SIMULATION OF FREE WATER CONTENT OF PASTE WITH FLY ASH

Somnuk Tangtermsirikul, and Warangkana Saengsoy
School of Building Facilities Engineering and Civil Engineering
Sirindhorn International Institute of Technology, Thammasat University
P.O. Box 22, Thammasat-Rangsit Post Office, Pathumthani 12121, Thailand
Phone (66-2) 986-9009 ext. 1908, Fax (66-2) 986-9009 ext. 1900
E-mail: somnuk@siit.tu.ac.th

Abstract

This study is aimed to investigate the free water content of fly ash-cement pastes. Experiments were conducted to obtain the free water content by using oven-drying method. The experimental results were used to construct a model for predicting free water content regarding time dependent properties of fly ash-cement pastes. In this model, gel water was considered as a part of hydration and pozzolanic products. From the experimental results, it was found that free water content of pastes decreased with respect to time due to water consumption by hydration and pozzolanic reactions. The replacement of cement by fly ash causes the relatively higher free water content at early age but tends to decrease in longer age due to pozzolanic reaction. The verification tests showed that the proposed model could be used to predict the free water content of the tested pastes with satisfactory accuracy.

1. Introduction

The water held in cement pastes can be classified into three phases: capillary water (free water), gel water (physically bound water), and chemically bound water (non-evaporable water) [1,2]. Free water or capillary water is the water present in the coarse capillary pore, unbound in the cement paste, which is freely accessible for the cement hydration. The water approximately 0.21 g is chemically bound per g of cement reacted during hydration, called chemically bound water or non-evaporable water, since it is an integrated part of the structure of the gel solid. Gel water or physically bound water is an amount of water adsorbed on the surface of the gel solid equivalent to approximately 0.19 g water per g of cement reacted if water to cement ratio is higher than 0.4.

Free water content of paste was simulated in this study for application in durability evaluation like drying shrinkage, carbonation, and chloride movement. Furthermore, the free water content can be used for evaluation of thermal properties such as specific heat, thermal conductivity, and thermal expansion coefficient since water is the important ingredient that possesses different properties from the others in concrete.

During hydration process, free water content will change with respect to time. The amount of free water in paste decreases with an increase in the degree of hydration.

Many researchers suggested that free water can be determined by loss upon drying at elevated temperature, most commonly at about 105 °C, or by freezing out, or by removing with a solvent [1,2,3]. In this study, the oven drying at 105 °C was used to measure the free water content.

Tatong [4] proposed a model for predicting free water content for simulating autogenous shrinkage but the model included the gel water content because free water was defined as water that was reactable with cementitious materials in her study. In this paper, free water which is defined as those excluding gel water will be studied.

RECEIVED 13 APRIL, 2002
ACCEPTED 6 SEPTEMBER, 2002

2. Experimental Program

2.1 Mix proportion and materials

A total number of six proportions of paste mixtures were cast and tested for free water content at various ages. The ratio of water to binder (w/b) and the replacement ratio of cement by fly ash f/(c+f)) were varied. The mix proportions of all samples are shown in Table 1. An example of description of the mixture designation is as follow; "w25r3" means the paste which has w/b of 0.25 and fly ash replacement ratio of 0.30.

The chemical compositions and physical properties of cement and fly ash are shown in Table 2 and Table 3, respectively.

Table 1: Mix proportion of the tested samples

Mixture Designation	w/b	f/(c+f)
w25r0	0.25	0
w25r3	0.25	0.3
w25r5	0.25	0.5
w40r0	0.40	0
w40r3	0.40	0.3
w40r5	0.40	0.5

Remarks: w: water, c: cement, f: fly ash, and b: binders (c+f).

Table 2: Chemical compositions of Portland cement type I and fly ash

Chemical Component (%)	Cement Type I	Fly Ash
SiO_2	20.99	45.88
Al_2O_3	5.18	26.20
Fe_2O_3	3.20	10.94
CaO	64.63	8.28
MgO	1.30	2.83
SO_3	2.61	1.04
Na_2O	0.04	0.90
K_2O	0.40	2.78
TiO_2	0.25	0.51
P_2O_5	0.05	0.10
LOI	1.17	0.17
Free Lime	0.75	0.18

Table 3: Physical properties of Portland cement type I and fly ash

Physical Properties	Cement Type I	Fly Ash
Specific Gravity	3.15	1.85
Specific Surface Area (cm^2/g)	3190	3460

2.2 Test of free water content

The experiment was conducted to obtain the free water content of fly ash-cement pastes. In this study, the oven drying at 105 °C was used to remove the free water.

Six proportions of paste mixtures were cast and sealed in plastic boxes in order to prevent the evaporation of the water. The plastic boxes were placed at room temperature until the test age (1, 3, 7 and 28 days) and then the specimens were demoulded to measure their initial weight. Then, the specimens were dried in an oven under a constant temperature of 105 °C. After one day of drying, the specimens were taken out and the weight loss was measured. Since only free water can evaporate at this temperature, the weight loss was the amount of free water of those specimens.

3. Experimental Results

From the experiment, it was found that free water of cement paste decreased with respect to time due to water consumption by hydration and pozzolanic reactions.

The time-dependent weight ratio of free water per unit weight of paste are shown in Fig. 1 to Fig. 5.

Fig. 1 and Fig. 2 show the effect of replacement ratio of fly ash. It was found that free water of paste without fly ash (w25r0 and w40r0) decreases rapidly at initial stage but nearly stops decreasing in longer age. In contrast, for the mixtures with fly ash, the rate of decreasing of free water is slow but still continues in longer ages. It can be explained that pozzolanic reaction of fly ash is the cause of the longer age reduction of the free water of the pastes with fly ash. During the initial stage pozzolanic reaction is very minor while hydration reaction of cement is the main reaction for this stage. The use of fly ash reduces the amount of cement so that the amount of water consumed by hydration reaction decreases. This causes the relatively higher free water content in mixtures with fly ash at early ages. At longer age, the pozzolanic reaction still continues but the hydration reaction becomes less significant so the free water of mixture with fly ash decreases in longer age.

The effect of water to total binder ratio (w/b) are shown in Fig. 3 to Fig. 5. It can be clearly explained that pastes with lower w/b has lower free water than that of pastes with higher w/b because of its smaller water content.

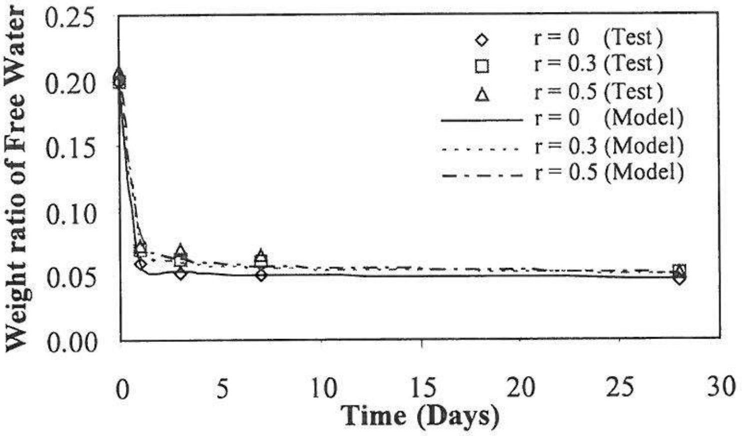

Fig. 1: Comparisons between test results and the model of weight ratio of free water of cement paste with fly ash replacement ratio of 0, 0.3 and 0.5, and w/b = 0.25

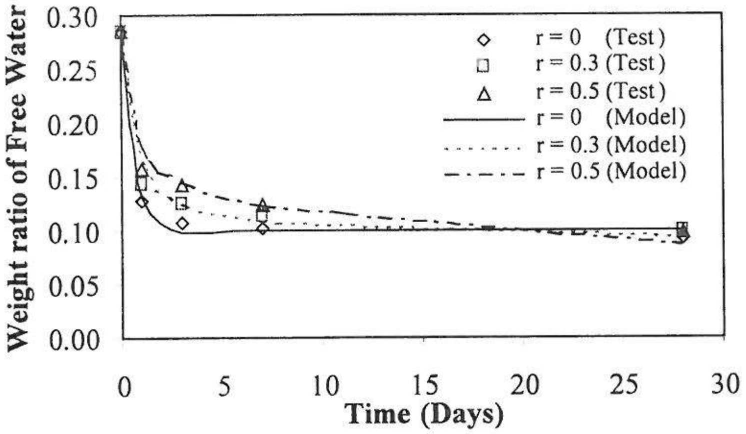

Fig. 2: Comparisons between test results and the model of weight ratio of free water of cement paste with fly ash replacement ratio of 0, 0.3 and 0.5, and w/b = 0.40

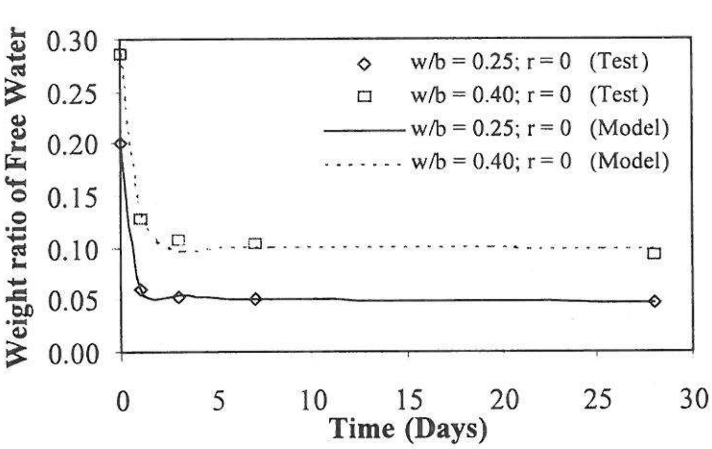

Fig. 3: Comparisons between test results and the model of weight ratio of free water of cement paste with w/b = 0.25 and 0.40

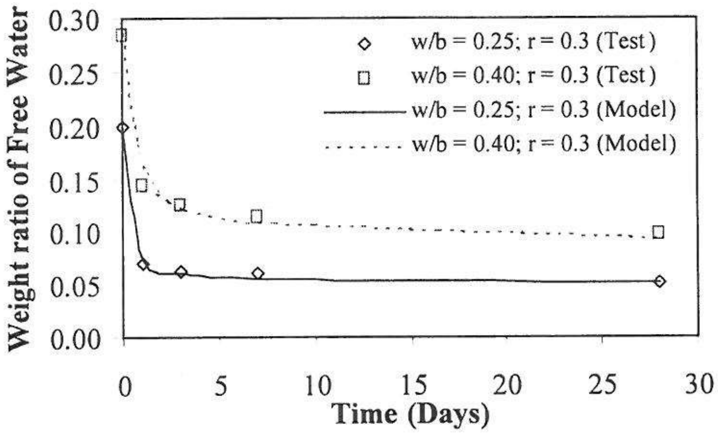

Fig. 4: Comparisons between test results and the model of weight ratio of free water of cement paste with fly ash replacement ratio of 0.3, and w/b = 0.25 and 0.40

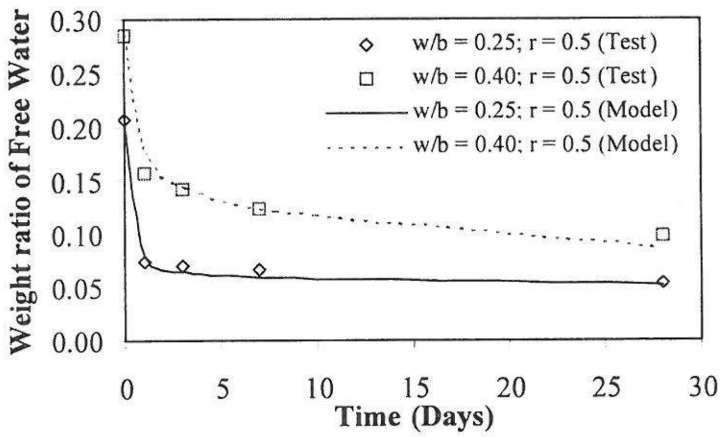

Fig. 5: Comparisons between test results and the model of weight ratio of free water of cement paste with fly ash replacement ratio of 0.5, and w/b = 0.25 and 0.40

4. Water Content Model

4.1 Free water content

The free water content of paste reduces with time due to water consumption in hydration process. The free water content at a certain age was proposed as in Eq. (1).

$$W_{wfree}(t) = W_{w0} - W_{whp}(t) - W_{wgel}(t) \quad (1)$$

$$W_{whp}(t) = \theta_f \cdot (W_c + W_f) \cdot \frac{\alpha_{avg}(t)}{100} \quad (2)$$

$$\theta_f = 0.21 - 0.13 \cdot r^{2.15} \quad (3)$$

$$\alpha_{avg}(t) = (1-r) \cdot \alpha_{hy}(t) + 0.4 \cdot r \cdot \tan^{-1}[13 \cdot \alpha_{poz}(t)] \quad (4)$$

where $W_{wfree}(t)$ and $W_{wgel}(t)$ are the weight of free water and gel water in paste at time t, respectively (kg/m^3). W_{wo} is the unit water content of the paste mixture (kg/m^3). $W_{whp}(t)$ is the weight of water consumed by hydration and pozzolanic reactions (kg/m^3). θ_f is the minimum ratio of water to binders for completing reactions. W_c and W_f are the weight of cement and fly ash in paste, respectively (kg/m^3). r is the replacement ratio of fly ash in total binder content by weight, $\alpha_{avg}(t)$ is the average degree of reaction of paste (%), $\alpha_{hy}(t)$ is the average degree of hydration of cement in the paste (%), $\alpha_{poz}(t)$ is the degree of pozzolanic reaction of fly ash in the paste at any age (%), and t is the age of paste (days).

It is noted in this paper that the state of complete reactions represents the state of complete hydration reaction and attaining the possibly maximum pozzolanic reaction.

The minimum water to cement ratio required to complete hydration of cement paste is considered in this study to be approximately equal to 0.21 [1,2,5]. In fly ash-cement paste, the minimum water content for completing reaction will be reduced with the increase of fly ash replacement. The minimum ratio of water to binders for completing reaction is assumed to be equal to 0.20 for paste with 30% of fly ash replacement, and 0.18 for paste with 50% of fly ash replacement.

4.2 Gel water content

The gel water content of paste increases with age following hydration and pozzolanic reactions since it is entrapped in the products of those reactions. The gel water content is affected by the amount of water content in the mixture and replacement ratio of cement by fly ash. Eq. (5) was applied to compute weight of gel water at a time considered.

$$W_{wgel}(t) = \theta_{gel} \cdot (W_c + W_f) \cdot \frac{\alpha_{avg}(t)}{100} \quad (5)$$

$$\theta_{gel} = (0.19 + 0.13 \cdot r^{2.15}) \cdot \phi_{w/b} \cdot \phi_r \quad (6)$$

where θ_{gel} is the ratio of gel water to binders in paste at the state of complete reactions (kg/m^3). w/b is the water to binder ratio and $\alpha_{avg}(t)$ is the average degree of reaction of paste from Eq. (4) (%). $\phi_{w/b}$ is the effect of water to binders ratio on gel water content at state of complete reactions, and ϕ_r is the effect of replacement ratio of cement by fly ash on gel water content at the state of complete reactions.

Considering at state of complete reactions, it is assumed that if the mixture has water content beyond the minimum amount of water required for completing the hydration of cement paste (θ_f), gel water will exist. Maximum gel water to cement ratio of cement paste was assumed equal to 0.19 if w/c is greater than or equal to 0.4 ($\theta_f + \theta_{gel}$) [1,2]. For cement paste with w/c from 0.21 to 0.4, the gel water content at complete hydration will vary from zero to 0.19 of the cement weight. Fig. 6 illustrates the ratio of gel water to binders in paste at the state of complete reactions (θ_{gel}).

At state of complete reactions, the average degree of reaction of paste ($\alpha_{avg}(t)$) was defined equal to 100 % which gel water content can be obtained from the ratio of gel water to binders in paste (θ_{gel}) and the binders weight. However, at any state of reactions, gel water content of paste is proportional to its average degree of reaction that is varying from 0 % to 100 %. Fig.7 shows the distribution of ratio to cement weight of free water, gel water, and hydrated water to cement in paste with various water to cement ratio at different state of reactions.

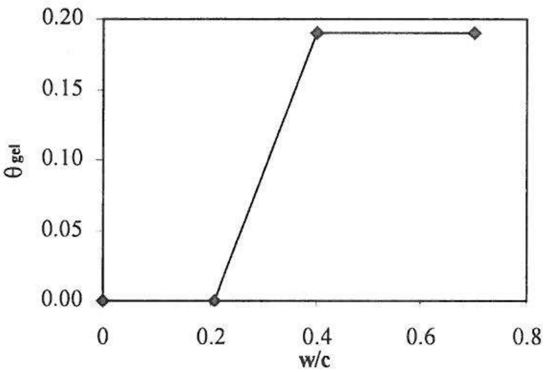

Fig. 6: The ratio of gel water to binders in paste at the state of complete reactions

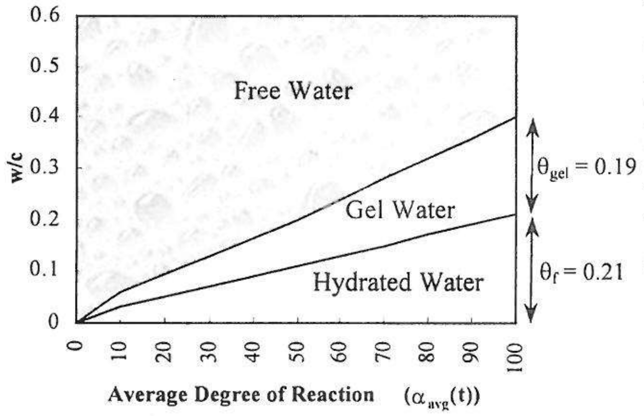

Fig. 7: The distribution of ratio to cement weight of free water, gel water, and hydrated water in paste with various water to cement ratio at different state of reactions

In fly ash-cement paste, the maximum gel water content at the state of complete reactions will increase with the increase of fly ash replacement. It is noted that this paper studies fly ash-cement paste with fly ash replacement up to 50% of total binder. θ_{gel} is expected to reduce if too much fly ash is incorporated. The maximum gel water content was assumed equal to 0.20 for paste with 30% of fly ash replacement, and 0.22 for paste with 50% of fly ash replacement. Effect of water to binders ratio on gel water content at state of complete reaction can be seen in Fig. 8. Effect of replacement ratio of cement by fly ash can be shown in Fig. 9 and Fig. 10.

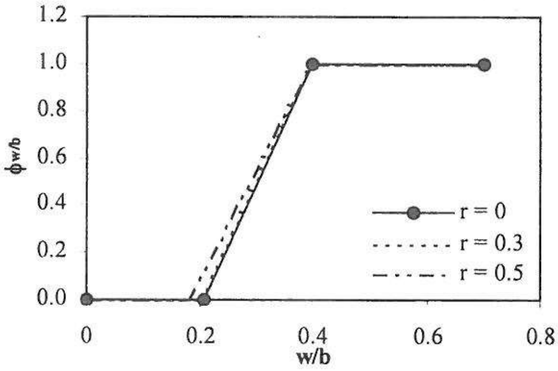

Fig. 8: Relationship between $\phi_{w/b}$ and w/b

For cement paste with water to binder ratio less than 0.21, the minimum water to binder ratio required to complete hydration, there is no gel water exists at the state of complete hydration because the water content was all consumed in hydration process. Maximum gel water to binder ratio considered in this study is assumed equal to 0.19 [1,2]. So, water content in cement paste with water to binder ratio greater than 0.4 become free water in capillary pores.

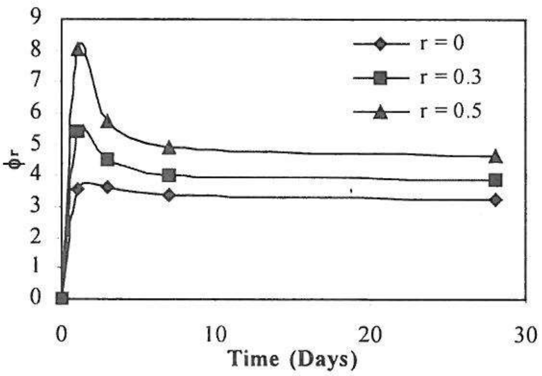

Fig. 9: Effect of replacement ratio of cement by fly ash ϕ_r of pastes with fly ash replacement ratio of 0, 0.3 and 0.5, and w/b = 0.25

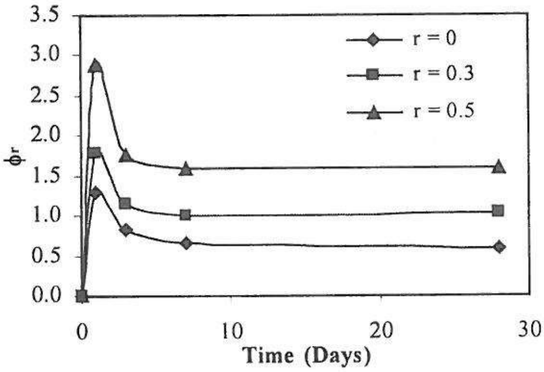

Fig. 10: Effect of replacement ratio of cement by fly ash ϕ_r of pastes with fly ash replacement ratio of 0, 0.3 and 0.5, and w/b = 0.40

The gel water content of paste changes with time due to hydration and pozzolanic processes. Replacement ratio of cement by fly ash also has an effect on gel water content of paste. Appropriately higher fly ash replacement ratio usually gives higher hydrated and pozzolanic products in long term. Since gel water is a part of hydrated and pozzolanic products, paste with higher replacement ratio of cement by fly ash gives higher gel water content. As previously mentioned that only up to 50% of fly ash replacement was studied in this paper, it is expected that gel water will reduce if too much fly ash is incorporated.

5. Degree of Hydration and Average Degree of Hydration

Degree of hydration of each cement compound (C_3A, C_3S, C_2S and C_4AF) is affected by water-cement ratio, concrete temperature and age [6]. Degree of hydration used in this study is shown in Fig. 11 to Fig. 14.

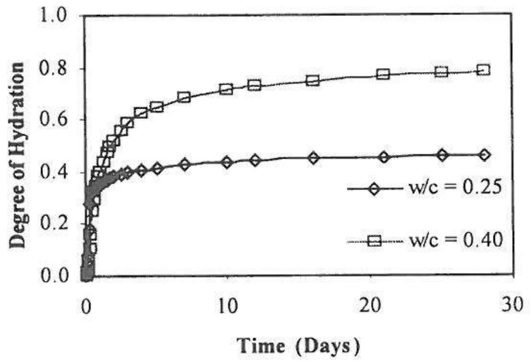

Fig. 11: Degree of hydration of C_2S of paste with w/c = 0.25, and 0.40 at 28°C

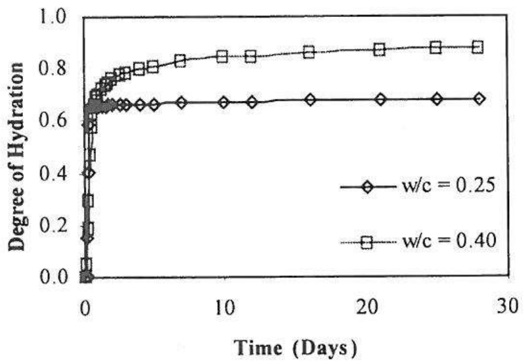

Fig. 12: Degree of hydration of C_3A of paste with w/c = 0.25, and 0.40 at 28°C

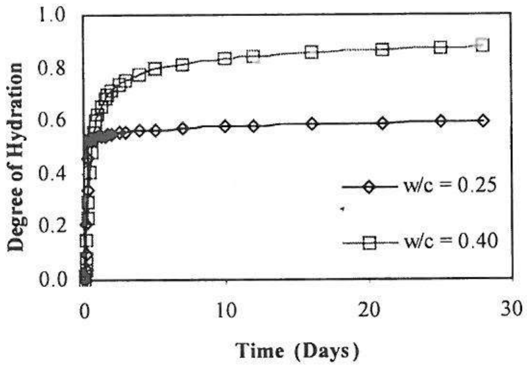

Fig. 13: Degree of hydration of C_3S of paste with w/c = 0.25, and 0.40 at 28°C

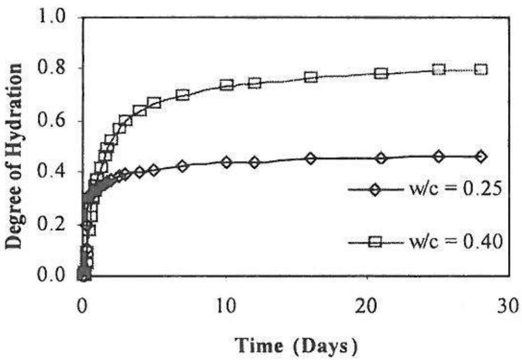

Fig. 14: Degree of hydration of C_4AF of paste with w/c = 0.25, and 0.40 at 28°C

The average degree of hydration of paste is defined as the weight fraction of hydrated cement per total cement in the paste mixture.

Under a simple assumption that hydration products from all cement composition (C_3S, C_2S, C_3A, C_4AF) entrapped the same amount of the gel water, the average degree of hydration was introduced as a weight average of the rate of hydration of its constituents for convenient application of the model.

$$\alpha_{hy}(t) = \frac{\sum_{i=1}^{4} m_i \alpha_i(t)}{\sum_{i=1}^{4} m_i} \quad (7)$$

where $\alpha_{hy}(t)$ is the average degree of hydration (%), 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 cement (%).

The examples of average degree of hydration of the pastes used in this study are shown in Fig. 15.

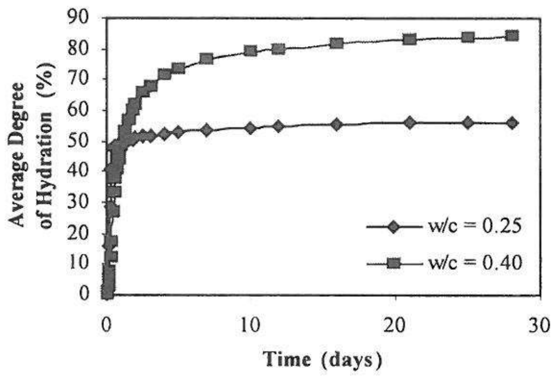

Fig. 15: The average degree of hydration of cement paste with w/c = 0.25 and 0.40 at 28°C

6. Degree of Pozzolanic Reaction

The 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 both in cement and fly ash, and fineness of fly ash [4]. The examples of degree of pozzolanic reaction of pastes used in this study are shown in Fig. 16.

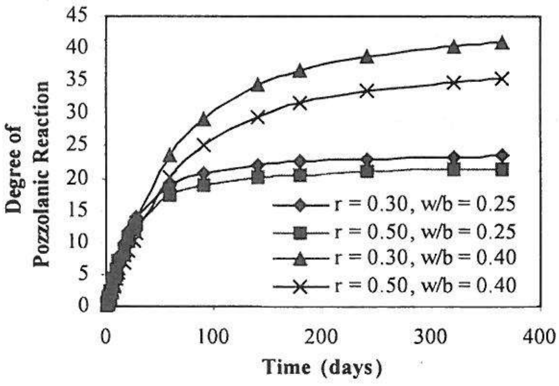

Fig. 16: The degree of pozzolanic reaction of cement paste with fly ash replacement ratio of 0.30 and 0.50, and w/b = 0.25 and 0.40 at 28°C

7. Retardation of Hydration Reaction by Fly Ash

The use of fly ash may retard the time of setting of concrete. Both Class F fly ash and Class C fly ash retard early hydration of C_3S

[7,8]. The retardation factor of C_3S hydration by fly ash was proposed by Tatong [4] as

$$\psi = [\{0.0866 \cdot (w/b)^{-2.443} - 1.032 \cdot w/b\} \cdot r^{2.151} + 1] \cdot (\alpha_{C_3S}/100)^{3.409 \cdot r^{1.952}} \quad (8)$$

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

$$\alpha_{C_3S,poz}(t) = \psi \cdot \alpha_{C_3S}(t) \quad (9)$$

where ψ is the retardation factor of C_3S hydration by fly ash. $\alpha_{C_3S,poz}(t)$ and α_{C3S} (t) are the degree of hydration of C_3S with and without replacement of cement by fly ash, respectively (%). r is the replacement ratio of fly ash in total powder content by weight and w/b is the water to binder ratio.

The retardation factor of C_3S hydration (ψ) of mix proportions used in this study is shown in Fig. 17.

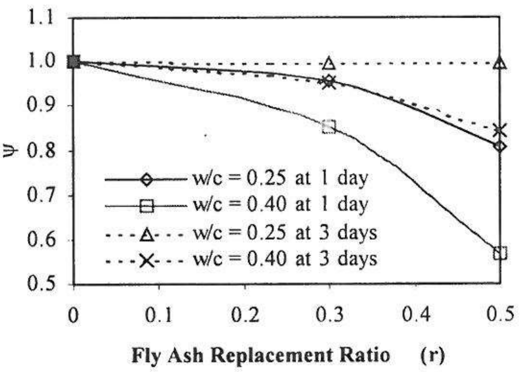

Fig. 17: The retardation factor of C_3S hydration (ψ) of paste with various fly ash replacement ratio, and w/b = 0.25 and 0.40 at 1 day and 3 days.

8. Verification of Free Water Content Model

The free water content at a certain time of the pastes were computed by using Eq. (1). The comparison between the analytical results and the test results are shown in Fig. 1 to Fig. 5. Fig. 1 and Fig. 2 show the effect of replacement ratio of fly ash. Fig. 3 to Fig. 5 show the effect of water to binder ratio. It is shown in the figures that the models are satisfactory to predict the free water content of the tested pastes. The model obviously shows, in Fig. 1 and Fig. 2, that the free water of pastes with fly ash tend to continue decreasing in long term when compared to that of the cement paste. The model also shows, in Fig. 3 to Fig. 5, that the pastes with higher w/b have higher free water content than those with lower w/b.

9. Conclusions

It can be concluded from the experimental results that free water content of pastes decreased with respect to time due to water consumption in hydration and pozzolanic processes. The replacement of cement by fly ash causes the relatively higher free water content at early age but tends to decrease in longer age due to pozzolanic reaction.

The verification showed that the proposed free water content model could be satisfactorily used to predict the free water content of the tested pastes.

10. References

[1] A. M. Neville, 1995, *Properties of Concrete*, Longman 4th edition.

[2] T.C. Powers, 1960. Physical Properties of Cement Paste, *Proceedings of the Fourth International Symposium on the Chemistry of Cement*, Washington D.C, V-1, pp. 577-613.

[3] I. Odler, 1998, *Lea's Chemistry of Cement and Concrete: Hydration, Setting, and Hardening of Portland Cement*, 4th ed., London, U.K: P. C. Hewlett. Arnold.

[4] Tatong S., 2001. "Autogenous Shrinkage Model for Fly Ash Concrete Considering Effect of Reactions, Pore structure, and Aggregate Restraint". Master Thesis. Sirindhorn International Institute of Technology and Faculty of Engineering, Thammasat University, Pathumthani, Thailand.

[5] L. Lam, Y.L Wong and C.S. Poon 2000. Degree of Hydration and

Gel/Space Ratio of High-Volume Fly Ash/Cement Systems. *Cement and Concrete Research,* V 30, pp. 747-756.

[6] Nipatsat N., 2000. "Model for Predicting Compressive Strength of Concrete by Considering Effect of Curing Temperature". Master Thesis. Sirindhorn International Institute of Technology and Faculty of Engineering, Thammasat University, Pathumthani, Thailand.

[7] Jawed, L. and Skanly, J. 1981. Hydration of Tricalcium Silicate in the Presence of Fly Ash. *Proceeding, Symposium N, Effects of Fly Ash Incorporation in Cement and Concrete, Materials Research Society*, Pittsburgh, 60-69.

[8] Grutzeck, M. W., Wei, Fajun, and Roy, D. M. 1984. Retardation Effects in the Hydration of Cement-Fly Ash Pastes. *Proceedings, Materials Research Society, Pittsburgh.*