decrease rapidly at the early stage of reaction with 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 (Isgor and Razaqpur, 2004; Kwak et al., 2006), however, this is not realistic especially during very early age where the specific heat varies significantly. Also, the effect of fly ash on specific heat of concrete has not been much studied in the past. As a result, the model for predicting the specific heat considering time, material and mix proportion dependent properties of fly ash concrete was proposed in this study.

5.2 Experimental Program

In this study, the test results conducted in the authors' previous study (Jitvturikrai, 2000) is used in the analysis. A test method to determine specific heat of hardened cement paste proposed by Schutter and Taerwe (1995) was adopted to be used in the experiment. The details of the experiment are mentioned below.

5.2.1 Mix proportion and materials.

Ordinary Portland cement (OPC) and lignite fly ash were used as cementitious materials. The chemical compositions and physical properties of the cement and fly ash are shown in Appendix C (Table C1). Properties of fine aggregates are shown in Table C2. The mix proportions of the tested mixtures are shown in Table 5.2. Cement-fly ash pastes and mortars with two different types of fine aggregate (natural river sand and crushed limestone sand) were produced and tested at 7 and 28 days of age. In each set, ratio of water to binder (*w/b*) and replacement ratio of cement by fly ash (r) were varied. Cement-fly ash pastes were tested to observe the effect of water and fly ash contents. The *w/b* was varied at 0.25 and 0.4 and fly ash to binder ratio was varied at 0, 0.3 and 0.5. Mortars were tested to observe the effect of aggregates. Fine aggregate to binder ratio by weight was varied at 1 and 3. An example of description of the mixture designation is as follow; "w25r3" means paste which has *w/b* of 0.25 and fly ash replacement ratio (r) of 0.30. Some mixtures of cement-fly ash pastes and mortars (mixtures number 2, 7, 8 and 9 in Table 5.2) were also tested at 1 and 3 days of age to investigate the specific heat of the pastes and mortars at early age. All samples were cast in PVC pipes which have 2.5-cm diameter and 5.0-cm length. After casting, the specimens were covered with aluminum foil in order to prevent the loss of moisture to the surrounding. After one day, the pipes were removed and all specimens were firmly wrapped by using aluminum foil in order to prevent the evaporation of water and to simulate the physical condition of the specimens to be similar to that inside the mass concrete (no moisture loss or gain). The seams of the aluminum 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 aluminum foil. Because the aluminum foil was very thin (0.02 mm.) and the foil had very high heat conductivity when compared to paste and mortar (190 kcal/m hr ^{o}C) (ASHRAE, 1993), the effect of aluminum foil on the specific heat of specimen can be neglected. The specimens were kept in the room temperature (28 $\pm$ 2 ^{o}C) and in seal-curing condition.

5.2.2 Specimen preparation and test procedure

Two specimens were cast for each mixture. For the first specimen, thermocouple was installed at the center of the specimen while for the second specimen thermocouple was placed mid height but near the side face (0.5 cm. from the surface of the specimens). The positions of the thermocouples are shown in Fig 5.1a. This effort was made firstly for taking into account the non-uniform temperature that might occur within the specimen during the test. However, it was found later from the test that the differences can be neglected. The specific heat, obtained from the tests, was then the average value of the two specimens. The apparatus and its setting for testing specific heat are shown in Figs 5.1b to 5.1d.

Table 5.1 Specific heat of the ingredients of concrete

Ingredients	Specific Heat (kcal/kg ^{o}C)
Cement	0.18 (Bentz, 2007)
Fly Ash	0.17 (Krishnaiah and Singh, 2006)
Water	1.00 (Schutter and Taerwe, 1995)
Quartz Sand	0.19 (ASHRAE, 1993)
Limestone	0.20 (Klieger and Lamond, 1994)
Air	0.24 (Rolle, 2000)
Hydrated Products	0.10*

* The value was obtained from regression analysis in this study.

Table 5.2 Mix proportions of the tested cement-fly ash pastes and mortars

Mix No.	Mixture Code	w/b	r	s/b	g/b
1	w25r0	0.25	0	0	0
2	w25r3	0.25	0.3	0	0
3	w25r5	0.25	0.5	0	0
4	w40r0	0.40	0	0	0
5	w40r3	0. 40	0.3	0	0
6	w40r5	0. 40	0.5	0	0
7	w40s1	0.40	0	1	0
8	w40s3	0.40	0	3	0
9	w40g3	0.40	0	0	3

Remarks: w/b: water to binder ratio, r: fly ash replacement ratio, s/b: natural river sand to binder ratio and g/b: crushed limestone sand to binder ratio.

From a previous study (Schutter and Taerwe, 1995), a test method to determine the specific heat of hardened cement paste was proposed. The specific heat was determined by measuring the temperature rise of the paste sample in a calorimeter caused by a certain energy supply. By using the same principle, the specimens were submerged in hot water in an insulated container. The heat supplied to the specimens was obtained from the hot water. Temperature of the hot water and the specimens were simultaneously recorded every thirty seconds by using a data logger. The measurement was conducted three times for each pair of specimens then the average value was used. The calculation of specific heat is shown in Eq. (5.1) to Eq. (5.3).

$$Q_w - Q_{loss} = Q_{sp} \tag{5.1}$$

$$m_w c_w \Delta T_w - m_w c_w \Delta T_{loss} = m_{sp} c_{sp} \Delta T_{sp} \tag{5.2}$$

$$c_{sp} = \frac{m_w c_w \left(\Delta T_w - \Delta T_{loss}\right)}{m_{sp} \Delta T_{sp}} \tag{5.3}$$

where Q_w is the total heat loss from water (kcal), Q_{loss} is the heat loss from water to the environment (kcal), Q_{sp} is the heat intake into the specimens (kcal). m_w and m_{sp} are the mass of water and specimen, respectively (kg). c_w and c_{sp} are the specific heat of water and specimen, respectively (kcal/kg ^oC). ΔT_w is the total temperature reduction of water (^oC), ΔT_{sp} is the temperature increase of specimen (^oC), and ΔT_{loss} is the temperature reduction of water due to loss of heat to the environment (^oC).

The tests were conducted in a room where temperature was controlled at 25 $\pm$ 1 ^oC. In order to measure temperature loss (ΔT_{loss}), the system with water only was used to record the temperature change of the water due to heat loss to the environment. The temperature was recorded by using data logger at an interval of thirty seconds. This calibration was done three times then the average value was calculated.

5.3 Experimental Results

5.3.1 Effect of age

As shown in Table 5.1, specific heat of water is the highest when compared to those of the other ingradients in concrete. From the experimental results, it was found that the specific heat of concrete decreased with a decrease in the amount of free water in concrete. As the reaction proceeds, the amount of free water in paste reduces with an increase in the amount of hydrated products so that the specific heat of paste decreases with age as can be seen from Figs. 5.2 and 5.3. Many researchers found that the increase in water content tended to increase the specific heat of concrete (Neville, 1995; Bentz, 2007; Waller et al., 1996; Klieger and Lamond, 1994)

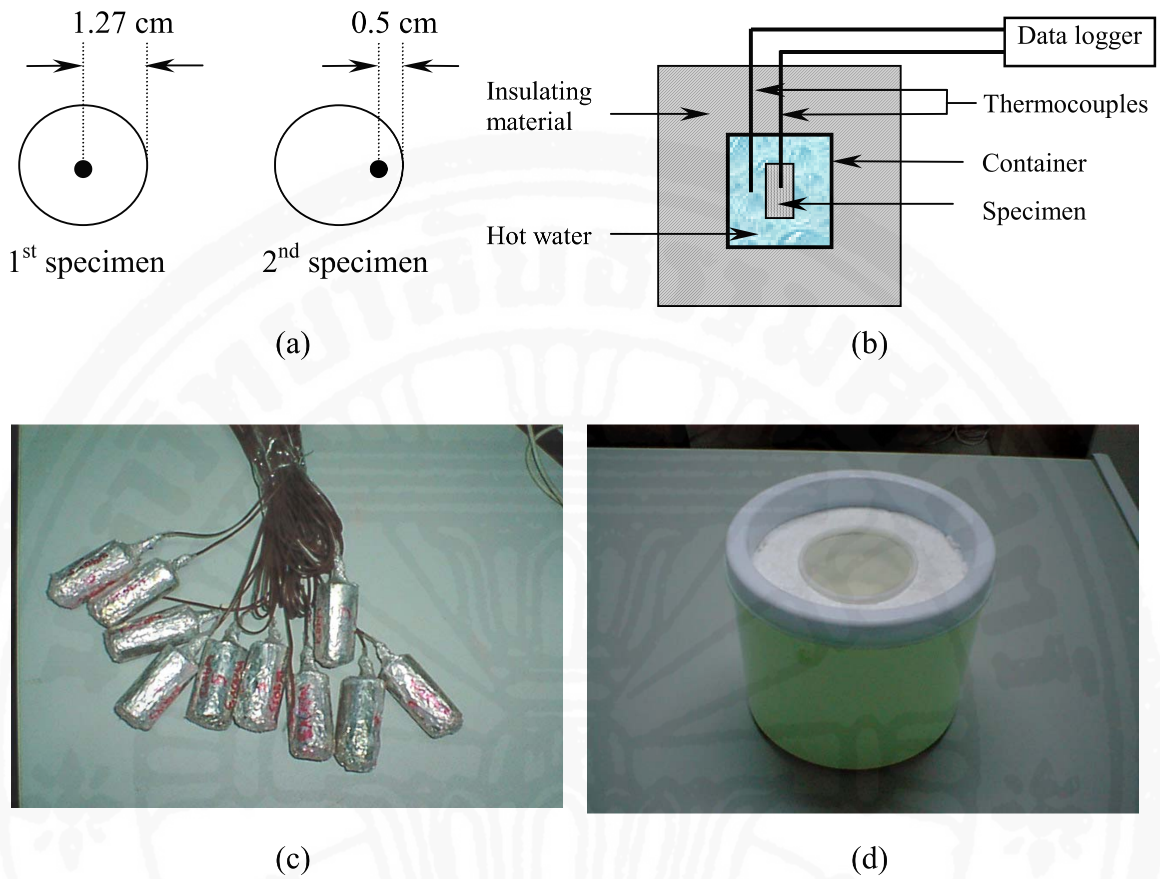

Fig 5.1 Apparatus for testing the specific heat (a) Positions of thermocouples, (b) Schematic illustration, (c) Sealed Specimens, (d) Insulated Container

5.3.2 Effect of *w/b*

The effect of water to binder ratio is shown in Fig. 5.2. Paste with lower water to binder ratio (*w/b* = 0.25) has lower specific heat than that with higher water content (*w/b* = 0.40). The specific heat of water is much higher than that of cement, so lower *w/b* gives lower specific heat.

5.3.3 Effect of fly ash

The effect of fly ash content is shown in Figs. 5.3 and 5.4. Specific heat of pastes with fly ash at young age is higher than that of cement paste but continues decreasing in 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 but tends to decrease at longer age due to pozzolanic reaction (Tangtermsirikul and Saengsoy, 2002). 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 fly ash is beneficial as cement replacing material to reduce temperature of mass concrete in addition to the lower heat generation.

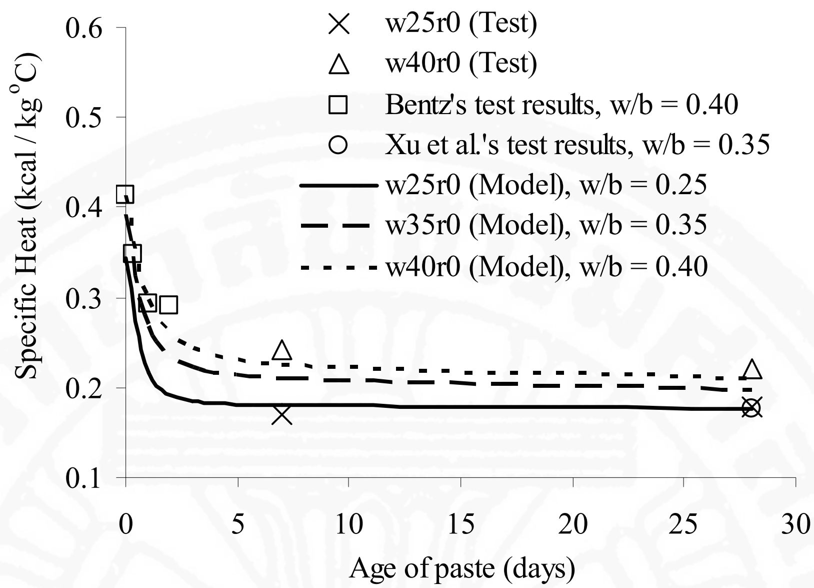

Fig 5.2 Comparison between predicted and authors' and other researchers 's test results of specific heat of cement pastes with *w/b* = 0.25, 0.35 and 0.40

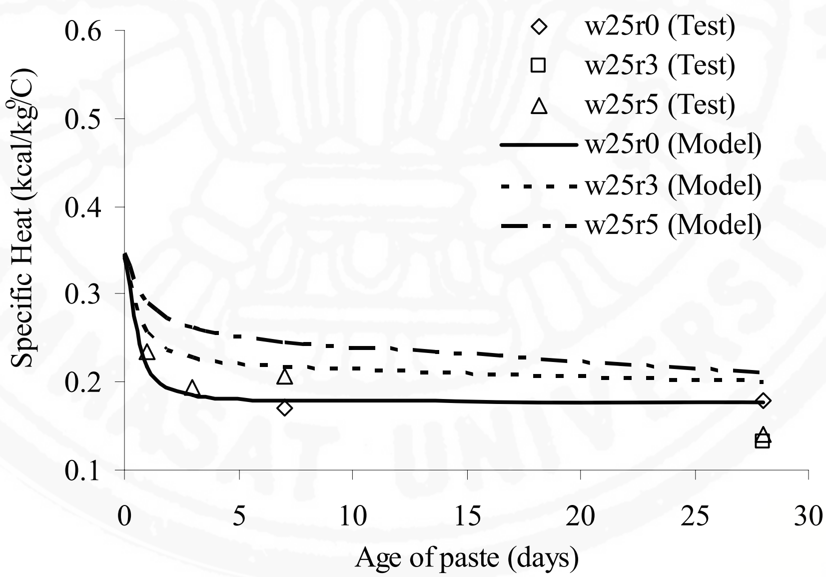

Fig 5.3 Comparison between predicted and test results of specific heat of cement-fly ash pastes with fly ash replacement ratios of 0, 0.3 and 0.5, and *w/b* = 0.25

5.3.4 Effect of fine aggregates

Figs 5.5 and 5.6 show 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.

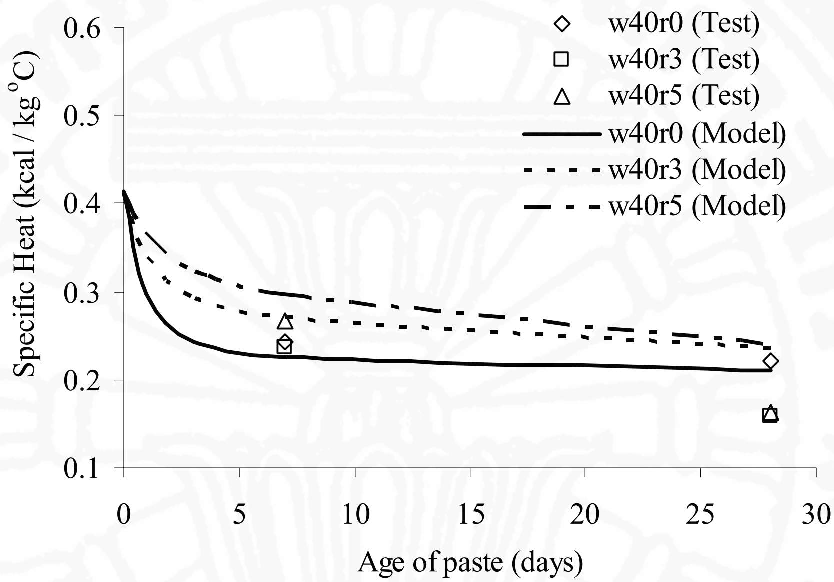

Fig 5.4 Comparison between predicted and test results of specific heat of cement-fly ash pastes with fly ash replacement ratios of 0, 0.3 and 0.5, and *w/b* = 0.40

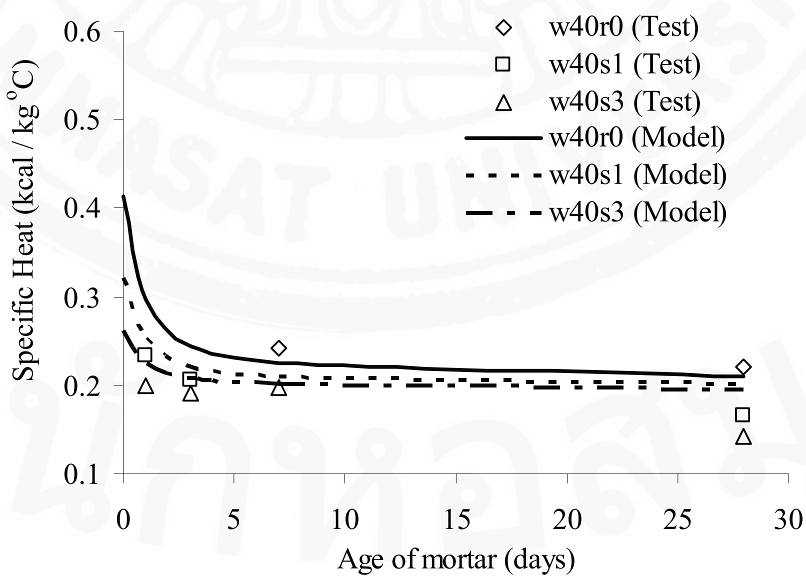

Fig 5.5 Comparison between predicted and test results of river sand mortars with *s/b* = 0, 1 and 3, and *w/b* = 0.40.

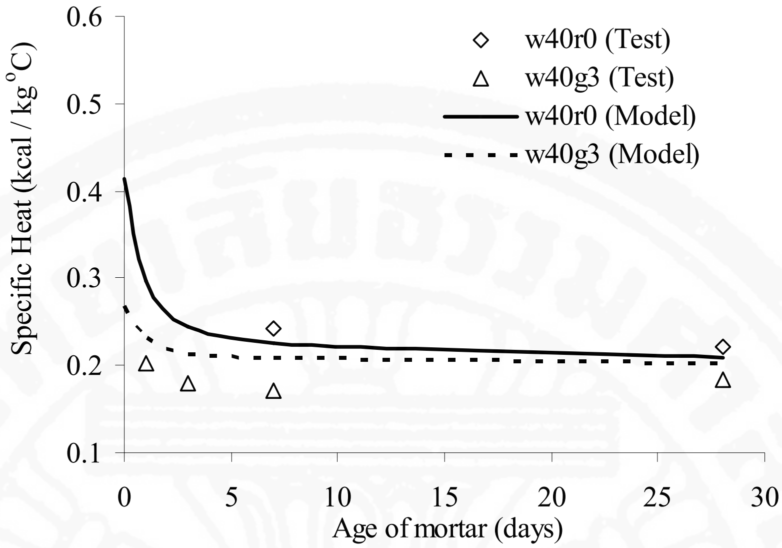

Fig 5.6 Comparison between predicted and test results of crushed limestone sand mortars with sand to binder ratios of 0 and 3, and *w/b* = 0.40

5.4 Specific Heat Model

Eq. (5.4) was proposed for estimating the value of specific heat of pastes, mortars and concrete. The specific heat of concrete was assumed to be computed based on the weight fraction of the ingredients and their individual specific heat. The ingredients include the still non-reacted cementitious materials, aggregates, free water, air and the hydrated and pozzolanic products. Their weight fraction relation can be determined as shown in Eq. (5.5). Because the weight of air is small, the weight of air is assumed to be zero. The weight fractions of unhydrated cement and non-reacted fly ash are calculated based on the average degree of hydration reaction of cement and the degree of pozzolanic reaction of fly ash as shown in Eq. (5.9) and Eq. (5.10), respectively. The details of the determination of the weight fractions of free water are shown in Eq. (5.13) and Chapter 4 (Eq. 4.1). The details of degree of hydration and degree of pozzolanic reaction are described in Chapter 3.

$$c(t) = w_g c_g + w_s c_s + w_{ra} c_{ra} + w_{fw}(t) c_w + w_{uc}(t) c_c + w_{ufa}(t) c_{fa} + w_{hp}(t) c_{hp} \quad (5.4)$$

$$w_{hp}(t) = 1.0 - (w_g + w_s + w_{fw}(t) + w_{uc}(t) + w_{ufa}(t)) \quad (5.5)$$

$$w_g = \frac{W_g}{UW_{con}} \quad (5.6)$$

$$w_s = \frac{W_s}{UW_{con}} \quad (5.7)$$

$$w_{ra} = \frac{W_{ra}}{UW_{con}} \quad (5.8)$$

$$w_{uc}(t) = (1 - \frac{\alpha_{hy}(t)}{100})w_{c0} \tag{5.9}$$

$$w_{ufa}(t) = (1 - \frac{\alpha_{poz}(t)}{100})w_{fa0} \tag{5.10}$$

$$w_{c0} = \frac{W_{c0}}{UW_{con}} \tag{5.11}$$

$$w_{fa0} = \frac{W_{fa0}}{UW_{con}} \tag{5.12}$$

$$w_{fw}(t) = \frac{W_{fw}(t)}{UW_{con}} = \frac{W_{fw0} - W_{whp}(t) - W_{wgel}(t)}{UW_{con}} \tag{5.13}$$

where c(t) is the specific heat of concrete at the considered age (kcal/ kg ^{o}C), w_g, w_s and w_{ra} are the weight fractions of coarse aggregate, fine aggregate and air, respectively, $w_{fw}(t)$, $w_{uc}(t)$, $w_{ufa}(t)$, and $w_{hp}(t)$ are the weight fractions of free water, unhydrated cement, non-reacted fly ash, and the products of hydration and pozzolanic reactions, respectively, at the considered age. w_{c0} and w_{fa0}, are the weight fractions of cement and fly ash at the time of mixing (at t = 0). $W_{wgel}(t)$ and $W_{whp}(t)$ are the weights of gel water in paste and water consumed by hydration and pozzolanic reactions at the considered age (kg/m^3 of concrete). W_g, W_s and W_{ra} are the weight of coarse aggregate, fine aggregate and air, respectively (kg m^3 of concrete), W_{c0}, W_{fa0}, and W_{fw0} are the weight of cement, fly ash and water at the time of mixing (at t = 0) (kg/m^3 of concrete). UW_{con} is the unit weight of concrete (kg/m^3 of concrete), c_g, c_s, c_{ra} c_w, c_c, c_{fa}, and c_{hp} are the values of specific heat of coarse aggregate, fine aggregate, air water, cement, fly ash, and the products of hydration and pozzolanic reactions, respectively (kcal/ kg ^{o}C). $\alpha_{hy}(t)$ and $\alpha_{poz}(t)$ are the average degree of hydration of cement and the degree of pozzolanic reaction of fly ash, respectively, at the considered age. t is the considered age (days).

As the reaction proceeds, the amount of free water in concrete reduces with an increase in the amount of the products of reactions and concrete converts from a fresh state to plastic and hardened states. So the specific heat of concrete decreases with time. As coarse aggregate, and fine aggregate are inert materials, their weight fractions remain constant throughout the reaction period. At the same time the volume of non-reacted cementitious materials (e.g. cement and fly ash) and free water reduces and the amount of reaction product increases with time.

The values of specific heat of other ingredients of concrete except for that of the hydration and pozzolanic products were obtained from previous studies as shown in Table 5.1. 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 paste samples and Eq. (5.4) together with the values of specific heat of concrete ingredients in Table 5.1. The specific heat of hydrated and pozzolanic products obtained from the back calculation was found to be about 0.10 kcal/ (kg ^{o}C).

5.5 Verification of Specific Heat Model

By using Eq. (5.4), and the specific heat of the ingredients of the concrete in Table 5.1, the specific heat of the tested pastes and mortars were computed. The comparison between the analytical results and the experimental results are shown in Figs. 5.2 to 5.6. It is shown in the figures that the specific heat model is nearly quantitatively satisfactory to predict the specific heat of the tested pastes and mortars. The model shows, in Fig. 5.2, that the pastes with higher free water content (w/b = 0.4) have higher specific heat than those with lower free water content (w/b = 0.25). The model also shows, in Figs. 5.3 and 5.4, 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 5.5 and 5.6 show that the proposed model is able to predict the lower values of specific heat of mortars relative to that of the cement paste.

The proposed model was also verified with test results from other researchers. As shown in Fig. 5.7, the model was compared with the test results conducted by Brown and Javaid (1970) 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 tested mix proportions are shown in Appendix C (Table C3). The model was also verified with the test results conducted by Xu and Chung (2000) as shown in Figs. 5.2 and 5.8, in which cement paste and mortar were tested at 28 days. The w/b was 0.35 for cement paste and mortar. The sand to binder ratio (s/b) was 1.0 for mortar. In Fig. 5.2, the model was also compared with the test results conducted by Bentz (2007) in which cement paste (w/b = 0.4) was prepared and tested at various ages. It was found that the proposed model can simulate the trend of specific heat of the authors' and the other researcher's test results with a certain degree of satisfaction.

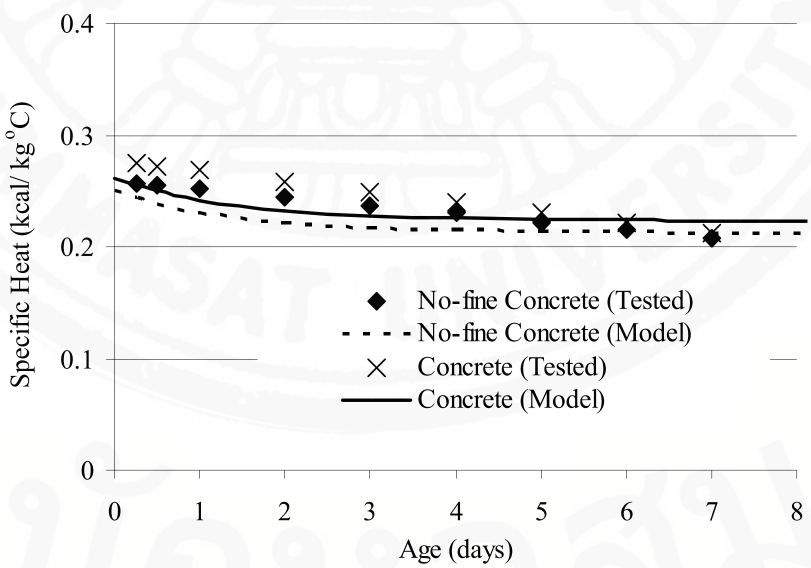

Fig 5.7 Comparison between predicted and Brown and Javaid's test results specific heat of no-fine concrete and concrete

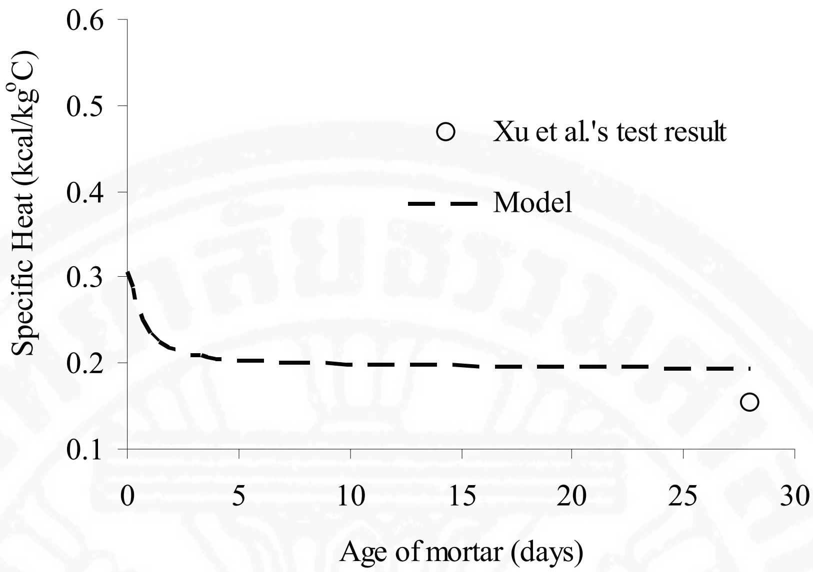

Fig 5.8 Comparison between predicted and Xu et al.'s test result of river sand mortar with *s/b* = 1, and *w/b* = 0.35.