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- Technical Paper -

EFFECT OF RELATIVE HUMIDITY ON HYDRATION REACTION OF CEMENT-FLY ASH PASTE

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ABSTRACT

The influence of relative humidity on the hydration reaction of cement-fly ash paste was elucidated by exploring specimens in various environmental conditions. The degree of hydration of both cement and fly ash of these pastes was quantified by using selective dissolution and a Rietveld XRD analysis. The results of the experiment revealed that when the paste specimens were exposed to a relatively lower ambient humidity, the degree of hydration of both the cement and the fly ash decreased. The hydration reaction of belite is more significantly affected by curing relative humidity than other cement components.

Keywords: relative humidity, hydration reaction, cement component, fly ash

1. INTRODUCTION

The mechanical properties and the durability of concrete depend largely on the progress of the hydration reaction and the effectiveness of the hydrates in producing a dense low permeability matrix. The drying of the concrete, particularly at an early age, caused by a poor curing regime, leads to restricted hydration in the surface layers and thus to higher porosity and permeability. [1]

Many aspects of cement hydration in relation to the curing of concrete have been discussed. Powers [2] concluded that hydration virtually ceased when concrete dried at a relative humidity lower than 80%. Jensen et al. [3] described the effect of relative humidity on the hydration of pure cement clinker minerals.

However, there is little in the literature that reveals the progress of hydration and the pozzolanic reaction in cement-fly ash mixes under lower than saturated conditions.

This research aims to elucidate the effect of curing conditions on the hydration reaction of cement-fly ash paste. The particular focus in this case was on the effect of the relative humidity on the hydration of cement and fly ash. The method used was a combination of XRD-Rietveld analysis and selective dissolution.

2. EXPERIMENTAL PROGRAMS

2.1 Materials and Mix Proportions

Ordinary Portland Cement Type I was used with mineral compositions as shown in Table 1. Fly ash type II according to JIS A6201 was used. The physical properties of the OPC and the fly ash are shown in Table 2. The paste samples were prepared with a water-to-binder ratio of 1.00 by volume. The replacement ratios of cement by fly ash were 0, 0.25, and 0.50. A polycarboxylate-based superplasticizer was used to control the fluidity of the paste.

Table 1 Mineral Compositions of Cement

C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
73.03	10.40	6.50	9.37

Table 2 Physical Properties of Cement and Fly Ash

	Density (g/cm^3)	Blaine Surface Area (cm^2/g)	Ignition Loss (%)
Cement	3.17	3520	0.56
Fly Ash	2.15	3970	1.25

The pastes were prepared in a mixer at low speed for 90 seconds and further mixed at high speed for 90 seconds. The specimens were prepared in cylinder moulds of 5cm in diameter and 10cm in height.

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All the specimens were sealed and placed in a controlled temperature room at 20±2 °C. After three days of mixing, the specimens were remolded and cured until the required age. The specimens were explored in five different environmental conditions: in water, in sealed curing, and at the relative humidity levels of 60%, 80%, and 95%. The relative humidity was controlled by the saturated salt solutions.

The hydration reaction in the paste samples was examined at 3, 7, 14, 28, and 56 days.

2.2 Measuring Method

(1) Measurement of Internal Relative Humidity

The internal relative humidity in the pastes was measured using a ceramic sensor. The dimension of ceramic sensor is 1 cm in diameter and 1 cm in height. The sensor was embedded in the centre of specimen during sample preparation. Then, it was connected to the data logger to record the electrical resistance at every ten minutes throughout the experiment. The relative humidity was calculated based on the electrical resistance as in Eq. 1

$$RH = -0.05\,(\rho - 327.5)^{0.42} + 100 \qquad (1)$$

where,

RH : relative humidity (%)

ρ : electrical resistance (Ω)

(2) Measurement of Degree of Hydration

The degree of hydration of the hydrated cement pastes was estimated with an XRD-Rietveld analysis. In the case of the pastes that had been incorporated with fly ash, the degree of hydration was estimated with a combined method using XRD-Rietveld analysis and selective dissolution [4, 5].

At the required age, the samples were cracked into small pieces and soaked in acetone to stop the hydration reaction and further dried at 105°C. Then, they were ground in a ball mill at a speed of 300 rpm for eight minutes.

The X-ray diffraction equipment used in the XRD-Rietveld analysis was a Rigaku. A CuK_α X-ray type was used. The experiments were performed in the range of 5-70° 2θ at 40 kV, 20 mA, 0.02° sampling width and 2°/min scan speed. The divergence slit, scattering slit and receiving slit were 1/2°, 1/2° and 0.3 mm, respectively. The standard corundum 10% by weight of sample was used as an internal reference. The sample and corundum were mixed in the ball mill at a speed of 100 rpm for three minutes. The software used in the Rietveld analysis for this study was SIROQUANT (version 3.0) [6].

As for selective dissolution, the unhydrated fly ash was determined using a solution of 2N HCl and 5% Na_2CO_3. At first, a 1g hydrated sample was prepared in a centrifuge tube. To this, 30 cm^3 of HCl solution was added. The tube was then shaken in an automatic shaking water bath at 60°C for 15 minutes following which, the sample was centrifuged at 4,000rpm for one minute to separate the solid and liquid phases. The liquid phase was decanted and the solid phase remaining in the tube was washed in hot water and centrifuged at 4,000rpm for one minute. The centrifuge tube was then filled with 30cm^3 of Na_2CO_3 solution, and shaken in a hot automatic shaking water bath at 80°C for 20 minutes after which the tube was centrifuged at 4,000rpm for one minute and the liquid phase was separated and decanted. The solid phase was washed in hot water and centrifuged at 4,000rpm for one minute. After decanting the liquid phase, the tube with the residue sample was dried at 110°C and weighed. The residue sample is unhydrated fly ash. The degree of hydration of the fly ash was calculated from the quantity of hydrated fly ash divided by quantity of unhydrated fly ash at 0 days [5, 7].

(3) Measurement of Loss on Ignition

The samples were dried at 105°C and further combustion at 950°C. After combustion, the samples were left in the furnace until the temperature was cooled down at about 500°C. Then, the samples were placed in the desiccator at room temperature until became a constant weight. The ignition losses of the samples were determined as their weight loss after dried at 105°C and combustion at 950°C.

3. RESULTS AND DISCUSSIONS

3.1 Internal Relative Humidity

The internal relative humidity changes of the pastes are shown in Figs. 1 to 3. The internal relative humidity was seen to decreases with respect to time. The internal relative humidity in paste at a relative humidity of 95% is almost identical to that in paste under sealed curing conditions. The internal relative humidity is seen to decrease with a reduction in the exposed ambient relative humidity.

The reduction of internal relative humidity in the sealed paste is due to the loss of moisture content in the hydration reaction. The additional loss of moisture content due to drying leads to a reduction in the internal relative humidity in pastes exposed to drying at reduced relative humidity levels.

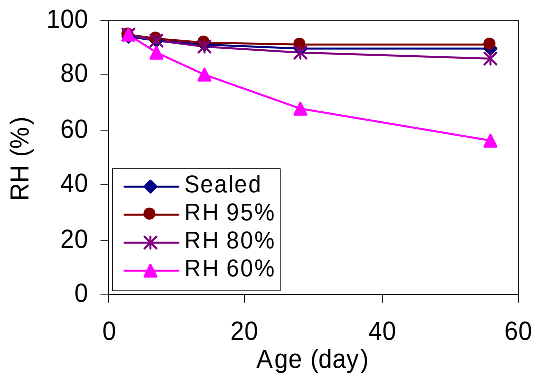

Fig. 1 Internal relative humidity of cement paste

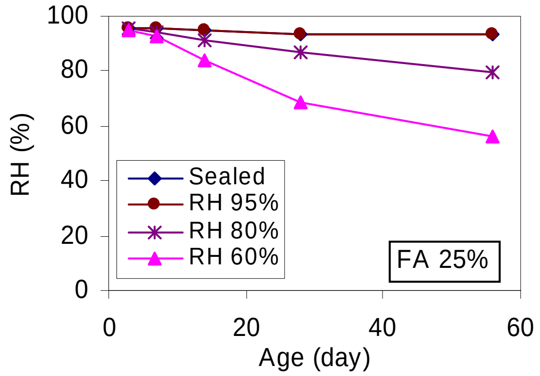

Fig. 2 Internal relative humidity of cement-fly ash paste with 25% fly ash

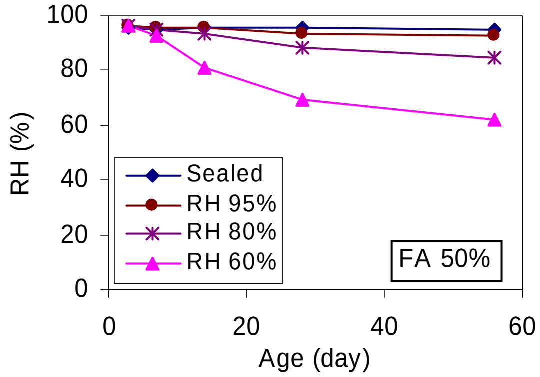

Fig. 3 Internal relative humidity of cement-fly ash paste with 50% fly ash

3.2 Degree of Hydration of Cement

(1) Effect of Replacement Ratio of Fly Ash

The effect of the replacement ratio of fly ash on the degree of hydration of cement is shown in Fig. 4. The degree of hydration of cement in cement paste is lower than that in cement-fly ash paste. The degree of hydration of cement increases with an increase in the replacement ratio of fly ash. The incorporation of fly ash in the paste mixture had an effect on the degree of hydration of cement since it increases the water-to-cement ratio even though the water-to-binder ratio is equal [8].

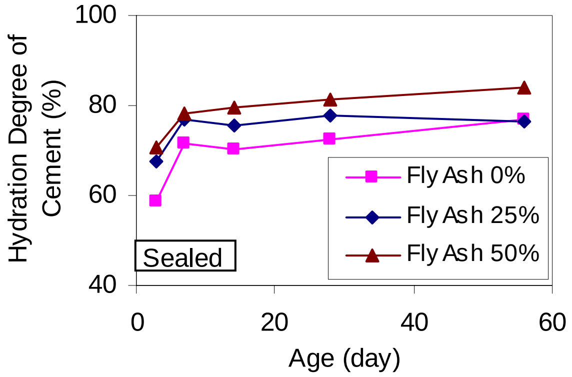

Fig. 4 Degree of hydration of cement in paste in sealed curing conditions with 0%, 25% and 50% fly ash

(2) Effect of Curing Condition and Ambient Relative Humidity

The degree of hydration of cement in pastes cured at various conditions is shown in Figs. 5 to 10. Figs. 5 to 7 show the degree of hydration of cement in pastes cured in water, in sealed curing and at a relative humidity of 95%. The degree of hydration in cement paste cured in water is slightly greater than the others. In the case of cement-fly ash pastes, there is no significant difference in the degree of hydration of cement among these curing conditions.

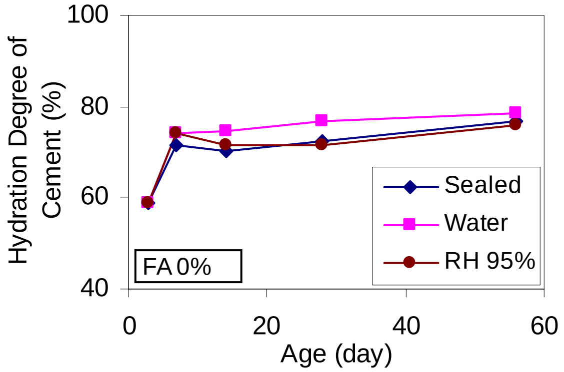

Fig. 5 Degree of hydration of cement in cement paste cured in water, in sealed curing and at relative humidity of 95%

Considering paste with a low water-to-binder ratio, self-desiccation leads to a reduction in the moisture content in paste. It was expected that the degree of hydration of cement in paste cured in water would be higher than that of the others since additional water from the surroundings is available as a supply for the hydration reaction.

In cement-fly ash pastes, the increase in water-to-cement ratio with the increase in the replacement ratio of fly ash might be sufficient for the cement to hydrate with no external water supply, as previously mentioned. As a result, it was possible to observe the comparable degree of hydration of cement in cement-fly ash pastes.

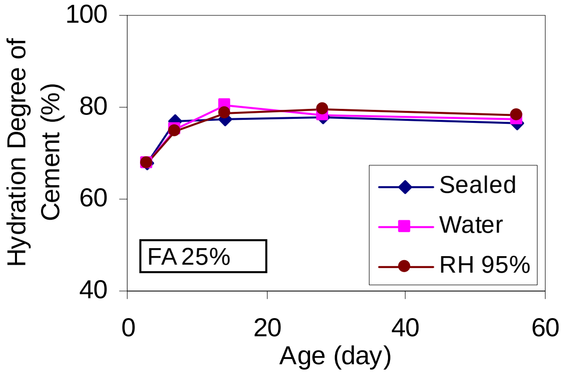

Fig. 6 Degree of hydration of cement in cement-fly ash paste with 25% fly ash cured in water, in sealed curing and at a relative humidity of 95%

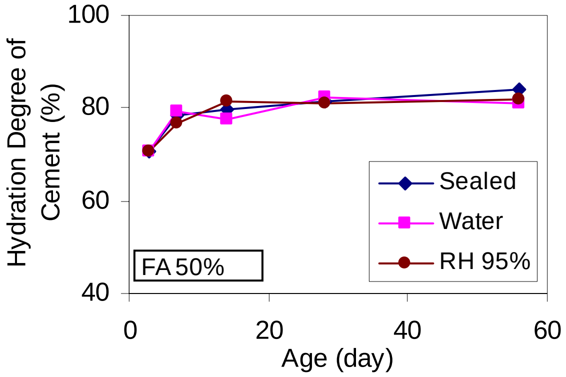

Fig. 7 Degree of hydration of cement in cement-fly ash paste with 50% fly ash cured in water, in sealed curing and at a relative humidity of 95%

In regard to the pastes that had been exposed to dry conditions, specifically low relative humidity, the loss of moisture content to the surroundings had a significant effect on the degree of hydration of cement.

The degree of hydration of cement in pastes explored at relative humidity levels of 60% and 80%, compared to those in sealed curing are shown in Figs. 8 to 10. The degree of hydration of cement in cement paste and paste with 50% fly ash decreases with a reduction in ambient relative humidity. On the other hand, the relative humidity has only a slight effect on the hydration degree of cement in paste with 25% fly ash. However, the reason for such this phenomenon is still unclear. More research is still needed in this area.

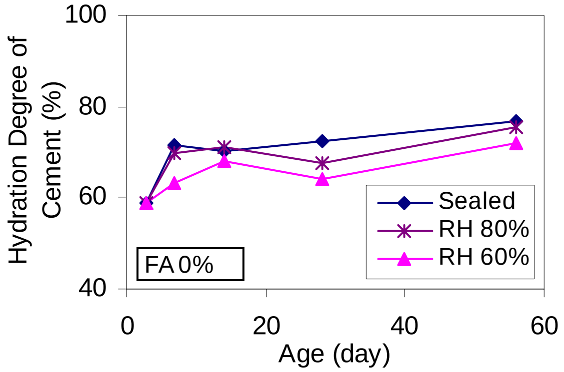

Fig. 8 Degree of hydration of cement in cement paste cured at relative humidity levels of 60% and 80% and sealed curing

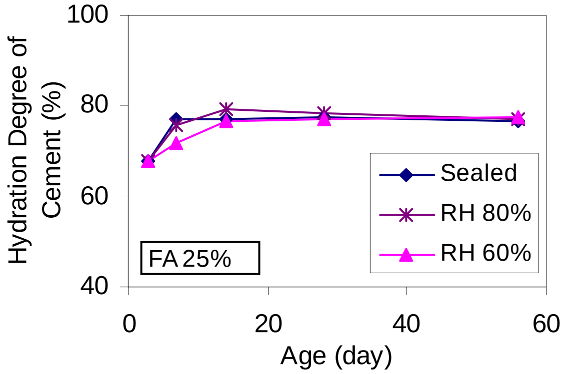

Fig. 9 Degree of hydration of cement in cement-fly ash paste with 25% fly ash cured at relative humidity levels of 60% and 80% and sealed curing

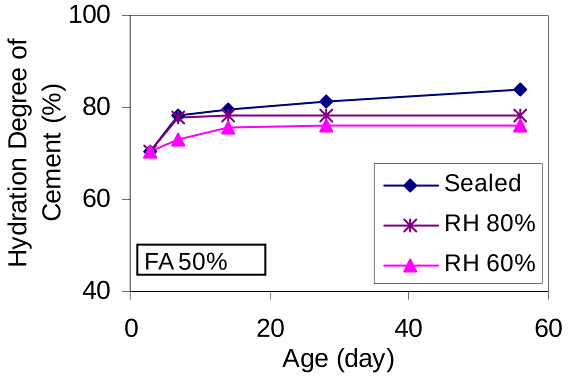

Fig. 10 Degree of hydration of cement in cement-fly ash paste with 50% fly ash cured at relative humidity levels of 60% and 80% and sealed curing

3.3 Degree of Hydration of Cement and Loss on Ignition

Loss on ignition is one of several ways to characterize the progress of hydration reaction. In general, loss on ignition is used to determine the bonding water in the hydrated product of paste.

Fig.11 shows the relationship between the total degree of hydration (cement and fly ash) and loss on ignition. In cement paste, the degree of hydration is shown satisfactorily correlated to the loss on ignition regardless of curing condition and relative humidity. In cement-fly ash pastes, the accuracy decreases with an increase in the fly ash replacement ratio. This inferior relationship is due to the bonding water in the hydrated product of cement-fly ash paste is different from that in the cement paste.

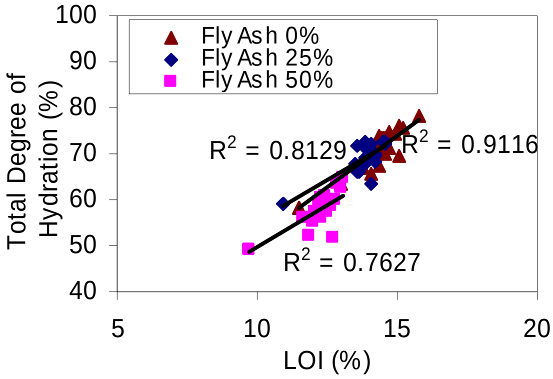

Fig. 11 Relationship between total degree of hydration (cement and fly ash) and loss on ignition

3.4 Degree of Hydration of Each Cement Component

The degree of hydration of each cement component in cement-fly ash paste with 50% fly ash is shown in Fig. 12. The degree of hydration of C_3S and C_3A increases at an early age and is nearly constant at a later age, while the degree of hydration of C_2S and C_4AF gradually increases.

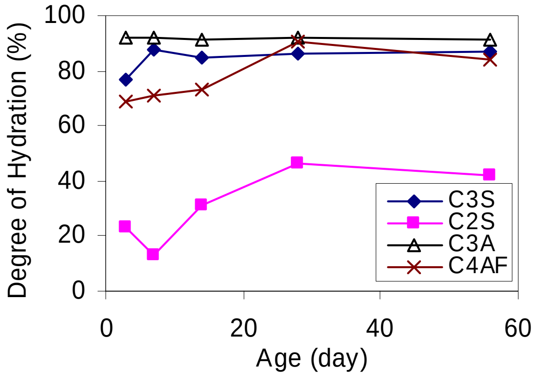

Fig. 12 Degree of hydration of each cement component in paste cured in water

The effect of curing at reduced relative humidity on the degree of hydration of each cement component is shown in Fig. 13 and Fig. 14.

The curing condition was seen to have a small effect on the hydration reaction of C_3S. Fig. 13 shows that degree of hydration of C_3S in paste under sealed curing is slightly higher than that at a relative humidity of 60%. The effect of the curing condition can be clearly seen in the hydration reaction of C_2S and C_4AF. At a reduced relative humidity, the hydration reaction of both C_2S and C_4AF is hardly increased at a later age. The degree of hydration of C_3A does not depend on curing conditions. The same tendency of result was reported by Jensen et al. [3]

In regard to the hydration characteristic of cement components, C_3S and C_3A react very rapidly with water and their hydration reaction is almost complete at an early age. In contrast, the hydration rates of C_2S and C_4AF are much slower than those of C_3S and C_3A. When the pastes are exposed to a low relative humidity, the moisture content in the paste decreases due to moisture diffusion occurring during drying in addition to the loss of moisture due to water consumption in the hydration reaction of C_3S and C_3A. As a result, an insufficient quantity of water remained for C_2S and C_4AF to hydrate at a later age.

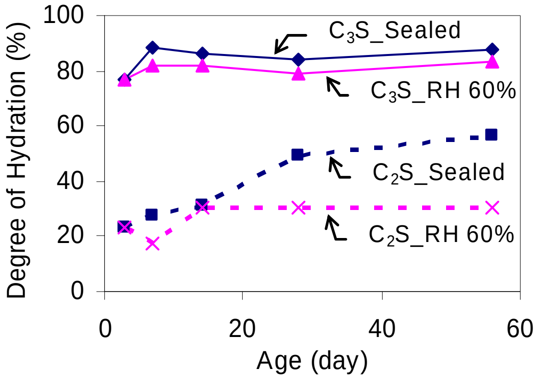

Fig. 13 Degree of hydration of C_3S and C_2S in cement-fly ash paste with 50% fly ash

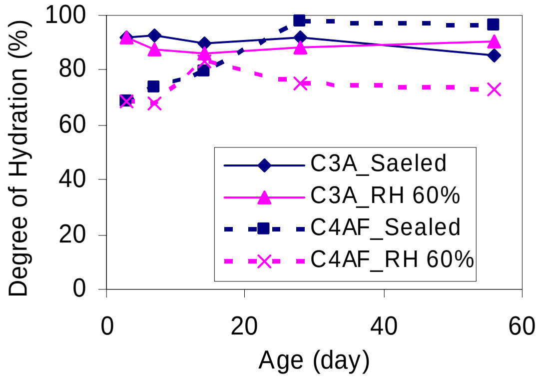

Fig. 14 Degree of hydration of C_3A and C_4AF in cement-fly ash paste with 50% fly ash

3.5 Hydration Degree of Fly Ash

The degree of hydration of fly ash in paste with a fly ash replacement ratio of 0.25 and 0.50 are shown in Fig. 15 and Fig. 16, respectively. The degree of hydration of fly ash in paste with 50% fly ash is remarkably impeded when exposed to a relative humidity of 60%.

It is generally known that in the pozzolanic reaction of fly ash, the $Ca(OH)_2$ produced during C_3S and C_2S hydration reacts with water and the silicate and aluminate phases of fly ash to produce calcium silicate hydrate and calcium aluminate hydrate. Since the hydration reaction of C_3S and C_2S is affected by the relative humidity, there is a possibility of its being affected by the pozzolanic reaction of fly ash in the same direction.

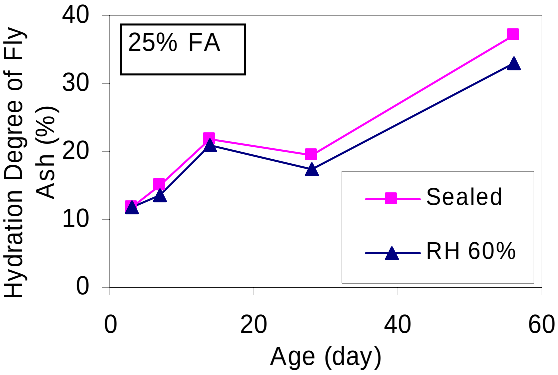

Fig. 15 Degree of hydration of fly ash in paste with fly ash replacement ratio of 0.25

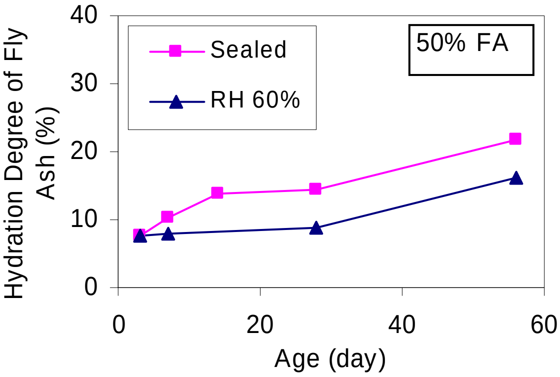

Fig. 16 Degree of hydration of fly ash in paste with fly ash replacement ratio of 0.50

4. CONCLUSIONS

(1) The degree of hydration of cement appears to be affected by a reduced curing relative humidity.

(2) The total degree of hydration satisfactorily correlates with the loss on ignition

(3) The hydration reaction of C_2S is more significantly affected by a reduced curing relative humidity than other cement components.

(4) The pozzolanic reaction of fly ash is affected by relative humidity as a consequence of a decreased rate of reaction of C_3S and C_2S.

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REFERENCES

[1] Patal R. G., et al.: Gradients of Microstructure and Diffusion Properties in Cement Paste Caused by Drying, Cem. Concr. Res., 15, (2), pp. 343-356, 1985

[2] Powers T. C., Portland Cement Ass, RX25, pp.178, 1947

[3] Jensen O. M., et al.: Clinker mineral hydration at reduced relative humidities, Cem. Concr. Res., 29, pp. 1505-1512, 1999

[4] Termkhajornkit P., Nawa T., Kurumisawa K.: A study of fly ash-cement hydration by Rietveld analysis and selective dissolution, JCI, Vol. 27, pp. 169-174, 2005

[5] Termkhajornkit P., Nawa T., Kurumisawa K.: Quantitative study on hydration of fly ash and Portland cement, Proceedings of ConMat'05, Vancouver, pp. 399, 2005

[6] Taylor J. C; Computer Programs for Standardless Quantitative Analysis of Minerals Using the Full Powder Diffraction Profile, Powder Diffraction, 6(1), March pp. 2-9, 1991

[7] Termkhajornkit P., et al.: Effect of Fly Ash on Autogenous Shrinkage, Cem. Concr. Res., 35, (3), pp. 473-482, 2005

[8] Termkhajornkit P., et al.: Effect of Water Curing Conditions on the hydration degree and compressive strengths of Fly Ash-Cement Paste, Cem. Concr. Comp., 28, pp. 781-789, 2006