Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 30 (2000) 747–756

Degree of hydration and gel/space ratio of high-volume fly ash/cement systems

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Received 22 July 1999; accepted 12 January 2000

Abstract

Although fly ash has been widely used in concrete as a cement replacement, little work has been done on determining the degree of hydration of high-volume fly ash/cement (FC) systems. In the present study, the degree of hydration of the cement in Portland cement (PC) paste was obtained by determining the non-evaporable water (Wn) content. The degree of reaction of the fly ash in FC pastes was determined using a selective dissolution method. Based on the relation between the degree of cement hydration and effective water-to-cement (w/c) ratio, the degree of hydration of the cement in FC pastes was also estimated. It was found that high-volume fly ash pastes underwent a lower degree of fly ash reaction, and in the pastes with 45% to 55% fly ash, more than 80% of the fly ash still remained unreacted after 90 days of curing while the hydration of the cement in high-volume fly ash pastes was enhanced because of the higher effective w/c ratio for the paste. This effect was more significant for the pastes with lower water-to-binder (w/b) ratios. Thus, preparing high-volume fly ash concrete at lower w/b ratios can result in less strength losses. This paper also introduces a model to describe the relationship between the w/c ratio and the degree of cement hydration and gel/space ratio. The gel/space ratios of the FC pastes, evaluated based on the proposed model, were found to be consistent with the gel/space ratio of PC pastes in terms of the relationship with compressive strength. The gel/space ratio data correlated (inversely) linearly with mercury intruded porosity, but the former correlated more with compressive strength than the latter.

Keywords: Fly ash; Cement paste; Hydration; Gel/space ratio

1. Introduction

High-volume fly ash concrete for structural use was first developed by the Canadian Centre for Mineral and Energy Technology (CANMET) in the late 1980s [1]. This type of concrete may contain more fly ash than cement by weight, and is usually prepared at the water-to-binder (w/b) ratios of about 0.3. It was reported to have acceptable early-age strength, high long-term strength and modulus of elasticity, low drying shrinkage and creep, and excellent durability when compared with Portland cement (PC) concrete with similar strength [2–5]. As more than 50 wt.% of the PC have been replaced in this type of concrete, it is believed that fly ash plays a significant cementing role [6].

Fly ash is known as a pozzolana which in itself possesses little or no cementitious value [7] and cannot react with water alone. Traditionally, fly ash used in structural concrete is limited to 15% to 25% cement replacement [6,8]. When a significant amount of fly ash is used, how it contributes to the strength development of the concrete and the hydration characteristics of this type of material are of significant research interest.

Feldman et al. [9] found that in high-volume fly ash/cement (FC) pastes, the fly ash commences reaction with $Ca(OH)_2$ between 3 and 7 days, but considerable amounts of $Ca(OH)_2$ and fly ash still remain unreacted after 91 days of hydration. The reaction products, mainly in the form of calcium silicate hydrates (CSH), have lower calcium-to-silica ratios (c/s). Berry et al. [10] indicated that in the early stages, fly ashes have the physical effect of a space filler, and are involved in the formation of ettringite (AFt). In the long-term, they are involved in the hydration reaction mainly as silico-aluminate binders. Xu et al. [11] and Xu and Sarkar [12] attributed the low early strength of high-volume FC systems to the effect of higher net water-to-cement ratio (w/c) due to fly ash replacement. They also indicated that the fly ash at later

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PII: S0008-8846(00)00213-1

ages have a twofold effect: it strengthens the contact between particles and also consumes $Ca(OH)_2$ to reduce the flaws associated with it. Berry et al. [6] proposed two cementing mechanisms for high-volume FC systems. The first was the 'enhanced' reaction of the PC due to a higher w/c ratio, with the consequent production of larger quantities of hydration products, exceeding the usual stoichiometric proportions. The second was the formation of additional cementing constituents through chemical reactions involving fly ash. Zhang [13] suggested that, as most of the ash particles remain unreacted even after a long period of curing, high-volume fly ash pastes can be considered as a composite material with the ash particles serving as reactive micro-aggregates.

The above studies provided a qualitative understanding of the hydration chemistry and microstructure of high-volume FC systems. However, it should be noted that although hydration characteristics of fly ash are common for all FC systems, there are substantial differences between low-volume (10% to 25% by weight) and high-volume (around 50% by weight) FC systems. A more quantitative understanding of the hydration process of FC systems with different levels of replacements is needed.

Moreover, it is known that the strength of concrete depends upon the gel/space ratio [14], which depends on the degree of hydration at a given age of the cementitious materials. Information on the degree of hydration of FC systems is also limited in other studies, except that by Ohsawa et al. [15] and Li et al. [16], who presented some data on the degree of hydration of fly ash and silica fume. Gopalan [17] also evaluated the gel/space ratios of fly ash concrete mixes from their compressive strength, assuming that the correlation between gel/space ratio and compressive strength for fly ash concrete was the same as for PC concrete. In some studies [6,9,10], although non-evaporable water (Wn) and $Ca(OH)_2$ content were determined, the obtained data did not lead to a quantitative determination of the degrees of cement hydration and fly ash reaction in high-volume fly ash systems where hydration reactions are more complex than plain PC systems. A quantitative determination of the degree of hydration of cement and fly ash will lead to a better understanding of the mechanism of strength development of high-volume fly ash concrete.

This paper presents extensive experimental results of a quantitative analysis of the hydration of FC pastes with different percentages of replacements and w/b ratios. The degree of hydration of plain PC pastes was determined based on the determination of Wn content. The degree of reaction of the fly ash in FC pastes was determined by means of the selective dissolution method of Ohsawa et al. [15] and Li et al. [16]. The compressive strength and $Ca(OH)_2$ content of the pastes were also determined. Attempts were made to evaluate the degree of cement hydration and gel/space ratios in FC systems. The results were compared with the compressive strength data and the mercury intrusion porosity data obtained previously [18,19].

2. Experimental details

2.1. Materials

The cementitious materials used in this study were a PC equivalent to ASTM Type I, and low calcium fly ash equivalent to ASTM Class F, both which are commercially available in Hong Kong. The material properties of these materials are shown in Table 1.

2.2. Preparation of cement pastes

FC pastes were prepared at the w/b ratios of 0.19, 0.24, 0.3, and 0.5. Fly ash was used as the replacement of cement at the levels of 25% and 45% by weight for the pastes at the w/b of 0.19 and 0.24, and 25 and 55% by weight for those at the w/b of 0.3 and 0.5. Plain PC pastes without any fly ash replacement were prepared at the same w/b ratios as the references. The pastes were mixed in a mechanical mixer with 5-l capacity, and cast in a 70.7 × 70.7 × 70.7-mm steel mould. A high range water reducing admixture (HRWRA) was added to the pastes with w/b of 0.19 and 0.24 to increase the workability. Special precaution was taken for the pastes at the w/b ratio of 0.5, which was mixed continuously in the mixer for 3 h before casting into steel moulds to prevent segregation. The steel moulds were removed 24 h after mixing, and the cubes were cured in water at 27°C.

2.3. Compression strength test

A compression test was carried out at the given ages, using a Denison compression machine. The fracture pieces of the cubes after the compression test were preserved for other tests. To stop the hydration reactions, the samples were soaked in acetone for 7 days, and were then placed in a vacuum desiccator overnight to remove the acetone. These samples were further dried at 60°C in an oven for 24 h and were ground in a mortar to pass through a 150-μm sieve.

Table 1
Properties of cement and fly ash

Properties	Cement	Fly ash
SiO_2 (%)	21.0	56.8
Fe_2O_3 (%)	3.4	5.3
Al_2O_3 (%)	5.9	28.2
CaO (%)	64.7	<3
MgO (%)	0.9	5.2
SO_3 (%)	2.6	0.7
Alkali as Na_2O (%)	0.4	0.14
Chloride content (%)	0.004	<0.005
Loss on ignition (%)	1.2	3.9
Density	3.15	2.31
Fineness (wet sieve, >45 μm) (%)		6.3
Specific surface area (cm^2/g)	3519	3860

2.4. Determination of non-evaporable water

Wn contents of the hydrated cement pastes were determined to evaluate the degree of hydration. For PC pastes, the degree of hydration can be determined based on that the hydration of 1 g of anhydrous cement produces 0.23 g of Wn [14].

All the calculations described in this subsection and the following subsections were carried out on the ignited basis (i.e. 1 g of sample was ignited at 950°C in an electric furnace for 1 h). The loss on ignition (LOI) of the as-received fly ash and cement, and hydrated cement pastes was calculated by:

$$\text{LOI}\ (\%) = 100 \times (\text{as-received weight} - \text{ignited weight})/\text{ignited weight} \quad (1)$$

The original fractions of fly ash (f) and cement (c) in a FC paste on an ignited basis were calculated by:

$$f \text{ or } c = \text{ignited weight of fly ash or cement} / (\text{ignited weight of fly ash} + \text{ignited weight of cement}) \quad (2)$$

where the ignited weight of fly ash or cement can be calculated by:

$$\text{Ignited weight} = \text{as-received weight}/(1 + \text{LOI}) \quad (3)$$

To determine the Wn content, 1 g of the hydrated sample obtained from Section 2.3 was dried in an oven at 110°C for 3 h, and was then ignited at 950°C in an electric furnace for 1 h. The Wn content of hydrated pastes on the ignited basis was calculated by Eq. (4):

$$\text{Wn}\ (\%) = 100 \times [(\text{dried weight of paste} - \text{ignited weight of paste}) / \text{ignited weight of paste} - \text{LOI of cement}] \quad (4)$$

The degree of hydration of the cement (α_c) in PC pastes is calculated by Eq. (5):

$$\alpha_c \text{ in PC pastes} = 100 \times \text{Wn}/0.23. \quad (5)$$

2.5. Determination $Ca(OH)_2$ in hydrated cement pastes

The $Ca(OH)_2$ content of hydrated cement pastes was determined by thermal gravimetry analysis (TGA), using the sample obtained from Section 2.3. The $Ca(OH)_2$ content was calculated based on the ignited weight of the sample.

2.6. Determination of the degree of reaction of fly ash

The determination of the degree of reaction of fly ash was based on a selective dissolution procedure using picric acid–methanol solution and water [15,16]. The principle of the procedure is that in a blended cement paste, fly ash reacts with calcium hydroxide to form acid-soluble hydration products. It is possible to dissolve the hydration products of cement and fly ash, and the unreacted cement components, leaving the remaining unreacted fly ash undissolved [15].

To determine the degree of reaction of fly ash, the insoluble residues of the as-received cement and fly ash, and the hydrated FC pastes in a solution of picric acid–methanol–water were determined. One gram of the ground sample was added to a beaker containing 9 g of picric acid and 60 ml methanol (AR Grade). The mixture was stirred using a magnetic stirrer for 15 min. Distilled water (40 ml) was added and the mixture was stirred continuously for another 45 min. The mixture was filtered through a Whatman No. 41 filter paper. The filter paper and the residue were further washed with methanol until the color of picric acid disappeared. They were then washed with about 300 ml distilled water at about 60°C. The filter paper and its content were transferred into a porcelain crucible. The crucible was ignited in an electric furnace at 300°C, 450°C and thereafter at 950°C, each for 1 h. The crucible was weighed after cooling to room temperature. Blank tests were carried out following the same procedure but without adding the sample. The residue from a blank test was used to correct the weight of residue of the sample. The residue per gram of ignited sample was calculated by Eq. (6):

$$\text{Residue per gram of ignited sample} = \text{corrected weight of residue} \times (1 + \text{LOI})/\text{weight of sample} \quad (6)$$

The unreacted fly ash per gram of ignited FC paste was given by:

$$\text{Unreacted fly ash per gram of ignited FC paste} = \text{residue per gram of ignited FC paste} - \text{residue per gram of ignited cement} \times c \quad (7)$$

The degree of reaction of fly ash α_f was thus given by:

$$\alpha t_{ptf}\ (\%) = 100 \times (1 - \text{unreacted fly ash per gram of ignited FC paste}) / (\text{residue per gram of fly ash} \times \text{f}) \quad (8)$$

In Eqs. (7) and (8), c and f are original fractions of cement and fly ash, determined according to Eq. (2).

3. Results and discussion

3.1. Compressive strength of the pastes

The results of the compressive strength test of the pastes are shown in Table 2. The corresponding compressive strength data of the concrete can be found in our other papers [19,20].

Generally, it is known that replacing cement by fly ash would lower the early strength (up to 28 days). It has been reported that preparing high-volume fly ash concrete at lower w/b ratios produces less negative effects on the compressive strength of the concrete [19]. Similar phenomenon is also observed for pastes prepared in this study. At lower w/b ratios, a 25% replacement had an insignificant negative effect on the compressive strength even at the age as early as 7 days. A 45% fly ash replacement resulted in 8% reduction in the 28-day compressive strength for the paste at the w/b ratio of 0.24. But at a w/b ratio of 0.3, a 55% fly ash replacement reduced the 28-day compressive strength by 28%, and at the w/b ratio of 0.5, the strength reduction was increased to 38%.

When compared with the compressive strength of the corresponding concrete [19,20], it was noted that the fly ash in concrete generally contributes better to strength than in pastes. This may be due to the improvement effect of fly ash in the interfaces between the cement matrix and aggregates in concrete with lower w/b ratio. But in concrete with a high w/b ratio and with a high-volume fly ash, the interfacial bond is weak even after a long period of curing.

3.2. Non-evaporable water and degree of hydration of PC pastes

The results of the determination of Wn content are shown in Table 3.

For PC pastes, the results clearly show that Wn content increased as the w/c ratio increased. At each age, the Wn content of the paste at the w/c ratio of 0.5 were substantially (50%) higher than that of the paste at the w/c ratio of 0.19. Based on the data of Wn, degrees of hydration of the PC pastes were determined according to Eq. (3). From Fig. 1, it can be seen that at the w/c ratio of 0.19, the degree of hydration was about 45% at 7 days of age. This value increased by only a few percentage at the age of 90 days. However, at the w/c value of 0.5, the degrees of hydration of the PC paste were 65% and 81%, respectively at the ages of 7 and 90 days. The lower degree of hydration for the pastes at lower w/c ratios can be attributed to the insufficient space available to accommodate more hydration products [14].

For FC pastes, the amount of Wn is dependent on w/b ratios and percentages of cement replacement. Overall, FC pastes had lower Wn contents than the PC paste at the same w/b ratio. The pastes at a higher w/b and with a lower fly ash replacement had higher Wn content. Furthermore, it is noted that in the FC pastes, the amount of Wn relative to the cement content (amount of Wn per 100 g of cement) of the paste was higher than in the PC paste, and the higher the fly ash content, the higher the relative Wn (Fig. 2). This is consistent with the results of Feldman et al. [9] and Berry et al. [10]. The higher relative Wn content in FC pastes can be attributed to (1) the contribution of fly ash reaction, and (2) the 'enhanced' hydration of the PC in FC pastes due to the relatively higher effective w/c ratio, as proposed by Berry et al. [6]. The latter is because when part of cement is replaced by fly

Table 2
Compressive strength of the pastes

w/b	Fly ash replacement (%)	Compressive strength (MPa)		
		7 days	28 days	90 days
0.19	0	85.6	116.0	133.9
	25	74.9	113.3	136.9
	45	54.7	94.9	116.1
0.24	0	74.7	103.7	119.0
	25	69.5	99.5	120.2
	45	56.0	95.0	104.5
0.3	0	67.2	80.9	97.6
	25	55.3	75.5	106.1
	55	31.0	58.9	79.0
0.5	0	21.8	37.5	54.2
	25	16.9	31.0	48.0
	55	10.0	23.3	42.3

Table 3
Wn content of PC and FC pastes (based on ignited weight)

w/b	Fly ash replacement (%)	Wn content (%)		
		7 days	28 days	90 days
0.19	0	10.32	10.96	11.71
	25	10.30	11.07	11.50
	45	10.18	10.76	11.14
0.24	0	11.99	12.39	13.76
	25	11.31	12.4	13.11
	45	10.39	11.16	11.70
0.3	0	14.20	14.68	15.66
	25	12.47	13.32	13.74
	55	9.92	10.74	12.71
0.5	0	15.00	16.87	18.62
	25	12.15	14.07	15.10
	55	9.65	11.08	13.62

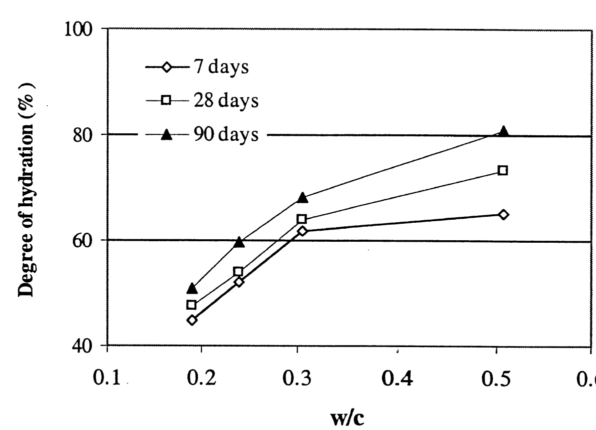
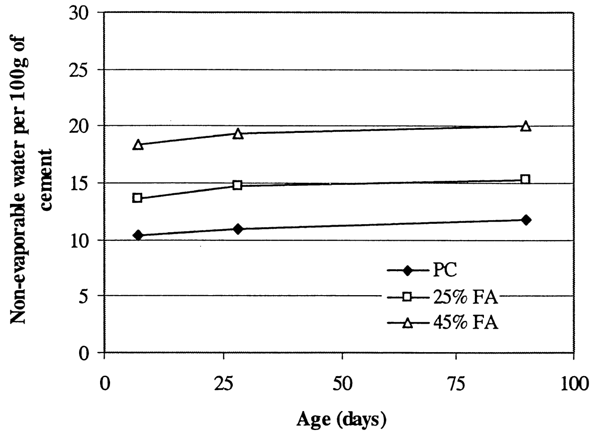
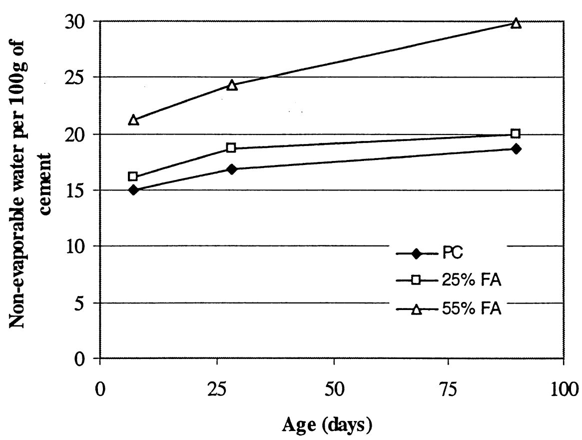


Fig. 1. Increased degree of hydration of PC pastes with increasing w/c ratios.



(a)



(b)

Fig. 2. Wn content relative to the cement content in PC and FC pastes (based on ignited weight). (a) w/b=0.19, and (b) w/b=0.5.

ash, the concentration of cement in the system is diluted, and the effective w/c ratio controlling the rate of cement hydration is relatively increased.

On the other hand, it is noted that at lower w/b ratios, the negative effects of high-volume fly ash on Wn content are small. At the w/b ratios of 0.19 and 0.24, a 45% fly ash replacement resulted in only small decreases in Wn content. But at the w/b ratio of 0.5, the fly ash replacements significantly reduced the Wn content. These are consistent with the results of the compressive strength test, and seem to indicate that the above-mentioned hydration enhancement effect in FC pastes with lower w/b ratios is more significant.

Since the processes of pozzolanic reaction are more complex than cement hydration, and the amount of water bound in the fly ash reaction products is uncertain, direction determination of the degree of hydration from the data of Wn for fly ash pastes has not yet been established.

Table 4
$Ca(OH)_2$ content of PC and FC pastes (based on ignited weight)

w/b	Fly ash replacement (%)	$Ca(OH)_2$ content (%)		
		7 days	28 days	90 days
0.3	0	11.8	12.55	12.83
	25	9.08	8.84	6.98
	55	5.5	4.05	3.03
0.5	0	15.32	14.79	15.78
	55	6.83	4.79	3.30

3.3. $Ca(OH)_2$ contents

It is generally considered that a fully hydrated PC, with typical C_3S and C_2S contents, will take up about 20 to 25 wt.% H_2O, and produces about 20 to 25 wt.% $Ca(OH)_2$ [6,21]. Thus, $Ca(OH)_2$ content can be used to determine the degree of hydration of cement in the PC pastes. However, as the pozzolanic reaction in FC system consumes $Ca(OH)_2$, the same principle cannot be used to determine the degree of hydration of FC systems.

In this study, $Ca(OH)_2$ content was determined for part of the samples and the results are shown in Table 4. For PC pastes, the results of $Ca(OH)_2$ content are consistent with the results of Wn content with an increasing trend with age.

For FC pastes, the $Ca(OH)_2$ content decreased as the fly ash content and curing age increased. The decrease in $Ca(OH)_2$ with curing ages indicates the progress of pozzolanic reaction that consumed $Ca(OH)_2$.

3.4. Degree of fly ash reaction

The hydration rates of the fly ash in the FC pastes are shown in Table 5. The data for the pastes at w/b ratios of 0.19 and 0.24 have been extracted from our previous study [19].

The results show that at 7 days, a measurable amount of pozzolanic reaction in the FC pastes has taken place. The reaction degree of about 5% of the fly ash may correspond to the initial attack on the fly ash particles by the alkali ions in the pore solution [6,10]. According to Berry et al. [6,10], even at ages as early as 7 days, fly ash particles are involved in chemical reactions forming ettringite (AFt). However,

Table 5
Degree of reaction of fly ash in FC pastes

w/b	Fly ash replacement (%)	Degree of reaction (%)		
		7 days	28 days	90 days
0.19	25	5.09	13.71	17.54
	45	4.85	10.84	14.8
0.24	25	5.65	13.94	22.56
	45	5.28	12.81	16.45
0.3	25	6.67	14.41	24.58
	55	4.98	11.21	17.03
0.5	25	6.4	12.23	29.52
	55	5.26	9.82	19.41

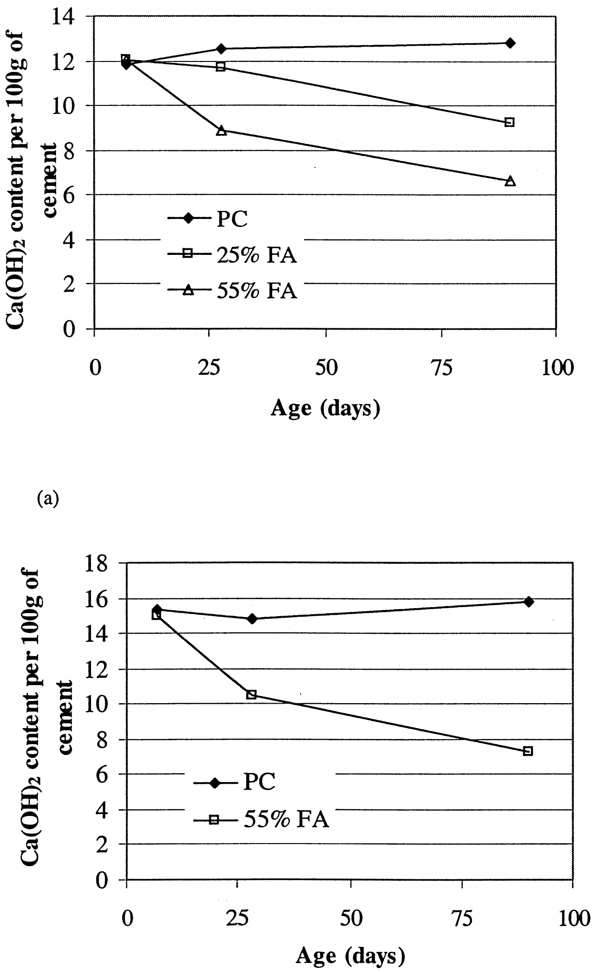


Fig. 3. $Ca(OH)_2$ content relative to the cement content in PC and FC pastes (based on ignited weight). (a) w/b = 0.3, and (b) w/b = 0.5.

5% fly ash reaction seemed to have little effect on the relative $Ca(OH)_2$ content in the fly ash pastes. At the age of 7 days, the FC pastes had the relative $Ca(OH)_2$ content similar to the PC pastes (Fig. 3). This might be due to the initial attack of fly ash, which was mainly involved in the formation of AFt that did not consume $Ca(OH)_2$, and the hydration of cement was enhanced in the fly ash pastes as has been mentioned above.

At the age of 28 days, the degree of fly ash reaction increased to about 10% to 14%. According to Berry et al. [6] and Xu and Sarkar [12], during the period of 7 to 28 days, many ash particles show some etching of the glassy materials, and $Ca(OH)_2$ on fly ash particles undergo redissolution and reaction. At this stage, deposits of reaction products, oriented radially to the fly ash surface, are observable as interfacial or boundary zones around some ash particles [6]. Evidence of fly ash reaction was also demonstrated by the reduced relative $Ca(OH)_2$ content (Fig. 3).

At 90 days, the measured degree of fly ash reaction was about three to four times of that at 7 days. An increase in the degree of fly ash reaction corresponded to a decrease in $Ca(OH)_2$ content, indicating active pozzolanic reaction. According to Berry et al. [6], Xu et al. [11], and Xu and Sarkar [12], at this age, etched fly ash surfaces and hydrated rims with broken fly ash particles are quite common. Various reaction products including hydrates of calcium silicates (CSH), aluminates (CAH), and aluminosilicates (CASH), would be expected to form, with consequent consumption of $Ca(OH)_2$ [6]. As both $Ca(OH)_2$ and CSH precipitate on the surfaces of fly ash particles, pozzolanic reaction at later ages strengthens the contact between cement and fly ash and between fly ash particles. This leads to a more densified and more homogeneous system, and a considerable long-term strength increase (Table 2).

It is noted that in general, the fly ash in the pastes with higher percentages of replacement underwent a lower degree of reaction. This might be due to the lower concentration of Ca^{++} ions in the pore solutions of the pastes. The w/b ratio seems to be another factor controlling the rate of fly ash reaction. As the w/b ratio increased from 0.19 to 0.24, the degree of reaction of fly ash was also increased. But as the w/b increased to 0.5, the degree of fly ash reaction at the age of 28 days was decreased, particularly for the paste with 55% fly ash. Apparently, a higher w/b ratio does not favor the hydration of cement pastes with high contents of fly ash. A higher w/b ratio dilutes the concentration of Ca^{++} in the pore solution of the pastes, and reduces the contact between the particles. Thus, for FC systems with a high w/b ratio and a high level of cement replacement, the compressive strength and the interfacial bond strength development require a longer period of curing.

The results show that, in cement pastes with high volumes of fly ash, more than 80% of the weight of the fly ash remained unreacted after 90 days of curing. This

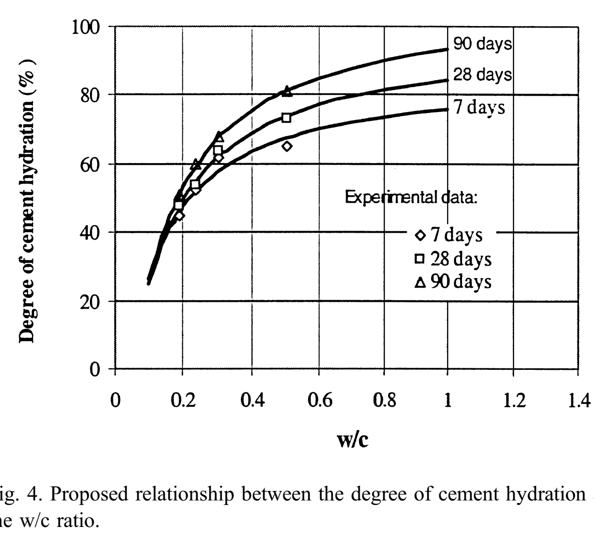


Fig. 4. Proposed relationship between the degree of cement hydration and the w/c ratio.

Table 6
Regression analysis of the degree of hydration of cement in PC pastes

Regression equation	Curing age (days)	Constants		Correlation coefficient, R^2
		a	*b*	
$\alpha_c = ae^{(-b/(w/c))}$	7	85.29	0.1172	0.9326
	28	96.58	0.1345	0.9883
	90	107.37	0.1405	0.999

implies that in the high-volume fly ash systems, the space filling effect is significant.

4. Analysis

4.1. Degree of hydration of cement in FC pastes

In the above section, the degree of hydration of the cement in PC pastes and the fly ash in FC pastes have been determined. The degree of hydration of the cement in FC pastes still remains unknown. The difficulties in determining the degree of cement hydration in FC pastes are due to the fact that the amount of water bound in fly ash reaction products is uncertain, and the pozzolanic fly ash reaction consumes $Ca(OH)_2$, both of which can be used for determining the degree of cement hydration in PC pastes. Nevertheless, from the data presented in the above section, it is known that the degree of hydration of cement strongly depends on the w/c ratio.

An equation describing the relationship between the degree of cement hydration and the w/c ratio can be written as:

$$\alpha_c = ae^{\frac{-b}{w/c}} \tag{9}$$

where α_c is the degree of hydration of cement in weight percent, w/c is the water-to-cement ratio, and *a* and *b* are empirical constants. According this model, the degree of hydration of cement initially increases as the w/c ratio increases, and is finally limited to a constant *a* as the w/c value increases to a large value. This is reasonable and is consistent with the experimental results. By means of statistical techniques, the data obtained in this study can be fitted into Eq. (9). The fitted profiles are shown in Fig. 4. The determined constants *a* and *b*, and the correlation coefficients of the fitting are given in Table 6. From Fig. 4 and Table 6, it can be seen that the experimental data have a good correlation with the model. At low w/c ratios, the curves are steep. A small increase in w/c value corresponds to a large increase in the degree of hydration. Gradually, the curves tend to be flattened. The increase in degree of hydration due to the increase of w/c ratio becomes insignificant. For example, as the w/c ratio is increased from 0.2 to 0.4, the degree of hydration at 28 days is increased by 40%, while if the w/c value is increased from 0.4 to 0.8, the degree of hydration is increased only by 17%. The model predicts that at the age of 90 days, complete hydration (100%) of the cement can be attained with a w/c ratio of about 2.

Attempts have also been made to estimate the degree of hydration of the cement in FC pastes using Eq. (9). As fly ash is partially reactive, the reactive part of fly ash should be taken into account in the effective w/c ratio of the fly ash pastes. The reactivity of fly ash can be quantified by a well-known cementing efficiency factor *k* [22], which depends on several conditions such as w/c ratio, curing age, and the type of ash. Thus, w/c in Eq. (9) was substituted by $w/(c+kf)$, where *c* and *f* are the original fractions of cement and fly ash in a FC blend based on ignited weight, and *k* is the cementing efficiency factor of the fly ash. In this study, data on *k* values are not available, but the degrees of fly ash reaction at different ages have been determined. Using the degree of fly ash reaction α_f to replace the *k* values, the degrees of hydration of the cement in FC pastes are calculated and given in Table 7.

It should be noticed that the estimated degrees of hydration of the cement in FC pastes are only approximations based on the proposed theoretical model that needs to be justified.

4.2. Gel/space ratios of PC and FC pastes

It is well-known that the compressive strength of concrete depends on the gel/space ratio determined from the degree of cement hydration and the w/c ratio [14]. A gel/space ratio is defined as the ratio of the volumes of the hydrated cement to the sum of the volumes of the hydrated

Table 7
Estimated degree of hydration of cement in FC pastes

w/b	Fly ash replacement (%)	$w/(c+\alpha_f f)$			Degree of hydration of cement, α_c (%)		
		7 days	28 days	90 days	7 days	28 days	90 days
0.19	25	0.249	0.242	0.239	53.3	55.4	59.7
0.19	45	0.332	0.318	0.309	60.0	63.3	68.1
0.24	25	0.312	0.304	0.296	58.6	62.1	66.8
0.24	45	0.416	0.393	0.383	64.3	68.6	74.4
0.3	25	0.397	0.387	0.376	63.5	68.3	73.9
0.3	55	0.638	0.583	0.556	71.0	76.7	83.4
0.5	25	0.662	0.648	0.578	71.5	78.5	84.2
0.5	55	1.061	1.009	0.849	76.4	84.5	91.0

cement and of the capillary pores [14]. For PC pastes, assuming that 1 ml of hydrated cement occupies 2.06 ml, the gel/space ratio is given by [14]:

$$x_{pc} = \frac{2.06 v_c \alpha_c}{v_c \alpha_c + \frac{w}{c}} \quad (10)$$

where x_{pc} is the gel/space ratio of the PC paste, v_c is the specific volume of anhydrous cement, α is the degree of hydration of cement, and w/c is the original water-to-cement ratio. In this study, the cement used had the density of 3.15, corresponding to $v_c = 1/3.15 = 0.317$.

For cement pastes containing fly ashes, volume stoichiometry for pozzolanic reaction is not well-established because the relevant data for FC systems are too scanty and too uncertain [23]. In contrast, the reaction between silica fume and $Ca(OH)_2$ in hydrated PC pastes is clearer. Wu and Young [24] suggested that silica fume could be used to model the interaction of fly ash or other reactive pozzolanic, with C_3S in PC. Young and Hansen [25] proposed that pozzolanic reactions could be represented by Eq. (11):

$$S + 1.5CH + 2.5H = C_{1.5}SH_{3.8} \quad (11)$$

where $S = SiO_2$, $CH = Ca(OH)_2$, and $H = H_2O$. Based on this relationship, they found that each volume unit of silica is capable of reacting with 2.08 volume units of $Ca(OH)_2$ to produce 4.6 volume units of pozzolanic CSH. This model has been used by Bentz and Garboczi [26] in digital simulation studies of mineral admixtures. With regard to the problems in the present study, as the volume of $Ca(OH)_2$ has been taken into account in calculating the volume of cement hydration products, 1 ml of reacted fly ash is therefore considered to occupy 2.52 (4.6−2.08) ml of space. Thus, Eq. (10) is modified to:

$$x_{fc} = \frac{2.06 v_c \alpha_c c + 2.5 v_f \alpha_f f}{v_c \alpha_c c + v_f \alpha_f f + w} \quad (12)$$

where x_{fc} is the gel/space ratio of FC pastes; v_c and v_f are the specific volumes, and α_f and α_f are the degrees of reaction of cement and fly ash, respectively; *c* and *f* are the original fractions of cement and fly ash in the FC blend on an ignited basis; and *w* is the weight of water mixed with per gram of ignited FC blend. In this study, the fly ash used had a density of 2.31, corresponding to $v_f = 1/2.31 = 0.433$.

It should be noted that the volume change of SiO_2 in a pozzolanic reaction is based on the CSH produced from the reaction having a molar ratio of C/S = 1.5. This is consistent with the work of Rodger and Groves [27]. In fact, lower Ca/Si ratios have been observed [24]. As the volume of $Ca(OH)_2$ is not included in the factor of 2.52 in Eq. (12), a lower Ca/Si ratio may only have a small effect on the calculation. On the other hand, it is also noted that the volume change of SiO_2 is larger than the anhydrous cement (2.52 vs. 2.06). This may be partially due to the lower density of the pozzolanic hydration products, and may indicate that pozzolanic reaction products are more effective in filling pores [28].

The gel/space ratios of PC pastes were calculated based on the data of degrees of cement hydration, obtained from Wn content. The gel/space ratios of the FC pastes were

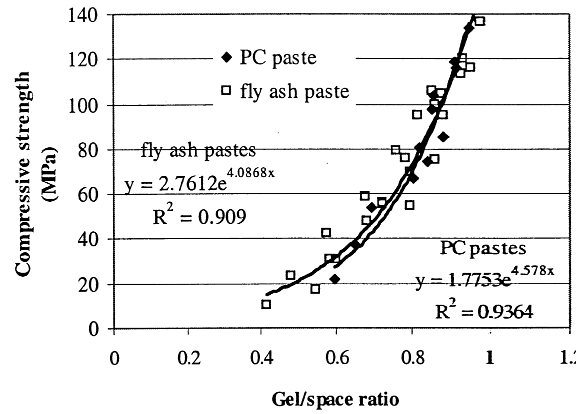


Fig. 5. Relationship between the compressive strength and the gel/space ratio of PC and FC pastes.

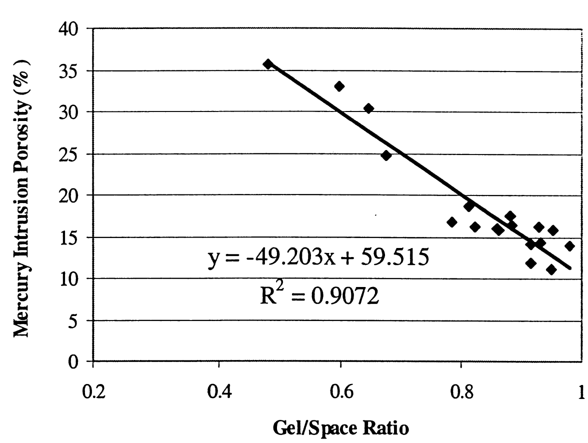
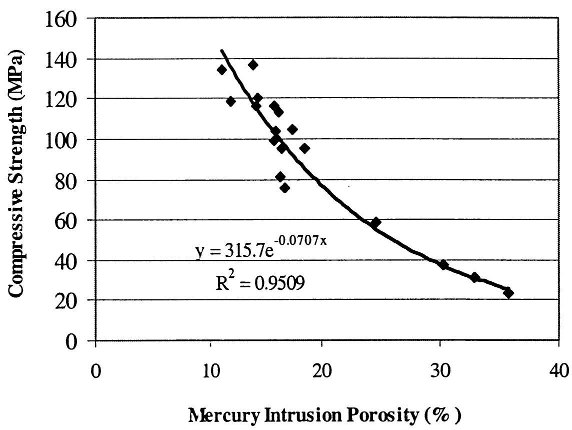


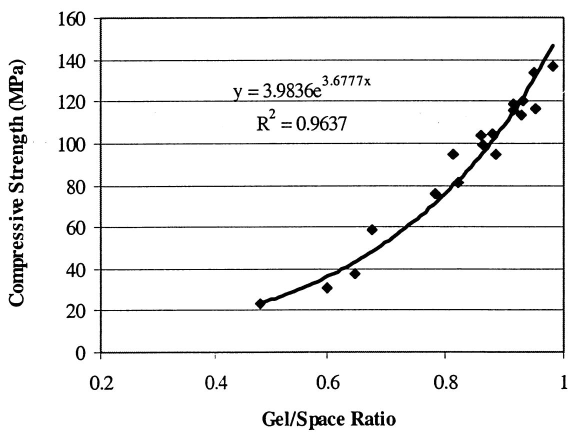
Fig. 6. Correlation between the gel/space ratio and mercury intruded porosity.

Table 8
Calculated gel/space ratios of PC and FC pastes

w/b	Fly ash replacement (%)	Gel/space ratios 7 days	28 days	90 days
0.19	0	0.8839	0.9144	0.9481
0.19	25	0.8643	0.9283	0.9800
0.19	45	0.7993	0.8845	0.9517
0.24	0	0.8445	0.8609	0.9139
0.24	25	0.7982	0.8626	0.9313
0.24	45	0.7236	0.8184	0.8803
0.3	0	0.8074	0.8238	0.8559
0.3	25	0.7214	0.7842	0.8555
0.3	55	0.5820	0.6768	0.7600
0.5	0	0.5975	0.6485	0.6932
0.5	25	0.5456	0.5996	0.6806
0.5	55	0.4157	0.4809	0.5742



(a)



(b)

Fig. 7. Relationship of compressive strength with: (a) mercury intruded porosity and (b) gel/space ratios.

calculated based on the data of the degree of cement hydration, which were estimated by the proposed model. The calculated results are shown in Table 8. It can be seen that at the low w/b ratios, a 45% fly ash replacement did not result in significant decreases in gel/space ratios. This is consistent with the results of Wn content and compressive strength tests.

When plotting the compressive strength data against the data on gel/space ratio, it is found that the trend for FC pastes and that for PC pastes almost coincide (Fig. 5). Mercury intrusion porosity data are available from our previous studies [18,19] for the pastes with the same w/b ratios and the same fly ash replacement levels, at the ages of 28 and 90 days. It is observed that the data of gel/space ratio correlate linearly with the data of porosity (Fig. 6). However, the gel/space ratio data correlate better with compressive strength than with the mercury porosity data (Fig. 7a and b). Thus, the proposed model has been proven to be able to estimate the degree of cement hydration and gel/space ratio in the FC systems.

5. Summary and conclusions

(1) The degree of cement hydration of the plain Portland cement pastes was determined by determining the non-evaporable water content, which was observed to increase with water-to-cement ratios and curing age.

(2) The degree of fly ash reaction in fly ash/cement pastes was determined using a selective dissolution procedure. At 7 days, a small percentage of the fly ash was reacted. At different curing ages, the degree of fly ash reaction depends on the fly ash content and the water-to-binder ratio of the paste. The paste with high volumes of fly ash undergoes a lower degree of fly ash reaction than a paste with less fly ash. At the age of 90 days, more than 80% of the fly ash in the pastes with 45% to 55% fly ash still remained unreacted.

(3) The degree of cement hydration in FC pastes was estimated based on the relation between the degree of cement hydration and effective w/c ratio, which was given by $w/(c+\alpha_f f)$, the weight ratio of water to cement plus reacted fly ash. The hydration of cement in high-volume fly ash pastes was enhanced due to the higher effective w/c ratio. The enhancement effect was significant for the pastes at low w/b ratios. Thus, high-volume fly ash should be prepared at lower w/b ratios.

(4) The gel/space ratio of FC pastes was evaluated based on the degrees of cement hydration and fly ash reaction. The volume stoichiometry of fly ash reaction was simplified using a model of silica fume. The calculated data of gel/space ratio for fly ash pastes are consistent with the data for PC pastes in terms of their relationship with compressive strength. In addition, the determined gel/space ratio in this study correlates linearly with the data on mercury intruded porosity. But when comparing the two parameters (viz. gel/space ratio and mercury intruded porosity), the former correlates better with compressive strength.

Acknowledgments

The authors wish to thank the Hong Kong Polytechnic University for funding support. The authors also wish to thank Mr. S.C. Kou, for carrying out the measurement of $Ca(OH)_2$ content at the Wuhan University of Technology. The assistance of Mr. T. Poon and Mr. W.K. Yu, final year BEng students, in carrying out some of the experimental work is also acknowledged.

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