

CHAPTER 8

FREE SHRINKAGE OF PASTE IN CONCRETE

8.1 General

Concrete was defined as a 2-phase material, the shrinkage occurs only in the paste phase, whereas the aggregate phase was considered to restrain the shrinkage by their particle interaction. The formulation of shrinkage restraint by the aggregate phase was explained in Chapter 6. In this chapter, the simulation of free shrinkage of paste phase is proposed.

The autogenous shrinkage model of paste in this research is based on semi-microscopic consideration. Large amount of autogenous shrinkage was observed for paste when water to binder ratio is decreased and when very dense structure is obtained. Autogenous shrinkage of paste varies with the water to binder ratio, chemical composition of cement and fly ash, fineness of cement and fly ash, and curing temperature.

8.2 Principle of Modeling

As the mechanisms of autogenous shrinkage can be considered as a combination of chemical phenomenon and physical phenomenon, then the autogenous shrinkage was separated into two terms of shrinkage as shown in Eq. (8.1). The first term is defined as the autogenous shrinkage by chemical process. The second term, autogenous shrinkage by physical effect is specified. In the process of the volume change, expansion is frequently involved. Then, the third term was defined for the chemical expansion strain contributed by fly ash in the cement-fly ash paste.

$$\varepsilon_{as}(t) = \varepsilon_{as,chem}(t) + \varepsilon_{as,phy}(t) - \varepsilon_{exp}(t) \quad (8.1)$$

where

- $\varepsilon_{as}(t)$ = autogenous shrinkage strain of cement paste with fly ash ($\times 10^{-6}$)
- $\varepsilon_{as,chem}(t)$ = autogenous shrinkage strain contributed by chemical effect ($\times 10^{-6}$)
- $\varepsilon_{as,phy}(t)$ = autogenous shrinkage strain contributed by physical effect ($\times 10^{-6}$)
- $\varepsilon_{exp}(t)$ = chemical expansion strain contributed by fly ash in the cement-fly ash paste ($\times 10^{-6}$)
- t = the time considered (days)

8.3 Autogenous Shrinkage by Chemical Effect

Autogenous shrinkage by chemical process represents the macroscopic volume reduction of the hydrated products derived from hydration reaction of each mineral compound in the cement and pozzolanic reaction of fly ash. From the assumption that hydration reaction of main compounds of cement (C_3A , C_4AF , C_3S , C_2S) hydrate independently, the autogenous shrinkage by chemical effect depends on the summation of the multiplication of degree of hydration and mass of each compound which represent the progression of hydration reaction in each compound. When cement is replaced by fly ash, the additional term of shrinkage by the effect of pozzolanic reaction should be included. The typical equation for shrinkage by chemical process was obtained in Eq. (8.2). However, each compound gives the different volume reduction when hydration reaction and pozzolanic reaction progress. Then, the parameters to control the volume reduction of different compounds which can be obtained by back analysis method are represented by A, B, C, D, and E as shown in Eq. (8.3) to Eq. (8.7).

$$\begin{aligned} \varepsilon_{as,chem}(t) = & \left(A \cdot m_{C_3A} \cdot \alpha_{C_3A}(t) \right) + \left(B \cdot m_{C_4AF} \cdot \alpha_{C_4AF}(t) \right) \\ & + \left(C \cdot m_{C_3S} \cdot \alpha_{C_3S}(t) \right) + \left(D \cdot m_{C_2S} \cdot \alpha_{C_2S}(t) \right) + \left(E \cdot m_{FA} \cdot \alpha_{poz}(t) \right) \end{aligned} \quad (8.2)$$

$$A = 14.2 \cdot \left(0.0016 \left(\frac{w}{b} \right)^{-4.68} - 0.05 \right) \cdot (-0.96F + 4.36) \cdot (7.35C_3A + 0.39) \cdot \left(\frac{\alpha_{C_3A}(t)}{100} \right)^{4.63 \cdot (-1.5F + 6.26)} \quad (8.3)$$

$$B = 0.045 \quad (8.4)$$

$$C = 10.8 \cdot \left(0.0016 \left(\frac{w}{b} \right)^{-4.68} - 0.05 \right) \cdot (-0.96F + 4.36) \cdot (7.35C_3A + 0.39) \cdot \left(\frac{\alpha_{C_3S}(t)}{100} \right)^{5.16 \cdot (-1.5F + 6.26)} \quad (8.5)$$

$$D = 0.053 \quad (8.6)$$

$$E = 1.200 \quad (8.7)$$

where

- $\varepsilon_{as,chem}(t)$ = autogenous shrinkage strain contributed by chemical effect ($\times 10^{-6}$)
- i = mineral compound of cement (C_3A , C_4AF , C_3S , C_2S)
- m_i = mass of each compound per cubic meter of cement paste at any water to binder ratio (kg/m^3)
- m_{FA} = mass of fly ash per cubic meter of cement-fly ash paste at any water to binder ratio (kg/m^3)
- $\alpha_i(t)$ = degree of hydration of each compound in cement (%)
- $\alpha_{poz}(t)$ = degree of pozzolanic reaction (%)
- $\frac{w}{b}$ = water to binder ratio
- C_3A, C_3S = ratio of mineral compound in cement by weight

$$\begin{aligned}
F &= \text{Blaine fineness of cement (cm}^2\text{/g)} \\
\alpha_{C_3A}(t) &= \text{degree of hydration of } C_3A \text{ (\%)} \\
\alpha_{C_3S}(t) &= \text{degree of hydration of } C_3S \text{ (\%)}
\end{aligned}$$

The effective parameters were determined from the results of autogenous shrinkage by chemical effect. Higher water to binder ratio causes larger autogenous shrinkage by chemical effect because of more progressive hydration. However, if the water to binder is increased too much, autogenous shrinkage will be reduced because there is not enough chemical compounds for hydration reaction. While the higher content of C_3A and C_3S and fineness causes faster reaction, resulting in the increase of autogenous shrinkage by chemical effect, especially at early age.

8.3.1 Degree of hydration and average degree of hydration

The rate of cement reaction or degree of hydration of each cement compound can be defined as the function of ratio of cumulative heat generated up to the time considered to the maximum cumulative heat generation of each mineral compound in cement. The cumulative heat generated was derived from the heat of hydration model based on the multi-component concept by Kishi and Maekawa (1996), and was modified by Jitvutikrai (2000). Specified chemical components of clinker materials are treated as the characteristic parameter and the influence of moisture content and powder material proportions in the mix is taken into consideration.

$$\alpha_i(t) = \frac{Q_i(t)}{Q_{i,\infty}} \cdot 100 \quad (8.8)$$

where

$$\begin{aligned}
Q_{C_3A,\infty} &= 207 \text{ kcal./kg} & Q_{C_4AF,\infty} &= 100 \text{ kcal./kg} \\
Q_{C_3S,\infty} &= 120 \text{ kcal./kg} & Q_{C_2S,\infty} &= 62 \text{ kcal./kg}
\end{aligned}$$

$$\begin{aligned}
Q_i(t) &= \text{the cumulative heat generated by each mineral compound in cement (kcal/kg)} \\
Q_{i,\infty}(t) &= \text{the final heat generation by each mineral compound (kcal/kg)} \\
i &= \text{mineral compound of cement (} C_3A, C_4AF, C_3S, C_2S \text{)}
\end{aligned}$$

The cumulative heat by each mineral compound in cement depends on properties of cement, water to cement ratio, and curing temperature. The computer program called COMH3 has been introduced to compute cumulative heat. The degree of hydration can be obtained as Eq. (8.8). The degree of hydration of mineral compounds of mix proportions used in this study are shown in Fig. 8.1 to Fig. 8.9.

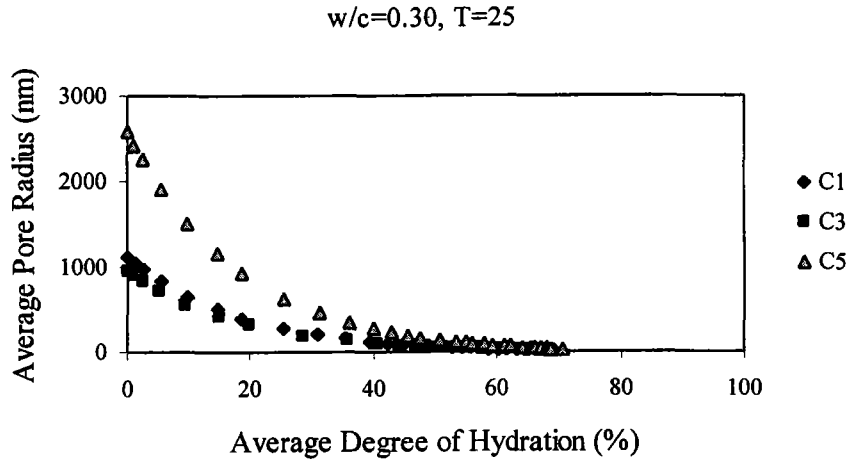


Fig. 8.1 Degree of hydration of type 1 cement with fineness $3190 \text{ cm}^2/\text{g}$, w/c=0.25 at 25°C

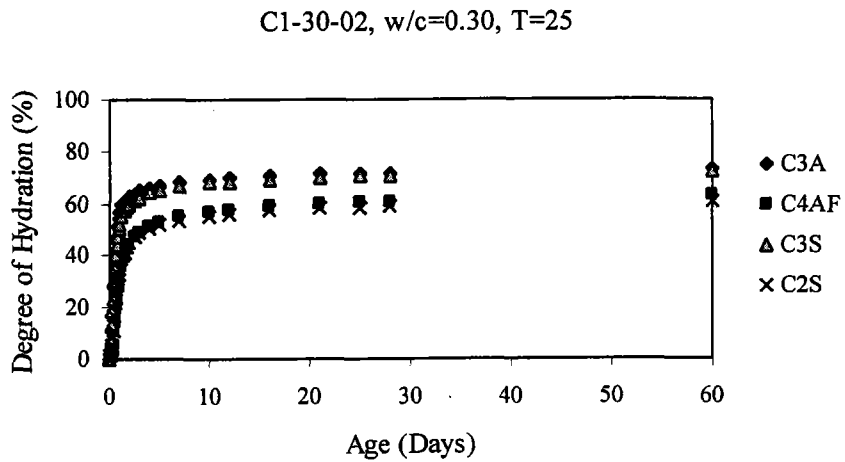


Fig. 8.2 Degree of hydration of type 1 cement with fineness $3190 \text{ cm}^2/\text{g}$, w/c=0.30 at 25°C

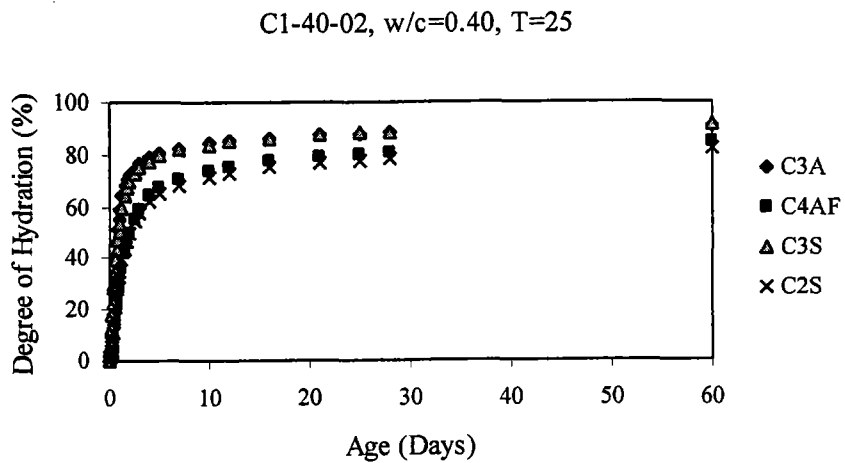


Fig. 8.3 Degree of hydration of type 1 cement with fineness $3190 \text{ cm}^2/\text{g}$, w/c=0.40 at 25°C

C3-30-02, w/c=0.30, T=25

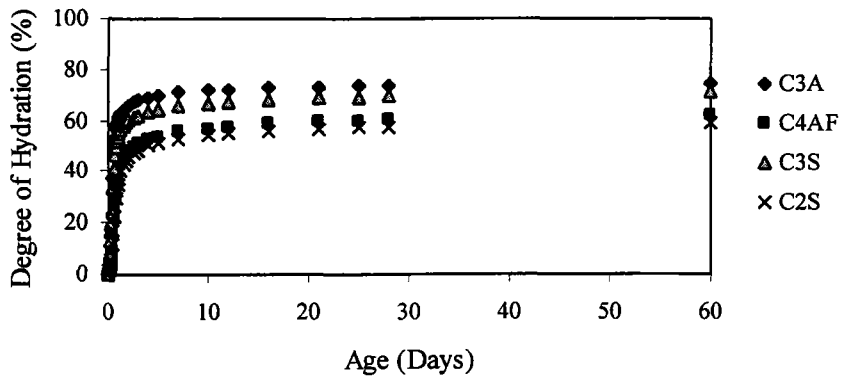


Fig. 8.4 Degree of hydration of type 3 cement with fineness 4770 cm²/g, w/c=0.30 at 25°C

C5-30-02, w/c=0.30, T=25

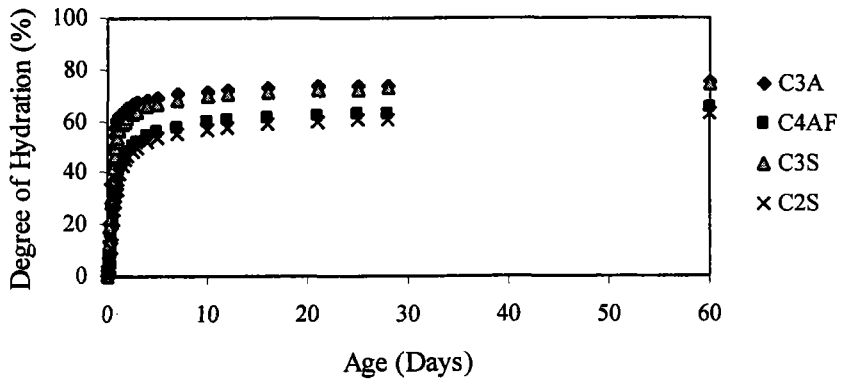


Fig. 8.5 Degree of hydration of type 5 cement with fineness 3760 cm²/g, w/c=0.30 at 25°C

C1-30-02, w/c=0.30, T=25

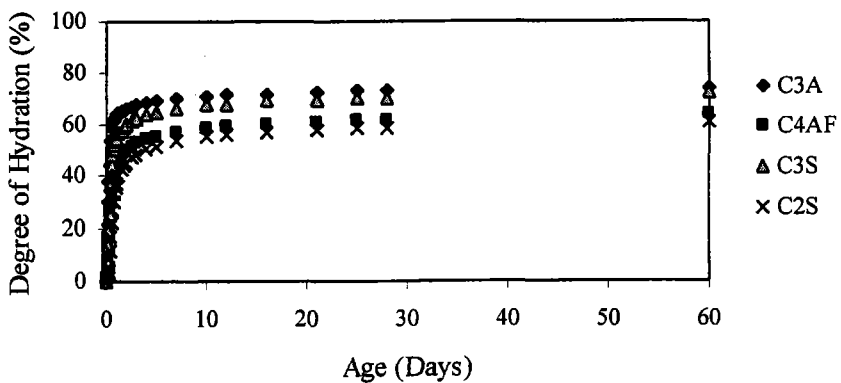


Fig. 8.6 Degree of hydration of type 1 cement with fineness 5570 cm²/g, w/c=0.30 at 25°C

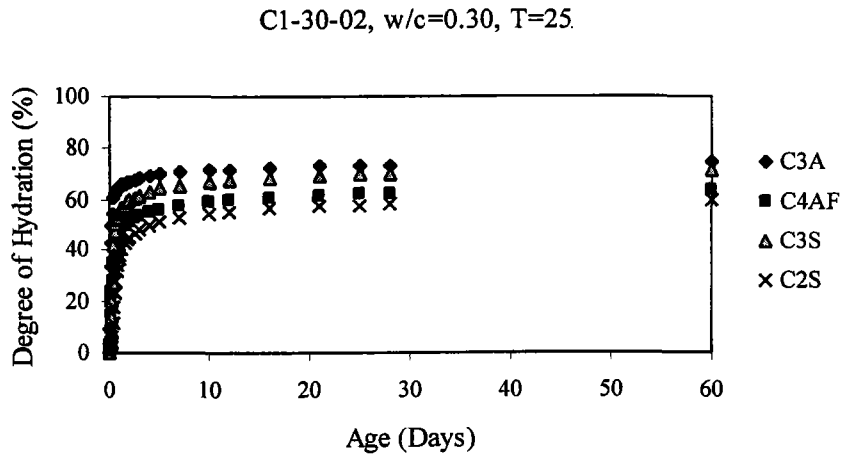


Fig. 8.7 Degree of hydration of type 1 cement with fineness 7430 cm²/g, w/c=0.30 at 25°C

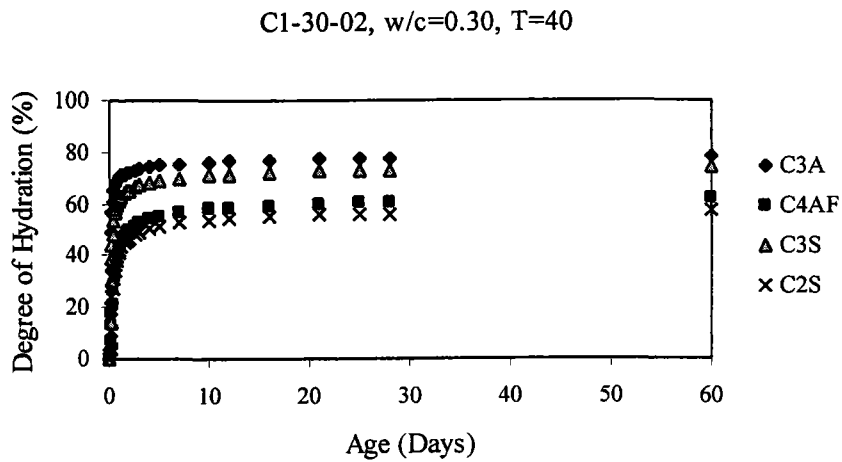


Fig. 8.8 Degree of hydration of type 1 cement with fineness 3190 cm²/g, w/c=0.30 at 40°C

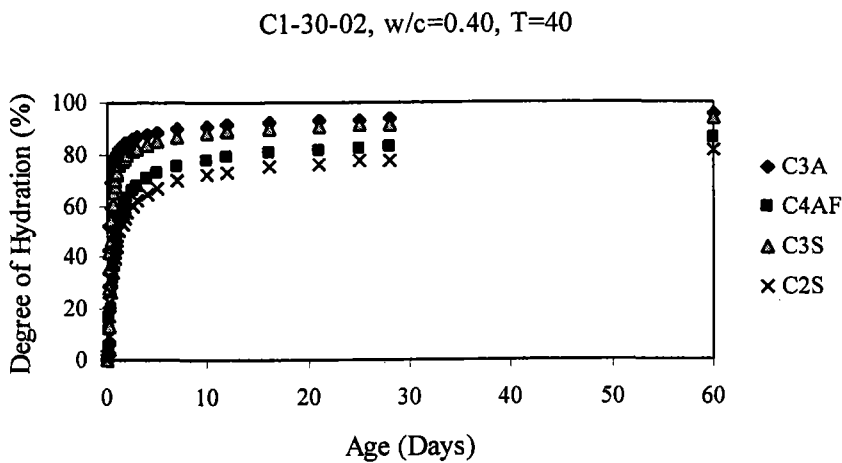


Fig. 8.9 Degree of hydration of type 1 cement with fineness 3190 cm²/g, w/c=0.40 at 40°C

The degree of hydration for many mix proportions was derived from multi-component hydration heat model. It was considered for the sake of convenience that the average degree of hydration would be applied in the model rather than the individual degree of hydration. The average degree of hydration can be computed from

$$\alpha_{\text{hy}}(t) = \frac{\sum_{i=1}^4 m_i \cdot \alpha_i(t)}{\sum_{i=1}^4 m_i} \quad (8.9)$$

where

- $\alpha_{\text{hy}}(t)$ = average degree of hydration (%)
- i = mineral compound of cement (C_3A , C_4AF , C_3S , C_2S)
- m_i = mass of each compound per cubic meter of cement paste at any water to binder ratio (kg/m^3)
- $\alpha_i(t)$ = degree of hydration of each compound in cement (%)

The effect of chemical composition of cement, water to cement ratio, temperature, and fineness were considered as to change degree of hydration too. Cement characteristics of Portland cement type 1, type 3 and type 5 were shown in Table A.1-A.2. The average degree of hydration from nonlinear heat conduction analysis program was shown as follows:

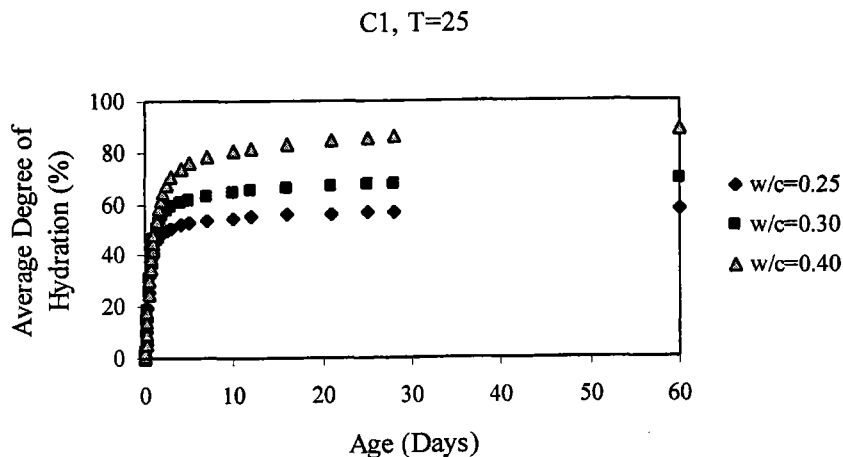


Fig. 8.10 Average degree of hydration of type 1 cement with fineness = $3190 \text{ cm}^2/\text{g}$, $w/c = 0.25, 0.30, \text{ and } 0.40$ at 25°C

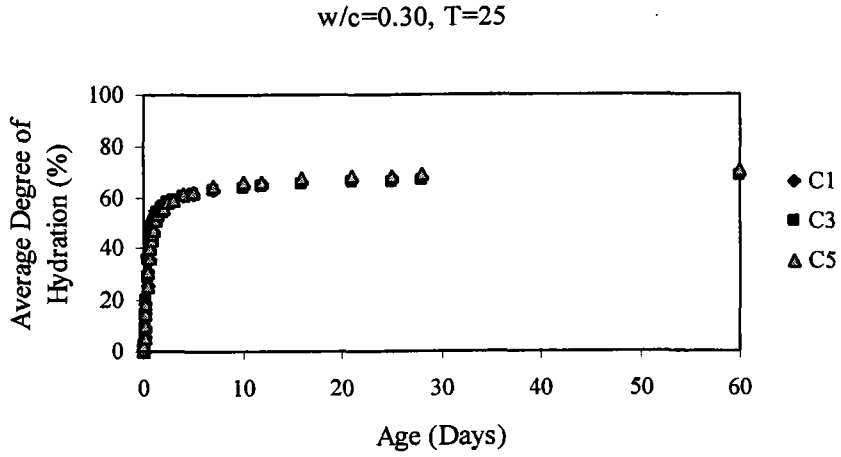


Fig. 8.11 Average degree of hydration of type 1, type 3, and type 5 cement with w/c = 0.30 at 25°C

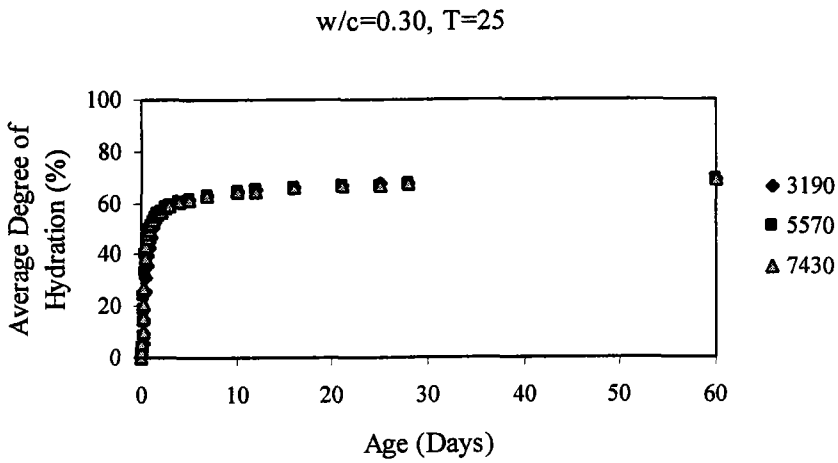


Fig. 8.12 Average degree of hydration of type 1 cement with fineness 3190, 5570, 7430 cm²/g, w/c = 0.30 at 25°C

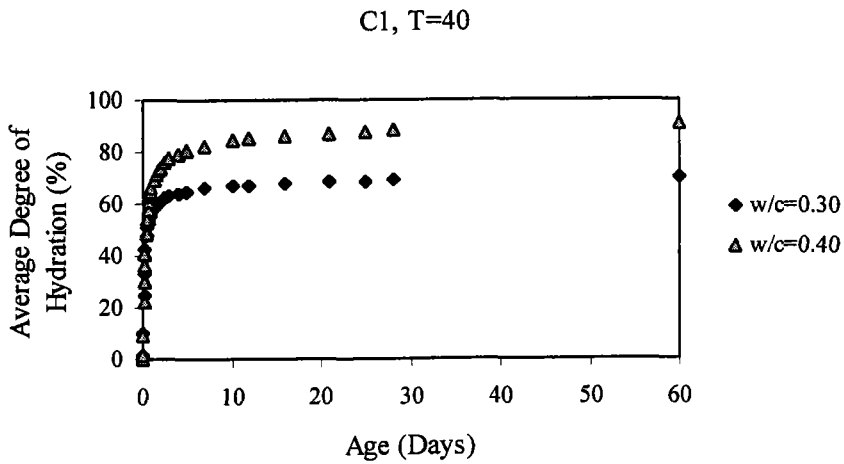


Fig. 8.13 Average degree of hydration of type 1 cement with fineness = 3190 cm²/g., w/c = 0.30 and 0.40 at 40°C

8.3.2 Degree of pozzolanic reaction

The principal product of the reactions of fly ash with alkali and calcium hydroxide in concrete is essentially the same as that of the hydration of Portland cement. A very small, immediate chemical reaction also takes place when fly ash is mixed with water, preferentially releasing calcium and aluminum ions to solution. The reaction of the fly ash continues to consume calcium hydroxide to form additional C-S-H as long as calcium hydroxide is present in the pore liquid of the cement paste. At room temperature the slower calcium-hydroxide activation prevails and the early alkali activation is minimized. As a result, pozzolanic reaction is retarded at early age of cement paste. The degree of pozzolanic reaction is assumed in this study as

$$\alpha_{\text{poz}}(t) = \frac{\tan^{-1}\left[\left(0.049 \cdot T - 0.186 \cdot \frac{w}{b} - 0.135\right) \cdot t\right]}{\tan^{-1}\left[\left(0.049 \cdot T - 0.186 \cdot \frac{w}{b} - 0.135\right) \cdot 365\right]} \cdot \alpha_{\text{poz}}(365) \quad (8.10)$$

$$\alpha_{\text{poz}}(365) = 100 - \left\{ (102 - 0.1 \cdot T) \cdot (0.416 + 0.0088 \cdot (w/b)^{-1.822}) \cdot \tan^{-1}\left\{ (7.927 \cdot (w/b)^{-1.546} - 15.699) \cdot [(\text{SiO}_2/\text{CaO}_{\text{eff}}) - (\% \text{SiO}_{2c}/\% \text{CaO}_c)] \right\} \right\} \quad (8.11)$$

$$\text{SiO}_2 = [(W_c \cdot \% \text{SiO}_{2c}) + (W_f \cdot \% \text{SiO}_{2f})]/100 \quad (8.12)$$

$$\text{CaO}_{\text{eff}} = [(W_c \cdot \% \text{CaO}_c) + \phi \cdot (W_f \cdot \% \text{CaO}_f)]/100 \quad (8.13)$$

$$\phi = \left\{ 1 - \exp[-a \cdot (\% \text{CaO}_f)] \right\} / \left\{ 1 + \exp[-a \cdot (\% \text{CaO}_f)] \right\} \quad (8.14)$$

$$a = 0.0048 \cdot (F_f/3000)^{3.0734} + 0.0245 \quad (8.15)$$

where

$\alpha_{\text{poz}}(t)$	=	degree of pozzolanic of paste at any age (%)
$\alpha_{\text{poz}}(365)$	=	degree of pozzolanic of paste at 365 days (%)
t	=	the time considered (days)
T	=	curing temperature ($^{\circ}\text{C}$)
w/b	=	water to binder ratio
$\% \text{CaO}_c$	=	calcium oxide content in cement (% by weight)
$\% \text{CaO}_f$	=	calcium oxide content in fly ash (% by weight)
$\% \text{SiO}_{2c}$	=	calcium oxide content in cement (% by weight)
$\% \text{SiO}_{2f}$	=	calcium oxide content in fly ash (% by weight)
CaO_{eff}	=	effective unit calcium oxide content in paste (kg/m^3)
SiO_2	=	silicon dioxide content in paste (kg/m^3)
ϕ	=	effectiveness of calcium oxide in fly ash
W_c	=	cement content in paste (kg/m^3)
W_f	=	fly ash content in paste (kg/m^3)
F_f	=	fineness of fly ash (cm^2/g)

The degree of pozzolanic reaction is affected by water to binder ratio, calcium oxide and silicon dioxide both in cement and fly ash, and fineness of fly ash. Because calcium oxide in fly ash is in different form from calcium oxide in cement, then calcium oxide in fly ash is assumed to give different effectiveness from calcium oxide in cement. The effectiveness of calcium oxide in fly ash is presented in Eq. (8.14). The degree of pozzolanic reaction of mix proportions used in this study are shown in Fig. 8.14 to Fig. 8.19.

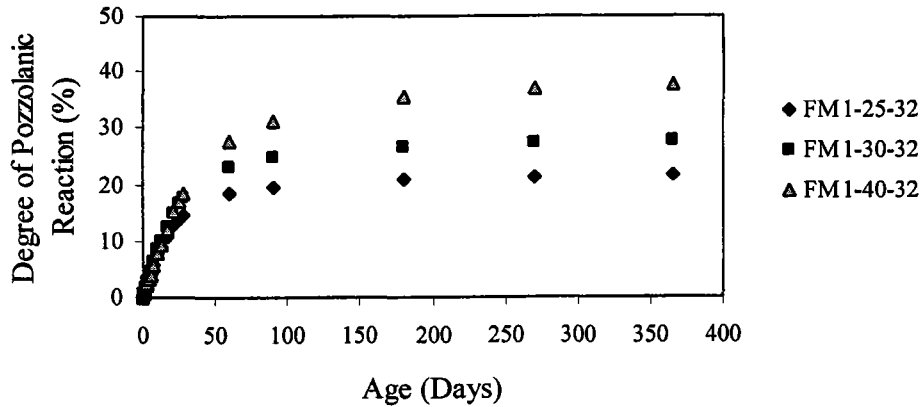


Fig. 8.14 Degree of pozzolanic reaction of fly ash FM1 with $r = 0.30$, $w/b = 0.25, 0.30$ and 0.40 at 25°C

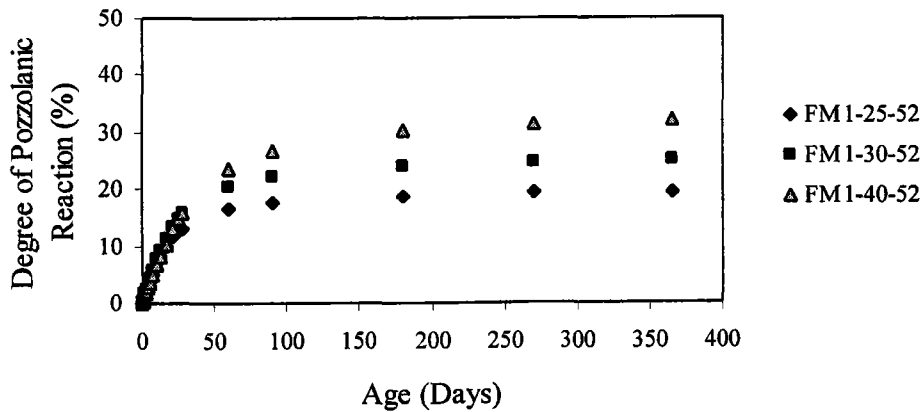


Fig. 8.15 Degree of pozzolanic reaction of fly ash FM1 with $r = 0.50$, $w/b = 0.25, 0.30$ and 0.40 at 25°C

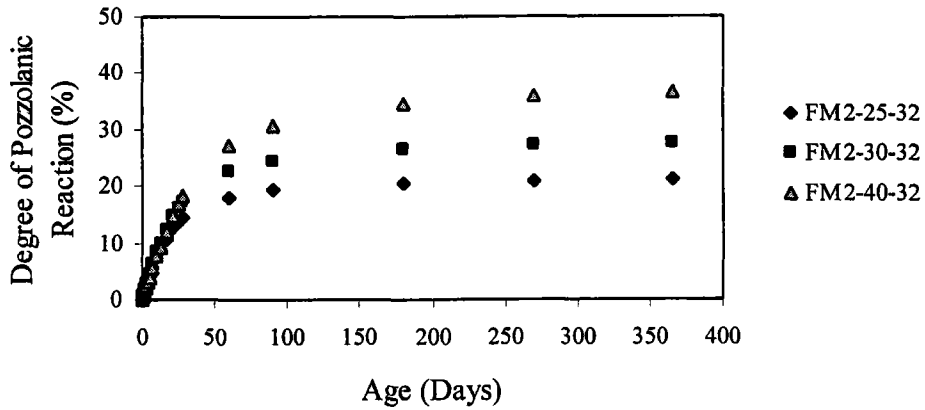


Fig. 8.16 Degree of pozzolanic reaction of fly ash FM2 with $r = 0.30$, $w/b = 0.25, 0.30$ and 0.40 at 25°C

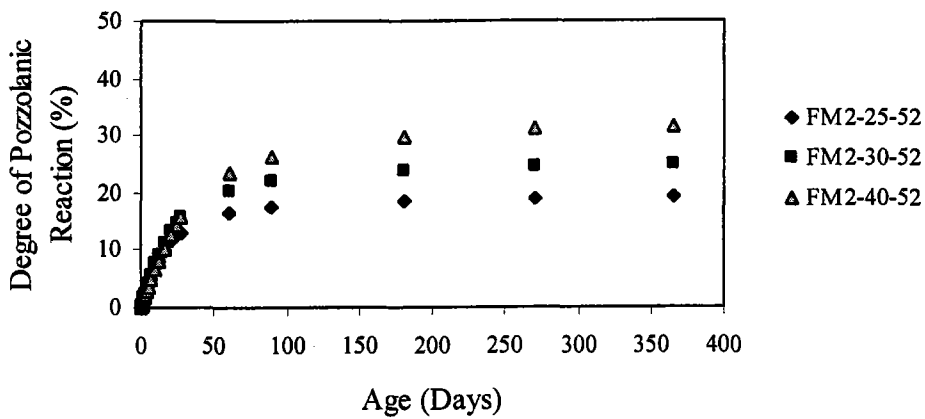


Fig. 8.17 Degree of pozzolanic reaction of fly ash FM2 with $r = 0.50$, $w/b = 0.25, 0.30$ and 0.40 at 25°C

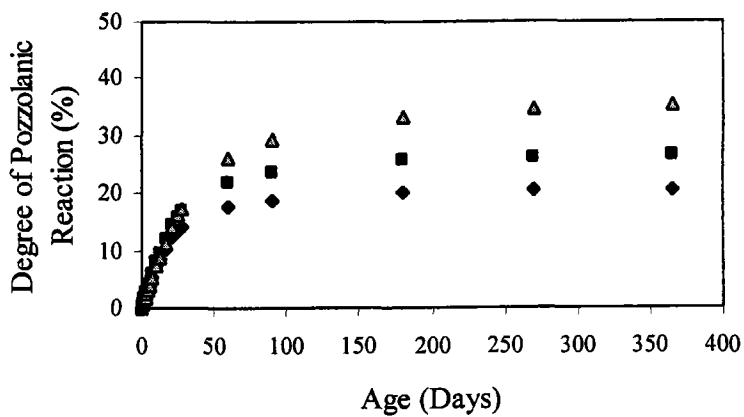


Fig. 8.18 Degree of pozzolanic reaction of fly ash FT with $r = 0.30$, $w/b = 0.25, 0.30$ and 0.40 at 25°C

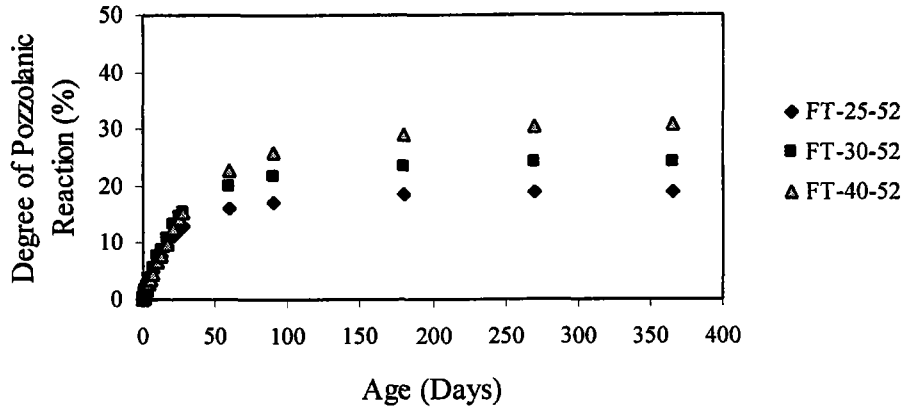


Fig. 8.19 Degree of pozzolanic reaction of fly ash FT with $r = 0.50$, $w/b = 0.25, 0.30$ and 0.40 at 25°C

8.3.3 Retardation of hydration reaction by fly ash

The use of fly ash may retard the time of setting of concrete. Jawed and Skalny (1981) found that Class F fly ash retards early C_3S hydration. Grutzeck, et al (1984) also found retardation with Class C fly ash. The retardation factor of C_3S hydration by fly ash is defined as

$$\psi = [(-7.633 \cdot r^2 + 5.219) \cdot (w/b + 0.053 \cdot r - 0.206)^{0.183 - 0.949 \cdot r}] \cdot (\alpha_{\text{C}_3\text{S}}/100)^{2.75 \cdot r - 0.495} \quad (8.16)$$

So, the degree of hydration of C_3S is reduced at early age to be

$$\alpha_{\text{C}_3\text{S},\text{poz}}(t) = \psi \cdot \alpha_{\text{C}_3\text{S}}(t) \quad (8.17)$$

where

- ψ = retardation factor of C_3S hydration by fly ash
- $\alpha_{\text{C}_3\text{S}}(t)$ = degree of hydration of C_3S without replacement of fly ash (%)
- $\alpha_{\text{C}_3\text{S},\text{poz}}(t)$ = degree of hydration of C_3S when replace cement with fly ash (%)
- r = replacement ratio of fly ash in total powder content by weight

The hydration of C_3S is retarded at early age resulting in lower autogenous shrinkage by chemical effect to be

$$\begin{aligned} \varepsilon_{\text{as,chem}}(t) = & \left(A \cdot m_{\text{C}_3\text{A}} \cdot \alpha_{\text{C}_3\text{A}}(t) \right) + \left(B \cdot m_{\text{C}_4\text{AF}} \cdot \alpha_{\text{C}_4\text{AF}}(t) \right) \\ & + \left(C \cdot m_{\text{C}_3\text{S}} \cdot \psi \cdot \alpha_{\text{C}_3\text{S}}(t) \right) + \left(D \cdot m_{\text{C}_2\text{S}} \cdot \alpha_{\text{C}_2\text{S}}(t) \right) + \left(E \cdot m_{\text{FA}} \cdot \alpha_{\text{poz}}(t) \right) \end{aligned} \quad (8.18)$$

8.4 Autogenous Shrinkage by Physical Effect

For the autogenous by physical effect, local thermodynamic and interface equilibrium are considered. Vapor and liquid interfaces in pore structure would be formed due to the pressure difference by capillary attraction. The total intensity of the tensile stress per unit concrete volume will depend on both the magnitudes of the tension and the area where it is applied. In this research the Shimomura and Maekawa's formulation (1996) for capillary stress which causes drying shrinkage is adopted as in Eq. (8.19). The stress-strain relationship, which describes the micro deformation of cement paste due to capillary stress, is assumed to be linear as shown in Eq. (8.20).

$$\sigma_{as,phy}(t) = \left(\frac{2\gamma \cdot A_s(t)}{r_{ave}(t)} \right) \times 10^{-5} \quad (8.19)$$

$$\varepsilon_{as,phy}(t) = \frac{\sigma_{as,phy}(t)}{E_s} \quad (8.20)$$

$$\varepsilon_{as,phy}(t) = \left(\frac{2\gamma \cdot A_s(t)}{r_{ave}(t)} \right) 10^{-5} / E_s \quad (8.21)$$

where

$\varepsilon_{as,phy}(t)$	=	autogenous shrinkage strain contributed by physical effect ($\times 10^{-6}$)
$\sigma_{as,phy}$	=	capillary stress (kgf/cm^2)
γ	=	surface tension of liquid water (N/m). The surface tension of water at constant temperature at 25°C is 72 N/m.
$A_s(t)$	=	area factor
$r_{ave}(t)$	=	average radius of the pore in cement paste (m)
E_s	=	elastic modulus for capillary stress (kgf/cm^2). In this study, E_s is assumed to be about $\frac{1}{4}$ of the ordinary value of the static elastic modulus of cement paste.
t	=	the time considered (days)

8.4.1 Average radius of pores

Typically, the size and range of pores present in the cement paste are distributed over several orders of magnitude. From the point of view of moisture transport, the overall cementitious micropore structure is divided into two basic components, which are capillary and gel pores. The capillary pores are actually empty space left between partially hydrated cement grain. Autogenous shrinkage by physical effect, which is caused by loss of water used up in hydration normally occurs due to self-desiccation of capillary pores. However, only the capillary pores, which are not permanently saturated can cause surface tension of liquid inside pores. In this study, we assumed that pore radius smaller than 6 nm. would be completely filled by water. According to a semi-microscopic approach, average pore radius is assumed to represent the pore size distribution. Some pore size distributions detected by mercury intrusion porosimetry (MIP) were tested at Thailand Institute of Scientific and Technological Research. The test results are shown in Appendix D. From the pore

size distribution, the volume of pore size which was assumed to be the saturated pores (smaller than 6 nm.) are excluded. Then, the average pore size is determined from average by volume of unsaturated pore as shown in Fig. 8.20.

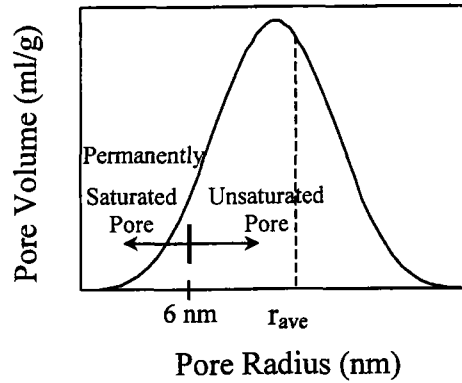


Fig. 8.20 The example of pore size distribution of paste

The average pore size decreases when degree of hydration and degree of pozzolanic reaction, C_3S and C_3A , and fineness of cement are increased, whereas water to binder ratio, and curing temperature are decreased. The autogenous shrinkage by physical effect, which affected by capillary tension increases with the decreasing of average pore radius. The model for average pore radius was proposed in this study as presented in Fig. 8.21 to Fig. 8.29. An equation to simulate average pore radius is shown in Eq. (8.22).

$$r_{ave}(t) = \left\{ (-48.99 \cdot (-0.241 + w/b)^{0.44}) + 1.9 \cdot \exp[9.39 \cdot (w/b - 0.244)^{0.07} + (-6.67 + \exp(-1.47 + 5.79 \cdot w/b)) \cdot \alpha_{ave}(t)/100] \right\} \cdot [1602.35 \cdot F^{-1.02} + 0.57] \cdot [0.94 + \exp(1.71 - 55.17 \cdot C_3A)] \quad (8.22)$$

$$\alpha_{ave}(t) = (1-r) \cdot \alpha_{hy}(t) + 0.4 \cdot r \cdot \tan^{-1}[13 \cdot \alpha_{poz}(t)] \quad (8.23)$$

where

- $\alpha_{ave}(t)$ = average reaction of paste (%)
- $\alpha_{hy}(t)$ = average degree of hydration of paste (%)
- $\alpha_{poz}(t)$ = degree of pozzolanic reaction of paste (%)

The retardation factor of C_3S hydration (ψ) is also applied to the average degree of hydration in Eq. (8.9) which is used to compute the average reaction of paste in Eq. (8.23).

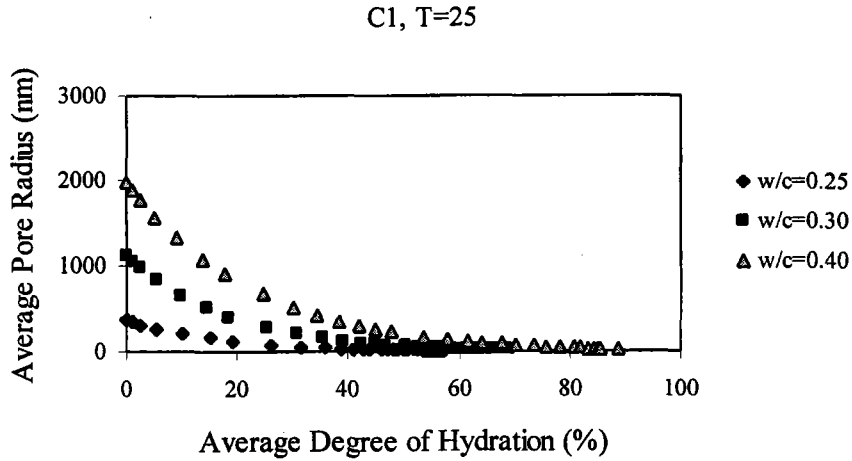


Fig. 8.21 Average pore radius of paste of type 1 cement with fineness = $3190 \text{ cm}^2/\text{g}$., $w/c = 0.25, 0.30,$ and 0.40 at 25°C

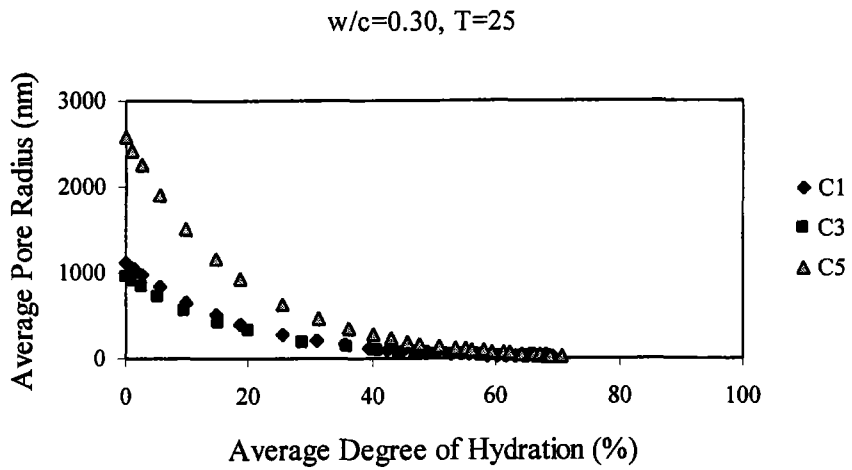


Fig. 8.22 Average pore radius of paste of type 1, type 3, and type 5 cement with $w/c = 0.30$ at 25°C

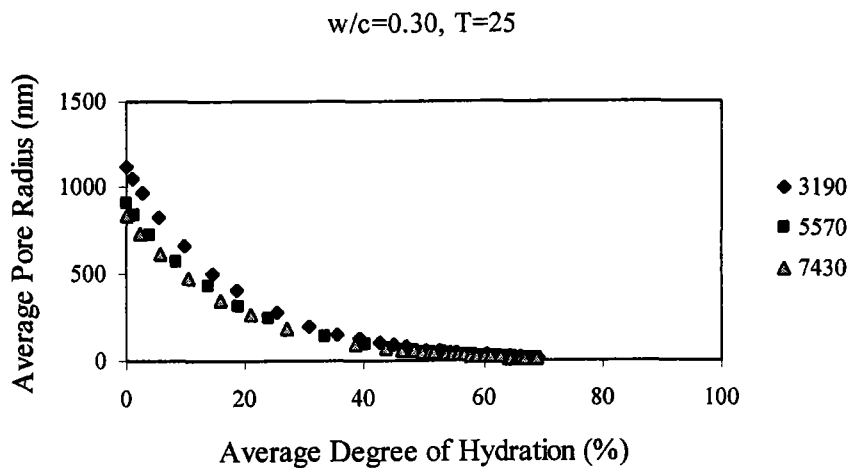


Fig. 8.23 Average pore radius of paste of type 1 cement with fineness $3190, 5570,$ $7430 \text{ cm}^2/\text{g}$, $w/c = 0.30$ at 25°C

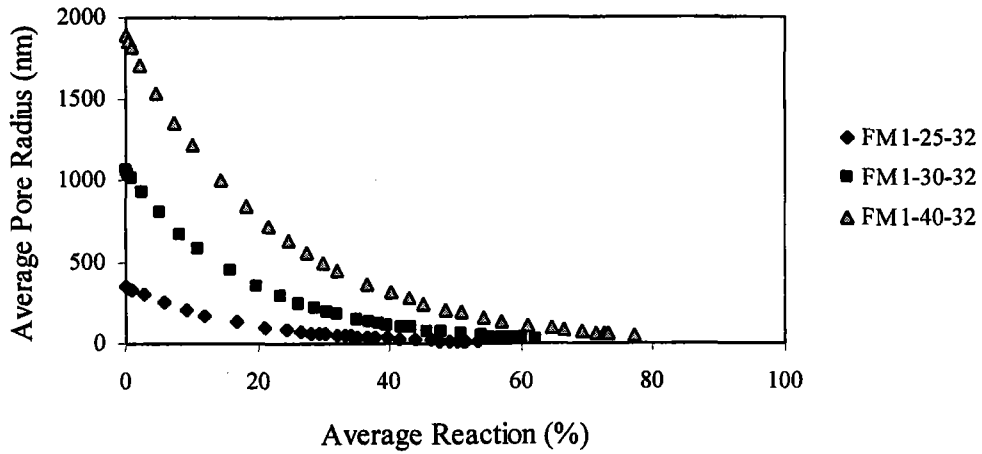


Fig. 8.24 Average pore radius of paste with fly ash FM1 with $r = 0.30$, $w/b = 0.25$, 0.30 and 0.40 at 25°C

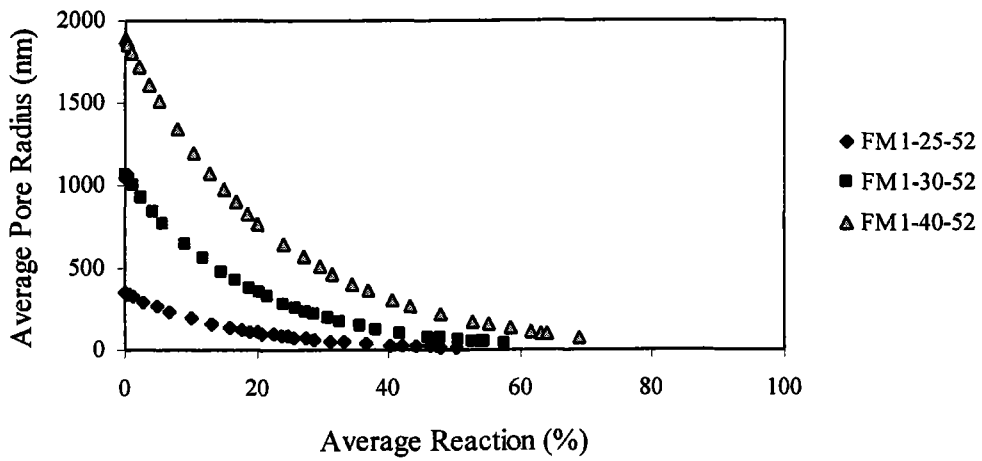


Fig. 8.25 Average pore radius of paste with fly ash FM1 with $r = 0.50$, $w/b = 0.25$, 0.30 and 0.40 at 25°C

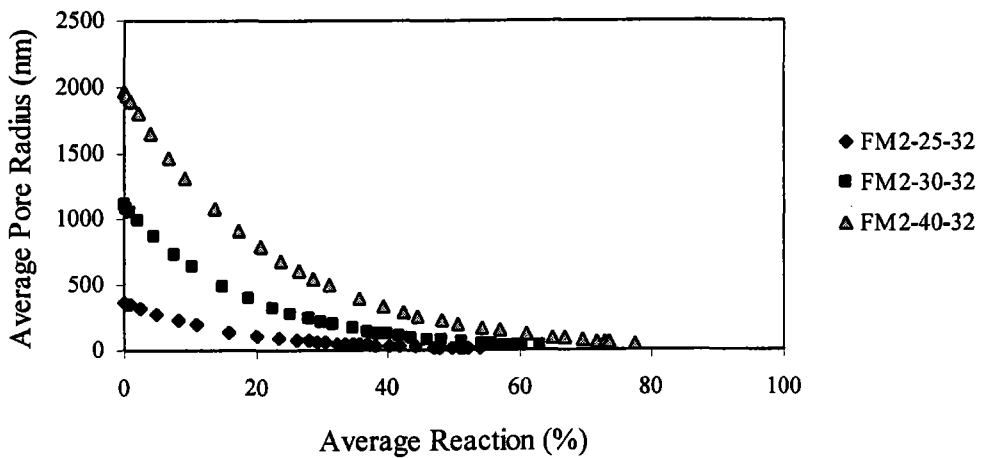


Fig. 8.26 Average pore radius of paste with fly ash FM2 with $r = 0.30$, $w/b = 0.25$, 0.30 and 0.40 at 25°C

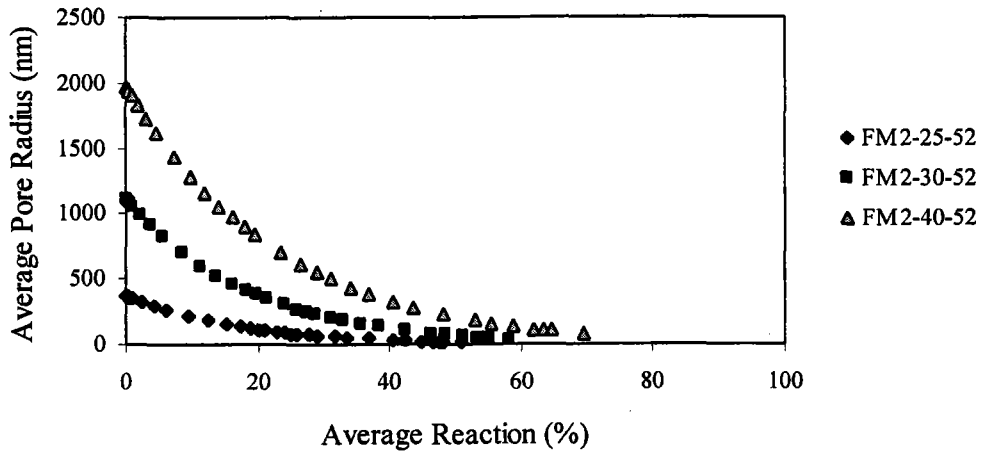


Fig. 8.27 Average pore radius of paste with fly ash FM2 with $r = 0.50$, $w/b = 0.25$, 0.30 and 0.40 at 25°C

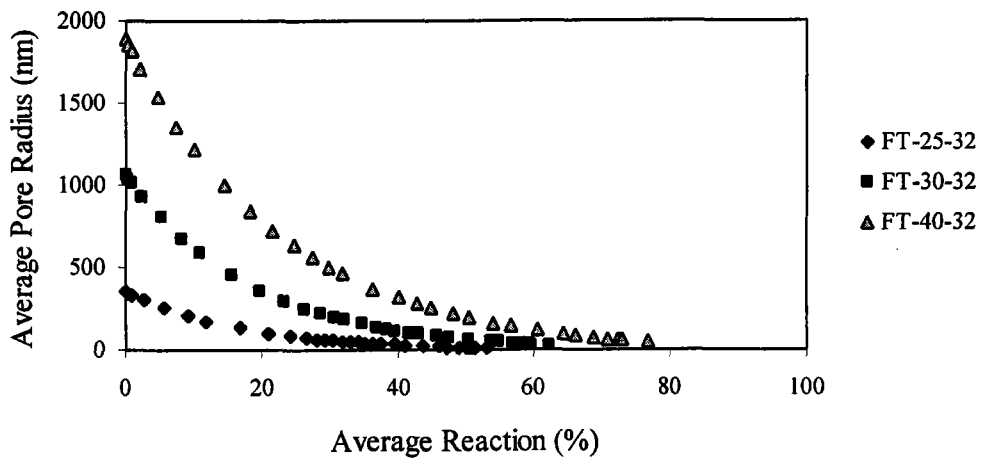


Fig. 8.28 Average pore radius of paste with fly ash FT with $r = 0.30$, $w/b = 0.25$, 0.30 and 0.40 at 25°C

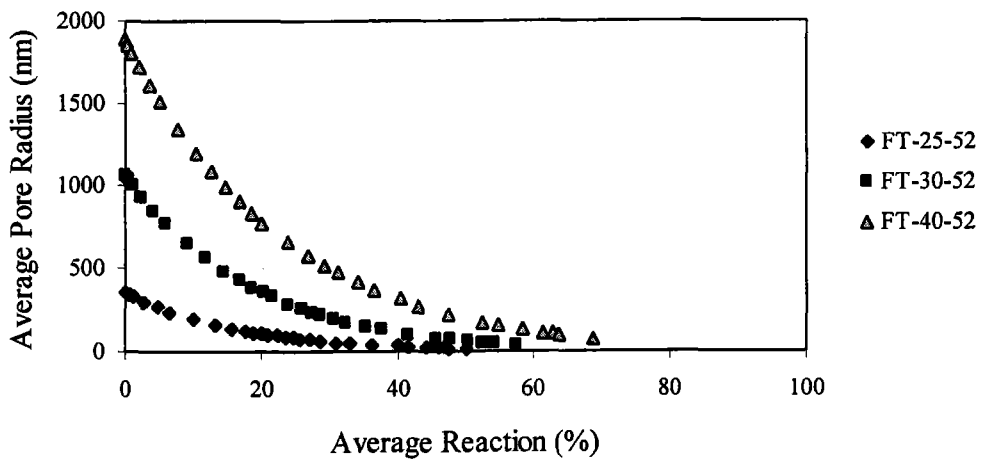


Fig. 8.29 Average pore radius of paste with fly ash FT with $r = 0.50$, $w/b = 0.25$, 0.30 and 0.40 at 25°C

8.4.2 Area factor

The capillary stress is applied on pore walls where liquid water exists. Therefore, area factor ($A_s(t)$) in Eq. (8.19) is defined as the free water content per unit paste volume. It has to be remembered that the free water content of paste reduces with time due to water consumption in hydration process. The minimum water to cement ratio, which is required to complete hydration of cement paste 0.21. In fly ash-cement paste, the minimum water content for completing reaction will be reduced with the increase of fly ash replacement. The minimum water content for completing reaction is equal to 0.20 for paste with 30% of fly ash replacement, and equal to 0.18 for paste with 50% of fly ash replacement. The free water content at a certain time ($V_w(t)$) can be estimated from the average reaction ($\alpha_{ave}(t)$) comparing with the completing reaction as

$$V_w(t) = V_{wo}(0) - (0.21 - 0.13 \cdot r^{2.15}) \cdot (W_c + W_f) \cdot \alpha_{ave}(t) / 100 \quad (8.24)$$

where

$V_w(t)$	=	volume of free water in paste at time t (m^3/m^3)
$V_{wo}(0)$	=	volume of water used in the mixture of paste (m^3/m^3)
W_c	=	weight of cement in paste (kg/m^3)
W_f	=	weight of fly ash in paste (kg/m^3)
r	=	replacement ratio of fly ash in total powder content by weight
$\alpha_{ave}(t)$	=	average reaction of paste (%)

So, area factor at any time can be determined from

$$A_s(t) = \frac{V_w(t)}{V_p} \quad (8.25)$$

where

$A_s(t)$	=	area factor
V_p	=	volume of paste = 1.0 (m^3)

8.5 Effect of Curing Temperature on Autogenous Shrinkage

The higher the temperature of the concrete, causing a rapid initial hydration, results in a non-uniform distribution of the cement gel with a poorer physical structure, which is probably more porous than the structure developed at normal temperatures. With a high temperature, there is insufficient time available for the products of hydration to diffuse away from the cement grains and for a uniform precipitation in the interstitial space. As a result, a concentration of hydration products is built in the vicinity of the hydrating cement grains, a process which retards subsequent hydration and, thus, the development of longer-term strength. While, cement hydrates at low temperature, and therefore hydrates slowly, there is ample time for the hydration products to diffuse and precipitate relatively uniformly.

The hydration products of higher temperature formed by rapid early hydration causes larger autogenous shrinkage than lower curing temperature at the initial state. High curing temperature will accelerate the early hydration and form hydration products with has a smaller volume than the concrete materials before hydrate. Then,

autogenous shrinkage by chemical effect of high curing temperature will increase rapidly at initial state. When time is longer, the rate of hydration of high temperature is lower and pore radius gets larger than normal temperature. Then, the surface tension of capillary pores becomes lower. As a result, autogenous shrinkage from self-desiccation by physical effect of high temperature in long term will be small. The curing temperature affects autogenous shrinkage in two manners. Firstly, it affects degree of hydration and average degree of hydration in Eq. (8.8) and Eq. (8.9), which depends on cumulative heat. Secondly, it affects the average pore radius in Eq. (8.22), which is modified to take into account the effect of temperature as

$$r_{ave}(t) = \{(-48.99 \cdot (-0.241 + w/b)^{0.44}) + 1.9 \cdot \exp[9.39 \cdot (w/b - 0.244)^{0.07} + (-6.67 + \exp(-1.47 + 5.79 \cdot w/b)) \cdot f(T) \cdot \alpha_{ave}(t)/100]\} \cdot [1602.35 \cdot F^{-1.02} + 0.57] \cdot [0.94 + \exp(1.71 - 55.17 \cdot C_3A)] \quad (8.26)$$

$$f(T) = -8.95 \times 10^{-4} \cdot \exp(-0.508 + 0.125 \cdot T) + 1.012 \quad (8.27)$$

where

T = curing temperature (°C)

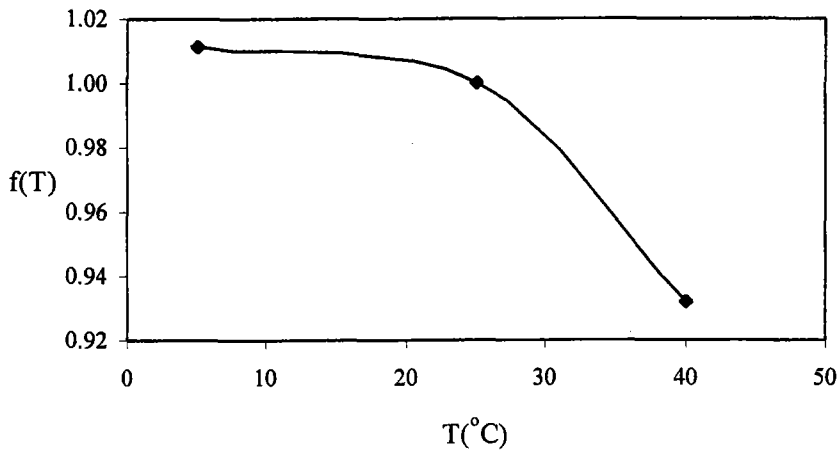


Fig. 8.30 The effect of curing temperature on average pore radius

8.6 Expansion

The chemical expansion, which compensates autogenous shrinkage, is believed to be the result of SO₃ content in fly ash. The SO₃ content in fly ash exists mainly in form of CaSO₄. When it reacts with water, it hydrates to form gypsum.

From the test results, it can be seen that the chemical expansion of fly ash-cement pastes increase with increasing of SO₃ content in fly ash and also replacement percentage of fly ash. Then, chemical expansion of fly ash-cement paste can be obtained as

$$\epsilon_{exp}(t) = (2.58 \cdot \%SO_3 + 109.42 \cdot r + 200 \cdot w/b - 60) \cdot \tan^{-1}[(0.4159 + 0.0337 \cdot \%SO_3) \cdot t] \quad (8.28)$$

where

- $\epsilon_{exp}(t)$ = chemical expansion of fly ash-cement paste ($\times 10^{-6}$)
- $\%SO_3$ = sulfur trioxide content in fly ash (% by weight)
- r = replacement ratio of fly ash in total powder content by weight
- w/b = water to binder ratio
- t = the time considered (days)

The examples of the chemical shrinkage from the model are shown in Fig. 8.31 to Fig. 8.33.

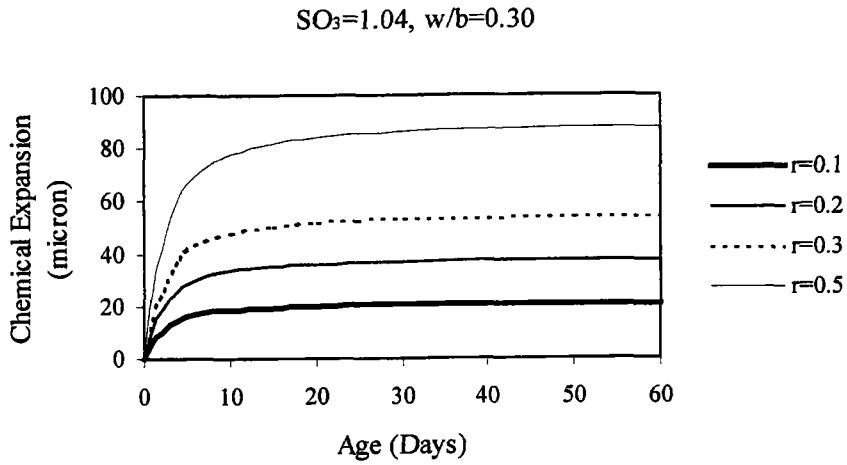


Fig. 8.31 Chemical expansion of cement-fly ash paste with different replacement percentage of fly ash (r)

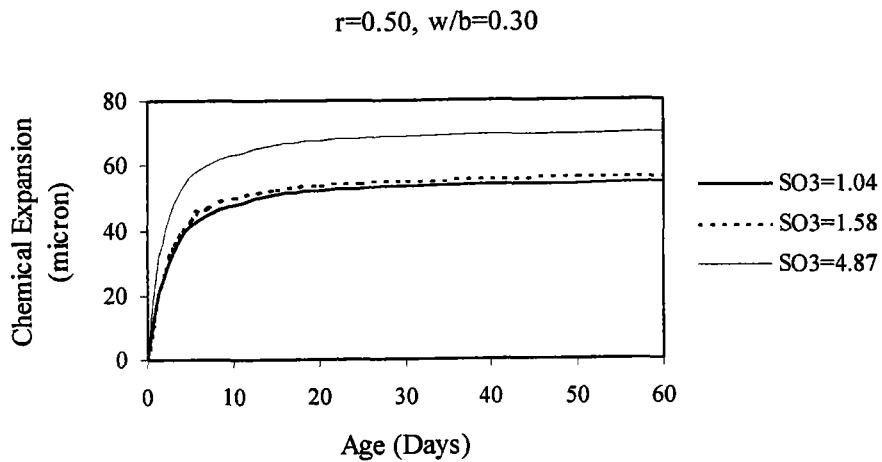


Fig. 8.32 Chemical expansion of cement-fly ash paste with different SO_3 percentage

SO₃=1.04, r=0.50

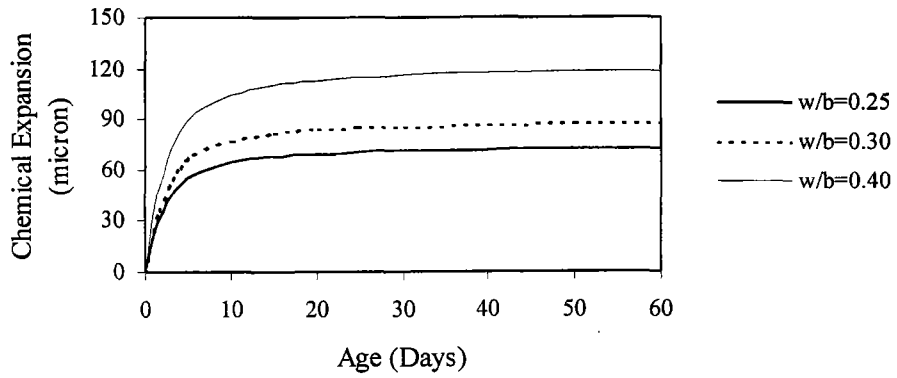


Fig. 8.33 Chemical expansion of cement-fly ash paste with different water to binder ratio (w/b)