

## CHAPTER 4

### THEORETICAL CONSIDERATIONS FOR THE EMPIRICAL FUNCTION OF THE AVERAGE DEGREE OF HYDRATION

#### 4.1 General

Some fundamental aspects of the chemistry of the hydration reaction are reviewed in this chapter. First, a brief account is given of Portland cement and its constituent oxides. Next, the hydration of cement is discussed. Finally, the parameters affecting the strength development of concrete are identified and classified according to their strength imparting mechanism.

#### 4.2 Portland Cement

Portland cement consists mainly of lime (CaO), silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and ferric-oxide (Fe<sub>2</sub>O<sub>3</sub>) which result in the formations of C<sub>2</sub>S, C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF. These compounds are called the major compounds. A brief discussion is given about the behavior of major compounds.

##### 4.2.1 Tricalcium silicate (C<sub>3</sub>S)

C<sub>3</sub>S is unstable at temperatures below 1,250°C, and it breaks down to C<sub>2</sub>S and CaO. This break down, however, is very slow. On the addition of water (Soroka 1979) setting takes place and the paste hardens within a few hours. The resulting solid gains strength mainly during the first week. Setting of C<sub>3</sub>S involves a hydration process. The hydration is exothermic and in the case of C<sub>3</sub>S the amount of heat liberated is about 120 cal/g (Neville 1990).

##### 4.2.2 Dicalcium silicate (C<sub>2</sub>S)

The hardened paste of C<sub>2</sub>S gains strength steadily and slowly for weeks and months, reaching a final strength which may be the same order as C<sub>3</sub>S. On addition of water, its hydration liberates a comparatively small amount of heat about 62 cal/g (Neville 1990).

##### 4.2.3 Tricalcium aluminate (C<sub>3</sub>A)

In its pure form, tricalcium aluminate reacts with water almost instantaneously giving a flash set accompanied by the evolution of large quantity of heat equal to about 207 cal/g (Neville 1990). Normal setting is achieved by adding gypsum to the mixture of C<sub>3</sub>A and water. The contribution of C<sub>3</sub>A is not certain to the strength of cement paste. It has unfavorable effects on the strength of cement paste if present in large quantities in the cement.

#### **4.2.4 Tetracalcium aluminoferrite ( $C_4AF$ )**

$C_4AF$  reacts with water rapidly and setting occurs within minutes. The heat of hydration is approximately 100 cal/g (Neville 1990). The strength of the set paste is uncertain.

### **4.3 Hydration of Cement**

The rate of hydration of Portland cement depends upon many factors, and the properties of hardened paste depend on its degree of hydration. The factors that affect the rate of hydration are described in this section.

#### **4.3.1 Ages of cement paste**

Except for dormant period, the rate of hydration is maximum at early ages. The rate decreases with age until a stage is reached when virtually no hydration takes place. The decrease in the hydration rate may be attributed to the formation of a dense layer of calcium silicate hydrate gel around the cement grains. The hydration process stops when:

1. No more water is available for reaction.
2. No more unhydrated cement is available.
3. Diffusion can not take place due to lack of spaces of sufficiently large space for creation of new solid hydration products.

#### **4.3.2 Cement composition**

The rate of hydration of Portland cement, and therefore its rate of hardening, depends mainly on its chemical composition. The rate of hydration of individual cement constituents ( $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ ) varies considerably as mentioned at the beginning of this chapter.

#### **4.3.3 Water to cement ratio**

Fresh cement paste is a plastic network of particles of cement in water. Since most of the products of hydration are colloidal during hydration the surface area of the solid phase increases enormously, and a large amount of free water becomes adsorbed on this surface. If no water movement to or from the cement paste is permitted, the reactions of hydration use up the water until too little is left to saturate the solid surfaces, and the relative humidity within the paste decreases. This is known as self-desiccation. However, in self-desiccated pastes with water to cement ratio in excess of 0.5, the amount of mixing water is sufficient for hydration to proceed at the same rate as when moist-cured. The lower the water to cement ratio, the lower the degree of hydration and the average rate of hydration as shown in Fig. 4.1. When the amount of water to cement ratio is increased, it causes high possibility for cement to contact with water. This has the effect of increasing average degree of hydration at long term. And it implies that cement is almost completely hydrated at w/c equal 0.6 and higher.

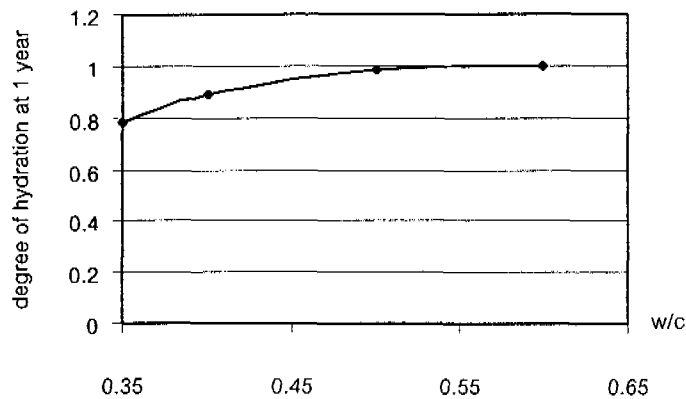


Fig. 4.1 Average degree of hydration at 1 year with various amount of water to cement ratio

#### 4.3.4 Temperature

By the accelerated initial hydration, which occurs at the elevated temperature, no uniform diffusion and sedimentation of the hydration products in the internal space between the cement grains can be achieved. When cement hydrates at a low temperature, and therefore hydrates slowly, there is ample time for the hydration products to diffuse and precipitate relatively uniformly throughout the interstitial space, among the cement grains. However, if the hydration is accelerated, as by the increased temperature, the high rate of reaction does not allow time for such diffusion and precipitation. Therefore, a high concentration of hydration products is built up in the zone surrounding the hydrating cement grains. The presence of this highly concentrated, dense and encapsulating layer, which forms an impermeable rim around the cement grain, should retard subsequent hydration.

It is believed that the dense zone of hydration products around the hydrating grain, created by rapid early hydration, significantly reduces the ultimate degree of hydration of the silicate phases.

The hydration products of a weaker physical structure are formed, more porous than usual, so that the larger portion of pores remains unfilled. The hydration level at the later age of concrete is lower, which causes significantly lower ultimate strengths.

So it is clear that the structures of hydration products formed by rapid early hydration are more porous than those formed at a lower temperature. If water permeability and water absorption is higher for concrete hardened at high temperature, it is believed that the durability of this concrete is lower too.

#### 4.4 Prediction of Degree of Hydration

In this study, the prediction of degree of hydration is based upon a multi-component division of cement and the rate of heat generation for each of these components under various temperature is based on modified Arrhenius's law (Maekawa and Kishi 1998). Mutual interactions among the reacting constituents during hydration and their dependence on the availability of water in the concrete micropore are also quantitatively formulated. Simultaneously, studying these phenomena at any point enables the tracing of microstructure development with increase in the degree of hydration for arbitrary temperature and water content.

In this study, the degree of hydration reaction is assumed to be equal to the ratio between cumulative heat at the time considered and the total cumulative heat at 100% hydration. The multi-component heat model proposed by Maekawa and Kishi(1998) is applied for determination of the amount of heat generated.

##### 4.4.1 Basic concepts of multi-component model

Four main compounds of cement namely  $C_3A$ ,  $C_4AF$ ,  $C_3S$ , and  $C_2S$  take part in the generation of hydration heat. When cement is mixed with water these compounds produce cementitious products. It can be realized that the hydration characteristics of cement are equivalent to the combination of the hydration process of the individual compounds and the hydration-heat is very near to the sum of the heat of hydration of the individual compounds when hydrates alone. Therefore, specified chemical components of clinkers minerals are treated as characteristic parameters; consequently, the hydration of cement blended with fly ash or slag is expressed as,

$$\begin{aligned} H &= \sum \rho_i H_i \\ &= \rho_{C_3A} (H_{C_3AET} + H_{C_3A}) + \rho_{C_4AF} (H_{C_4AFET} + H_{C_4AF}) \\ &\quad + \rho_{C_3S} H_{C_3S} + \rho_{C_2S} H_{C_2S} + \rho_{SG} H_{SG} + \rho_{FA} H_{FA} \end{aligned} \quad (4.1)$$

where  $H_i$  : the heat generation rate of mineral i per unit weight  
 $i$  : mineral compound ( $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ )  
 $\rho_i$  : the weight composition ratio

$H_{C_3AET}$  and  $H_{C_4AFET}$  : both are heat generation rates in the process of formation of ettringite

The Arrhenius' law can be extended to the composite of different chemical reaction of clinker minerals as a single fictitious material by means of the average heat rate and variable activation energy. These are uniquely specified in terms of the accumulated heat of the cement through several adiabatic temperature rise tests. According to the Arrhenius' law, the temperature dependent rate of hydration heat is expressed with the coefficients representing the interaction among the constituents as,

$$H_i = \gamma_i \beta_i \lambda_i \mu_i s_i H_{i,t_0} (Q_i) \exp \left\{ -\frac{E_i}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right\} \quad (4.2)$$

$$Q_i = \int H_i dt \quad (4.3)$$

- where
- $E_i$  : the activation energy of component  $i$
  - $R$  : the gas constant
  - $H_{i,T_0}$  : the reference heat generation rate of component  $i$  at constant temperature  $T_0$
  - $\gamma$  : a coefficient expressing the delaying effect of chemical admixture and fly ash in the initial hydration exothermic process
  - $\beta_i$  : a coefficient expressing the reduction in heat generation rate due to the reduced availability of free water
  - $\lambda$  : a coefficient expressing the change of the heat generation rate of blast furnace slag and fly ash due to the lack of calcium hydroxide in the liquid phase
  - $\mu$  : a coefficient expressing changes in the heat generation rate in terms of the difference of mineral composition of Portland cement
  - $s_i$  : a coefficient for changing the reference heat rate according to the fineness of powders

#### 4.4.2 Determination of hydration heat of each cement compound

Although the multi-component model can predict the amount of heat generated accurately, the calculations in the multi-component model are time-consuming. Since the thermal activity of cement compound is related to the accumulated heat, the iterations are then necessary in the computation. The computer program called COMH3 has been introduced to handle this problem.

However, the original multi-component computer program seems not to be practical for the application of strength prediction model. Therefore, in this study, the empirical formula is rationally developed.

$$Q_{c3a} = \{[(1.756 \times T - 628.49) \times \ln(w/b) + 908.72 \times w/b - 802.77] \times t^{-0.57 \times (w/b)^2} + 0.53 \times w/b - 0.0007 \times T - 0.059\} + \{(1.95 \times T - 860.96) \times \ln(w/b) + 1265.02 \times w/b - 1325.1\} / \exp(t) + \{(-2.45 \times T + 928.62) \times \ln(w/b) - 1331.2 \times w/b + 1399.69\} \quad (4.4)$$

$$Q_{c3s} = \{(0.77 \times T - 251.49) \times \ln(w/b) + 314.14 \times w/b - 291.58\} \times t^{-0.5 \times (w/b)^2} + 0.54 \times w/b + 0.0056 \times T - 0.28\} + \{(0.89 \times T - 411.57) \times \ln(w/b) + 556.75 \times w/b - 630.1\} / \exp(t) + \{(-1.15 \times T + 434.09) \times \ln(w/b) - 561.44 \times w/b + 644.17\} \quad (4.5)$$

$$Q_{c2s} = \{[(-0.24 \times T + 63.55) \times \ln(w/b) - 147.12 \times w/b + 121.63] \times t^{-1.79 \times (w/b)^2} + 1.95 \times w/b - 0.003 \times T - 0.22\} + \{(-0.2 \times T - 24.73) \times \ln(w/b) - 42.5 \times w/b - 41.03\} / \exp(t) + \{(0.15 \times T + 13.11) \times \ln(w/b) + 66.2 \times w/b + 17.32\} \quad (4.6)$$

$$Q_{c4af} = \{[(-0.77 \times T + 266.98) \times \ln(w/b) - 551.85 \times w/b + 460.38] \times t^{(0.0025 \times T - 0.94) \times \ln(w/b) + (2.22 \times w/b - 1.54)} + [(-0.63 \times T + 70.87) \times \ln(w/b) - 269.04 \times w/b + 100.35] / \exp(t) + \{(0.49 \times T - 107.37) \times \ln(w/b) + 356.06 \times w/b - 176.68\} \quad (4.7)$$

#### 4.4.3 Comparison between the multi-component heat model and the empirical formula

The model of Cumulative Heat of each main compound was applied to simulate the Cumulative Heat results from The multi-component model proposed by Maekawa and Kishi (1998). In the graph, the multi-component model results are appeared in the form of a dot while the empirical-formula results are appeared in the form of a line as shown in Fig. 4.2 and Fig. 4.7.

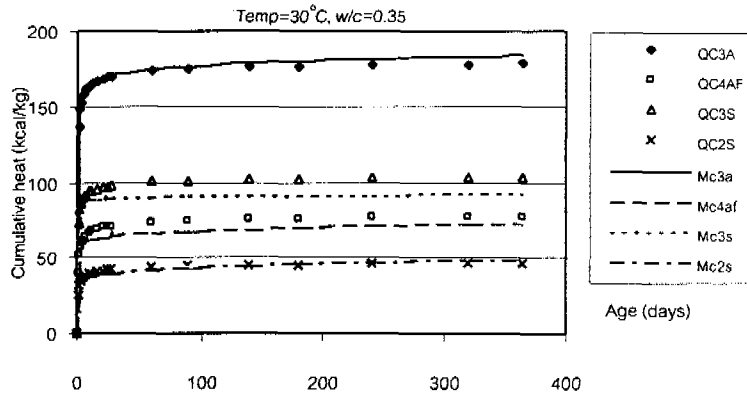


Fig. 4.2 Comparison of cumulative heat of each compound between the empirical model and the multi-component model at  $w/c = 0.35$  and temperature =  $30^{\circ}\text{C}$

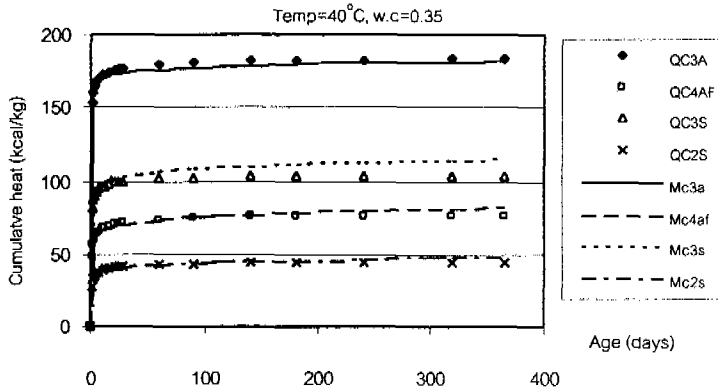


Fig. 4.3 Comparison of cumulative heat of each compound between the empirical model and the multi-component model at  $w/c = 0.35$  and temperature =  $40^{\circ}\text{C}$

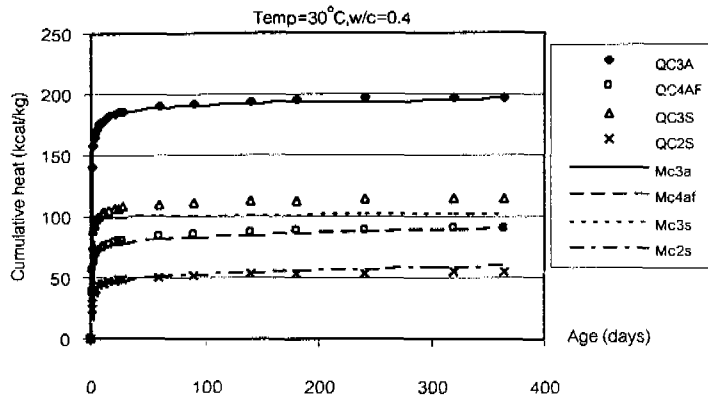


Fig. 4.4 Comparison of cumulative heat of each compound between the empirical model and the multi-component model at  $w/c = 0.40$  and temperature =  $30^{\circ}\text{C}$

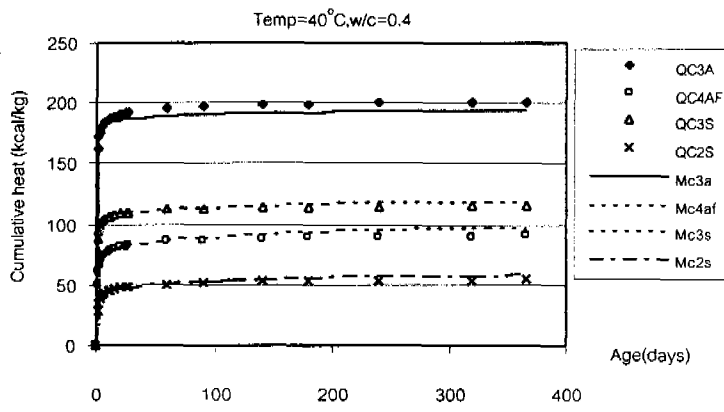


Fig. 4.5 Comparison of cumulative heat of each compound between the empirical model and the multi-component model at  $w/c = 0.40$  and temperature =  $40^{\circ}\text{C}$

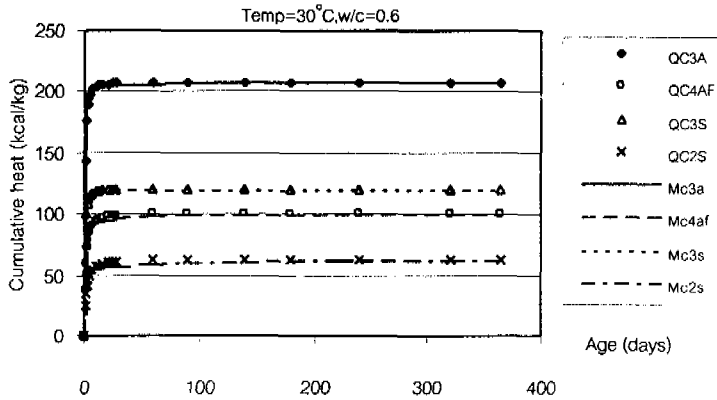


Fig. 4.6 Comparison of cumulative heat of each compound between the empirical model and the multi-component model at  $w/c = 0.60$  and temperature =  $30^{\circ}\text{C}$

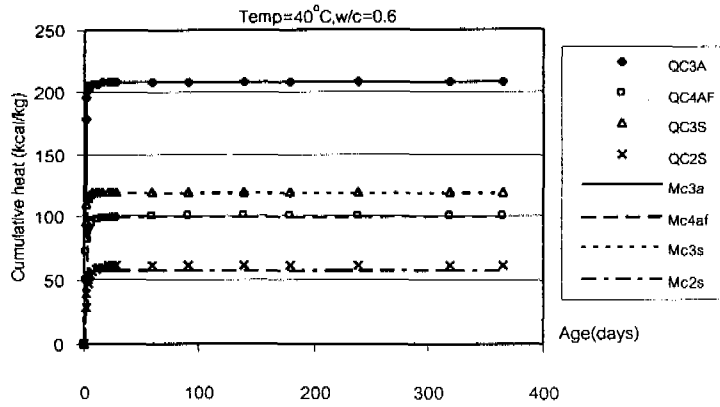


Fig. 4.7 Comparison of cumulative heat of each compound between the empirical model and the multi-component model at  $w/c = 0.60$  and temperature =  $40^{\circ}\text{C}$

#### 4.4.4 Determination of degree of hydration in strength development model

In this strength model, degree of hydration is considered to closely relate with the amount of heat generated by cementitious material. The degree of hydration of cement paste is defined as the average degree of hydration of all cement compounds. The degree of hydration of each compound is defined as the ratio of heat generated during the time step to the maximum heat generation of each mineral compound in cement which are given by

$$\alpha_i(t) = \frac{Q_i(t)}{Q_{i,\infty}} \quad (4.8)$$

where  $\alpha_i(t)$  : the degree of hydration at the considered time,  $t$ , of each oxide compound (%)

$Q_i(t)$  : the cumulative heat generated by each oxide compound in cement at the considered time,  $t$  (kcal/kg)

$Q_{i,\infty}$  : the final heat generation by each oxide compound where

$$\begin{aligned} Q_{c3a,\infty} &= 207 \text{ kcal/kg} & Q_{c4af,\infty} &= 100 \text{ kcal/kg} \\ Q_{c3s,\infty} &= 120 \text{ kcal/kg} & Q_{c2s,\infty} &= 62 \text{ kcal/kg} \end{aligned}$$

The cumulative heat generated model of the independent hydration concept approach enables evaluation of the average degree of hydration of cement as a weighted average of the independent rate of hydration of its constituents.

$$\alpha_{av}(t) = \frac{\sum_{i=1}^4 m_i \times \alpha_i(t)}{\sum_{i=1}^4 m_i} \quad (4.9)$$



$$m_i = \frac{\gamma_i \times C}{100} \quad (4.10)$$

where  $\alpha_{av}(t)$  : the average degree of hydration at the considered time, t (%)  
 $m_i$  : mass of each compound per cubic meter of concrete at any water to binder ratio  
 $\gamma_i$  : percentage of each compound in cement (%)  
 $C$  : cement content in the mixture ( $\text{kg/m}^3$ )

Coming up to this part, the average degree of hydration for arbitrary temperature and water content could be predicted as shown in Fig. 4.8. to Fig. 4.23.

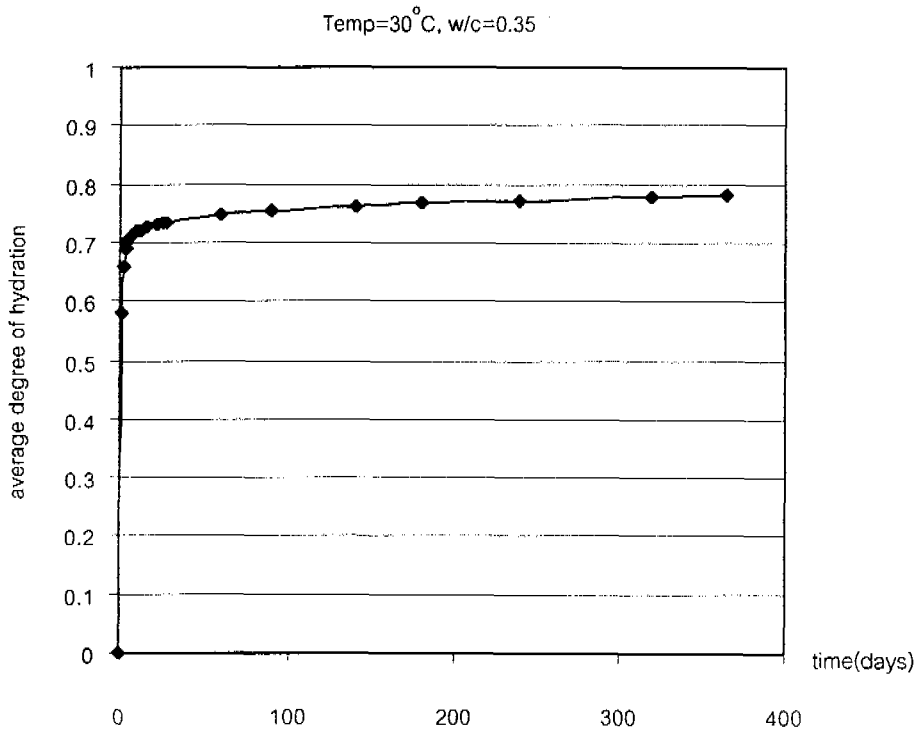


Fig. 4.8 The average degree of hydration at any considered age t and cured at room temperature by controlling w/c = 0.35

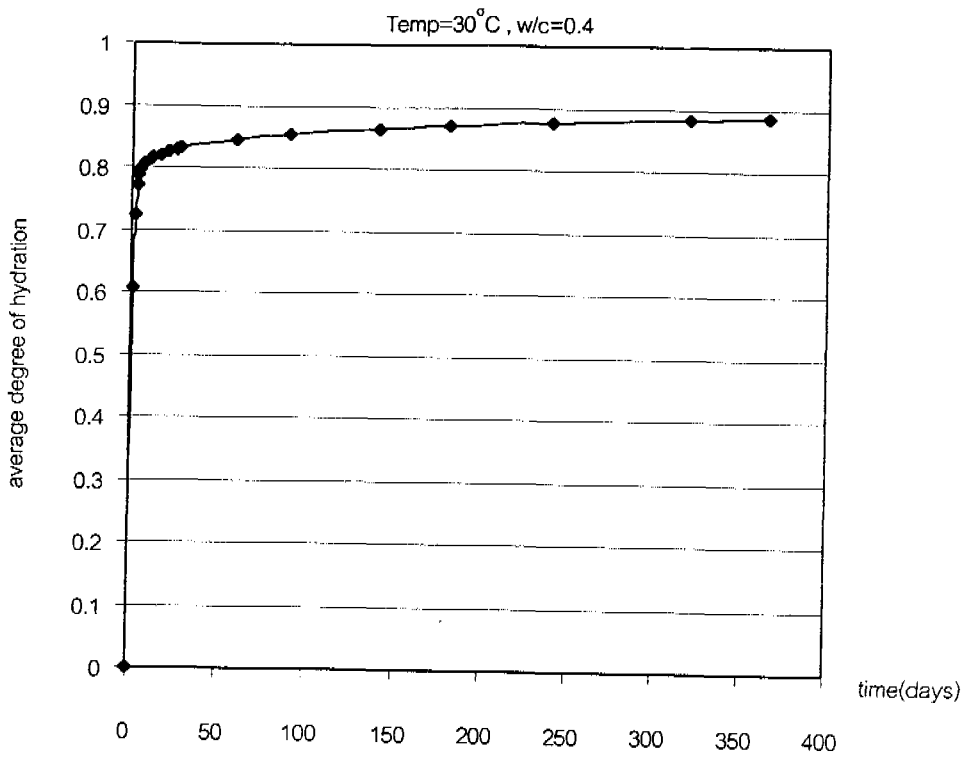


Fig. 4.9 The average degree of hydration at any considered age  $t$  and cured at room temperature by controlling  $w/c = 0.4$

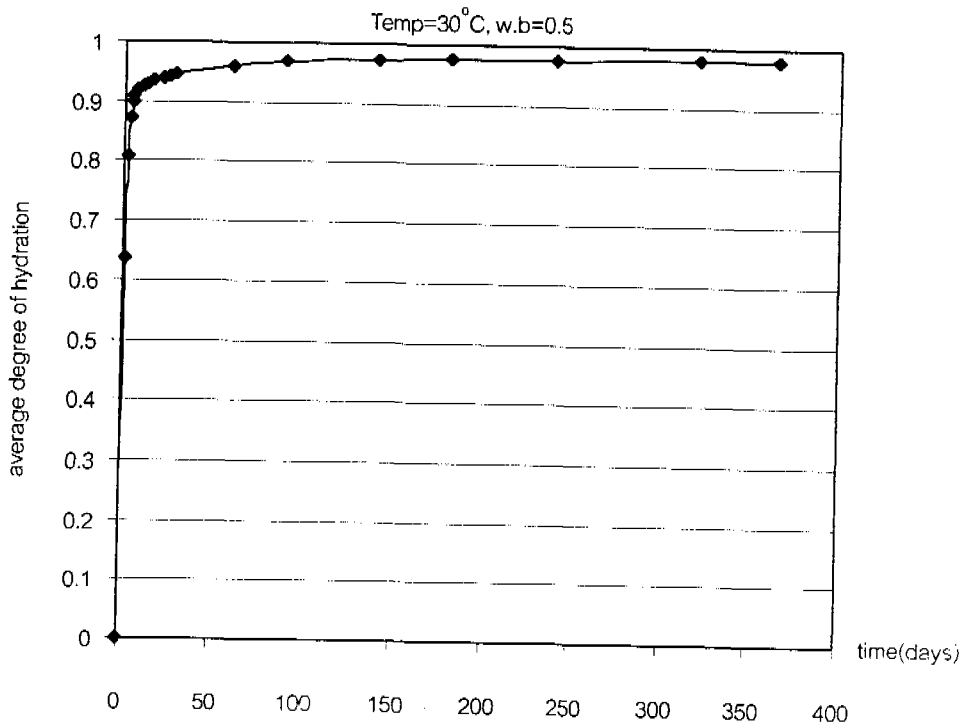


Fig. 4.10 The average degree of hydration at any considered age  $t$  and cured at room temperature by controlling  $w/c = 0.5$

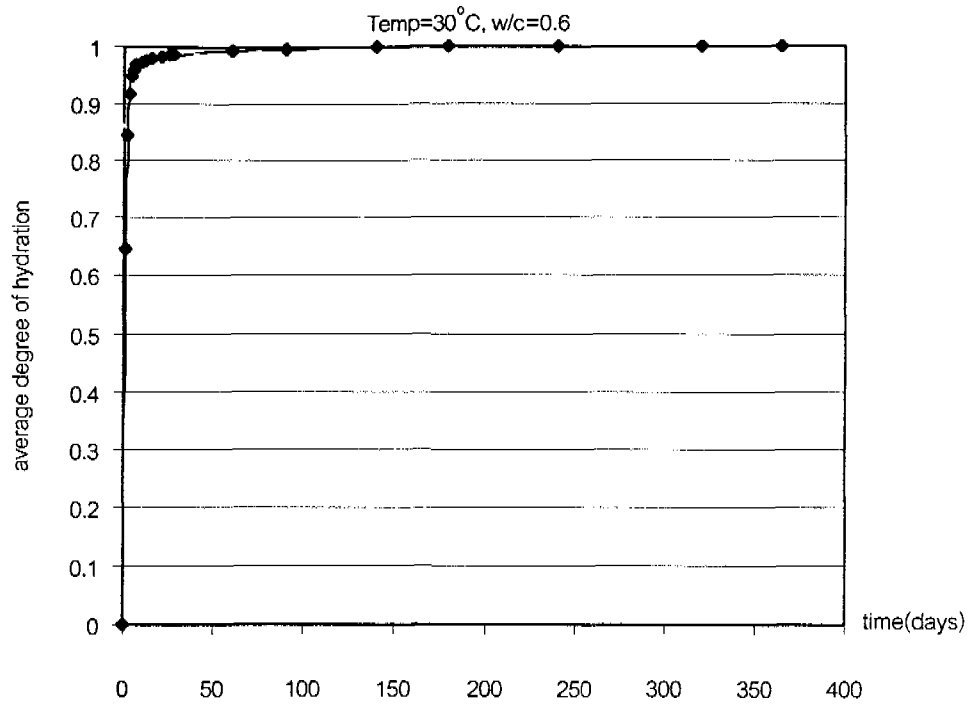


Fig. 4.11 The average degree of hydration at any considered age  $t$  and cured at room temperature by controlling  $w/c = 0.6$

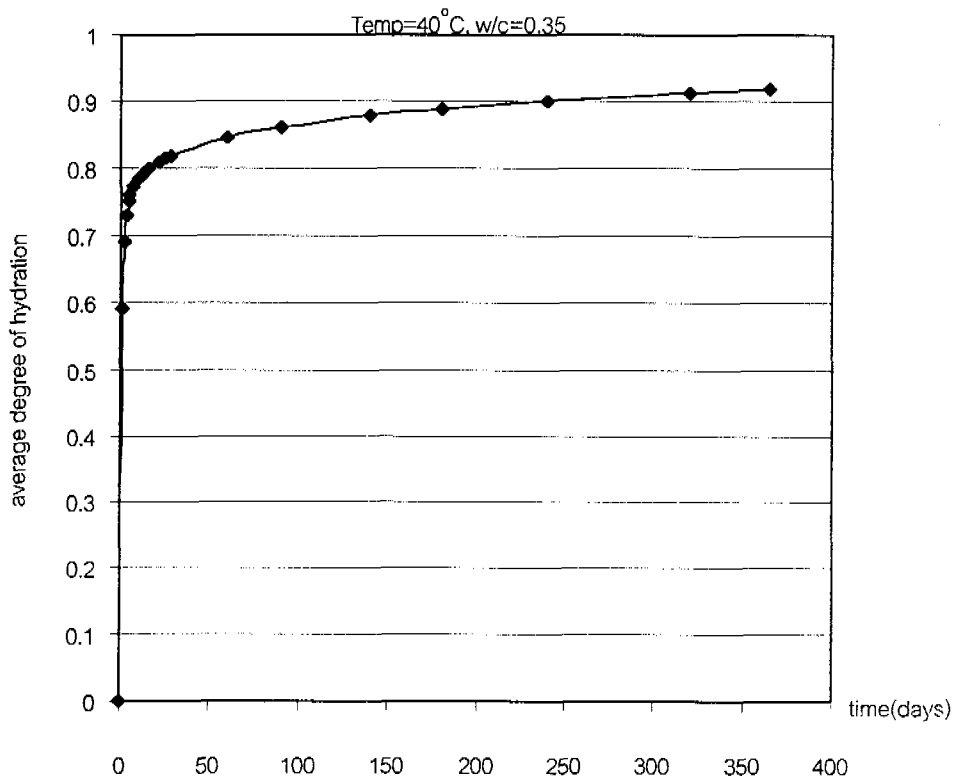


Fig. 4.12 The average degree of hydration at any considered age  $t$  and cured at 40°C by controlling  $w/c = 0.35$

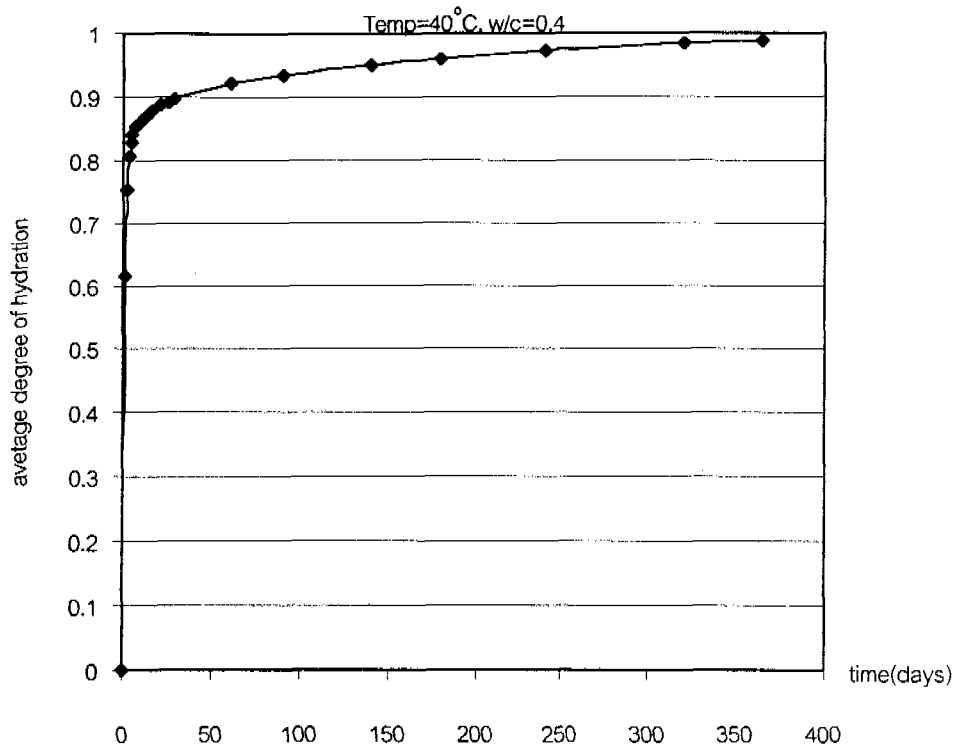


Fig. 4.13 The average degree of hydration at any considered age  $t$  and cured at  $40^{\circ}\text{C}$  by controlling  $w/c = 0.4$

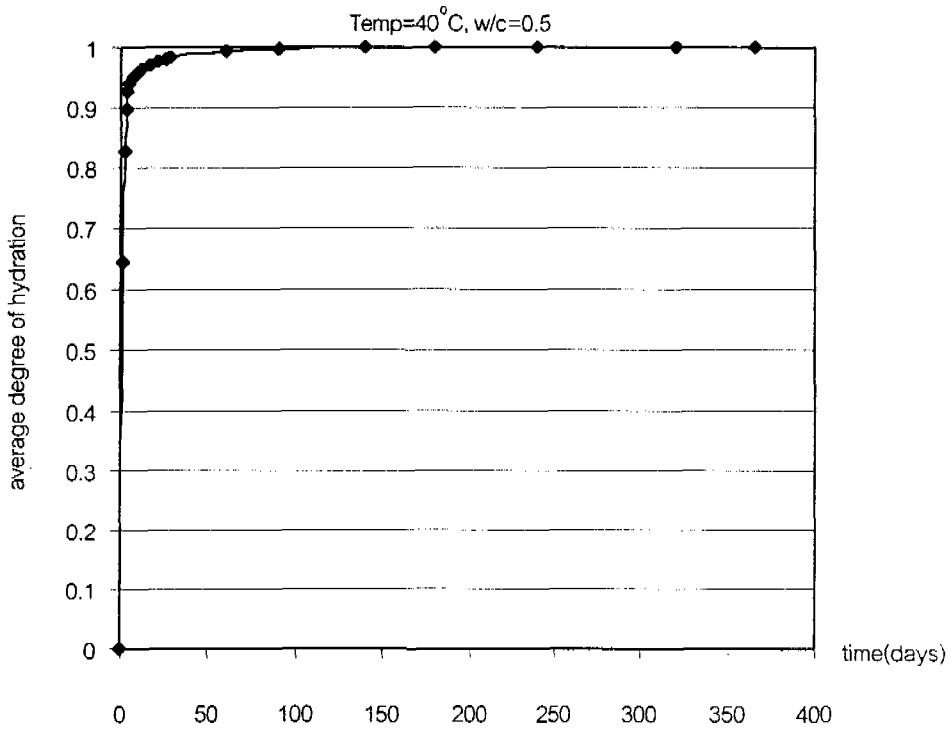


Fig. 4.14 The average degree of hydration at any considered age  $t$  and cured at  $40^{\circ}\text{C}$  by controlling  $w/c = 0.5$

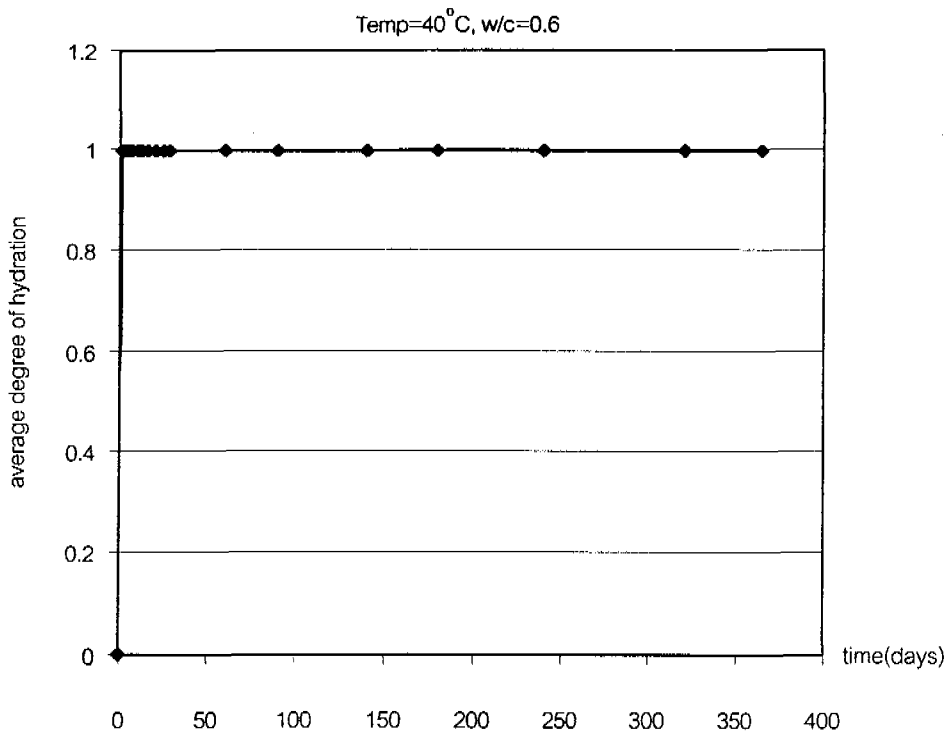


Fig. 4.15 The average degree of hydration at any considered age t and cured at 40°C by controlling w/c = 0.6

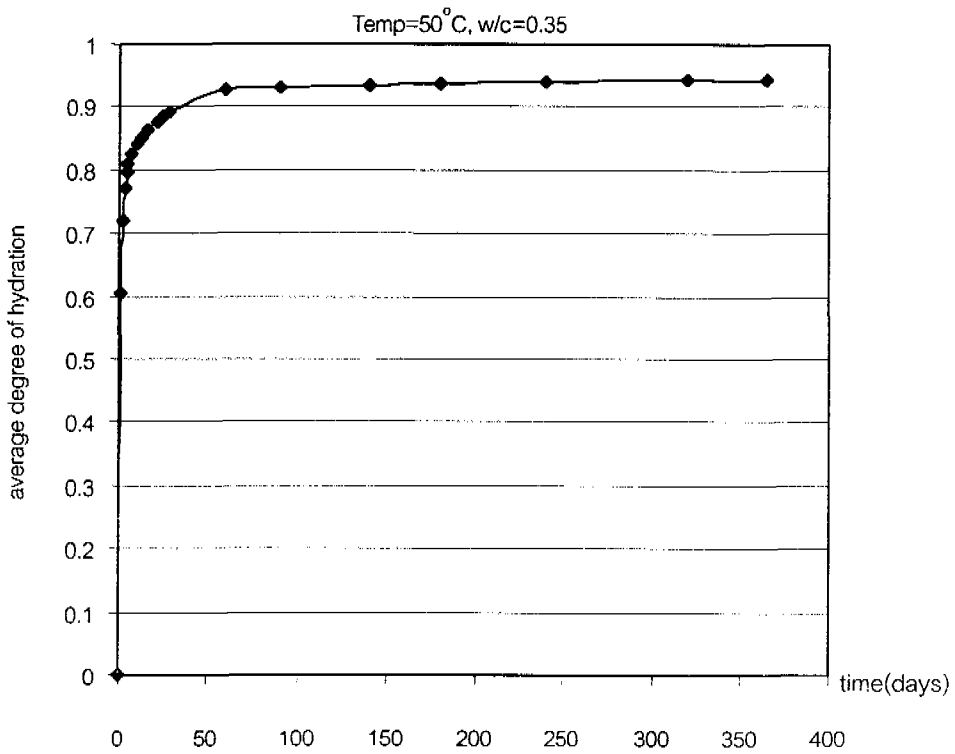


Fig. 4.16 The average degree of hydration at any considered age t and cured at 50°C by controlling w/c = 0.35

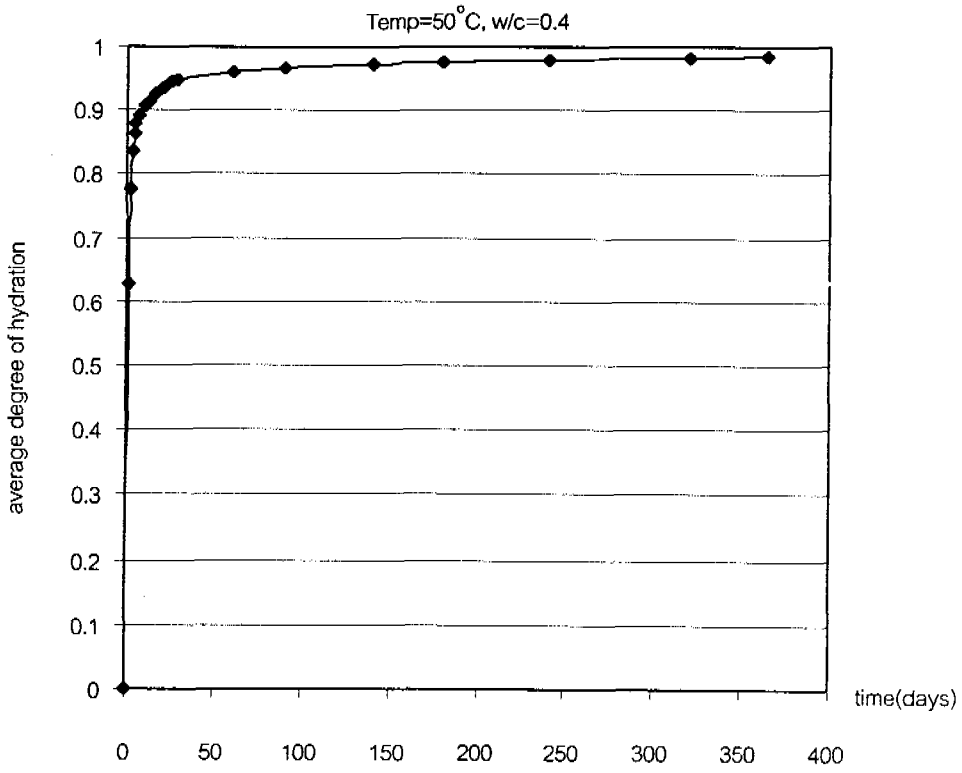


Fig. 4.17 The average degree of hydration at any considered age  $t$  and cured at  $50^{\circ}\text{C}$  by controlling  $w/c = 0.4$

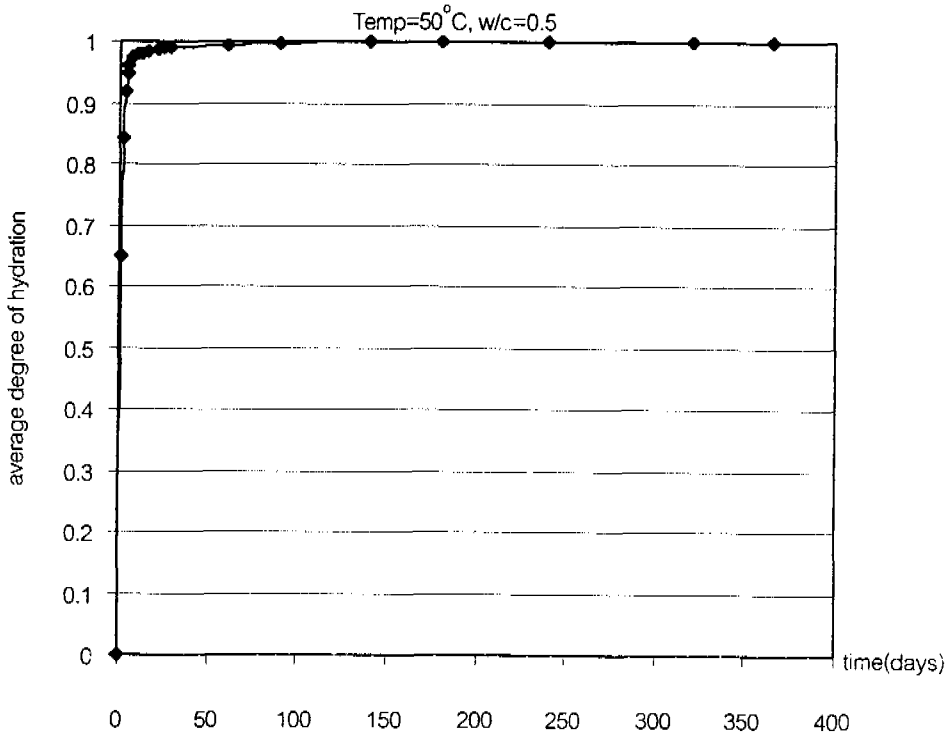


Fig. 4.18 The average degree of hydration at any considered age  $t$  and cured at  $50^{\circ}\text{C}$  by controlling  $w/c = 0.5$

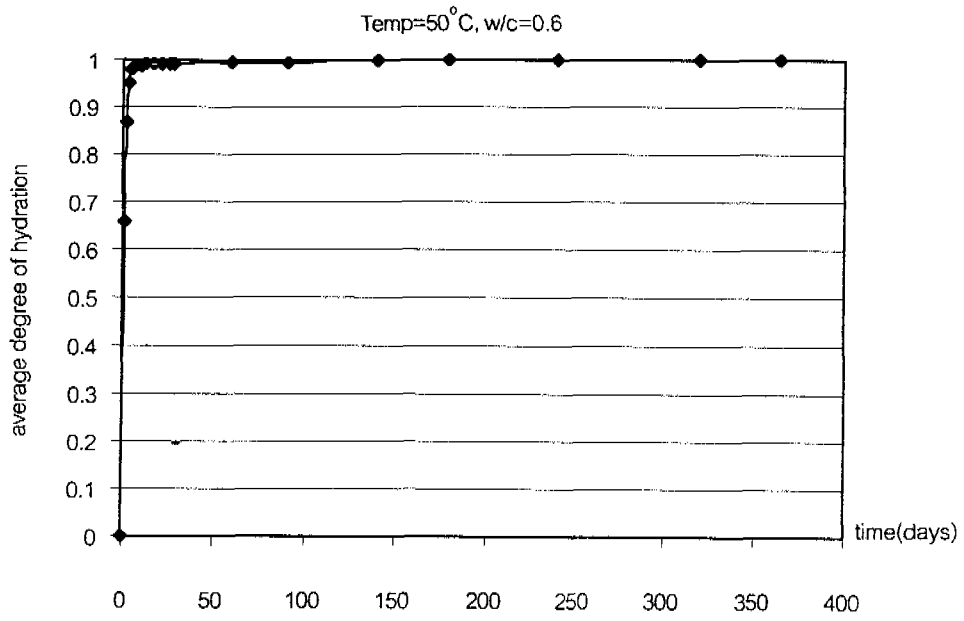


Fig. 4.19 The average degree of hydration at any considered age  $t$  and cured at 50°C by controlling  $w/c = 0.6$

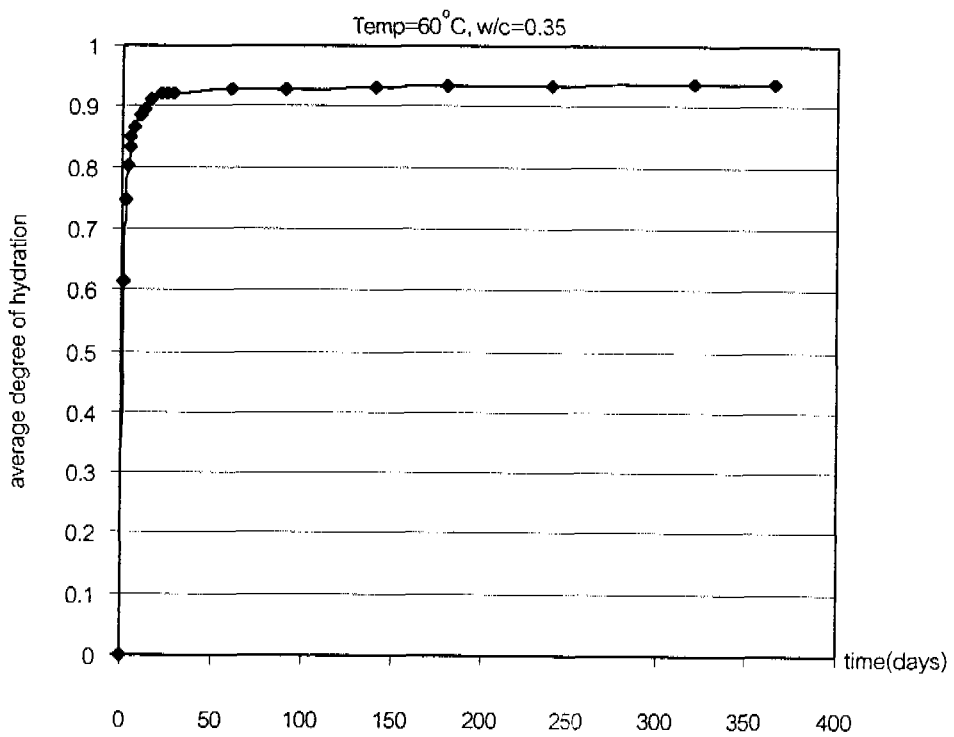


Fig. 4.20 The average degree of hydration at any considered age  $t$  and cured at 60°C by controlling  $w/c = 0.35$

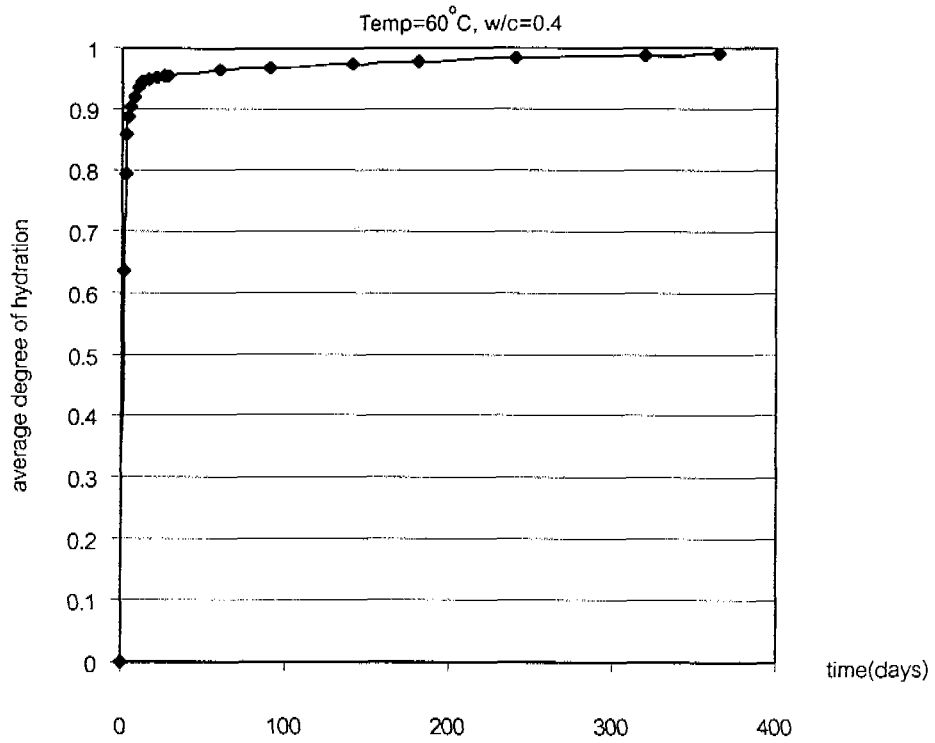


Fig. 4.21 The average degree of hydration at any considered age  $t$  and cured at  $60^{\circ}\text{C}$  by controlling  $w/c = 0.4$

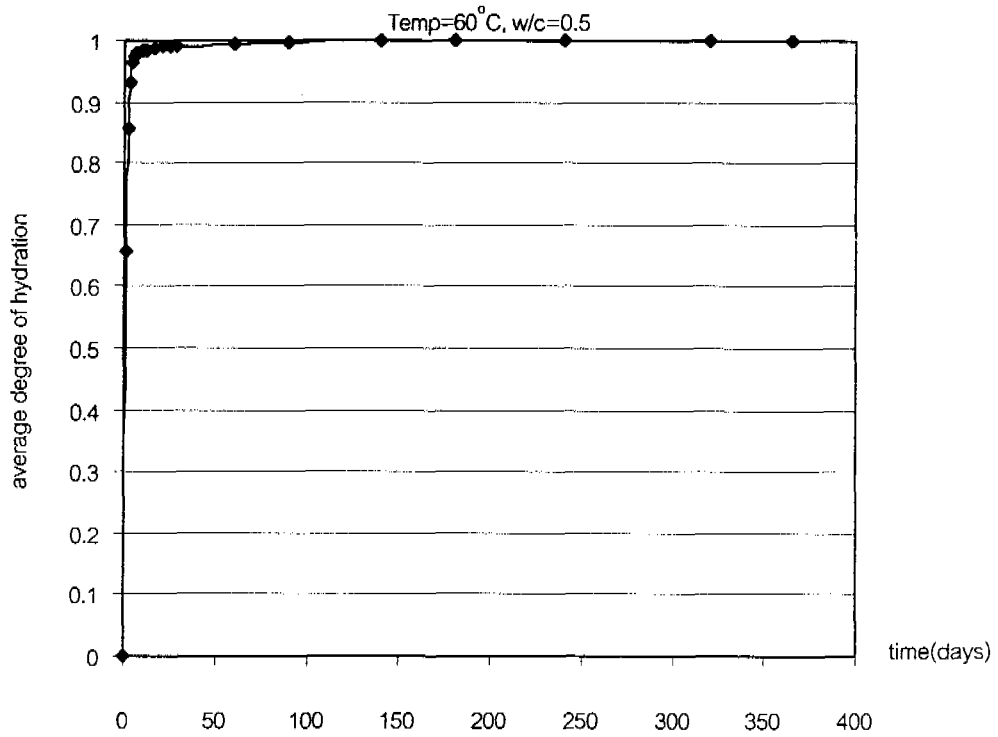


Fig. 4.22 The average degree of hydration at any considered age  $t$  and cured at  $60^{\circ}\text{C}$  by controlling  $w/c = 0.5$



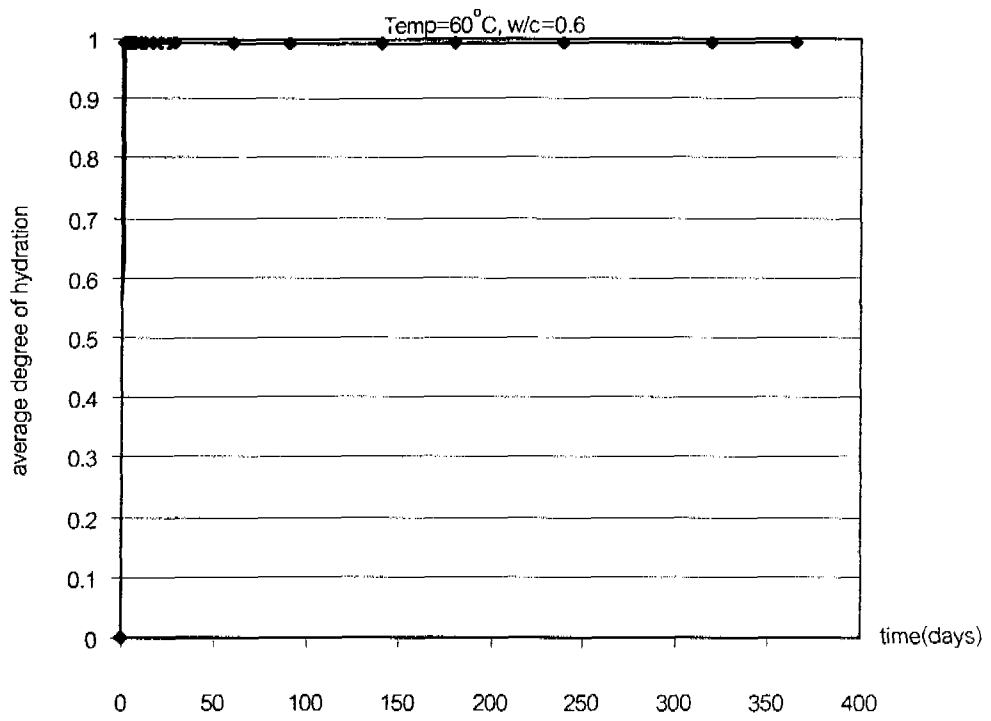


Fig. 4.23 The average degree of hydration at any considered age  $t$  and cured at  $60^{\circ}\text{C}$  by controlling  $w/c = 0.6$