Chapter 3
Computerized Model for Predicting Adiabatic Temperature of Mass Concrete

3.1 General

In order to predict the temperature of mass concrete, the rate of heat generated from hydration reaction and pozzolanic reaction must be predictable. Several mathematical models (Poppe and Schutter, 2006; Cervera et al., 2002; Evsukoff et al., 2006; Bentz et al., 1998; Meinhard and Lackner, 2008; Schutter and Taerwe, 1995; Maekawa et al. 1999 and Saengsoy and Tangtermsirikul, 2003) were formulated and most of the heat models were computed based on the degree of hydration reaction and pozzolanic reaction as well as the maximum heat generated from each cement compound, etc. However, only few models (Saengsoy., 2002) and Maekawa et al., 1999) considered the effect of fly ash. Saengsoy. (2002) proposed a model for predicting the adiabatic temperature rise of mass concrete and some parts of the model were modified in this study in order to improve the accuracy and to take into account the physical accretion of fly ash especially for the use of high volume fly ash. The model included quantitative estimation of degree of reactions, free water content, specific heat and then temperature of concrete in adiabatic condition. The details of the model are explained in this chapter. The heat obtained from the adiabatic condition was used as the input in the model to predict semi-adiabatic temperature for mass concrete.

3.2 Determination of Degree of Hydration

Saengsoy (2002) proposed the model to predict the degree of hydration of each cement compound by incorporating the effect of water to binder ratio, concrete temperature and age. In her study, the degree of hydration of each cement compound at each constant concrete temperature can be formulated as a function of water to binder ratio and age as shown in Eq. (3.1) to Eq. (3.4). The constant values A, B, C, D, E, F, G and H) used in these equations are shown in Appendix A. The time step used in the model is one hour. In this study, the model was modified in order to increase the accuracy especially at early age. The factors η_{C3A} and η_{C3S} are shown in Eq. (3.5) and Eq. (3.6).

$$\alpha_{C_3A}(t) = \eta_{C3A} \cdot \frac{1-\exp[A \cdot \tan^{-1}\{B \cdot (w/b)^C \cdot t\}]}{1+\exp[\{D \cdot (w/b)^3 + E \cdot (w/b)^2 + F \cdot w/b + G\} \cdot \tan^{-1}(H \cdot t)]} \times 100 \quad (3.1)$$

$$\alpha_{C_3S}(t) = \eta_{C3S} \cdot \frac{1-\exp[\{A/(B+\exp(C \cdot w/b))\} \cdot \tan^{-1}(D \cdot t)]}{1+\exp[\{E \cdot (w/b)^3 + F \cdot (w/b)^2 + G \cdot w/b + H\} \cdot t^{\{I/(J+\exp(K \cdot w/b))\}}]} \times 100 \quad (3.2)$$

$$\alpha_{C_2S}(t) = \frac{1-\exp[\{A/(B+\exp(C \cdot w/b))\} \cdot \tan^{-1}\{D \cdot (w/b)^E \cdot t\}]}{1+\exp[F \cdot t^G]} \times 100 \quad (3.3)$$

$$\alpha_{C_4AF}(t) = \frac{1-\exp[A \cdot \tan^{-1}\{B \cdot (w/b)^C \cdot t\}]}{1+\exp[\{D \cdot (w/b)^3 + E \cdot (w/b)^2 + F \cdot w/b + G\} \cdot \tan^{-1}\{H \cdot (w/b)^I \cdot t\}]} \times 100 \quad (3.4)$$

where, $\alpha_{C_3A}(t)$, $\alpha_{C_3S}(t)$, $\alpha_{C_2S}(t)$, and $\alpha_{C_4AF}(t)$ are degrees of hydration at the considered age of C_3A, C_3S, C_2S, and C_4AF, respectively (%). w/b is water to binder ratio by weight and t is age of concrete (days).

$$\eta_{C3S} = 0.2\alpha_{C_3S}(t-1)^4 - 0.4\alpha_{C_3S}(t-1)^3 + 0.2\alpha_{C_3S}(t-1)^2 - 0.05\alpha_{C_3S}(t-1) + \left(\left(w/b \times \frac{W_c + W_f}{UW}\right) + 0.97\right) \tag{3.5}$$

$$\eta_{C3A} = -0.18\alpha_{C_3A}(t-1)^4 + 0.24\alpha_{C_3A}(t-1)^3 - 0.15\alpha_{C_3A}(t-1)^2 + 0.01\alpha_{C_3A}(t-1) + \left(\left(w/b \times \frac{W_c + W_f}{UW}\right) + 1\right) \tag{3.6}$$

where, $\alpha_{C_3A}(t-1)$ and $\alpha_{C_3S}(t-1)$ are degrees of hydration at one hour before the considered age of C_3A and C_3S (%). W_c and W_f are the weight of cement and fly ash, respectively (kg). UW is unit weight of concrete (kg).

It is remarked that the degree of hydration was proposed for each 10°C step of concrete temperature (i.e. 10, 20, and 30°C). To determine the degree of hydration at any constant concrete temperature in between those steps, the linearly interpolation was applied. The concept for taking into account the effect of continuous temperature variation on degree of hydration is given in section 3.8. Eqs (3.5) and (3.6) were proposed for the time step of one hour. For the time step less than one hour, Eqs (3.5) and (3.6) may need future modification.

Examples of degree of hydration of each cement compound at various concrete temperatures are shown in Fig. 3.1 to Fig. 3.4.

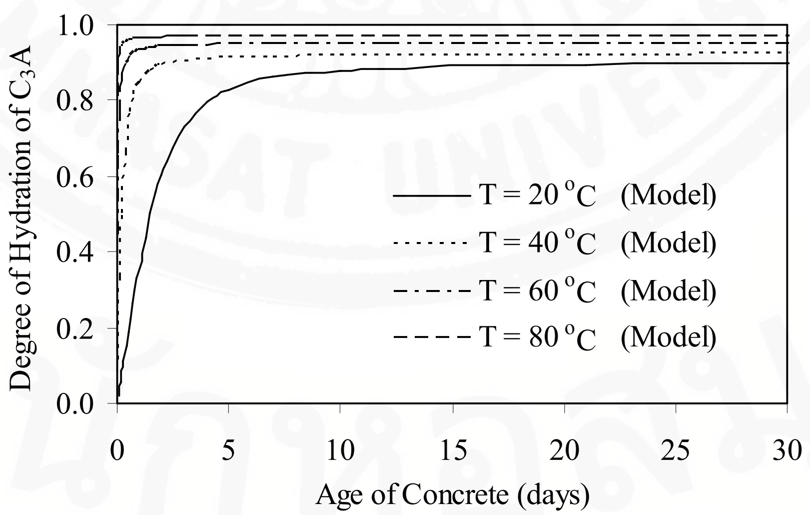

Fig. 3.1 Degree of hydration of C_3A of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

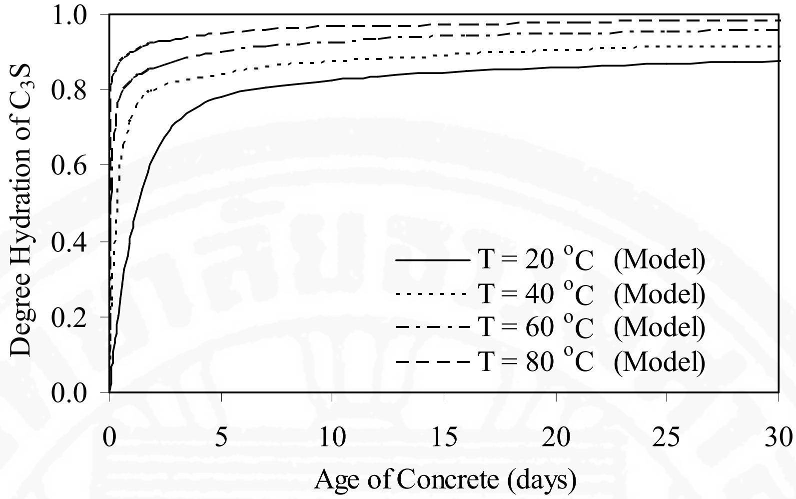

Fig. 3.2 Degree of hydration of C_3S of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

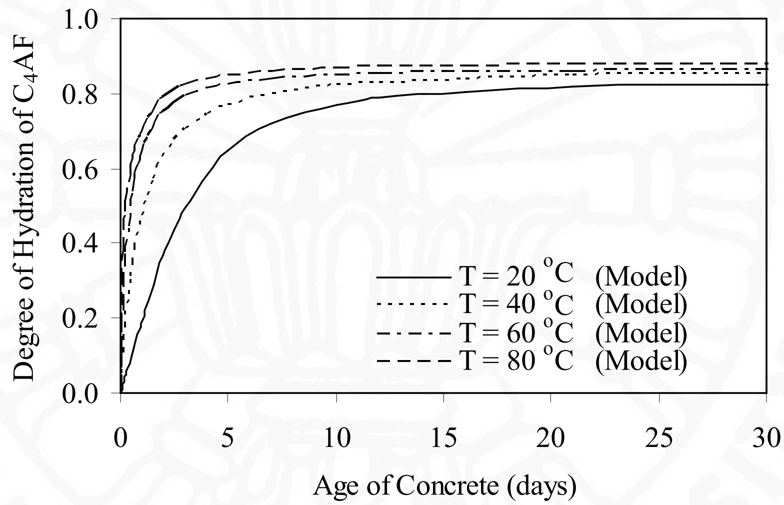

Fig. 3.3 Degree of hydration of C_4AF of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

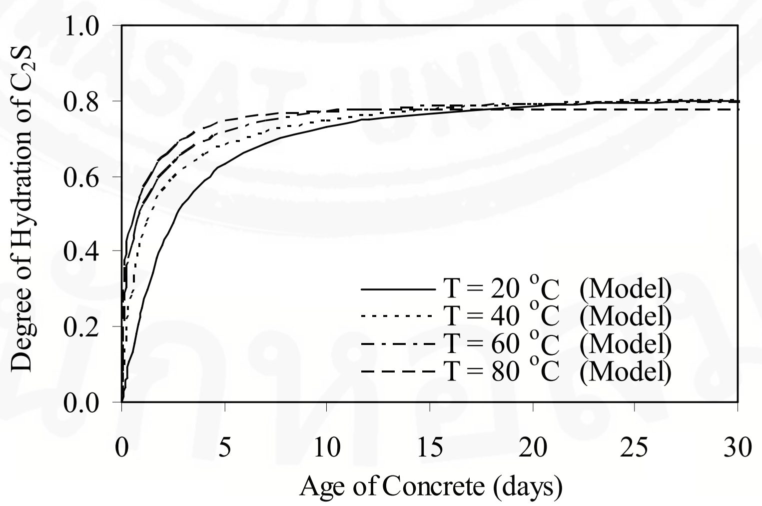

Fig. 3.4 Degree of hydration of C_2S of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

3.3 Verification of the Equations for Calculating Degree of Hydration

The proposed empirical formulas for determining degree of hydration were compared with that obtained from the multi component heat generation model (COMH3) proposed by Kishi and Maekawa (1996) and modified by Jitvutikrai (2000) as shown in Fig. 3.5 to Fig. 3.8.

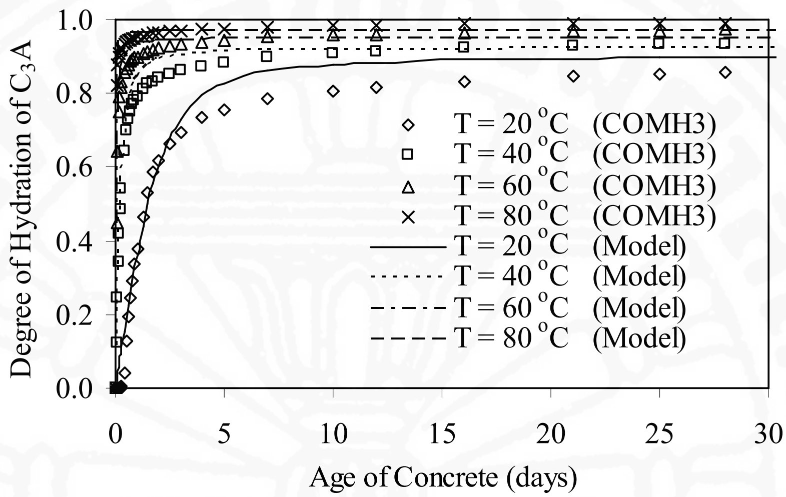

Fig. 3.5 Comparison between the degree of hydration obtained from proposed model and COMH3 of C_3A of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

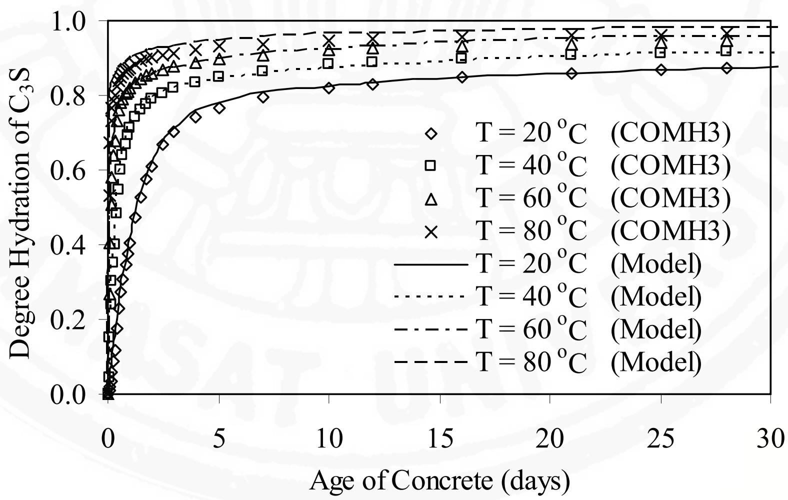

Fig. 3.6 Comparison between the degree of hydration obtained from proposed model and COMH3 of C_3S of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

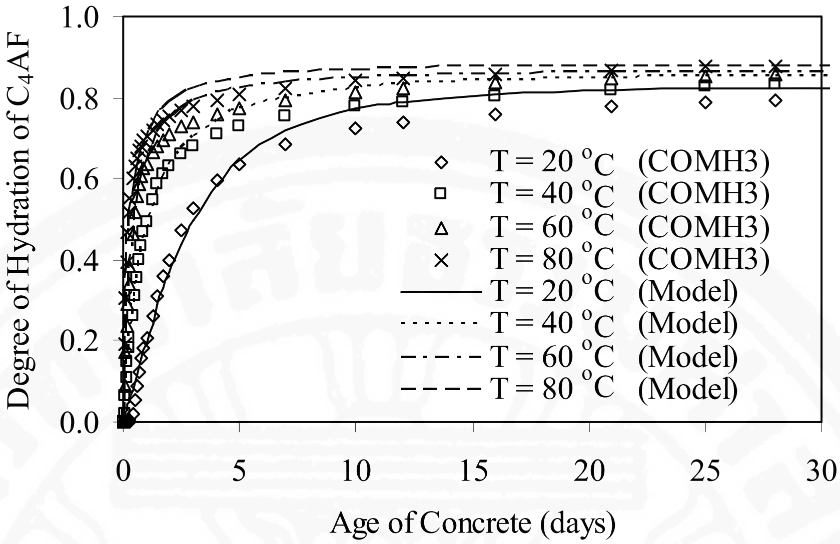

Fig. 3.7 Comparison between the degree of hydration obtained from proposed model and COMH3 of C_4AF of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

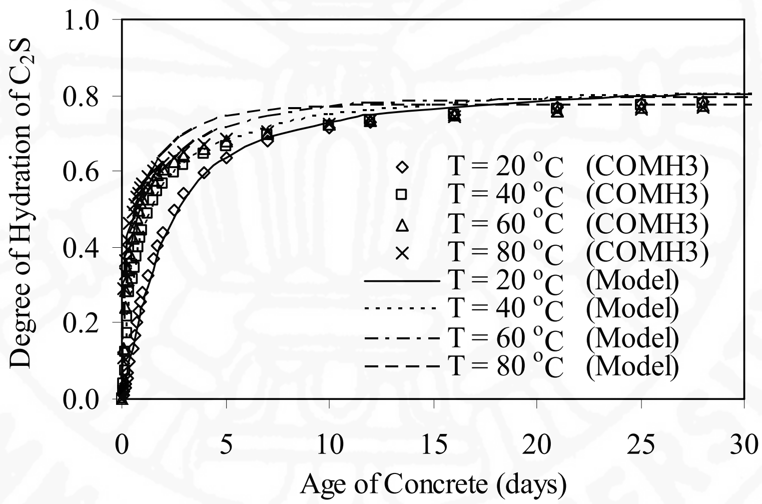

Fig. 3.8 Comparison between the degree of hydration obtained from proposed model and COMH3 of C_2S of concrete with w/b = 0.4 at 20, 40, 60, and 80°C

3.4 Average Degree of Hydration

The average degree of hydration of paste is defined as the weight fraction average of the degree of hydration of all cement compounds in the paste mixture.

By a simple assumption that hydration process of each cement compound (C_3S, C_2S, C_3A, C_4AF) is independent, the average degree of hydration of cement shown in Eq. (3.7) was introduced as a weight average of the rate of hydration of its constituents for convenient application of the model. Examples of average degree of hydration of pastes are shown in Fig. 3.9.

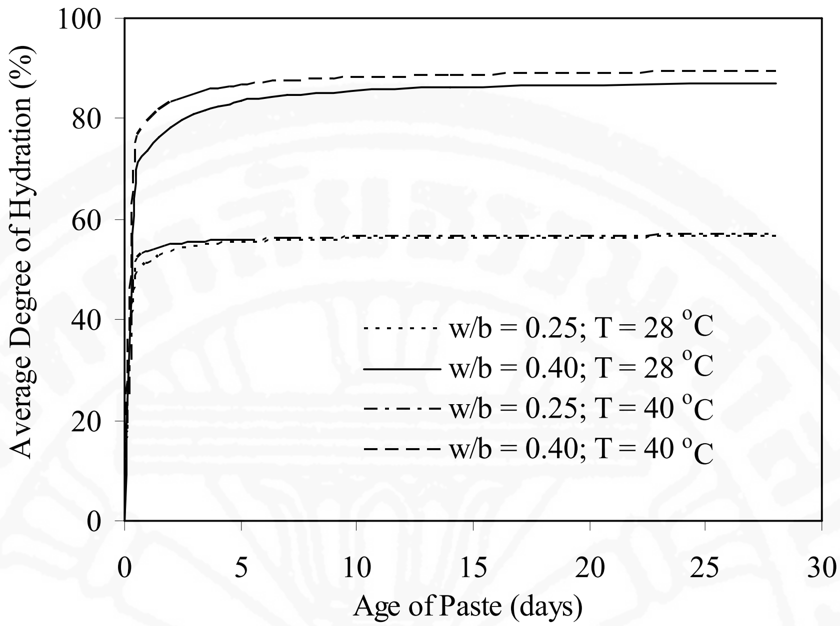

Fig. 3.9 Average degree of hydration of cement paste with w/b = 0.25 and 0.40 at 28°C and 40°C

$$\alpha_{hy}(t) = \frac{\sum_{i=1}^{4} m_i \alpha_i(t)}{\sum_{i=1}^{4} m_i} \tag{3.7}$$

where $\alpha_{hy}(t)$ is the average degree of hydration of cement (%), i is the mineral compound of cement (C_3S, C_2S, C_3A, C_4AF), m_i is the mass of each compound per cubic meter of cement paste (kg/m^3), and $\alpha_i(t)$ is the degree of hydration of each compound in the cement (%).

3.5 Verification for the Average Degree of Hydration

The degree of hydration of cement paste with various water to binder ratios tested by Lam et al. (2000) was adopted to be compared with the proposed average degree of hydration equation. In their test, the degree of hydration was obtained by determining the non-evaporable water content. The paste specimens were cast with the dimensions of 70.7 × 70.7 × 70.7 mm. and cured in water at 27°C. Therefore, the paste specimens were considered to have a constant temperature at 27°C in the calculation.

The comparison between the degree of hydration obtained from the proposed model and the test results obtained from Lam et al. (2000) is shown in Fig. 3.10.

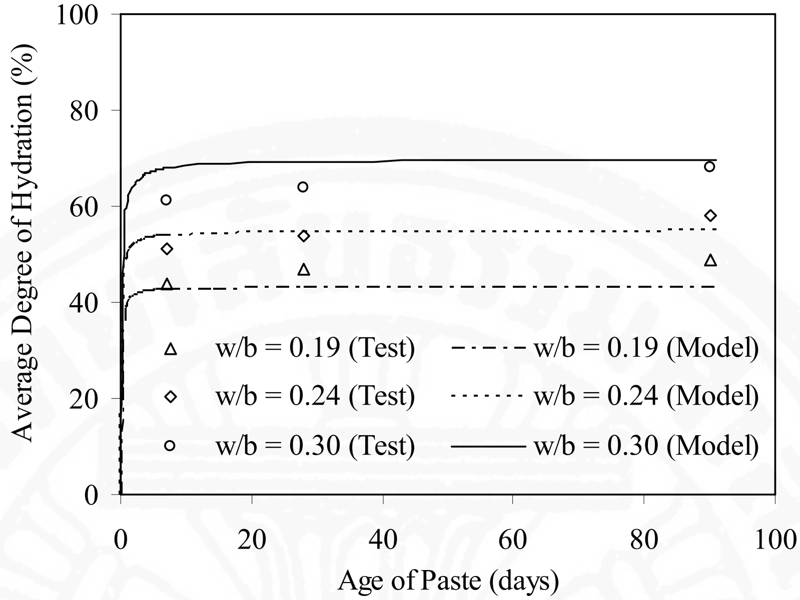

Fig. 3.10 Comparison between the average degree of hydration obtained from the proposed model and the test results of cement pastes with w/b = 0.19, 0.24 and 0.30 at 27°C (Lam et al., 2000)

3.6 Degree of Pozzolanic Reaction

Degree of pozzolanic reaction of paste is defined as the weight fraction of already reacted fly ash per total fly ash in the paste mixture.

The degree of pozzolanic reaction was considered affected by water to binder ratio, contents of calcium oxide and silicon dioxide in cement and fly ash, and fineness of fly ash (Tatong 2001). The equations of degree of pozzolanic reaction used in this study are shown in Eq. (3.8) to Eq. (3.13).

$$\alpha_{poz}(t) = \frac{\tan^{-1}[(0.049 \cdot T^{0.496} - 0.186 \cdot w/b - 0.135) \cdot t]}{\tan^{-1}[(0.049 \cdot T^{0.496} - 0.186 \cdot w/b - 0.135) \cdot 365]} \cdot \alpha_{poz}(365) \tag{3.8}$$

$$\alpha_{poz}(365) = \left[100 - \left\{ \begin{array}{l} (102 - 0.1 \cdot T) \cdot (0.416 + 0.0088 \cdot w/b^{-1.822}) \cdot \\ \tan^{-1}\left\{ (7.927 \cdot w/b^{-1.546} - 15.699) \cdot \left(\frac{SiO_2}{CaO_{eff}} - \frac{\%SiO_{2c}}{\%CaO_c} \right) \right\} \end{array} \right\} \right] \cdot \left[(1 - \%LOI/100) \cdot \{0.948 \cdot \tan^{-1} \cdot (7.227 \times 10^{-4} \cdot F_f)\}\right] \tag{3.9}$$

$$SiO_2 = [(W_c \cdot \%SiO_{2c}) + (W_f \cdot SiO_{2f})]/100 \tag{3.10}$$

$$CaO_{eff} = [(W_c \cdot \%CaO_c) + \varphi \cdot (W_f \cdot \%CaO_f)]/100 \tag{3.11}$$

$$\varphi = \frac{1 - \exp(-a \cdot \%CaO_f)}{1 + \exp(-a \cdot \%CaO_f)} \tag{3.12}$$

$$a = 0.0048 \cdot (F_f / 3000)^{3.0734} + 0.0245 \tag{3.13}$$

where $\alpha_{poz}(t)$, and $\alpha_{poz}(365)$ are the degree of pozzolanic reaction at any age of paste and at 365 days of paste, respectively (%). t is the considered age of paste (days), T is concrete temperature (°C), and w/b is the water to binder ratio. $\%CaO_c$, and $\%SiO_{2c}$ are calcium oxide content and silicon dioxide content in cement, respectively (% by weight of cement). $\%CaO_f$, and $\%SiO_{2f}$ are calcium oxide content and silicon dioxide content in fly ash, respectively (% by weight of fly ash). CaO_{eff} is the effective unit calcium oxide content in paste (kg/m^3). SiO_2 is the total silicon dioxide content in paste (kg/m^3). W_c, and W_f are weight of cement and fly ash in paste, respectively (kg/m^3). φ is effectiveness of calcium oxide in fly ash, and F_f is Blaine's fineness of fly ash (cm^2/g).

Examples of degree of pozzolanic reaction of pastes are shown in Fig. 3.11 and Fig. 3.12.

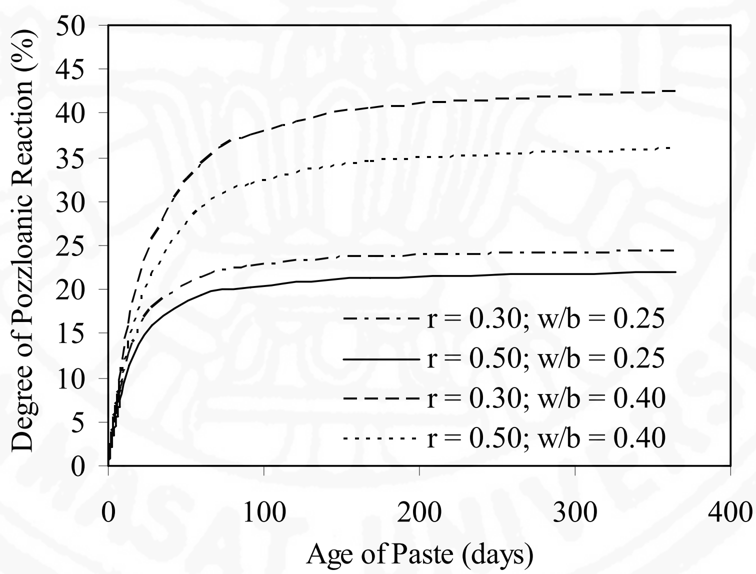

Fig. 3.11 Degree of pozzolanic reaction of paste with fly ash replacement ratio (r) of 0.30 and 0.50, and w/b = 0.25 and 0.40 at 28°C

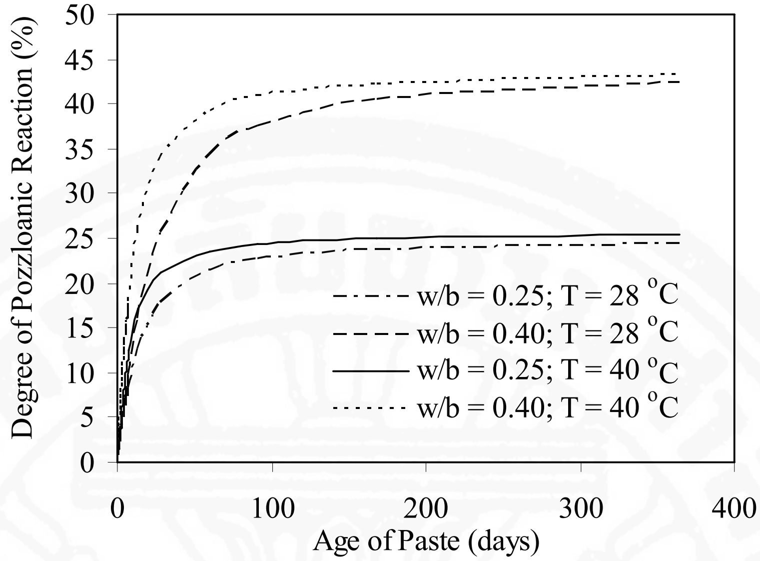

Fig. 3.12 Degree of pozzolanic reaction of paste with fly ash replacement ratio (r) of 0.30 and w/b = 0.25 and 0.40 at 28°C and 40°C

3.7 Effect of Fly Ash on Hydration Reaction

3.7.1 Dispersion effect of fly ash on hydration reaction

The addition of fly ash can accelerate cement hydration by the dispersion effect. The reduction of cement content reduces the total heat output from cement hydration but does not necessarily proportionally reduce the initial rate of heat evolution because fine powders are known to accelerate cement hydration. The initial rate of heat evolution of cement in fly ash concrete mixture increased progressively with increasing fly ash content. Bai et al. (2002) found the same phenomena when high volume fly ash was used. Saengsoy (2008) also found that the increase of the replacement ratio of fly ash accelerated the degree of hydration of cement in paste at early age (see Fig. 3.13). However, the difference of hydration reaction at later age was not significant.

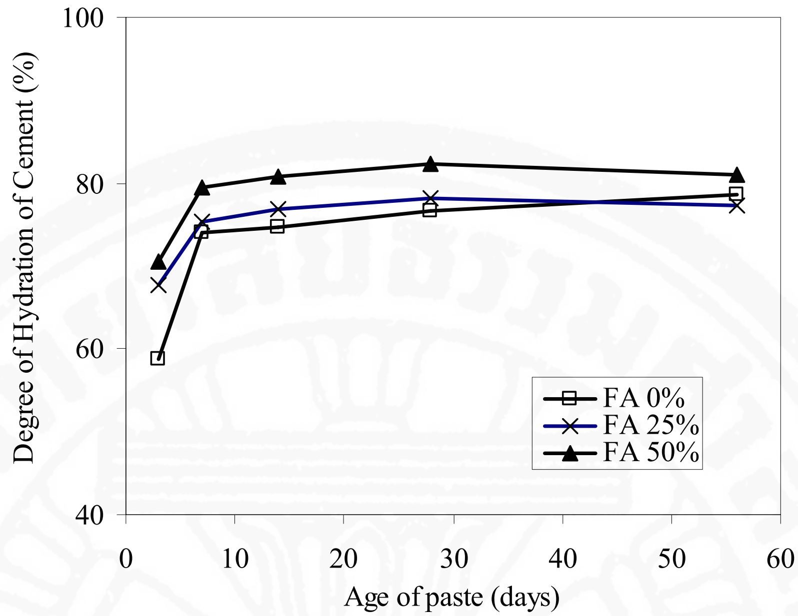

Fig. 3.13 Degree of hydration of cement in cement-fly ash paste with 0%, 25% and 50% of fly ash replacement, w/b = 0.32, cured in water at 20ºC (Saengsoy, 2008)

The physical acceleration effect was considered as a factor to accelerate the hydration reaction of cement. This effect is similar to that occurs in case of limestone powder (LS). Addition of the limestone filler causes an increase in the maximum hydration production rate (Poppe and Schutter, 2006). The physical acceleration at early age mainly affects the hydration reaction at early age of C_3A and C_3S. In this study, the dispersion factors (φ) were introduce to take into account the effect of physical acceleration of fly ash on the early age hydration of C_3A and C_3S as shown in Eqs. (3.14) and (3.15).

$$\varphi_{C_3S} = -1.6612\left(\frac{\alpha_{C_3S}(t-1)}{100}\right)^4 + 3.8991\left(\frac{\alpha_{C_3S}(t-1)}{100}\right)^3 - 2.4864\left(\frac{\alpha_{C_3S}(t-1)}{100}\right)^2 - 0.2045\left(\frac{\alpha_{C_3S}(t-1)}{100}\right) + 0.942\times\tan^{-1}\left(\left(F_f\times\frac{W_c+W_f}{UW}\right)^r\right) \quad (3.14)$$

$$\varphi_{C_3A} = 1.0281\left(\frac{\alpha_{C_3A}(t-1)}{100}\right)^4 - 1.5095\left(\frac{\alpha_{C_3A}(t-1)}{100}\right)^3 + 0.4181\left(\frac{\alpha_{C_3A}(t-1)}{100}\right)^2 - 0.1354\frac{\alpha_{C_3A}(t-1)}{100} + 0.78\times\tan^{-1}\left(\left(F_f\times\frac{W_c+W_f}{UW}\right)^r\right) \quad (3.15)$$

where, φ_{C_3S} and φ_{C_3A} are the dispersion factors of C_3S and C_3A. F_f is Blaine's fineness of fly ash (cm^2/g).

It is remarked that Eqs (3.14) and (3.15) were proposed for the time step of one hour. For the time step less than one hour, Eqs (3.14) and (3.15) may need future modification.

3.7.2 Retardation of hydration by fly ash

Fly ash physically accelerates but chemically retards the hydration reaction of cement. The addition of fly ash delays the time of setting of concrete. Both Class F fly ash and Class C fly ash retard early hydration of C_3S. The retardation factor of C_3S hydration, ψ, by fly ash was proposed by Tatong (2001). However, the effect of concrete temperature was not included in her model. As mentioned in the previous section, the rate of hydration reaction depends on concrete temperature. Higher concrete temperature results in faster hydration reaction. The retardation effect of fly ash also varies according to temperature. It was found from the analysis that fly ash seriously retarded the hydration of C_3S especially at temperature lower than 20 ^{o}C. In this study, the temperature factor (κ) was introduced to the retardation factor of fly ash to take into account the effect of concrete temperature especially for temperature lower than 20 ^{o}C. The temperature factor used in this study is shown in Fig. 3.14 and Eq. (3.16).

$$\psi = \kappa[\{0.0866 \cdot (\text{w/b})^{-2.443} - 1.032 \cdot \text{w/b}\} \cdot \text{r}^{2.151} + 1] \cdot (\alpha_{C_3S}(t)/100)^{3.409 \cdot \text{r}^{1.952}} \quad (3.16)$$

where ψ is the retardation factor of C_3S hydration by fly ash. $\alpha_{C_3S}(t)$ is the degree of hydration of C_3S for the mix without fly ash (%). r is replacement ratio of fly ash in total powder content by weight and w/b is water to binder ratio. κ is the temperature factor.

Examples of retardation factor of C_3S hydration (ψ) of some paste mixtures are shown in Fig. 3.15.

Finally, the degrees of hydration of C_3A and C_3S of cement can be calculated from

$$\alpha_{C_3S,\ poz}(t) = \psi \cdot \varphi_{C_3S} \cdot \alpha_{C_3S}(t) \quad (3.17)$$

$$\alpha_{C_3A,\ poz}(t) = \varphi_{C_3A} \cdot \alpha_{C_3A}(t) \quad (3.18)$$

where $\alpha_{C_3S,\ poz}(t)$ and $\alpha_{C_3A,\ poz}(t)$ are the degree of hydration of C_3S and C_3A, respectively, with consideration of dispersion and retardation effects of fly ash (%)

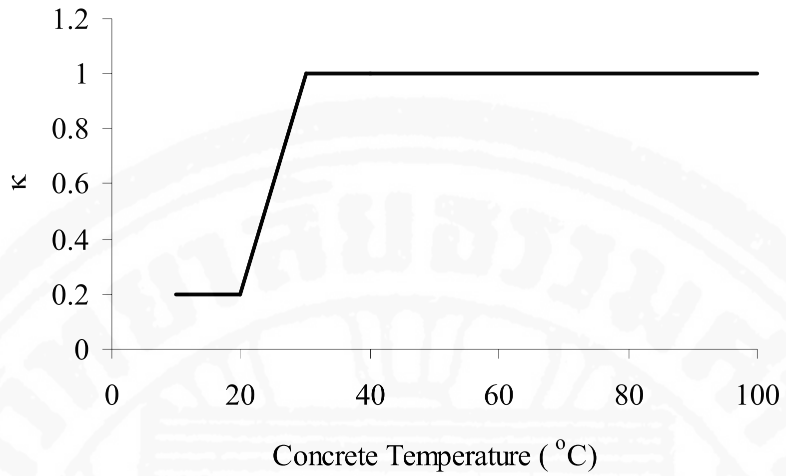

Fig. 3.14 Effect of temperature on retardation of C_3S hydration by fly ash (κ)

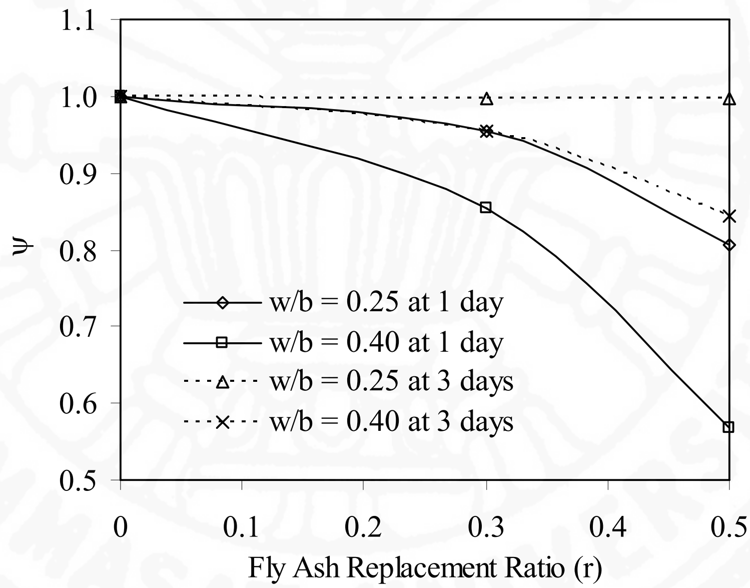

Fig. 3.15 Retardation factor of C_3S hydration (ψ) of paste with various fly ash replacement ratio, and w/b = 0.25 and 0.40 at 1 day and 3 days

3.8 Effect of Temperature Variation on Degree of Reactions

The degree of hydration and degree of pozzolanic reaction were formulated based on constant concrete temperature. As the temperature of concrete typically changes with respect to time (especially in mass concrete), a simple concept was introduced to determine the degree of reactions in case of varied concrete temperature.

In the computation, the degree of reactions was computed every time step (Δt) of the concrete age. Considering at initial concrete temperature, the degree of hydration and degree of pozzolanic reaction of concrete at the age of Δt were calculated from Eq. (3.1) to Eq. (3.4), and Eq. (3.8), respectively. Since heat generated in a period of time causes the temperature rise in concrete that consequently affects the degree of reactions, the degree of reactions at the next time step of concrete can be computed by using the equations at the updated concrete temperature.

Fig. 3.16 and Fig. 3.17 show the schematic illustration of the process for computing the degree of reactions of concrete when the concrete temperature continuously increases. The dashed lines in Fig. 3.16 exhibited the degree of reactions at the constant concrete temperatures (i.e. T_1, T_2, T_3, and T_4). In the computation, for instance, if the temperature of concrete is initially at T_1, the degree of reactions will follow the curve T_1 and can be represented by the solid curve c_1. At next time step, if the temperature of concrete changes to T_2, the degree of reactions consequently follows the curve T_2. At the time that temperature changes, the degree of reactions at the end of the previous temperature is used to start the calculation of degree of reactions at the new concrete temperature. The degree of reactions at the end of the next time step (and new concrete temperature also) can then be obtained. The process of calculation is repeated as the temperature of concrete continues to increase.

Finally, the degree of reactions of concrete is the connection of those solid curves as shown in Fig. 3.17.

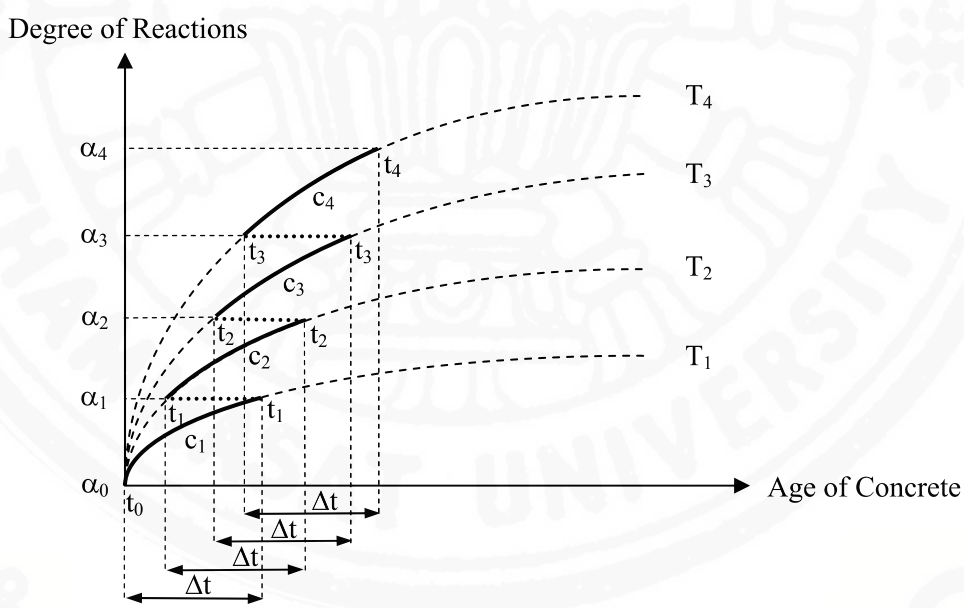

Fig. 3.16 Schematic illustration of the process for computing the degree of reactions

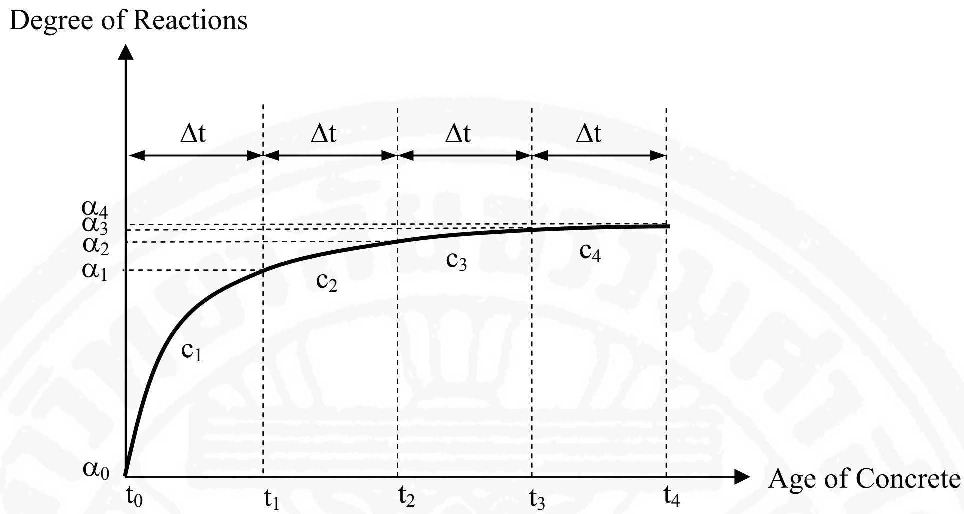

Fig. 3.17 Schematic illustration of the computed degree of reactions

3.9 Effect of Relative Water Content on the Degree of Reactions

The effect of the relative water content was taken into consideration for computing degree of hydration and degree of pozzolanic reaction. The equations for determining degree of hydration and degree of pozzolanic reaction previously mentioned are applicable for concrete with relative water content equals to 100 % (water-saturated concrete). At the lower relative water content, the rates of degree of reactions were computed based on the rate at 100% relative water content and the relative water content in a linear relationship manner as can be seen from Eq. (3.19). The rates of reactions were assumed to be linearly proportional to the relative water content in such a way that the reduction of the relative water content causes the reduction in the rate of reactions.

$$\frac{d\alpha_{i,C_w}(t)}{dt} = \frac{C_w}{100} \cdot \frac{d\alpha_i(t)}{dt} \tag{3.19}$$

where $\frac{d\alpha_{i,C_w}(t)}{dt}$ is the rate of reactions with considering the effect of relative water content (%/day). $\frac{d\alpha_i(t)}{dt}$ is the rate of reactions at 100 % relative water content (%/day). C_w is the relative water content (%) which can be expressed as in Eq. (3.20).

$$C_w = \frac{W_e}{W_{sat}} \cdot 100 \tag{3.20}$$

where C_w is the relative water content (%). W_e, and W_{sat} are the weight of evaporable water at 105 °C in the non-saturated concrete and the weight of the saturated water content of concrete, respectively (kg/m^3) (Khunthongkaew and Tangtermsirikul 2002).

It is noted that the relative water content was simply assumed to have a linear effect on the rate of reactions. However, its effectiveness seems to be nonlinear in reality, so this effectiveness may need future clarification.

3.10 Total Heat Generation for Concrete

The hydration of cement is accompanied by heat evolution, which causes a temperature rise in concrete. Cement consists of four major oxide compounds minerals which are C_3S, C_2S, C_3A, and C_4AF. Their proportion varies according to the type of cement. The hydration reaction rate of each cement compound varies with its reactivity. Their hydration products are also dissimilar. The hydration of C_3S, and C_2S produce both calcium silicate hydrates (CSH) and calcium hydroxide ($Ca(OH)_2$), while C_3A, and C_4AF produce ettringite or monosulphate by reacting with gypsum. After the gypsum is consumed, calcium aluminate hydrates and calcium ferro aluminate hydrates are produced. The reactions of each cement compound and fly ash are shown in Table 3.1.

All reactions are accompanied by some amount of heat generation. For the concrete incorporated with fly ash, the overall heat generation typically reduced mainly due to the reduction of cement content. However, the pozzolanic reaction of fly ash also produces heat and needs to be considered. By assuming that all exothermic reactions in concrete are independent, the total heat generation of concrete can be computed from the summation of the heat liberated from the reaction of each cement compound including the formation of ettringite and monosulphate, and the reaction of fly ash as

$$Q(t) = Q_{C_3S}(t) + Q_{C_2S}(t) + Q_{C_3A}(t) + Q_{C_4AF}(t) + Q_{C_3AET}(t) + Q_{C_4AFET}(t) + Q_{FA}(t) \quad (3.21)$$

where $Q(t)$ is the cumulative heat generation of concrete at age t (kcal/kg of concrete). $Q_{C_3S}(t)$, $Q_{C_2S}(t)$, $Q_{C_3A}(t)$, $Q_{C_4AF}(t)$, and $Q_{FA}(t)$ are the cumulative heat generation at age t of C_3S, C_2S, C_3A, C_4AF, and fly ash, respectively (kcal/kg of concrete). $Q_{C_3AET}(t)$ and $Q_{C_4AFET}(t)$ are cumulative heat generation at age t by ettringite and monosulphate formation from the reactions between C_3A, and C_4AF and gypsum, respectively (kcal/kg of concrete). t is the age of concrete (days).

Table 3.1 Reactions of each cement compound and fly ash (Mindess 1981)

Cement Compounds	Reactions
C_3A	$2C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_6A\underline{S}_3H_{32}$ $2C_3A + C_6A\underline{S}_3H_{32} + 4H \rightarrow 3C_4A\underline{S}H_{12}$ $C_3A + 6H \rightarrow C_3AH_6$
C_4AF	$C_4AF + 3C\underline{S}H_2 + 21H \rightarrow C_6(A,F)\underline{S}_3H_{32} + (A,F)H_3$ $2C_4AF + C_6(A,F)\underline{S}_3H_{32} + 7H \rightarrow C_4(A,F)\underline{S}H_{12} + (A,F)H_3$ $C_4AF + 9H + 4CH \rightarrow C_4(A,F)H_{13}$
C_3S	$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$
C_2S	$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$
Fly Ash	Reactions
S A	$2S + 3CH \rightarrow C_3S_2H_3$ $2A + 3CH \rightarrow C_3A_2H_3$

Remarks: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O, $\underline{S}$ = SO_3

3.11 Cumulative Heat Generation by Ettringite and Monosulphate Formation

Gypsum is introduced in Portland cement in order to prevent rapid hardening due to C_3A and C_4AF hydration. C_3A, and C_4AF react with gypsum to produce ettringite that is rapidly formed and accompanied by a high rate of heat evolution. The heat evolution is stagnated when gypsum is depleted due to the consumption in ettringite formation. In accordance with the shortage of gypsum, the ettringite then reacts with non-reacted C_3A or C_4AF and converts to monosulphate. The hydration heat generation of C_3A, and C_4AF is assumed to begin once the ettringite and monosulphate formation reactions have completed after the depletion of gypsum.

In this study, the heat generation during ettringite formation and conversion to monosulphate are analytically combined for the simplicity purpose. The periods of time taken to complete the ettringite and monosulphate formation reactions are varied according to the gypsum content in cement and concrete temperature. The higher gypsum content requires longer time to finish the reactions, while higher concrete temperature accelerates the rate of reactions.

The cumulative heat generation of ettringite and monosulphate formation at completed state of reactions considerably depends on the gypsum content in cement. High percentage by weight of gypsum in cement usually gives the large amount of heat production in the ettringite and monosulfate formation according to an extension of the ettringite and monosulphate formation reactions by more gypsum. Even though concrete temperature affects the rate of reactions, it is assumed that different concrete temperature with equal gypsum content results in the same cumulative heat at the end of ettringite and monosulphate formation reactions.

The cumulative heat generation by ettringite and monosulphate formation reactions at state of complete reactions can be expressed as in Eq. (3.22) and Eq. (3.23), respectively, and shown in Fig. 3.18.

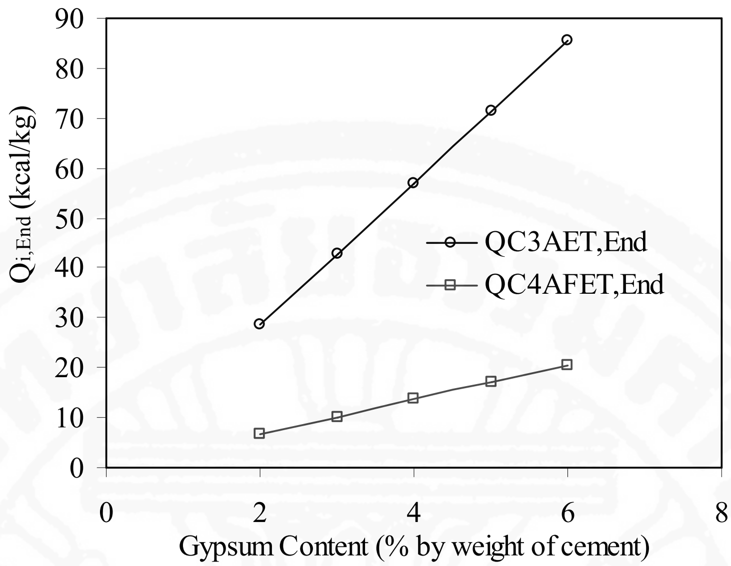

Fig. 3.18 Cumulative heat generation of the ettringite and monosulphate formation by C_3A and C_4AF at the state of complete reactions with various gypsum contents in cement

$$Q_{C_3AET,End} = 14.25 \cdot \%Gyp \quad (3.22)$$

$$Q_{C_4AFET,End} = 3.4 \cdot \%Gyp \quad (3.23)$$

where $Q_{C_3AET,End}$, and $Q_{C_4AFET,End}$ are the cumulative heat generation by C_3A-gypsum and C_4AF-gypsum ettringite and monosulphate formation reactions at state of complete reactions of ettringite and monosulphate formation, respectively (kcal/kg of gypsum). %Gyp is the gypsum content in cement (% by weight of cement).

During the process of ettringite and monosulphate formation reactions, the cumulative heat generation was simply assumed to have time-dependent increment with the reduction in heat producing rate. After the reactions have been completed, no heat from ettringite and monosulphate formation was produced and the cumulative heat generation by ettringite and monosulphate formation reactions becomes constant.

As the formation of ettringite is governed by the amount of gypsum and ettringite subsequently transformed into monosulphate, the cumulative heat generation of ettringite and monosulphate formation was consequently formulated as a function of gypsum content in cement and concrete temperature. However, the cumulative heat generation of ettringite and monosulphate would not be greater than that at the state of complete reactions which were given in Eq. (3.22), Eq. (3.23) and Fig. 3.18.

The cumulative heat generation of ettringite and monosulphate formation at a constant concrete temperature by C_3A and C_4AF can be expressed as

$$Q_{C_3AET}(t) = \frac{(0.4973 \cdot T^{1.1571} + 58.1539) \cdot t}{-0.9147 + \exp[(0.0089 \cdot T^{0.9615} + 0.4303) \cdot t]} \cdot w_{Gyp}$$

$$Q_{C_3AET}(t) \le Q_{C_3AET,End} \cdot w_{Gyp} \tag{3.24}$$

$$Q_{C_4AFET}(t) = \frac{(0.1186 \cdot T^{1.1571} + 13.8753) \cdot t}{-0.9147 + \exp[(0.0089 \cdot T^{0.9615} + 0.4303) \cdot t]} \cdot w_{Gyp}$$

$$Q_{C_4AFET}(t) \le Q_{C_4AFET,End} \cdot w_{Gyp} \tag{3.25}$$

where $Q_{C_3AET}(t)$, and $Q_{C_4AFET}(t)$ are cumulative heat generation at age t by the ettringite and monosulphate formation from the reaction of gypsum with C_3A, and C_4AF, respectively (kcal/kg of concrete). w_{Gyp} is the weight ratio of gypsum to the unit weight of concrete. T is concrete temperature (°C) and t is the age of concrete (days)

The computed results of cumulative heat generations of the ettringite and monosulphate formations by C_3A, and C_4AF with various gypsum contents at 30°C of concrete temperature are shown in Fig. 3.19 and Fig. 3.20, respectively.

Fig. 3.21 and Fig. 3.22 show examples of cumulative heat generation of the ettringite and monosulphate formation by C_3A and C_4AF with 6 % gypsum content in cement at various concrete temperatures.

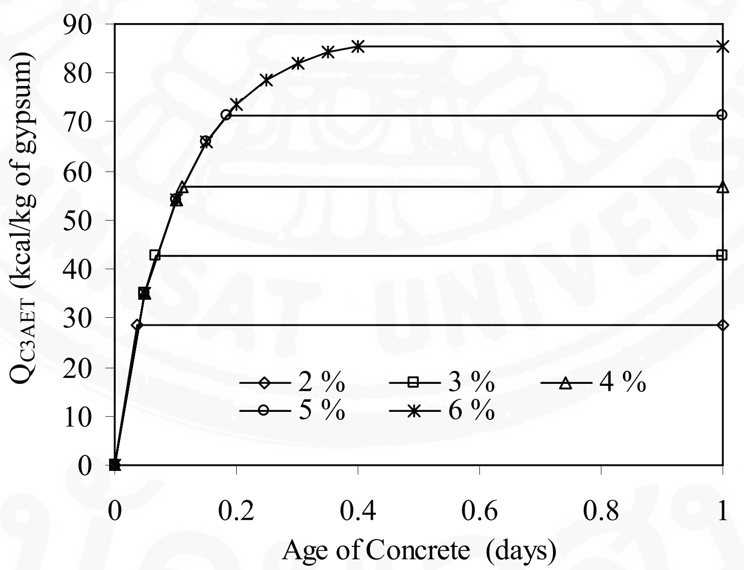

Fig. 3.19 Cumulative heat generation of the ettringite and monosulphate formation by C_3A with various gypsum contents at 30°C

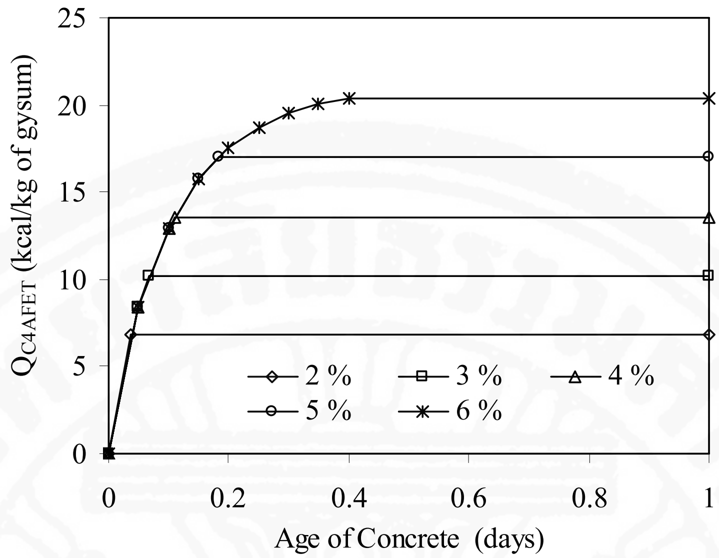

Fig. 3.20 Cumulative heat generation of the ettringite and monosulphate formation by C_4AF with various gypsum contents at 30°C

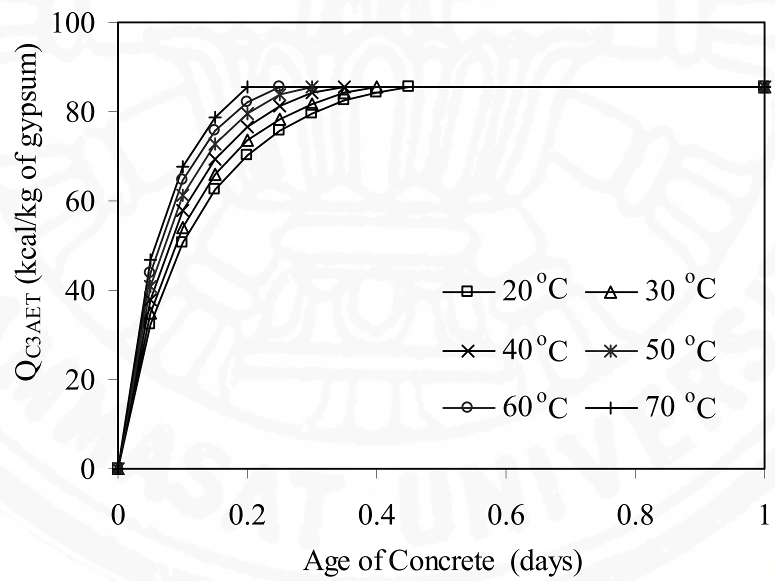

Fig. 3.21 Cumulative heat generation of ettringite and monosulphate formation by C_3A with 6 % of gypsum content in cement at various concrete temperatures

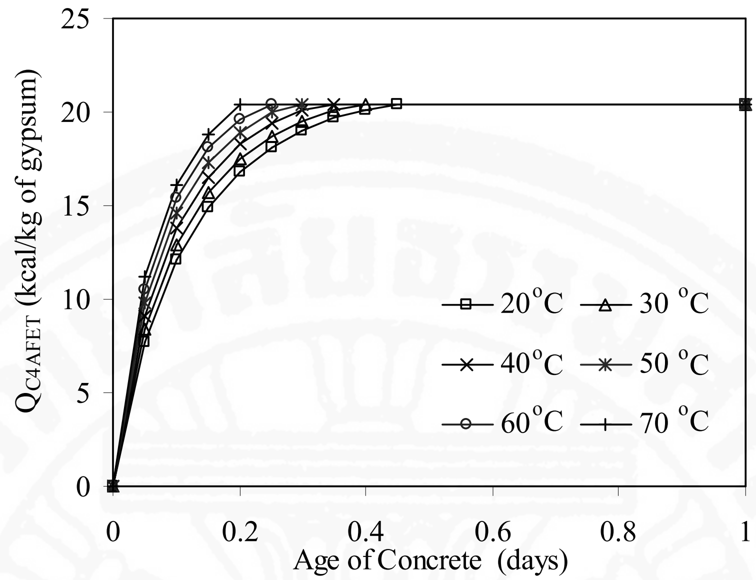

Fig. 3.22 Cumulative heat generation of ettringite and monosulphate formation by C_4AF with 6 % of gypsum content in cement at various concrete temperatures

3.12 Cumulative Heat Generation of Cement Compounds

When cement reacts with water, cementitious products are formed and heat liberated at the same time. The hydration process of each cement compound is regarded to be independent from each other. The heat generation of cement is consequently equivalent to the sum of the heat generated by each compound.

The cumulative heat generation of each cement compound is considered to be linearly related to its degree of reaction and its content in the concrete as shown in Eq. (3.26).

For C_3S, and C_2S, the whole amount presented in the concrete is available for generating heat in this part while only the amount of C_3A, and C_4AF, left from being used in the ettringite and monosulphate formations, are considered to hydrate and generate heat in addition to those generated in the ettringite and monosulphate formation. The effective quantity of cement compound to produce heat can be expressed as in Eq. (3.27) and Eq. (3.28).

$$Q_i(t) = \frac{\alpha_i(t)}{100} \cdot Q_{i,max} \cdot w_i \tag{3.26}$$

For C_3S, and C_2S;

$$w_i = w_{i0}\,\Phi \tag{3.27}$$

For C_3A, and C_4AF;

$$w_i = (w_{i0} - w_{iET} - w_{iMN})\,\Phi \tag{3.28}$$

where $Q_i(t)$ is the cumulative heat generation at age t of each cement compound (kcal/kg of concrete). $\alpha_i(t)$is the degree of hydration at age t of each cement compound(%). $Q_{i,max}$ is the cumulative heat generation of each cement compound at complete hydration (kcal/kg of the cement compound). w_i is the effective weight ratio of each cement compound available to generate heat in 1 m^3 of concrete to the unit weight of concrete (no unit). w_{i0} is weight ratio of each cement compound to the unit weight of concrete at time of mixing (no unit) .w_{iET}, and w_{iMN} are weight ratio to the unit weight of concrete of the related cement compounds (C_3A, C_4AF) that had been used to form ettringite and monosulphate, respectively which can be calculated from the stoichiometric balance equations (Sumranwanich and Tangtermsirikul 2002). i is mineral compound of cement (C_3S, C_2S, C_3A, and C_4AF), and t is age of concrete (days). Φ is the effective weight factor.

Normally, some part of cement particle does not react due to the adherence of cement particle. The use of high volume fly ash replacement leads to better reaction of cement particle because of better dispersion of cement particles. As a result, another factor, Φ, was introduced into the model as shown in Eq. (3.29).

$$\Phi = -6.19r^6 + 14.3r^5 - 9.16r^4 - 0.20r^3 + 1.06r^2 + 0.38r + 0.8 \qquad (3.29)$$

where, Φ is the dispersion factor. r is the replacement ratio of fly ash in total powder content by weight.

Various researchers (Saengsoy, 2002 and Maekawa et al., 1999) proposed values of cumulative heat of hydration of each mineral compound of cement (C_3S, C_2S, C_3A, and C_4AF) at complete hydration. As shown in Table 3.2, the values are somehow different which may results from the use of different raw material or different cement producing process. In the study of Saengsoy (2002), the maximum heat of each cement compound for cement produced in Thailand were proposed and those values were used in this study. Fig. 3.23 shows examples of calculated cumulative heat generation of C_3S, C_2S, C_3A, and C_4AF at different degree of hydration using Eq. (3.26) to Eq. (3.28) for the system without fly ash.

Table 3.2 Theoretical heat of hydration of cement compositions at complete hydration

Major Phase	Hydration Heat (kcal/kg of the compound)	
	Saengsoy (2002)	Maekawa et al. (1999)
C_3S	105	120
C_2S	50	62
C_3A	190	207
C_4AF	85	100

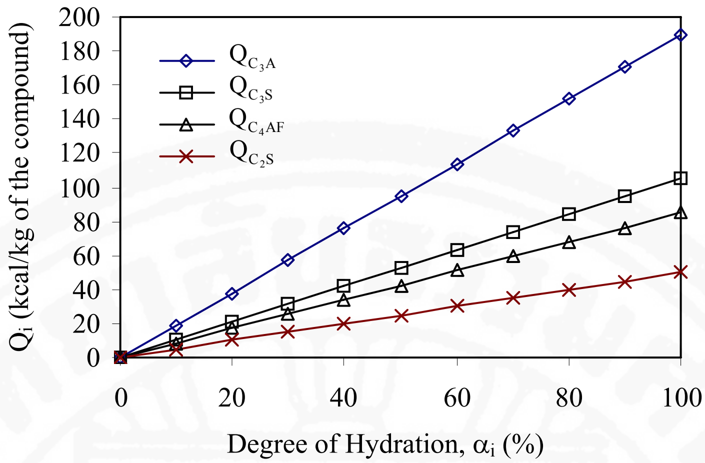

Fig 3.23 Cumulative heat generation of C_3S, C_2S, C_3A, and C_4AF at difference state of degree of hydration

The weight ratio to the unit weight of concrete of C_3A and C_4AF that had been used to form ettringite and monosulphate was assumed for simplicity under the following assumptions:

Eighty percent of gypsum weight in cement is accessible for reacting with C_3A to produce ettringite while another twenty percent of gypsum is available to react with C_4AF. Half of the ettringite weight individually formed by C_3A and C_4AF is assumed to convert into monosulphate.

The weight ratios to the unit weight of concrete of C_3A that had been used to form ettringite and monosulphate can be calculated from Eq. (3.30) and Eq. (3.32), respectively.

$$w_{C_3AET} = \frac{270}{516} \cdot 0.8 \cdot w_{Gyp} \tag{3.30}$$

$$w_{C3AMN} = \frac{540}{1254} \cdot 0.5 \cdot w_{ET,C3A} \tag{3.31}$$

$$w_{ET,C_3A} = \frac{1254}{516} \cdot 0.5 \cdot w_{Gyp} \tag{3.32}$$

where w_{C3AET}, and w_{C3AMN} are the weight ratios to the unit weight of concrete of C_3A that had been used to form ettringite and monosulphate, respectively. $w_{ET,C3A}$ is the weight ratio to the unit weight of concrete of ettringite formed by the reaction of C_3A with gypsum. w_{Gyp} is the weight ratio of gypsum to the unit weight of concrete.

The weight ratio to the unit weight of concrete of C_4AF that had been used to form ettringite and monosulphate can be calculated from Eq. (3.33) and Eq. (3.35), respectively.

$$w_{C_4AFET} = \frac{486}{516} \cdot 0.2 \cdot w_{Gyp} \quad (3.33)$$

$$w_{C_4AFMN} = \frac{486}{1283} \cdot 0.5 \cdot w_{ET,C_4AF} \quad (3.34)$$

$$w_{ET,C_4AF} = \frac{1283}{516} \cdot 0.5 \cdot w_{Gyp} \quad (3.35)$$

where w_{C_4AFET}, and w_{C_4AFMN} are the weight ratio to the unit weight of concrete of C_3A that had been used to form ettringite and monosulphate, respectively. w_{ET,C_4AF} is the weight ratio to the unit weight of concrete of ettringite formed by the reaction of C_4AF with gypsum. w_{Gyp} is the weight ratio of gypsum to the unit weight of concrete.

3.13 Cumulative Heat Generation of Fly Ash

Pozzolanic reaction of fly ash also produces heat. The pozzolanic reaction of fly ash is controlled by the calcium hydroxide, released from cement hydration, and the reactive phases in fly ash.

The cumulative heat generation of fly ash was computed based on the degree of pozzolanic reaction and fly ash content in concrete as shown in Eq. (3.36).

$$Q_{FA}(t) = \frac{\alpha_{poz}(t)}{100 \cdot} \cdot Q_{FA,\max} \cdot w_{fa} \quad (3.36)$$

where $Q_{FA}(t)$ is the cumulative heat generation at age t of fly ash (kcal/kg of concrete), $\alpha_{poz}(t)$ is the degree of pozzolanic reaction at age t (%), $Q_{FA,max}$ is the maximum cumulative heat generation of fly ash (kcal/kg of fly ash), and w_{fa} is the weight ratio of fly ash in 1 m^3 of concrete to the unit weight of concrete (no unit).

In this study, the cumulative heat generation of fly ash at the maximum pozzolanic reaction was assumed to be a function of calcium oxide content in fly ash which was slightly modified from that proposed by Sarker et al. (1999) as shown in Eq. (3.37) and Fig. 3.24.

$$Q_{FA,\max} = 100 + 1.75 \cdot \%CaO_f \quad (3.37)$$

where $\%CaO_f$ is calcium oxide content in fly ash (% by weight of fly ash)

The values obtained from the proposed function were close to the range reported by Evsukoff et al. (2006). In their study, the maximum cumulative heat generation of fly ash is in the range between 119.5 to 150.6 kcal/kg.

3.14 Computerized Program for Simulating Temperature of Mass Concrete

The input parameters required in this computerized program are initial temperature, mix proportion, and properties of cement, fly ash, water and aggregates. The computerized program initially calculated the degree of reactions, then the total heat generation, free water content and specific heat of concrete. The details of free water content model and specific heat model are mentioned in the later chapters (Chapters 4 and 5, respectively). Once the total heat generation, and specific heat are acquired, the temperature rise of concrete can be determined. The analytical process is shown in the flow chart in Fig.3.25.

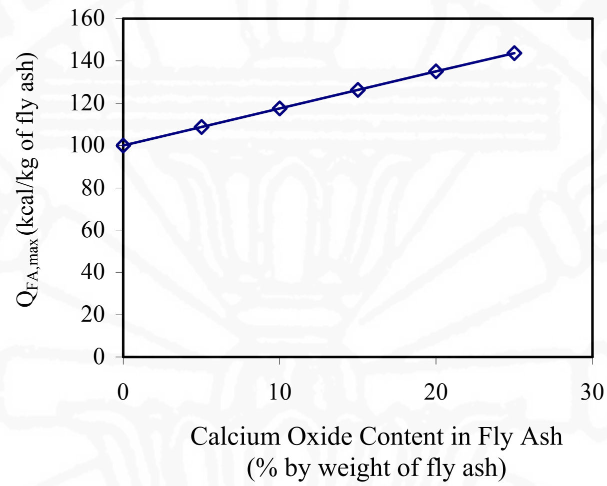

Fig 3.24 Cumulative heat generation of fly ash at maximum pozzolanic reaction of fly ash with various calcium oxide content

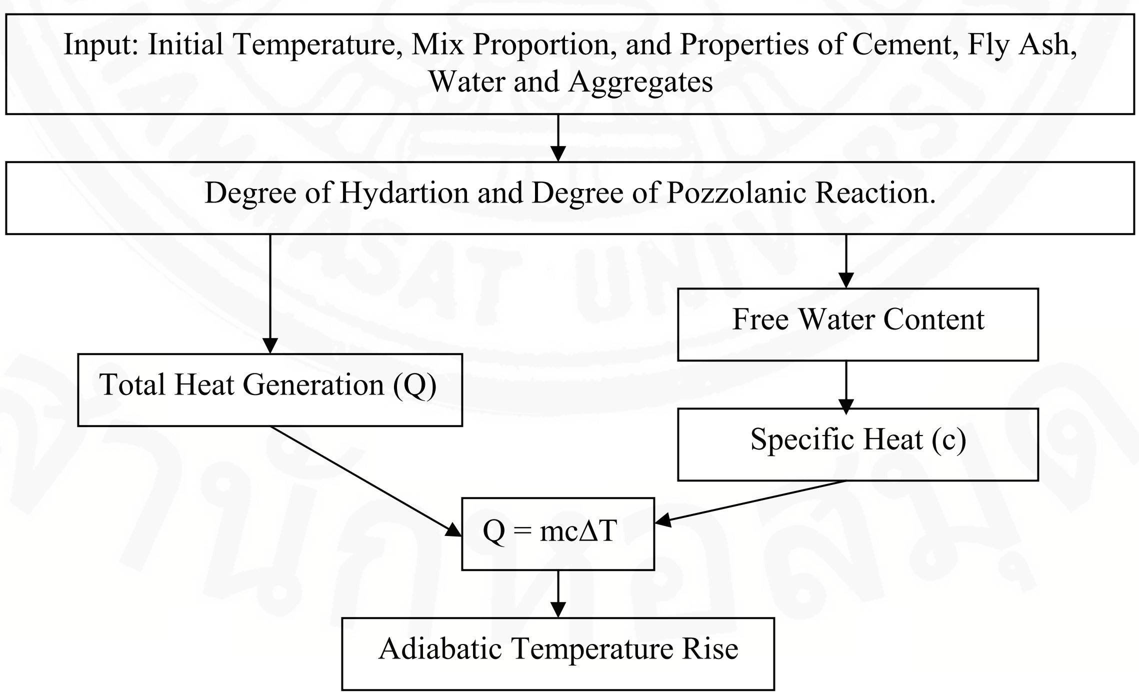

Fig. 3.25 Flow chart of modeling for simulating adiabatic temperature of mass concrete

3.15 Verification of the Proposed Models by Adiabatic Test Results

The adiabatic temperature rise of Portland cement mixture and blended cement mixture with 20% fly ash replacement conducted by Suzuki et al. (1990) were adopted for verification. For cement-only mixtures, three unit cement contents weights (200 kg/m^3, 300 kg/m^3, 400 kg/m^3) were examined for ordinary Portland cement (OPC) denoted as OPC200, OPC300, and OPC400. The adiabatic temperature rise of cement blended with fly ash was also carried out with three binder contents of 200 kg/m^3, 300 kg/m^3, and 400 kg/m^3 denoted as FA200, FA 300, and FA 400, respectively. The tests were conducted at three different levels of initial temperature (10°C, 20°C, 30°C). The concrete mix proportions and mineral composition of the tested cement and fly ash are shown in Appendix B (Table B1 and Table B2, respectively). Since the cement used was supposed to be made in Japan, the maximum heat of each cement compounds proposed by Maekawa et al. (1999) as shown in Table 3.2 were used in the verification. The comparison between the temperature computed by the model and the test results of Portland cement mixtures and blended cement mixtures are shown in Fig. 3.26 to Fig. 3.31.

The verification shows that the proposed model could predict the temperature of almost all test results with the satisfactory accuracy. The model could predict the temperature of the mixtures both with and without fly ash and at several different initial temperatures. The model predicted higher early age temperature than that of the test results for the mixtures with fly ash at initial temperature of 10 °C, however, the use of concrete with initial temperature 10 °C is not practical in Thailand. Nevertheless, in order to get more precisely predicted results, the improvement of the model for fly ash concrete at low initial temperature may be needed in the future.

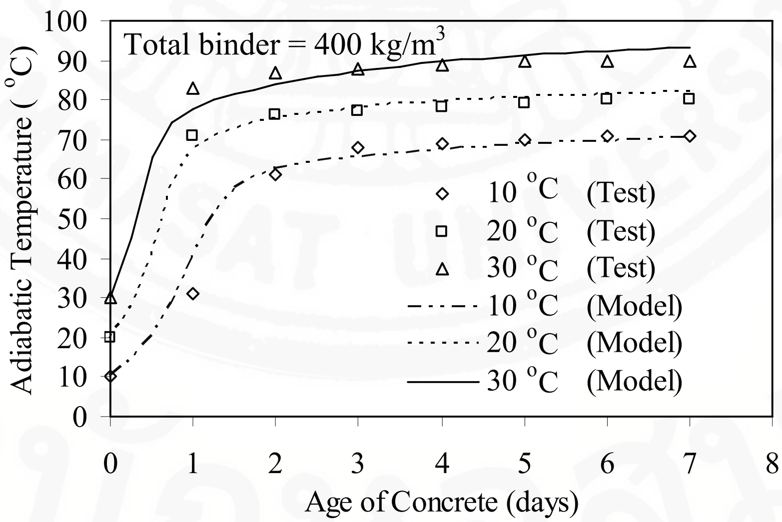

Fig. 3.26 Comparison between the computed temperature of Portland cement mixture (OPC400) and the test results with several initial temperatures

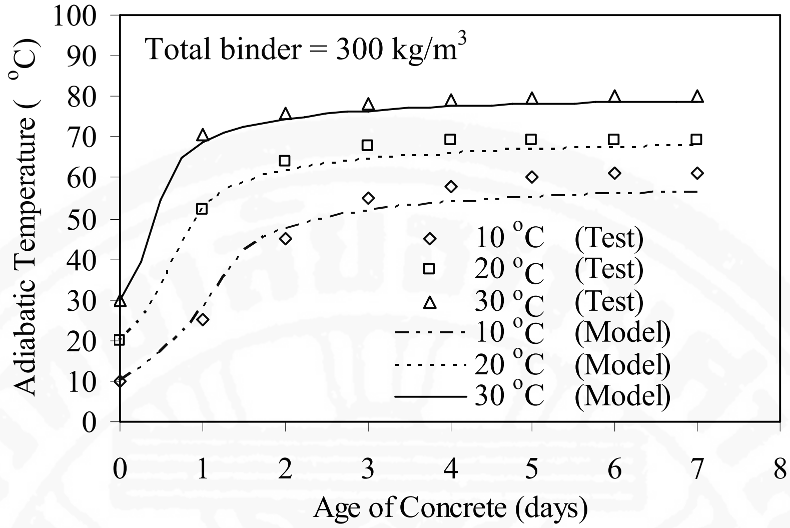

Fig. 3.27 Comparison between the computed temperature of Portland cement mixture (OPC300) and the test results with several initial temperatures

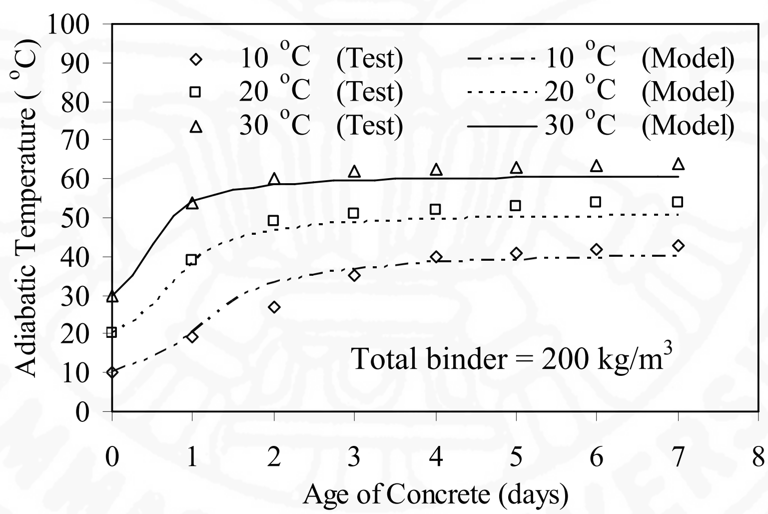

Fig. 3.28 Comparison between the computed temperature of Portland cement mixture (OPC200) and the test results with several initial temperatures

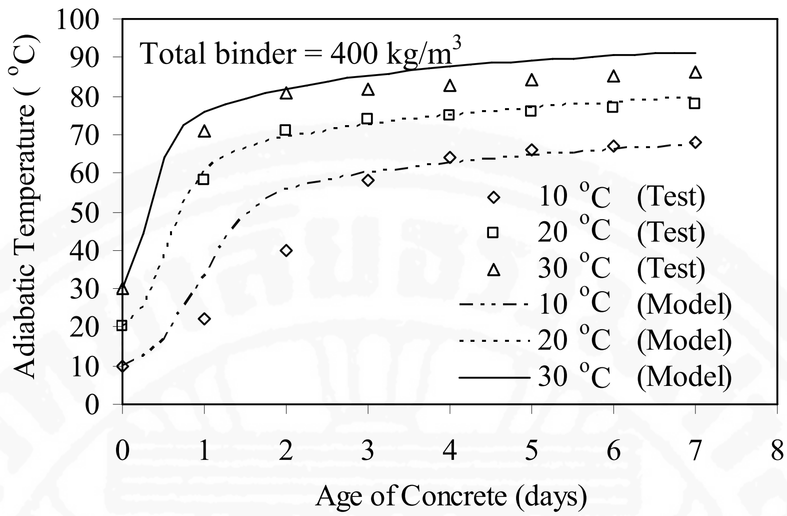

Fig. 3.29 Comparison between the computed temperature of blended cement mixture with 20% fly ash replacement (FA400) and the test results with several initial temperatures

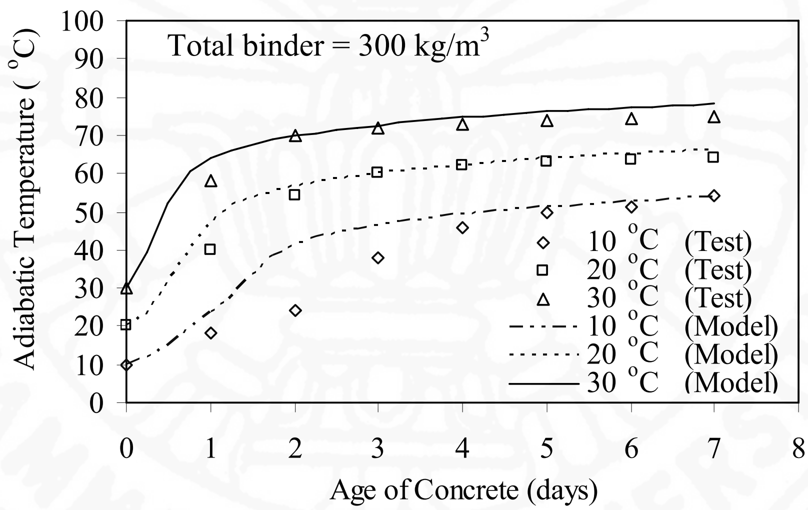

Fig. 3.30 Comparison between the computed temperature of blended cement mixture with 20% fly ash replacement (FA300) and the test results with several initial temperatures

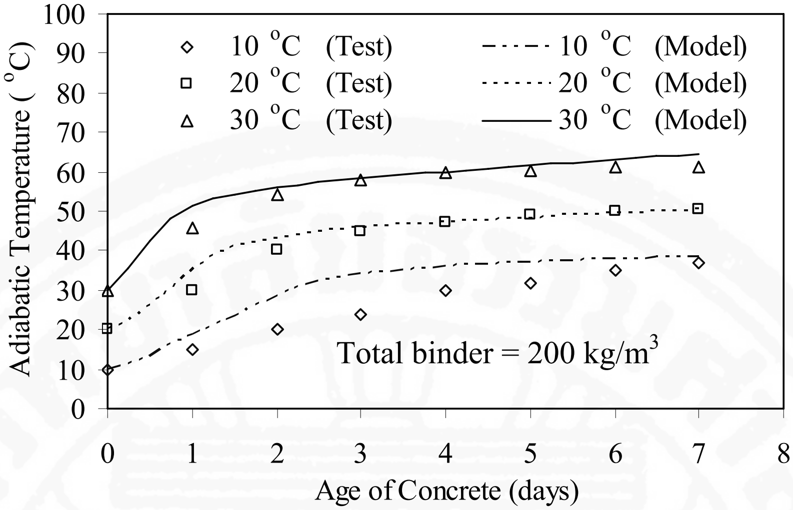

Fig. 3.31 Comparison between the computed temperature of blended cement mixture with 20% fly ash replacement (FA200) and the test results with several initial temperatures

The test results on adiabatic temperature of concretes having different water to binder ratios obtained by Bentz et al. (1998) were used to compare with the predicted temperatures derived from the proposed model as shown in Fig. 3.32. The mix proportions and mineral composition of the cement used are shown in Appendix B (Table B3 and Table B4, respectively). The maximum heat of each cement compounds proposed by Maekawa (1999) as shown in Table 3.3 were used in the verification. From the compared result, the model could satisfactorily predict the temperature of the adiabatic test results of concretes with different water to binder ratios.

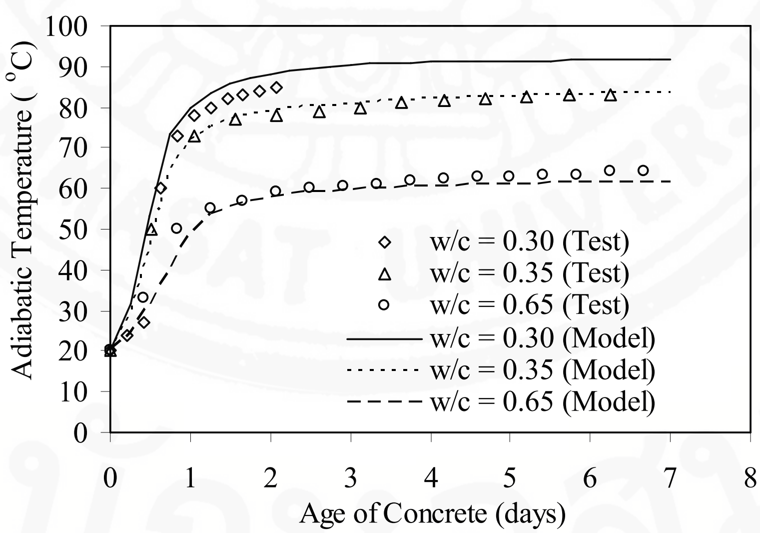

Fig. 3.32 Comparison between the temperature of concrete with difference water to binder ratios computed by the proposed model and the test results