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Hydration of high-volume fly ash cement pastes

Ya Mei Zhang [a], Wei Sun [a,*], Han Dong Yan [b]

[a] Department of Materials Science and Engineering, Southeast University, 2, Si Pai Lou, Nanjing 210096, People's Republic of China

[b] National Hua Qiao University, Quanzhou 362011, People's Republic of China

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Abstract

The hydration processes of high-volume fly ash cement paste were investigated by examining the non-evaporable water content, the CH content, the pH of pore solution and the fraction of reacted fly ash, curing at either 20°C or elevated temperatures after an initial curing at 20°C. The replacement percentage levels of fly ash were 40%, 50% and 60% by weight, respectively. The results revealed that the non-evaporable water content in high-volume fly ash cement pastes does not develop as plain cement pastes does, so it may be improper to apply the non-evaporable water content to evaluate the hydration process in high-volume fly ash cement matrix. The reduction in CH content increases with the progressing of hydration process and varies linearly with the logarithm of curing age. The addition of 3.0% of Na_2SO_4 could accelerate the pozzolanic reaction of fly ash at early ages. At 20°C, the pH of pore solution of high-volume fly ash cement paste was reduced to a great extent at early ages and it continued to decline at later ages due to the inclusion of large amount of fly ashes. At elevated temperatures, however, this trend was not found. The fraction of reacted fly ash directly reflects the pozzolanic reactivity of fly ash both at normal and elevated temperatures. There is some inherent correlation between the reduction in CH content, the pH of pore solution and the fraction of reacted fly ash. For specified matrix, the consumption of CH and the pH of pore solutions change linearly with the increase of the fraction of reacted fly ash.

Keywords: Fly ash; High-volume; Cement; Hydration; Non-evaporable water; CH; Pore solution; Fraction of reacted fly ash

1. Introduction

Many published literatures [1–7] have reported studies of the hydration of fly ash cement pastes. As is for pure cement pastes, non-evaporable water content and calcium hydroxide (CH) are usually measured to indicate the reaction progress in fly ash cement pastes. Some researchers [8,9] have also investigated the variation of the fraction of reacted fly ash and the alkalinity of pore solution in fly ash cement pastes with curing age.

Obviously, the objective of all the research work is to reveal the hydration kinetics of fly ash cement pastes in order to exploit the potential power of fly ash in cement-based composites. However, it appears to be quite difficult to describe the reaction degree in a simple way because the reactions involved in fly ash cement pastes are very complex, thus the compositions of hydration products cannot be exactly determined, and sometimes, contradictory results are even obtained by different researchers.

Meland [1] suggested that the water involved in the pozzolanic reaction comes from CH and that no extra water is chemically combined in the formation of pozzolanic products. Investigation by Marsh et al [1] showed that the water provided by CH is not the only water that takes part in the pozzolanic reaction. It seems that the hydrate formed at early and intermediate ages has higher water content than that specified in the formula $C_3S_2H_3$. Berry et al. [3] reported that the non-evaporable water content in early age fly ash cement pastes is higher than in plain cement pastes, but it does not keep on increasing continuously with age, which raises the difficulty to interpret the hydration process from the non-evaporable water content point.

As a matter of fact, most researchers [1–7] have also been interested in CH content in fly ash cement paste. Although the CH content in fly ash cement pastes is the eventual result of the product between cement and water and the consumption of CH by pozzolanic hydration of

* Corresponding author. Tel.: +86-25-3361361 Ext 4195; fax: +86-25-7712719/3359241.

E-mail address: sunwei@seu.edu.cn (W. Sun).

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fly ash, the reduction in CH content appears to be able to indicate the pozzolanic activity of fly ash.

Fraay [10] has reported the strong influence of the pH of the pore solution on the pozzolanic activity of fly ash. His research illustrates that the glass structure of the fly ash appears to be broken down substantially only beyond a pH of about 13.2 or 13.3. Huang [8] has examined the reaction degree of fly ash in a fly ash–$Ca(OH)_2$–water system by chemical method and found that the pH value can be applied to express the pozzolanic activity of fly ash. A fall of pH usually indicates the occurrence of reaction of fly ash. The lower the pH is, the higher the degree of reaction in fly ash is.

Since the incorporation of fly ash in cement pastes can reduce the alkalinity of pore solution, efforts have been made to apply high-volume of fly ash to improve the durability of glass fiber reinforced cement (GRC) [11–13]. Therefore, it is of significance to conduct researches not only on the non-evaporable water and CH content, but also the pH of pore solution, the degree of reacted fly ash and their relationships in high-volume fly ash cement matrix.

In the current investigation, the authors wish to present some results of the hydration of high-volume fly ash cement pastes. Investigations into the non-evaporable water and CH content in high-volume fly ash cement pastes will be reported, and the results of the pH of pore solution, the fraction of reacted fly ash and their relations with CH content will be discussed as well.

Table 1
Chemical compositions of cement and fly ashes (%)[a]

Items	Cement	SFA	INFA	NFA
SiO_2	21.1	45.47	57.74	55.88
Fe_2O_3	5.19	7.76	6.34	6.49
Al_2O_3	4.97	31.11	27.08	25.84
CaO	64.52	2.74	3.36	4.77
MgO	1.08	1.10	1.10	1.31
K_2O	–	0.64	–	–
Na_2O	–	0.35	–	–
SO_3	2.30	1.49	0.18	0.16
f-CaO	0.63	0.31	0.30	0.21
LOI	1.19	5.04	3.61	4.04

[a] C – Cement, SFA – Fly ash from Shanghai, INFA, NFA – Fly ash from Nanjing, LOI – Loss on ignition.

2. Experiments

2.1. Materials and mixture proportions

The chemical compositions and physical properties of cement and three air classified fly ashes used in all the experiments are given in Tables 1 and 2, respectively. Fly ashes were collected from two sources. NFA and INFA are from the same furnace, but have different particle size distribution. The particle size distribution of the three fly ashes is shown in Fig. 1.

All the specimens for determining the non-evaporable water and CH content had a water binder ratio of 0.33. The fly ash replacement percent for cement was 40%, 50% and 60% by weight. Specimens without fly ash were also cast for the comparison purpose. No admixtures were added.

Eight series of specimens were cast, as listed in Table 3. In S4(A) and S6(A), 3% of Na_2SO_4 was added to study its influence on the hydration of fly ash cement paste. Some specimens were cured in 20°C water till prescribed ages, others were pre-cured in 20°C water for

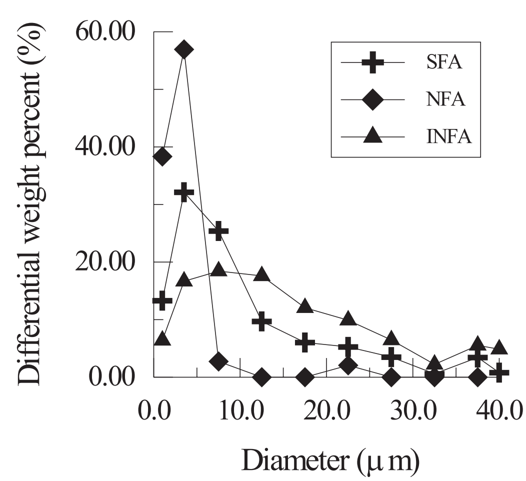

Fig. 1. Particle size distribution of fly ashes.

Table 2
Physical properties of cement and fly ashes

	Density (g/cm^3)	Specific area (cm^2/g)	45 μm sieve residue (%)	Water demand ratio[a]	Compressive strength ratio at 28 days[a]
C	3.1	3200	9.2	100	100
SFA	2.3	5960	1.7	89	97
NFA	2.35	7210	1.3	88	97
INFA	2.35	5330	8.8	92	91

[a] *Note*: Measured in accordance with GBJ146-90.

Table 3
Test series

	Series							
	C	S4	S5	S6	S4(A)	S6(A)	N6	IN6
Fly ash	–	SFA	SFA	SFA	SFA	SFA	NFA	INFA
Fly ash content (%)	0	40	50	60	40	60	60	60
Na_2SO_4 (%)	0	0	0	0	3	3	0	0

7 or 28 days and then put in 50°C water or 80°C water, respectively.

2.2. Measurements of non-evaporable water and CH content

Specimens were first split into small pieces and put in anhydrous ethanol to cease the further hydration, then ground until the particles all passed the 80 μm sieve. Finally, powder samples were dried at 60°C till constant weight.

The non-evaporable water content was examined by heating dry powder samples to 950°C to constant weight in an oven.

The non-evaporable water content is calculated according to the following equation:

$$w_{ne} = \frac{w_1 - w_2}{w_2} - \frac{r_{fc}}{1 - r_{fc}},$$

where, w_{ne} is the non-evaporable water content. w_1 and w_2 are the weight of specimens before and after ignition, respectively.

$$r_{fc} = p_f r_f + p_c r_c$$

where, p_f and p_c are the weight percent of fly ash and cement, respectively. r_f and r_c are the loss on ignition of fly ash and cement, respectively.

Since the f-CaO content in cement and three fly ashes is very limited (Table 1), its influence can thus be ignored, a chemical glycerine anhydrous ethanol method for examing the f-CaO content in cement was used to determine the CH content in fly ash cement paste. First, about 1 g dry powder samples and 15 ml glycerine anhydrous ethanol reacted together with a few Strontium Nitrate as activator under 100°C. Then, reaction products were titrated with standard benzoic acid anhydrous ethanol solution. The f-CaO content was calculated and converted into the content of $Ca(OH)_2$. The CH content presented in this paper is based on the weight of ignited samples. In order to find the relationship between CH content and the fraction of reacted fly ash, reduction in CH content was calculated according to the following equation:

$$(W_{CH})_R = (W_{CH})_{PC}(c/c+f) - (W_{CH})_{PC\text{–}FA},$$

where $(W_{CH})_R$ is the reduction in CH content (%), $(W_{CH})_{PC}$ the CH content in plain cement pastes (%), $(c/c+f)$ the weight percentage of cement, and $(W_{CH})_{PC\text{–}FA}$ is the CH content in fly ash cement pastes (%).

In practice, the hydration rate of PC is accelerated in the presence of pozzolanic materials (including fly ash), it then may result in a negative value of CH reduction at the early stages of hydration. This equation is based upon the assumption that the CH produced per unit weight of Portland cement at a given curing time is independent of the hydration environment of the Portland cement.

2.3. Measurements of the pH value of pore solution

The method applied to measure the alkalinity of pore solution is similar to that of Longuet's and Barneyback's [14]. Specimens were $\varnothing 72 \times 45$ mm^2 cylinders, which were subjected to the compressive loading of 1600 kN under a specified apparatus until no water could flow out from it at every desired age. The water-to-binder ratio was 0.50, and the binder sand ratio was 0.50. Expressed solution was titrated immediately after collection with standard hydrochloric acid solution.

2.4. Measurements of the fraction of reacted fly ash

The picric acid–methanol–water solution procedure similar to that described by Li and Roy [9] was used to determine the fraction of reacted fly ash

$$x = 1 - \frac{s_s - p_c s_c}{p_f s_f},$$

where x is the fraction of reacted fly ash, s_s the residue per gram of specimens, s_c and s_f are the residue per gram of plain cement paste and residue per gram of fly ash, p_c and p_f are the weight percentage of cement and fly ash of specimens, respectively.

3. Results and brief discussion

3.1. Non-evaporable water

Fig. 2 shows the non-evaporable water content of SFA fly ash cement pastes cured in 20°C water. It can be

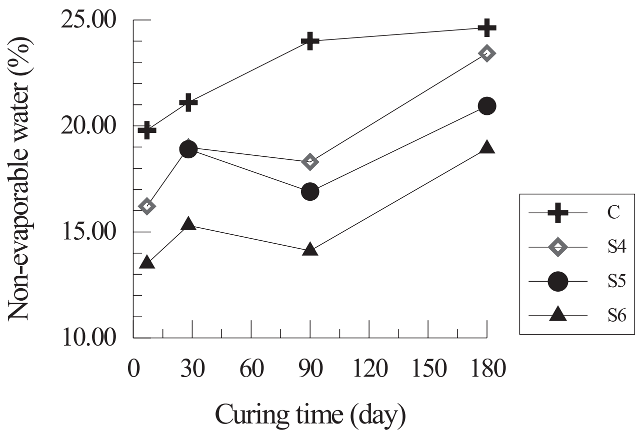

Fig. 2. Variation of the non-evaporable water content with age and fly ash content. Curing regime: 20°C water.

seen that the non-evaporable water in high-volume fly ash cement pastes is lower than that in plain cement pastes at the same age, and it decreases with the increase of fly ash content. The non-evaporable water contents of high-volume fly ash cement pastes at 90 days are smaller than those at 28 days, but increase again at 180 days. Similar results can also be found in Berry's paper [3]. No explanation has ever been made. May be the combining formation of water in fly ash cement paste varies with ages, and the drying process during the preparation for the powder specimens has caused the loss of some water in hydrates.

Fig. 3 shows the non-evaporable water contents of various pastes cured in 20°C water. The addition of 3% of Na_2SO_4 increases the non-evaporable water content of high-volume fly ash cement pastes at 7 and 28 days. For pastes including smaller fly ash particles, their non-evaporable water contents are higher than those with larger particles.

From Fig. 4, it may be found that the non-evaporable water content of all the pastes including plain cement pastes cured at elevated temperatures does not necessarily grow with age. For both C and S4 pastes, the non-evaporable water content decreases with age when pastes are cured in 80°C water. At elevated curing temperatures, the type, composition and morphology of the reaction products will certainly be different from those at normal curing temperature. Therefore, it might not be appropriate to use non-evaporable water content to describe the hydration process of high-volume fly ash cement pastes.

3.2. Reduction in CH content

Fig. 5 shows the variation of CH content by weight of total cementitious materials with curing age.

Based on the above assumption, a reduction of the CH content equivalent to null seems to mean the addition of fly ash has no effect on the hydration of the system at all. A positive CH reduction, however, indicates that pozzolanic reaction from fly ash has happened and consumed some CH produced by the hydration between cement and water. A negative result reveals that extra CH is formed due to the addition of fly ash, that is, the addition of fly ash accelerates the hydration of

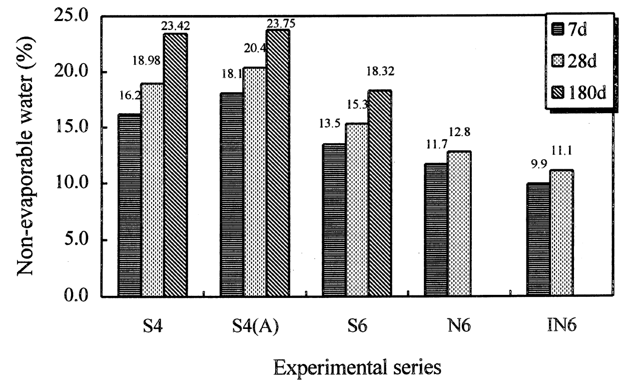

Fig. 3. The non-evaporable water content of fly ash cement pastes of various series. Curing regime: 20°C water.

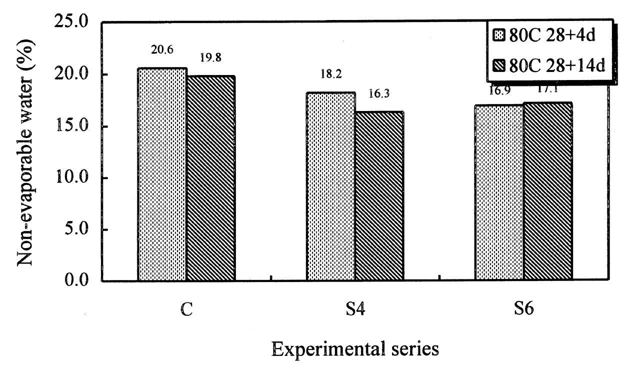

Fig. 4. The non-evaporable water content of specimens. Curing regime: 28 days in 20°C water and 4/14 days in 80°C water.

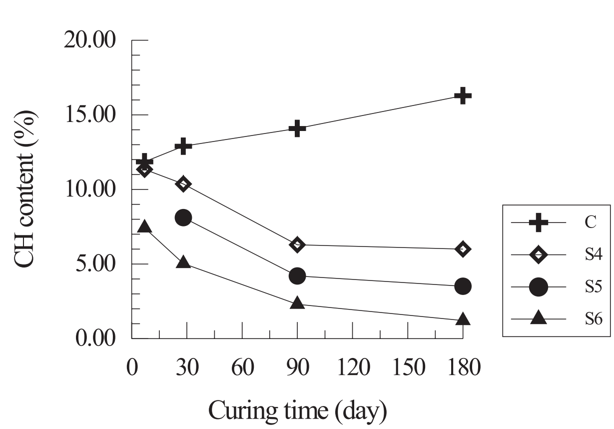

Fig. 5. Variation of CH content with age and fly ash content. Curing regime: 20°C water.

cement. From Fig. 5 to Fig. 7, it is evident that the incorporation of high-volume of fly ash in cement pastes may accelerate the hydration at early ages. But the reduction in CH content becomes positive and keeps on increasing with age. It is noticeable that, for specimens of the same ages, the difference of the reduction in CH content due to the different content of fly ash in pastes is not so obvious as that of CH content. Additionally, the CH content decreases with the increase of the content of fly ash, however, the reduction in CH increases with it.

Fig. 6 reveals that an approximate linear relation between CH reduction and logarithm of curing age t exists. From Fig. 7, it can be found that the reduction in CH content of S4(A) is positive at 7 days, which indicates the activating effect of Na_2SO_4 on the pozzolanic reaction of fly ash. For N6, the pozzolanic reaction of fly ash is also exhibited at 7 days because of the fine particles of fly ash NFA. At elevated curing temperatures, the CH reduction reaches a very high level in a short time and raises with age (Fig. 8). The higher the fly ash replacement percent is, the less the reduction in CH content is.

3.3. pH of pore solution

Fig. 9 describes the variation of the pH of pore solution with age. For specimens cured in 20°C water, the

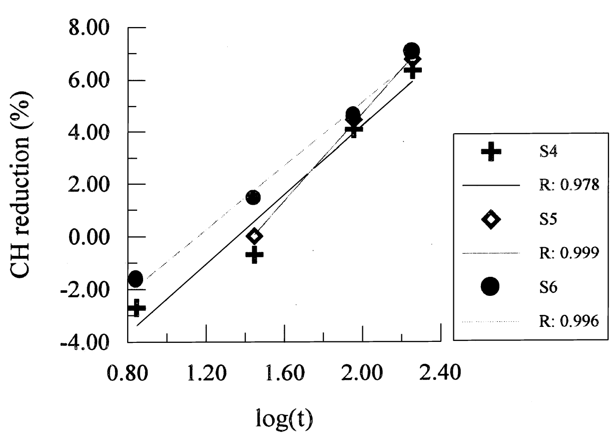

Fig. 6. The plot of the reduction of CH vs log(t).

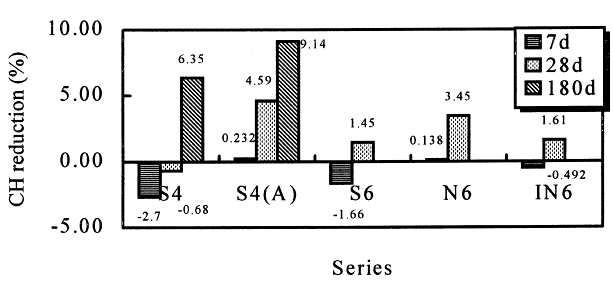

Fig. 7. Variation of the reduction of CH content of specimens of different series. Curing regime: 20°C water.

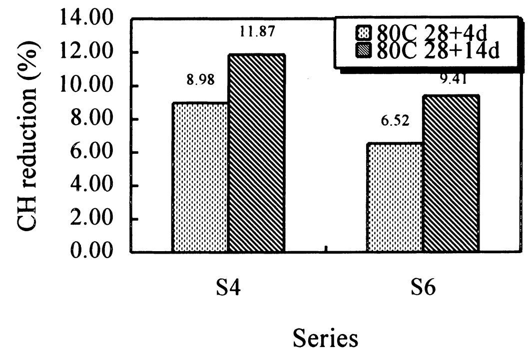

Fig. 8. The reduction of CH content of specimens. Curing regime: 28 days in 20°C water and 4/14 days in 80°C water.

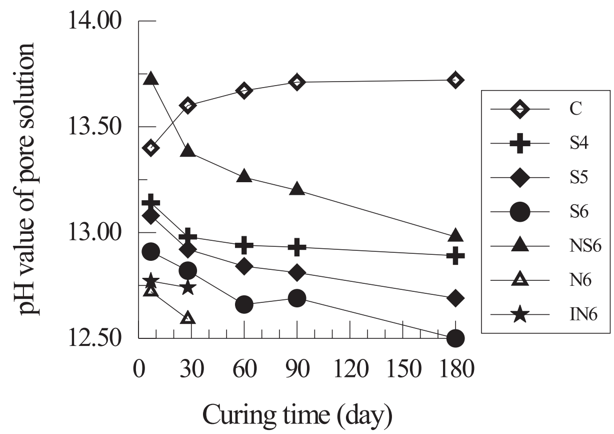

Fig. 9. The pH value of pore solution of specimens. Curing regime: 20°C water.

pH value of pore solution of high-volume fly ash cement pastes decreases continuously with curing age. For the same age specimens, it decreases with the increase of fly ash content. For specimens of the same fly ash content, specimens with finer ashes exhibit lower pH value than those with coarser ashes. It is noticeable that the decline of pH value mostly happens at the early ages. At later ages, however, the change is much slower. The addition of 3% of Na_2SO_4 raises the pH value of specimens at 7 days, which is higher than that of plain cement mortars, but at 28 days and later ages, the pH value of S6(A) declines sharply and keeps on decreasing with age.

Figs. 10 and 11 give the pH value of pore solutions of various specimens cured at 50°C and 80°C, respectively. When the curing temperature is elevated, the relationship between pH value and age found in specimens cured in 20°C water does not appear any more. Contrarily, at 80°C, the pH value of S6 shows a little increase with age. It is also evident that the pH value reaches a very low level at the very early ages when specimens are subjected to high temperatures.

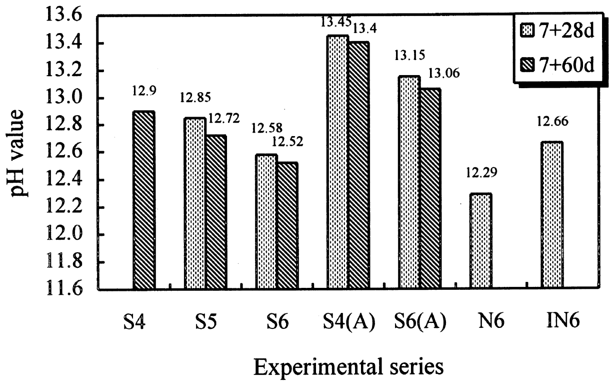

Fig. 10. The pH value of pore solutions of specimens. Curing regime: 7 days in 20°C water and 28/60 days in 50°C water.

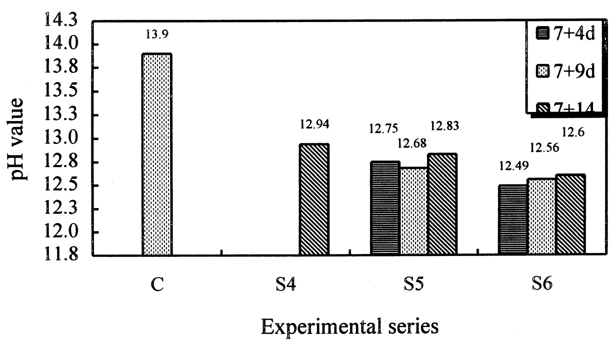

Fig. 11. The pH value of pore solutions of specimens. Curing regime: 7 days in 20°C water and 4/9/14 days in 80°C water.

3.4. Fraction of reacted fly ash

The relationship between the fraction of reacted fly ash (per unit weight of fly ash) and the content of fly ash and curing age is given in Figs. 12–14. From Fig. 12, it can be seen that the fractions of reacted fly ash at 7 days are very similar at the three replacement levels, but differ obviously at later ages for different replacement levels. It indicates that although the pozzolanic activity of fly ash is weaker at early ages than at later ages, there is ample lime available for reaction with fly ash, even at high fly ash levels. At the same ages, pastes including higher content of fly ash have lower fraction of reacted fly ash, which means that the degree of pozzolanic reaction is reduced due to the higher replacement level of fly ashes in pastes. At 180 days, the fractions of reacted fly ash in pastes S4, S5, S6 reach 36.24%, 33.02% and 28.59%, respectively. Additionally, there is an approximate linear relationship between fraction of reacted fly ash and the logarithm of curing age.

The addition of 3% of Na_2SO_4 also raises the fraction of reacted fly ash at early ages, but the difference at 180 days is only a little.

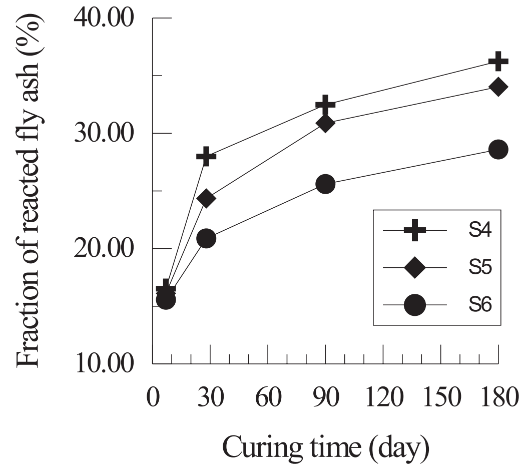

Fig. 12. The variation of the fraction of reacted fly ash with age and fly ash content. Curing regime: 20°C water.

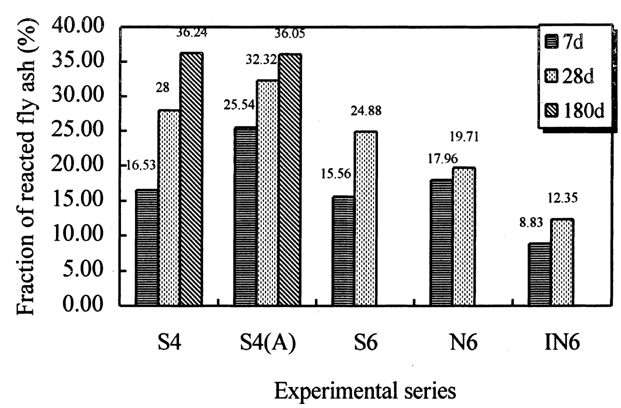

Fig. 13. The variation of the fraction of reacted fly ash of specimens. Curing regime: 20°C water.

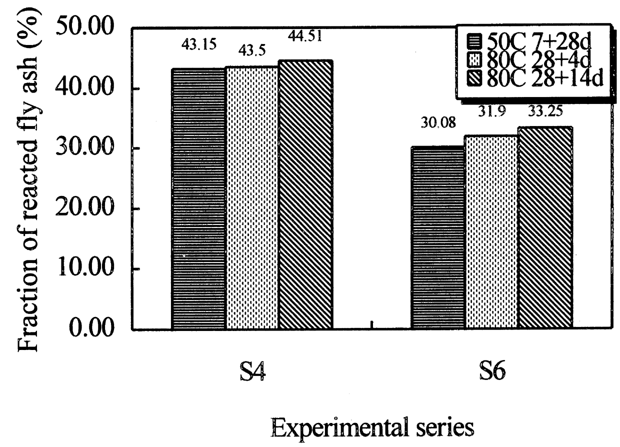

Fig. 14. The fraction of reacted fly ash of specimens at high temperatures. Curing regime: 7 days in 20°C water and 28 days in 50°C water 28 days in 20°C water and 4/14 days in 80°C water.

At elevated temperatures, the fraction of reacted fly ash reaches a high level in a short time, but increases only a little at later ages (Fig. 14).

3.5. Relationship between the fraction of reacted fly ash and the reduction in CH and pH

Fig. 15 shows that there appears to be an inherent connection between the fraction of reacted fly ash and the reduction in CH content in specified fly ash cement pastes. When the constituents of binders are changed, such correlation no longer exists.

Fig. 16 is a plot of the pH values of pore solution vs the fraction of reacted fly ash. For specified matrices, the pH value of pore solution decreases with the increase of the fraction of reacted fly ash.

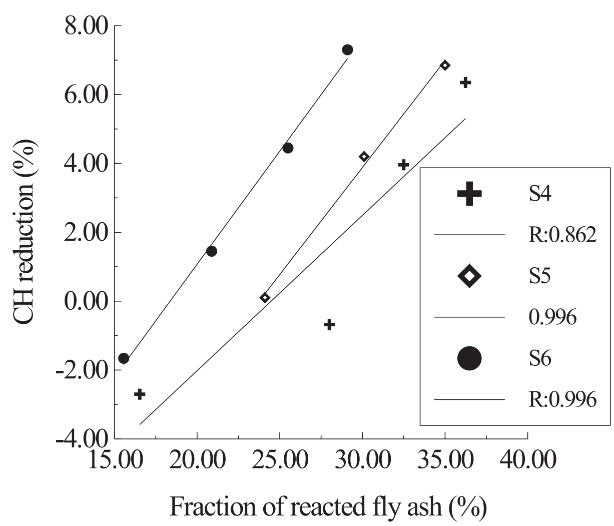

Fig. 15. The reduction in CH content vs the plot of the fraction of reacted fly ash. Curing regime: 20°C water.

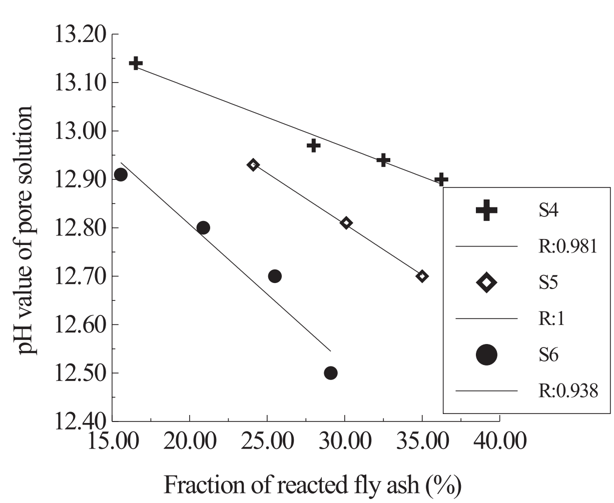

Fig. 16. The pH value of pore solution vs the plot of the fraction of reacted fly ash. Curing regime: 20°C water.

3.6. Brief discussion

The experimental results reveal that the reduction in CH content, the pH of pore solution and the fraction of reacted fly ash of high-volume fly ash cement pastes cured at normal temperature can reflect the reaction degree of fly ash from different aspects. However, there are some inherent correlations between them. On the one hand, the pozzolanic reaction of fly ash can cause the decline of the alkalinity of pore solution, and in the meantime consume the CH from the hydration of cement. On the other hand, a high alkaline environment is much beneficial to the pozzolanic reaction of fly ash. Therefore, the reaction extent of fly ash with Na_2SO_4 is higher than those without it up to 28 days, and the rate of pozzolanic reaction of fly ash at earlier ages is much higher than at later ages. For specimens with higher fly ash content, its pH of pore solution is relatively lower due to the lower cement content, therefore, its fraction of reacted fly ash is lower when compared with specimens having lower fly ash content, under the same conditions.

The study of the hydration of high-volume fly ash cement pastes can provide useful information for assessing the pozzolanic efficiency of fly ash. The investigation by the authors shows that the strength of high-volume fly ash cement concrete within 365 days also increases linearly with the logarithm of curing age [13]. An equation considering major factors such as the content of fly ash, water binder ratio and curing age is therefore put forward to assessing the efficiency of fly ash.

4. Conclusions

The non-evaporable water content in high-volume of fly ash cement pastes cured at normal temperature does not develop as plain cement pastes does. At elevated temperatures, it does not necessarily increase with age either. Therefore, it may be improper to apply the non-evaporable water content to evaluate the hydration process in high-volume fly ash cement matrix.

For specimens cured in 20°C water, the reduction in CH increases with the hydration progress and it varies linearly with the logarithm of curing age. The higher the content of fly ash is, the more the reduction in CH is.

The addition of 3% of Na_2SO_4 may accelerate the pozzolanic reaction of fly ash at early ages, which may be revealed from the increased non-evaporable water content and the reduction in CH content.

The pH of pore solution of high-volume fly ash cement pastes is reduced to a great extent at early ages and it continues to decline at later ages. At elevated temperatures, however, this trend is not found, perhaps due to the varied solubility of alkalis.

The fraction of reacted fly ash directly reflects the pozzolanic reactivity of fly ash curing at either 20°C or elevated temperatures after an initial curing at 20°C.

There are some inherent correlations between the reduction in CH content, the pH of pore solution and the fraction of reacted fly ash. For specified matrix, the consumption of CH and the pH of pore solutions change linearly with the increase of the fraction of reaction of reacted fly ash.

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