

An analysis of high-strength concrete made with significant amounts of low-calcium fly ash

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Abstract

The findings of a laboratory investigation on high strength concrete made with significant amounts of low calcium fly ash are presented in this publication. Compressive strength, heat of hydration, chloride diffusivity, degree of hydration, and pore architectures of fly ash/cement concrete and matching pastes were among the metrics examined. The experimental findings demonstrated that concrete with a water-to-binder (w/b) ratio of 0.24 and a fly ash content of 45% could be produced with a 28-day compressive strength of 80 MPa. When compared to plain cement concrete or concrete made with less fly ash, this concrete has a lower strength. The test findings demonstrated that the fly ash contributed more to strength at lower w/b ratios than it did in mixes made at higher w/b ratios. The study measured the cement and fly ash reaction rates in the cementitious materials. The outcomes showed that fly ash has two functions in concrete: (i) it serves as a pozzolana and (ii) it acts as a microaggregate. Also, it was discovered that fly ash's strength contribution to concrete was superior to that of equal cement/fly ash pastes, indicating that the fly ash had strengthened the interfacial bond between the paste and the concrete's particles. The outcomes of the mercury intrusion porosimetry (MIP) test likewise showed this improvement

Keywords: Fly ash; Concrete; Compressive strength; Hydration; Pore size distribution

1. Introduction

In both regular and high strength concrete, low calcium fly ash (ASTM Class F) has been utilised in place of cement on a large scale [1,2]. While the replacement level in high strength concrete is often just 15 to 25% [2], it can be as high as 50% in average strength concrete [3,4]. Reduced heat generation and improved durability qualities are the major goals of employing fly ash in high strength concrete. A 20% fly ash percentage, however, would not be enough to control the excessive heat of hydration in concrete mixes made at low water-to-binder (w/b) ratios.

A laboratory study at the Hong Kong Polytechnic University [5] examined the rise in temperature brought on by the hydration of huge concrete blocks (1000 x 1000 x 1000 mm). It was found that for 50 MPa concrete, a 25% fly ash replacement

reduced the maximum temperature of the concrete by 6°C, whereas for 100 MPa concrete, a 20% fly ash replacement did not result in a lower temperature rise. This seems to suggest that a normal amount of fly ash does not significantly reduce the temperature rise caused by cement hydration in concrete at a lower w/b ratio.

In the past, mass concrete, such as roller compacted dams and highway base courses [3], that contained large amounts of low-calcium fly ash was mostly employed in applications where great strength and high levels of workability were not necessary. The Canada Centre for Mineral and Energy Technologies (CANMET) created high volume fly ash concrete for structural usage in 1985 [4,5]. The percentage of fly ash in the cementitious elements of this type of concrete ranges from 50 to 60 percent. To achieve a high level of workability, superplasticizers (high-range water reduction admixtures) are utilised. Successful uses of this type of concrete include piles and columns with compressive strength requirements of 45 MPa at 28 days and 50 MPa at 120 days, respectively [3].

It is known that fly ashes generally have negative effects on the concrete strength, particularly at early ages [6]. Using large quantities of this material in concrete seem to be in contradiction to the original aims of preparing high strength concrete. However, as observed by many researchers [7 - 9], fly ash concrete may have better strength performance when they are prepared at lower w/b ratios. Lam et al. [9] demonstrated that at a w/b = 0.5, a 45% fly ash replacement resulted in about 30% reduction in 28-day compressive strength, but at a w/b = 0.3, the strength reduction was reduced to 17%. Also, the advances of concrete admixture technology allow concrete mixtures to be prepared with lower w/b ratios. It is therefore believed that high strength concrete can be obtained with large volumes of fly ash.

The present study was based on our previous studies on fly ash concrete with a w/b ratio of >0.3 [9,10], and aimed to produce high strength concrete with a high fly ash content. The concrete mixtures were prepared at the w/b ratios of 0.24 and 0.19. Low-calcium fly ash was used in the proportions of 0%, 25%, and 45% of the total mass of cementitious materials. The parameters studied included compressive strength, heat of hydration, chloride diffusivity, degree of hydration, and pore structures of fly ash/cement concrete and the corresponding pastes.

2. Experimental program

Materials

The cement used was a commercially available Portland cement equivalent to ASTM Type I. The fly ash used was a commercially available low calcium fly ash equivalent to ASTM Class F. The aggregates used were a 10-mm nominal maximum size crushed granite and natural river sand. A naphthalene-based superplasticizer was used to give a proper workability for the concrete mixtures. The solid content of the superplasticizer was 38.5%. The properties of the cement and the fly ash are

Table 1
 Properties of cement and fly ash

Properties	Cement	Fly ash
SiO ₂ (%)	21.0	56.8
Fe ₂ O ₃ (%)	3.4	5.3
Al ₂ O ₃ (%)	5.9	28.2
CaO (%)	64.7	<3
MgO (%)	0.9	5.2
SO ₃ (%)	2.6	0.7
Alkali as Na ₂ O (%)	0.4	0.14
Chloride content (%)	0.004	<0.005
LOI (%)	1.2	3.9
Density	3.15	2.31
Fineness (wet sieve, >45 μm, %)		6.3
Specific surface area (cm ² /g)	3519	3860

Table 2
 Properties of aggregates

Properties	Sand		10 mm Granite	
	Sieve (mm)	Passing (%)	Sieve (mm)	Passing (%)
Sieve analysis	10	100	14	100
	5	99	10	94
	2.36	96	5	21
	1.18	87	2.36	4
	0.6	70		
	0.3	26		
	0.15	2		
Density	2.63		2.62	

given in Table 1, and the properties of the aggregates are given in Table 2.

Concrete mixtures and cement pastes

Two series of concrete mixtures were prepared, with the w/b ratios of 0.24 and 0.19, respectively. Fly ash was used in the proportions of 0%, 25%, and 45% of the total cementitious materials. The concrete mixtures were proportioned and mixed using a pan mixer of 0.11 m³ in capacity. The superplasticizer was added together with the mixing water. The dosage of the superplasticizer was adjusted to give a slump of 200 to 230 mm for the concrete mixtures. The details of the concrete mixtures are given in Table 3. The concrete specimens prepared included 100-mm standard cubes and 100 mm (diameter) by 200 mm (height) standard cylinders. In parallel, 70.7 mm standard cubes of fly ash/cement pastes, with the same w/b ratios and fly ash replacement level as the concrete mixtures, were also prepared. All the specimens were cast in steel moulds, and were cured in water at 27°C after demoulding after 1 day.

Compression test

The compressive strength of the cube specimens of concrete and paste was tested with a Denison compression machine at the loading rate of 0.2-0.4 N/mm²/s.

Table 3
 Proportioning of concrete mixtures

w/b Ratio	% Fly ash	Constitution (kg/m ³)					Superplasticizer (l/m ³)
		Water ^a	Cement	Fly ash	Sand	Granite	
0.24	0	150	637	0	711	936	18.4
0.24	25	150	475	158	681	924	18.3
0.24	45	148	347	283	639	920	23.7
0.19	0	135	702	0	641	949	35.1
0.19	25	133	512	173	620	932	34.7
0.19	45	130	372	305	608	927	33.8

^a Water in the superplasticizer that has a water content of 61.5% not included.

Determination of heat of hydration of cement and cement/fly ash pastes

The heat of hydration of the pastes with the w/b ratio of 0.24 and the fly ash replacements of 0%, 25%, and 45% were tested using a JAF isothermal conduction calorimeter system. Thirty grams of cement or cement + fly ash and a designed amount of water was hand mixed in a thin plastic bag. The bag was placed in the calorimeter. The rate of heat evolution and the cumulative heat evolution of the cement hydration were then obtained and recorded by a microcomputer.

Determination of chloride diffusivity of concrete

The method used to measure the chloride diffusivity of the concrete was a rapid determination procedure in accordance with ASTM C1202-94 [11]. The test concrete specimens were 100 mm in diameter and 50-mm thick, which were sliced from the prepared concrete cylinders. The chloride diffusivity of the specimens was expressed as an electrical indication: the total charge passed in coulomb during the test period of 6 h.

Determination of degree of hydration

The samples for the degree of hydration test were obtained from the crushed paste cubes after the compression test. To stop the hydration, the samples were immersed in acetone for 7 days. The samples were then placed in a vacuum desiccator overnight to remove the acetone and were dried at 60 °C in an oven for 24 h. The dried samples were ground in a mortar to pass through a 150-µm sieve.

The determination of the degree of hydration of cement was based on the hydration of 1 g of anhydrous cement produces 0.227 g of non-evaporable water [12]. The determination of the degree of reaction of fly ash was based on a selective dissolution procedure using picric acid-methanol solution and water [13,14]. The principle of the procedure is, in a fly ash/cement system, fly ash reacts with calcium hydroxide (CH) 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 [13].

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

$$\text{LOI}(\%) = \frac{\text{weight of the sample before ignition} - \text{weight of sample after ignition}}{\text{weight of sample after ignition}} \times 100 \quad (1)$$

To determine the non-evaporable water content of the plain cement pastes, the samples of the hydrated plain pastes were dried in an oven at 110 °C for 3 h. One gram of the dried sample was then ignited and the non-evaporable water

content of plain cement pastes on the ignited basis was calculated by Eq. (2)

$$\begin{aligned} \text{Non — evaporable water content of cement paste (\%)} \\ = \frac{[(\text{weight of sample dried at } 110^\circ\text{C} \\ - \text{weight of sample ignited at } 950^\circ\text{C}) \\ / \text{weight of sample ignited at } 950^\circ\text{C} \\ - \text{loss on ignition of cement}] \times 100. \end{aligned} \quad (2)$$

The degree of hydration of plain cement pastes was calculated by Eq. (3):

$$\text{Degree of hydration (\%)} = \frac{\text{non-evaporable water}}{0.227} \times 100 \quad (3)$$

The degree of reaction of fly ash was determined by measuring the insoluble residues of the as-received cement and fly ash, and the hydrated fly ash/cement pastes when dissolved in a solution of picric acid-methanol- water. 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. Forty milliliters of distilled water 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. The residue per gram of sample on ignited basis was calculated by Eq. (4):

$$\begin{aligned} \text{Residue of sample (\%)} \\ = \frac{\text{weight of residue} \times (1 + \text{LOI})}{\text{weight of sample}} \times 100 \end{aligned} \quad (4)$$

The percentage of unreacted fly ash on the ignited basis was given by:

$$\begin{aligned} \text{Unreacted fly ash (\%)} \\ = \frac{\text{residue of hydrated fly ash cement paste} \\ - \text{residue of as received cement}}{\text{original fraction of cement}} \times 100 \end{aligned} \quad (5)$$

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

$$\begin{aligned} \text{Degree of reaction of fly ash (\%)} \\ = \frac{(1 - \text{unreacted fly ash}) \times 100}{\text{residue of as received fly ash} \\ / \text{original fraction of fly ash}} \end{aligned} \quad (6)$$

In Eqs. (5) and (6), original fractions of cement + original fraction of fly ash = 1, also on the ignited basis.

Measurement of the pore structure of concrete and paste

The porosity and pore size distribution of the concrete and paste samples were measured using a mercury intrusion

porosimeter (MIP) with a maximum mercury intrusion pressure of 210 MPa. The paste samples for the measurement were obtained from the crushed cubes after the compression test. The concrete samples for MIP measurement were small cylindrical cores of 21 mm in diameter and 20 mm in height, drilled from the concrete cube specimens at mid height. Both the paste and the concrete samples were soaked in acetone to stop the hydration, and were dried at 60°C for 24 h before the measurement. A cylindrical pore geometry and a contact angle θ of 140° were assumed [12,15]. The mercury intruded pore diameter d at a pressure of P was calculated by $d = 4\gamma \cos \theta / P$, where $\gamma = 0.483 \text{ Mm}^{-1}$, the surface tension of mercury [12].

3. Experimental results

Compressive strength of concrete

The compression test of the concrete mixtures was performed on the 100-mm cubes at the ages of 3, 7, 28, and 90 days. The results are given in Table 4.

At the w/b of 0.24, the mix with 25% fly ash showed slightly lower compressive strength at the ages of 3 and 7 days, but higher compressive strength at the ages of 28 and 90 days, when compared with the reference mix without fly ash. The mix with 45% fly ash showed a 28-day compressive strength of 89.4 MPa, which was 8% lower than that of the reference mix. The negative effect of using fly ash on concrete strength appeared to be insignificant. However, lowering the w/b ratio to 0.19 did not further improve the concrete strength.

Compressive strength of pastes

The compression test of the pastes was performed on the 70.7-mm cubes at the ages of 7, 28, and 90 days. The results are shown in Table 5.

A comparison between the strength developments of the fly ash concrete and the corresponding pastes seems to indicate that the strength contribution of fly ash in concrete was better than in the pastes at the ages after 28 days. In Fig. 1, the strength values are expressed as the relative percentage values to the strength of the paste and concrete

Table 4
 Compressive strength of the concrete mixes

w/b Ratio	% Fly ash	Compressive strength (MPa)			
		3 Days	7 Days	28 Days	90 Days
0.24	0	70.0	79.5	97.4	110.2
0.24	25	62.3	74.6	105.9	124.5
0.24	45	42.5	56.3	89.4	107.2
0.19	0	78.0	83.5	96.8	114.5
0.19	25	66.8	74.2	102.3	123.6
0.19	45	41.7	56.4	88.5	109.2

Table 5
 Compressive strength of the pastes

w/b Ratio	% Fly ash	Compressive strength (MPa)		
		7 Days	28 Days	90 Days
0.24	0	74.7	103.7	119
0.24	25	69.5	99.5	120.2
0.24	45	56.0	95.0	104.5
0.19	0	85.7	116.0	133.9
0.19	25	74.9	113.3	136.9
0.19	45	54.7	99.0	116.1

without fly ash (the reference mixes). At a w/b of 0.24, the fly ash concrete showed almost the same initial relative strength values as the pastes with the same fly ash replacements. At the age of 28 days, the concrete with 25% fly ash replacement showed higher relative strength value than the corresponding paste. At the age of 90 days, both the concrete with 25% and 45% fly ash replacements showed higher relative strength values than the corresponding pastes. Similar results were also observed for the pastes and concrete at the w/b of 0.19.

It should be noted that lowering the w/b ratio from 0.24 to 0.19 resulted in an average 10% compressive

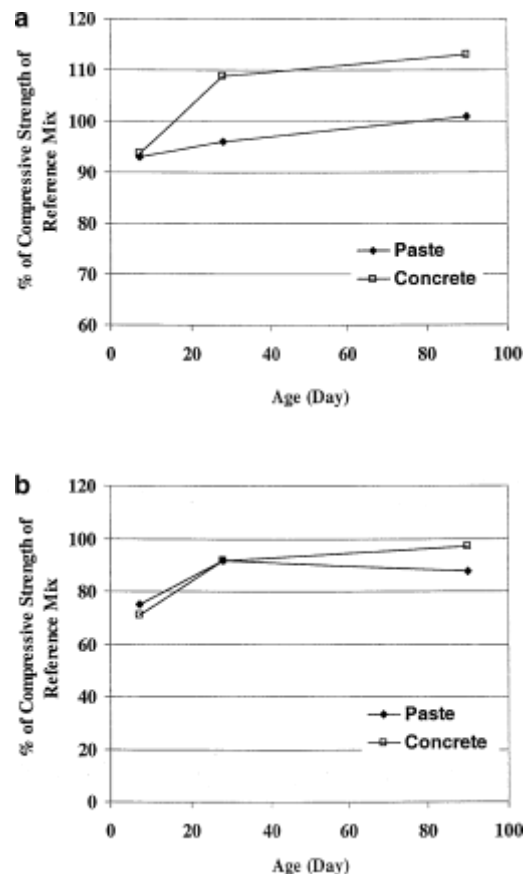


Fig. 1. Strength performance of fly ash pastes and concrete at w/b = 0.24: (a) 25% fly ash and (b) 45% fly ash.

Table 6
 Heat of hydration of the pastes at w/b of 0.24

w/b Ratio	% Fly ash	Maximum rate of heat evolution (W/kg)	Time of reaching the maximum rate (h)	Cumulative heat evolution during the first 72 h (kJ/kg)
0.24	0	2.40	10.9	211.7
0.24	25	1.84	11.5	178.7
0.24	45	1.27	12.5	134.9

strength increase for the fly ash/cement pastes (Table 5), although it did not increase the strength of the corresponding concrete (Table 4).

Heat of hydration of pastes

The heat evolution profiles of the pastes at the w/b of 0.24 were measured. The results are shown in Table 6 and Fig. 2. As the percentage of PFA replacement increased, both the maximum rate of heat evolution and the cumulative heat evolution during the first 72 h decreased. The time of reaching the maximum rate of heat evolution was delayed.

It can be noted that the reduction in heat evolution was smaller than the reduction in cement content due to the fly ash replacement. A 25% fly ash replacement resulted in only 16% reduction in the cumulative heat evolution, and a 45% fly ash replacement resulted in 36% reduction in the cumulative heat evolution. This might be due to the higher

effective water-to-cement (w/c) ratio for cement hydration when part of the cement was replaced by fly ash. Fly ash might also contribute to the heat evolution even at the initial curing age. Thus, fly ash replacement at the level of 20% may not be sufficient to suppress the temperature rise of high strength concrete in some cases.

Chloride diffusivity

The chloride diffusion test was carried out at the ages of 28 days and 90 days. The results are expressed as the total charge in coulomb passed through the concrete specimen during the test period of 6 h, and are given in Table 7.

The samples with fly ash replacement showed a significant reduction in the total charge passed. At the w/b of 0.24, a 45% fly ash replacement resulted in, respectively, 62% and 84% reductions in the coulomb passed at the ages of 28 and 90 days. These results are consistent with the results of Poon et al. [10] for concrete mixes at higher w/b ratios.

However, lowering the w/b ratio did not further reduce the chloride diffusivity of the fly ash concrete mixes. The total charge passed through the fly ash concrete mixes at the w/b of 0.19 were almost the same as those at the w/b of 0.24. In contrast, about 34% reduction was recorded for the plain concrete when the w/b ratio was reduced from 0.24 to 0.19.

Degree of cement hydration and pozzolanic reaction

The non-evaporable water content and the degree of hydration of the plain cement pastes are shown in Table 8. The results show low degree of hydration of the cement paste at low w/c ratios. At the age of 7 days, about 50% of the cement hydrated and the degree of hydration only increased a few percent from 7 to 90 days.

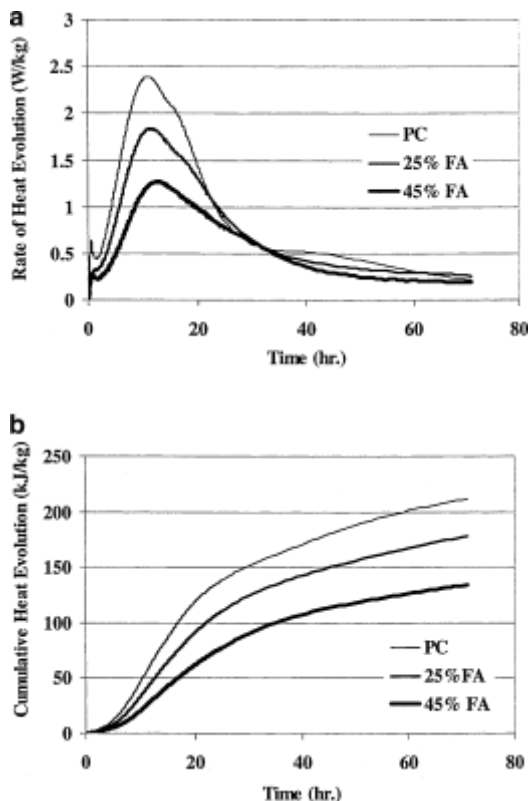


Fig. 2. Heat of hydration of the pastes at a w/b of 0.24: (a) rate of heat evolution and (b) cumulative heat evolution.

Table 7
 Results of chloride diffusion test

w/b Ratio	% Fly ash	Total charge passed (C)	
		28 Days	90 Days
0.24	0	1892	1133
0.24	25	810	181
0.24	45	718	160
0.19	0	1260	750
0.19	25	882	199
0.19	45	768	175

Table 8
 Non-evaporable water content and degree of hydration of plain cement pastes

w/b Ratio	% Fly ash	Non-evaporable water (%)			Degree of hydration (%)		
		7 Days	28 Days	90 Days	7 Days	28 Days	90 Days
0.24	0	12.0	12.4	13.8	52.8	54.6	60.6
0.19	0	10.3	11.0	11.7	45.5	48.3	51.6

The results of the degree of pozzolanic reaction of the fly ash in the fly ash/cement pastes at different ages are shown in Table 9. At the age of 7 days, the degree of reaction of fly ash in the pastes was about 5%. At the age of 90 days, the degree of reaction of the fly ash ranged from 14.8% to 22.6%, depending on the fly ash content and the w/b ratio of the paste. For a given age, the degree of reaction of the fly ash in the pastes with a lower w/b ratio or a higher fly ash content was lower than in the pastes with a relatively higher w/b ratio or a lower fly ash content.

Porosity and pore size distribution of concrete and pastes

The MIP test was carried out at the ages of 28 and 90 days for both the paste and concrete samples. The results are summarised in Table 10 and Table 11. The pore size distribution of the concrete mixes at the w/b of 0.24 is shown in Fig. 3.

For fly ash/cement pastes, as the fly ash content increased, the average pore diameters decreased, but the measured porosity increased. Lowering the w/b ratio resulted in lower porosity for both the plain cement paste and the fly ash/cement pastes. For the concrete samples, the fly ash replacements also reduced the average pore diameters, but did not increase the porosity as the case in the pastes. At the w/b of 0.19, the fly ash replacements resulted in higher concrete porosity when compared with the case of w/b = 0.24.

4. Discussion

Properties of high strength concrete with high fly ash content

The results of the present study have shown that with a fly ash content of 45%, concrete with a 28-day compressive strength of 80 MPa could be obtained at the w/b of 0.24. As mentioned earlier in this paper, fly ash concrete at lower w/b ratios had better strength performance. When compared to our previous results [9], it can be seen that the fly ash concrete at lower w/b ratios yielded higher relative (i.e., to the plain cement concrete) 28-day compressive strength (Fig. 4).

A plot of concrete chloride diffusivity against concrete strength is given in Fig. 5 for different levels of fly ash replacement (some of the data were extracted from our previous work [10]). The data show that the high strength concrete prepared with a high fly ash content had lower chloride diffusivity than the equivalent plain cement concrete or the concrete with lower fly ash contents. The isothermal conduction calorimetry results also demonstrated that the high strength concrete with a high fly ash content is effective in suppressing excessive heat evolution in fresh concrete.

However, it was noted that a higher dosage of superplasticizer was required for the mix with 45% fly ash (see Table 3). This was due to the higher volume fraction of fine particles in the mix. When part of cement was replaced by the same mass of fly ash, the total volume of the cementitious materials increased because of the lower density of the fly ash. This made it difficult to prepare a workable concrete mixture. Adding excessive amount of superplasticizer may cause strong segregation of different materials and result in poorer concrete. Thus, the advantages of further lowering w/b ratio are limited. In this present investigation, large quantities of superplasticizer had been used for preparing the concrete mixtures at the w/b of 0.19. Although a lower w/b ratio at 0.19 resulted in lower porosity and higher compressive strength for the pastes, it did not reduce the concrete porosity, and did not further improve the concrete strength and durability properties.

Table 9
 Degree of reaction of fly ash in fly ash cement pastes

w/b Ratio	% Fly ash	Degree of reaction of fly ash (%)		
		7 Days	28 Days	90 Days
0.24	25	5.7	13.9	22.6
0.24	45	5.3	12.8	16.5
0.19	25	5.1	13.7	17.5
0.19	45	4.9	10.8	14.8

Table 10
 Average pore diameter of pastes and concrete

w/b Ratio	% Fly ash	Average pore diameter of paste (µm)		Average pore diameter of concrete (µm)	
		28 Days	90 Days	28 Days	90 Days
0.24	0	0.0410	0.0484	0.0359	0.0314
0.24	25	0.0264	0.0278	0.0248	0.0187
0.24	45	0.0206	0.0192	0.0185	0.0160
0.19	0	0.0371	0.0386	0.0325	0.0444
0.19	25	0.0251	0.0241	0.0232	0.0217
0.19	45	0.0169	0.0164	0.0180	0.0172

Table 11
 Porosity of pastes and concrete

w/b Ratio	% Fly ash	Porosity of paste (%)		Porosity of concrete (%)	
		28 Days	90 Days	28 Days	90 Days
0.24	0	16.01	11.91	7.72	6.86
0.24	25	15.89	14.31	6.27	5.37
0.24	45	18.59	17.50	7.09	5.66
0.19	0	14.2	11.17	7.95	6.96
0.19	25	16.19	13.99	8.35	7.63
0.19	45	16.47	15.87	7.23	7.69

Different effects of fly ash in concrete and in cement pastes

It is interesting to note that the beneficial effects of fly ash in cement pastes and in concrete are different. This can be noticed from both the results of MIP and the results of the strength test. Replacing cement by fly ash increased the porosities of the pastes, but the porosities of the concrete were reduced. These observations are consistent with our previous results comparing the effects of fly ash on plain cement and cement mortars [10]. Also, the strength enhancement effect of fly ash in concrete was better than in the

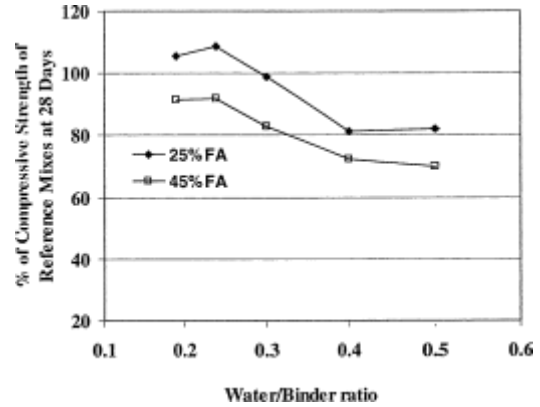


Fig. 4. Strength performance of fly ash concrete with different w/b ratios.

corresponding pastes (Fig. 1). Both results indicate an improvement effect on the interfacial zone between the cement matrix and the aggregate when fly ash is added to the concrete [16].

Degree of hydration in fly ash/cement systems at low w/b ratios

A number of papers have been published on the microstructure development and hydration mechanism of high volume fly ash/cement system [17 - 19]. In general, like other mineral admixtures, fly ash contributes to concrete properties by both the filler effect and the pozzolanic effect [19]. However, the relative importance of these effects has not been quantitatively identified. The results presented here on the degree of cement hydration and pozzolanic reaction may lead to a better understanding of the strengthening mechanism of fly ash concrete.

The results show that at 7 days, a measurable amount of pozzolanic reaction in the fly ash/cement system 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 [19,20]. According to Berry

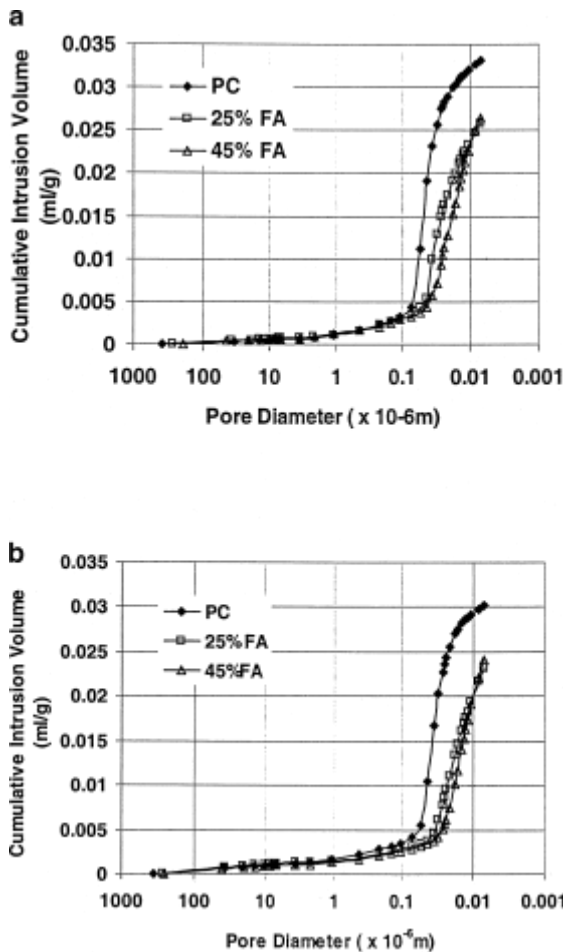


Fig. 3. Pore size distribution of the concrete mixes at w/b = 0.24: (a) 28 days and (b) 90 days.

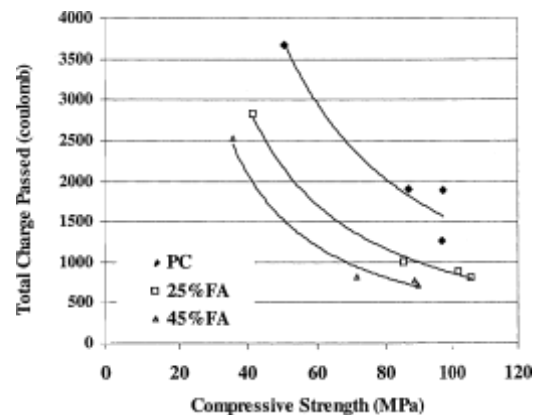


Fig. 5. Effect of fly ash on chloride diffusivity of concrete with equivalent compressive strength.

et al. [19,20], even at the ages as early as 7 days, fly ash particles are involved in chemical reactions forming ettringite (AF_t). At this stage, the physical effect of space filling and the formation of AF_t are important factors in strength development [19].

At 28 days of curing, the degree of fly ash reaction increased to more than 10%. At this age, according to Xu and Sarkar [18], hydration products are well established. CH on the fly ash particles undergoes re-dissolution and reacts with the fly ash and a considerable amount of the fly ash particles have been reacted. As can be seen from the results of strength test in this paper, the increased degree of fly ash reaction minimised the strength differences between the fly ash/cement pastes/concrete and the reference plain cement pastes/concrete. Some fly ash concrete had higher strength than the reference plain cement concrete (Table 4), although at this age, there are still more than 80% fly ash playing the role of space filler or micro-aggregates.

At the age of 90 days, the fly ash pastes had a degree of fly ash reaction between 14.8% and 22.6%. It is generally accepted that the pozzolanic reaction in the fly ash/cement systems becomes dominant at the ages after 28 days [16,19,20]. The reaction between the fly ash and the CH forms gel-like calcium silicate hydrates (C-S-H) which have lower calcium-to-silicate ratios (C/S) [18]. The reacted fly ash resulted in an average 20% increase in compressive strength, and a 77% drop in total coulomb passed for fly ash concrete during the period from 28 to 90 days (Tables 4 and 7). In comparison, the plain cement concrete showed an increase of about 16% in compressive strength and a decrease of 40% in total coulomb passed.

The results also show that in the pastes with lower w/b ratios, the cement or the fly ash underwent a lower degree of hydration/reaction. This is because there is less water available for the reaction and less space for the reaction products to form. It is interesting to note that in the plain cement pastes at the w/b of 0.24 or 0.19, only 50-60% of the cement were reacted at 90 days. This implies that about 40% to 50% of the cement play the role as micro-aggregates like most of the fly ash particles in the fly ash/cement system. Thus, it is not difficult to understand that at lower w/b ratios, the difference in strength between the plain cement concrete and the fly ash concrete is small.

5. Conclusions

(1) High strength concrete with a 28-day compressive strength of 80 MPa could be obtained with a w/b ratio of 0.24, and with a fly ash content of 45%. Such a concrete has a lower heat of hydration and chloride diffusivity when compared to the equivalent plain cement concrete.

(2) In concrete mixes prepared at lower w/b ratios, the contribution to strength by fly ash was better than in the

mixes prepared with higher w/b ratios. Also, the strength contribution of fly ash in concrete was better than in the equivalent fly ash/cement pastes.

(3) In plain cement pastes at the w/c ratios of 0.19 and 0.24, about 50% of the cement hydrated at the age of 7 days. From 7 to 90 days, the increase in the degree of hydration was not significant.

(4) In fly ash/cement pastes at the w/b ratios of 0.19 and 0.24, about 5% of the fly ash reacted at the age of 7 days. From 7 to 90 days, the degree of reaction of the fly ash ranged from about 15% to 23%, depending on the w/b ratios and the percentages of fly ash replacement. Fly ash in the pastes at lower w/b ratios and with higher fly ash replacement levels had lower degree of reaction.

(5) In the plain cement pastes and the fly ash/cement pastes prepared at the w/b ratios of 0.19 and 0.24, about 40% of the cement and 80% of the fly ash remained unreacted at the age of 90 days. These unreacted cement and fly ash particles served as micro-aggregates, which also contributed to the strength of the cementitious material.

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