

# Quantitative evaluation of mineral admixtures on the properties, pore structure, and durability of cement-based composites

Chinlai Lee<sup>1</sup>, Maochieh Chi<sup>2,\*</sup> and Ran Huang<sup>3</sup>

<sup>1</sup>Institute of Materials Engineering, National Taiwan Ocean University, Keelung 200, Taiwan, ROC

<sup>2</sup>Department of Fire Science, WuFeng University, Chiayi County 621, Taiwan, ROC, e-mail: jackchi@wfu.edu.tw; jackchi1023@gmail.com

<sup>3</sup>Department of Harbor and River Engineering, National Taiwan Ocean University, Keelung 200, Taiwan, ROC

\*Corresponding author

## Abstract

The influence of water/cementitious material ratio, silica fume, and fly ash as partial Portland cement replacement materials on the properties, pore structure, and durability of cement-based composites was evaluated by conducting compressive strength test, mercury intrusion porosimetry test, water absorption, rapid chloride penetration test, and scanning electron microscopy (SEM). Water/cementitious material ratio, and replacement percentage of silica fume and fly ash have significant effects on the pore structure and durability of cement-based composites. Composites with silica fume or fly ash have a denser structure than the control composite on SEM micrographs. Silica fume has about 5–10 times as much effect as fly ash, according to results of multiple linear regression analyses of testing data.

**Keywords:** fly ash; mercury intrusion porosimetry; multiple regression analysis; SEM; silica fume.

## 1. Introduction

In the past decades, concrete manufacturers have accepted several industrial by-products such as silica fume, ground grain blast-furnace slag, and fly ash as mineral admixture or supplementary cementitious materials in their products [1]. Reduction of Portland cement quantity in traditional concrete has been an interesting and important topic motivated by environmental, economic, and technical requirements. The application percentage of fly ash ranges from 20% (low volume fly ash) to >50% (high volume fly ash) of the total cementitious materials [2], and the application percentage of silica fume is around 10%. Nowadays, high-volume fly ash concrete has been developed for sustainable or green concrete and is becoming popular [3, 4]. However, lower early-age strength was found in high-volume fly ash concrete and deforming schedule would be adjusted in construction projects [5]. The two applications

of fly ash for concrete production have been clarified as being a microfiller (microaggregate) and a supplementary cementitious material (pozzolana) [6]. By increasing the interface strength and densifying the microstructure, silica fume has been verified to be effective in improving both the mechanical characteristics and durability of cementitious composites [7–10]. Normal composites with small amounts of silica fume would not reduce their early-age strength in comparison with high-fly-ash concrete [11–13]. Generally, the combination of fly ash and silica fume in concrete would have a positive effect on strength and durability [14, 15]. However, most studies have placed emphasis on qualitative discussions based on experimental evidence. There is little research work on the comparative performance of different pozzolanic concretes by qualitative discussion and quantitative analysis at the same time.

To quantify the effect of each parameter, such as water/cementitious ratio (w/c), fly ash content, and silica fume content, on the properties and durability of concrete, the traditional approach used in modeling properties of concrete is regression analysis using experimental data to determine unknown coefficients in the equations. Several mathematical models have been suggested to describe the relation between the components and behavior of materials. Bhanjaa and Sengupta [16] investigated the compressive strength of silica fume concrete using statistical methods to predict the 28-day compressive strength of silica fume concrete with w/c ratios and silica fume replacement percentages. Bouzoubaa and Fournier [17] determined the optimization of the fly ash content in non-air-entrained and non-superplasticized concrete using a statistical program to analyze the test results. Tanyildizi [18] investigated the effect of polypropylene fiber and silica fume on the mechanical properties of lightweight concrete exposed to high temperatures experimentally and statistically. Several studies related to mortar or concrete were performed using statistical methods. However, no quantitative results were demonstrated on the difference of fly ash and silica fume contents on the properties and durability of concrete. This study included comprehensive experimental work and statistical analysis to consider the effect and quantitative evaluation of the w/c ratio, fly ash content, and silica fume content on the properties, pore structure, and durability of cement-based composites.

## 2. Experimental

### 2.1. Materials

The cement used was type I ordinary Portland cement (OPC) conforming to American Society for Testing and Materials

(ASTM) standard C150-05. Silica fume and typical class F fly ash were used for partial cement replacement (by weight). The physical properties and chemical compositions of cement, silica fume, and fly ash are listed in Tables 1, 2. River sand was used and the specific gravity, water absorption, and the fineness modulus of fine aggregates are 2.58, 1.9%, and 2.93, respectively. A type G superplasticizer with a specific gravity of  $1.06 \pm 0.02$  and a water-reducing rate of 15% was used.

## 2.2. Mixture and specimen preparation

Mixture design is given in Table 3. Silica fume (5 wt.%, 10 wt.%) and fly ash (15 wt.%, 25 wt.%) were used at various combinations. The w/c ratios were 0.45 and 0.65 and the sand/binder ratio was 2.75. The cubic specimens were cast and kept in steel molds for 24 h, and then the specimens were demolded and moved into a curing room until testing.

## 2.3. Methods

Compressive strength tests of the specimens were conducted according to ASTM C109-08. For each mixture, three  $50 \times 50 \times 50$  mm cubic specimens were prepared and tested for each mixture at the age of 7, 28, 56, and 91 days, respectively. Mercury intrusion porosimetry test in accordance with ASTM D 4404-84 was conducted by injecting mercury into the dried specimens. Specimens aged 91 days were dried in an oven at  $105^\circ\text{C}$  for 24 h before testing. Progressive pressure increment was applied to mercury, and the intrusion of mercury at each increment was monitored. The corresponding intruded volume was used to compute pore size distribution and the Washburn equation used to calculate the diameter of cylindrical pores is given as Eq. (1) [12, 19]:

$$d = \frac{-\Phi\gamma\cos\theta}{p} \quad (1)$$

where  $d$  is the diameter of the cylindrical pore,  $\Phi$  is the factor of pore shape,  $\gamma$  is the surface tension of mercury,  $\theta$  is the contact angle of mercury, and  $p$  is the applied pressure. In this study, the contact angle selected was  $130^\circ$ , the surface tension of mercury was assumed to be 0.485 N/m, the measuring pressure ranged from 0.7 to 210 MPa, and the measurable pore size ranged from 0.003 to 360  $\mu\text{m}$ . The rapid chloride penetration test was performed on specimens at the age of 91 days according to ASTM C1202-05. The chloride ions are transported in concrete under an applied voltage. As the chloride flux becomes constant, the governing equation that describes transport processes in solution is the Nernst-Planck equation. Under the influence of an electrical field across the

**Table 2** Chemical compositions of cement, silica fume, and fly ash.

Chemical compositions (%)	Cement	Silica fume	Fly ash
Calcium oxide, CaO	63.87	0.4	2.4
Silicon dioxide, SiO <sub>2</sub>	20.89	91.5	57.2
Aluminum oxide, Al <sub>2</sub> O <sub>3</sub>	5.61	0.2	20.8
Ferric oxide, Fe <sub>2</sub> O <sub>3</sub>	3.13	0.7	8.1
Sulfur trioxide, SO <sub>3</sub>	2.2	0.5	0.4
Sodium oxide, Na <sub>2</sub> O	0.12	0.6	–
Potassium oxide, K <sub>2</sub> O	0.68	1.3	0.8
Magnesium oxide, MgO	2.93	1.5	2.2
Loss on ignition, L.O.I.	0.73	1.5	2.1
Others	1.4	1.8	0.55

specimen, only the migration is of paramount importance in the electrochemical desalination process, and then the diffusion coefficient of chloride ions,  $D_{\text{Cl}}$  ( $\text{m}^2/\text{s}$ ), is calculated as Eq. (2) [20]

$$D_{\text{Cl}} = \frac{J_{\text{Cl}}RTl}{zFC\Delta E} \quad (2)$$

where  $J_{\text{Cl}}$  is constant flux of chloride in the downstream cell ( $\text{mol}/\text{m}^2 \text{ s}$ ),  $R$  the universal gas constant (8.3 J/mol K),  $T$  the absolute temperature (K),  $l$  the width of specimen,  $z$  the electrical charge of chloride,  $F$  the Faraday constant (96,500 C/mol),  $C$  the concentration of chloride ion ( $\text{mol}/\text{l}$ ), and  $\Delta E$  the strength of the electric field between the anode and cathode (V/m). Water absorption was obtained in accordance with ASTM C642-06. Scanning electron microscopy (SEM) was performed using a HITACHI S-4800 microscope equipped with an energy dispersive spectroscope. Specimens with a dimension of  $10 \times 10 \times 3$  mm were obtained from 10 mm cubes at the age of 91 days. Representative samples were air-dried first, followed by resin impregnation. The impregnated specimens were ground and softly polished with sand paper down to 0.25  $\mu\text{m}$ .

In statistics, regression analysis is a method for investigation of the relation between a dependent variable and one or more independent variables. It is also used to infer causal relations between variables in restricted circumstances and to explore the forms of these relations. In linear regression, the model specification is that the dependent variable  $Y_i$  is a linear combination of the parameters (but need not be linear in the independent variables). Multiple linear regression attempts to model the relation between two or more explanatory variables and a response variable by fitting a linear equation to observed data. Every value of the independent variable  $X$  is associated with a value of the dependent variable  $Y$ . If two variables are correlated, then knowing the score on one variable will allow you to predict the score on the other variable. Multiple linear regression is simply an extension of this principle that allows us to predict one variable on the basis of several other variables. In this study, three independent variables were used to estimate their influence on the properties, pore structure, and durability of cement-based composites.

**Table 1** Physical properties of OPC, silica fume, and fly ash.

Physical properties	OPC	Silica fume	Fly ash
Specific gravity	3.16	2.2	2.06
Specific surface area ( $\text{m}^2/\text{g}$ )	0.352	22.5	0.405

**Table 3** Mixture proportions of silica fume and fly ash composites.

Mixture no	w/c	Water (kg/m <sup>3</sup> )	Cement (kg/m <sup>3</sup> )	Silica fume (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Fine aggregate (kg/m <sup>3</sup> )	SP (kg/m <sup>3</sup> )
A	0.45	245.8	555.7	–	–	1485.0	2.2
AS5	0.45	244.5	527.9	27.8	–	1485.0	3.5
AS10	0.45	243.8	500.1	55.6	–	1485.0	4.2
AF15	0.45	243.0	472.3	–	83.4	1485.0	5.0
AF25	0.45	242.4	416.8	–	138.9	1485.0	5.6
AS5F10	0.45	241.6	472.3	27.8	55.6	1485.0	6.4
AS5F20	0.45	240.5	416.8	27.8	111.1	1485.0	7.5
B	0.65	320.9	490.9	–	–	1350.0	–
BS5	0.65	320.9	466.4	24.5	–	1350.0	–
BS10	0.65	320.9	441.8	49.1	–	1350.0	–
BF15	0.65	320.9	417.3	–	73.6	1350.0	–
BF25	0.65	320.9	368.2	–	122.7	1350.0	–
BS5F10	0.65	320.9	417.3	24.5	49.1	1350.0	–
BS5F20	0.65	320.9	368.2	24.5	98.2	1350.0	–

Thus, multiple regression analysis was used as a statistical technique to determine the relations between the w/c ratio; the replacement of silica fume and fly ash; and the properties, pore structure, and durability of cement-based composites. We could construct a linear equation containing all those variables. In general then, multiple regression analysis will estimate a linear equation of the form

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 \quad (3)$$

The dependent variable  $Y$  represents the properties, pore structure, and durability of cement-based composites. The other variables,  $X_1$ ,  $X_2$ ,  $X_3$ , are independent variables, defined as follows:  $X_1$ , w/c ratio;  $X_2$ , silica fume content (%); and  $X_3$ , fly ash content (%). Ordinary least squares linear multiple regressions are used to predict dependent variables measured at the interval or ratio level.

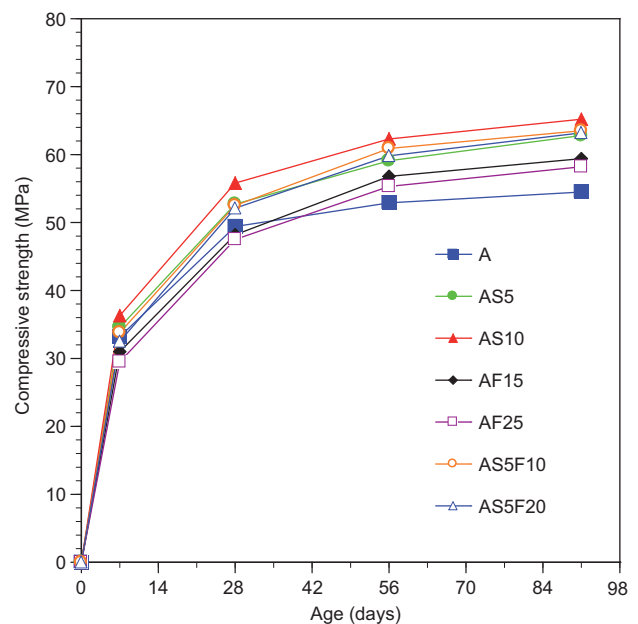
### 3. Results and discussion

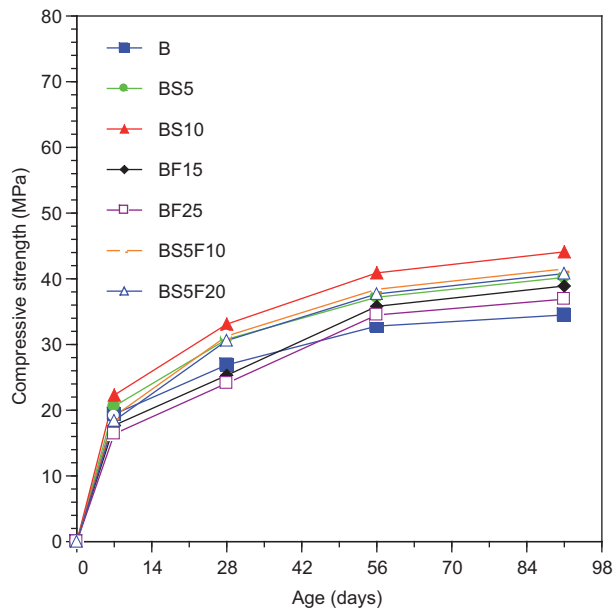
#### 3.1. Compressive strength

The compressive strength test results are given in Figures 1, 2 and Table 4. As expected, the compressive strength increases with an increasing age and a decreasing w/c ratio. The compressive strength of control specimen (A) with a w/c of 0.45 has a compressive strength of 33.2 MPa at the age of 7 days, 49.4 MPa at the age of 28 days, 52.9 MPa at the age of 56 days, and 54.5 MPa at the age of 91 days, respectively. The strength of specimens (AS5 and AS10) with addition of 5% and 10% silica fume shows an increase of 4.2–15.2% and 9.3–19.6% from 7 to 91 days, respectively. In contrast, the strength of specimens (AF15 and AF25) with 15% and 25% fly ash replacement has a decrease of 6.6–2.4% and 11.1–3.9% at the ages of 7 and 28 days, respectively. However, the strength of AF15 and AF25 increased after 56 days. The factors affecting the strengths of fly ash specimens and silica fume specimens are particle filling effect and pozzolanic reaction. Silica fume

has a much finer particle size (225,000 cm<sup>2</sup>/g) and a higher SiO<sub>2</sub> concentration (91.5%) than fly ash (4050 cm<sup>2</sup>/g; SiO<sub>2</sub>, 57.2%). A higher pozzolanic activity is demonstrated in silica fume specimens at an early age.

AS5F10 and AS5F20 specimens have almost the same compressive strengths as compared with AS5 and AS10 specimens at the age of 28 days. The compressive strengths of AS5F10 and AS5F20 are 63.5 and 63.2 MPa at the age of 91 days, which are 16.5% and 16% higher than that of the control specimen, respectively. Increasing fly ash amount in silica fume specimens does not significantly affect the compressive strength, which indicates the dosage effect of fly ash on compressive strength is limited. A similar trend is observed for the

**Figure 1** Compressive strength vs. age at the w/c of 0.45.



**Figure 2** Compressive strength vs. age at the w/c of 0.65.

specimens with a w/c ratio of 0.65. The strength of BS5 and BS10 shows an increase of 6.2–16.5% and 15–27.8% from 7 to 91 days, respectively. On the other hand, the strength of BF15 and BF25 has a decrease of 8.8–6% and 15.5–10.4% at the ages of 7 and 28 days, respectively. The positive effect of silica fume on compressive strength is more prominent in the specimens with a higher w/c ratio. The effect of w/c ratio on fly ash specimens is not as significant as on silica fume specimens.

The multiple regression analysis of 91-day compressive strength was conducted using Statistical Package for the Social Sciences (SPSS, version 13, New York, NY, USA). The independent variables include w/c ratio ( $w$ ), silica fume content ( $S, \%$ ), and fly ash content ( $F, \%$ ). The linear regression equation correlating the compressive strength ( $f'_c$ , MPa)

with w/c ratio, silica fume content, and fly ash content is obtained as follows:

$$f'_c (\text{MPa}) = 102.46 - 102.92w + 1.29S(\%) + 0.16F(\%); R^2 = 0.99 \quad (4)$$

The effect on the compressive strength is related to the coefficients of the independent variables. The coefficient of silica fume content is higher than that of fly ash content and the ratio is about 8 (1.29/0.16). The significance of the above correlation is that the compressive strength is primarily reduced by the increase of w/c ratio, and secondarily increased by the silica fume and fly ash replacement level. It indicates that the w/c ratio is still a control variable on compressive strength of cement-based composites and silica fume contents have more pronounced effect than fly ash contents. The effects of silica fume contents on compressive strength are about 8 times (1.29/0.16=8) as many as the fly ash contents.

### 3.2. Porosity and pore size distribution

The mercury intrusion porosimetry test was carried out for the specimens at the age of 91 days. By tracking pressure and intrusion volume at each increment, pore volume and pore size distribution were obtained, and the critical pore size (the pore size in the maximum logarithm differential intrusion volume) and the porosity (fraction of pore volume over total volume) would be computed. The cumulative intrusion volume, capillary pore intrusion volume, gel pore intrusion volume, porosity, and critical pore size are summarized in Table 5. As expected, specimens with a w/c ratio of 0.45 have less cumulative intrusion volume, lower porosity, and smaller critical pore size than those of with a w/c ratio of 0.65. At a w/c of 0.45, the control specimen (A) achieves cumulative intrusion volume of 0.1429 ml/g (capillary pore intrusion volume of 0.0859 ml/g and gel pore intrusion volume of 0.0570 ml/g). The cumulative intrusion volume of specimens (AS5 and AS10) with addition of 5% and 10% silica fume shows a decrease of 19.94% and 25.53%, respectively. The cumulative

**Table 4** Relative percentages of compressive strength for the cement-based composites.

Mixture no	w/c	Silica fume (%)	Fly ash (%)	Relative increase percentage (%)			
				7 days	28 days	56 days	91 days
A	0.45	–	–	100.0	100.0	100.0	100.0
AS5	0.45	5	–	104.2	106.7	111.7	115.2
AS10	0.45	10	–	109.3	113.0	117.8	119.6
AF15	0.45	–	15	93.4	97.6	107.4	109.0
AF25	0.45	–	25	88.9	96.1	104.5	106.8
AS5F10	0.45	5	10	101.8	106.3	115.1	116.5
AS5F20	0.45	5	20	97.9	105.5	113.0	116.0
B	0.65	–	–	100.0	100.0	100.0	100.0
BS5	0.65	5	–	106.2	114.5	113.4	116.5
BS10	0.65	10	–	114.9	123.1	124.7	127.8
BF15	0.65	–	15	91.3	94.0	109.2	112.8
BF25	0.65	–	25	84.5	89.6	105.2	107.0
BS5F10	0.65	5	10	98.4	116.4	117.1	120.3
BS5F20	0.65	5	20	94.8	113.8	114.9	118.3

**Table 5** Intrusion volume of mercury, porosity, and critical pore size.

Mixture no	Cumulative intrusion volume (ml/g)	Capillary pore intrusion volume (ml/g)	Gel pore intrusion volume (ml/g)	Porosity (%)	Critical pore size (nm)
A	0.1429	0.0859	0.0570	26.9	70
AS5	0.1144	0.0615	0.0529	22.1	45
AS10	0.1107	0.0519	0.0588	21.2	41
AF15	0.1328	0.0716	0.0612	23.4	60
AF25	0.1355	0.0736	0.0619	23.7	66
AS5F10	0.1220	0.0661	0.0559	23.0	48
AS5F20	0.1262	0.0723	0.0539	23.2	53
B	0.1453	0.0944	0.0509	27.9	83
BS5	0.1154	0.0684	0.0470	24.9	53
BS10	0.1122	0.0671	0.0451	23.8	47
BF15	0.1342	0.0855	0.0487	26.2	76
BF25	0.1372	0.0914	0.0458	26.8	80
BS5F10	0.1231	0.0734	0.0497	24.9	57
BS5F20	0.1276	0.0728	0.0548	25.3	60

intrusion volume decreases with an increasing silica fume addition. The reduction in the total pore volume is due to the high pozzolanic reactivity and the pore-filling effect of the very small particles of silica fume.

The cumulative intrusion volume of specimens (AF15 and AF25) with 15% and 25% fly ash replacement shows a decrease of 7.07% and 5.18%, respectively. The cumulative intrusion volume of mercury has a less decrease with an increasing fly ash addition. At the same time, AF15 and AF25 specimens also have less decrease than AS5 and AS10 specimens. The percentage of the total pore volume decreased with the addition of fly ash due to its pozzolanic activity. However, the dosage of fly ash to improve porosity is limited. The main reason is the unavailability of sufficient quantities of  $\text{Ca}(\text{OH})_2$  during the period of pozzolanic reaction.

The cumulative intrusion volume of specimens (AS5F10 and AS5F20) with 5% silica fume replacement mixed 10% or 20% fly ash replacement shows a decrease of 14.63% and 11.69%, respectively. The cumulative intrusion volume of AS5F10 and AS5F20 specimens is higher than AS5 and AS10 specimens and lower than AF15 and AF25 specimens. When silica fume and fly ash were used, the pozzolanic reaction with calcium hydroxide reduced the content of calcium hydroxide and increased the content of C-S-H in the interface and, as a result, increased the density of this layer. Silica fume is more reactive than fly ash due to its having a greater surface area and higher  $\text{SiO}_2$  content. A similar trend is observed for the specimens with a w/c of 0.65. At w/c of 0.65, the control specimen (B) achieves cumulative intrusion volume of 0.1453 ml/g. The cumulative intrusion volume of specimens BS5 and BS10 shows a decrease of 20.59% and 22.78%, and BF15 and BF25 shows a decrease of 7.07% and 5.18%, respectively. The cumulative intrusion volume of specimens with fly ash has less decrease than those of with silica fume. The cumulative intrusion volume of specimens BS5F10 and BS5F20 shows a decrease of 15.28% and 12.18%, respectively. Specimens with a w/c ratio of 0.65 have more cumulative intrusion volume than those of with a w/c of 0.45. However, the effect

of w/c ratio on fly ash specimens is not as significant as on silica fume specimens.

The critical pore size is defined as the pore size in the maximum logarithm differential intrusion volume. Lowering the w/c ratio resulted in smaller critical pore size for all specimens. The critical pore size decreases with the increase of silica fume replacement for the specimens with a w/c of 0.45 and 0.65. The addition of fly ash also decreases the critical pore size compared with that of the control specimen with a w/c of 0.45 and 0.65. However, the critical pore size increases with the increase of fly ash replacement. At the w/c of 0.45, the specimens (AS5 and AS10) with addition of 5% and 10% silica fume had the critical pore size of 45 and 41 nm, the specimens (AF15 and AF25) with 15% and 25% fly ash replacement had the critical pore size of 60 and 66 nm, and the specimens (AS5F10 and AS5F20) with silica fume of 5% mixed 10% and 20% fly ash replacement had the critical pore size of 48 and 53 nm, respectively. A similar trend was obtained for the specimens with a w/c of 0.65. At the w/c of 0.65, specimens BS5 and BS10 had the critical pore size of 53 and 47 nm, specimens BF15 and BF25 had the critical pore size of 76 and 80 nm, and specimens AS5F10 and AS5F20 had the critical pore size of 57 and 60 nm, respectively. Specimens with a w/c ratio of 0.65 had a bigger critical pore size than those of with a w/c of 0.45.

On the basis of the analysis of the critical pore size, it was shown that both the silica fume and fly ash content and the w/c ratio had a significant effect on the critical pore size. The multiple regression analysis of critical pore size was conducted using SPSS. The independent variables include the w/c ratio ( $w$ ), silica fume content ( $S, \%$ ), and fly ash content ( $F, \%$ ). The linear regression equation correlating the critical pore size ( $N$ , nm) with w/c ratio, silica fume content, and fly ash content is obtained as follows:

$$N(\text{nm})=34.98+65.91w-1.01S(\%)-0.21F(\%); R^2=0.90 \quad (5)$$

The effect on critical pore size is related to the coefficient of the independent variables. The coefficient of silica fume content is higher than that of fly ash content and the ratio is about

5 (-1.01/-0.21). The significance of the above correlation is that the critical pore size is primarily reduced by the decrease of w/c ratio, and secondarily increased by the silica fume and fly ash replacement level. It indicates that the w/c ratio is still a control variable on critical pore size of cement-based composites and silica fume contents have more pronounced effect than fly ash contents. The effects of silica fume contents on critical pore size are about 5 times (-1.01/-0.21=5) as many as the fly ash contents.

### 3.3. Water absorption

Table 6 lists the water absorption of the different mixes. It can be seen that the water absorption of specimen with a w/c ratio of 0.45 is lower than that of with a w/c ratio of 0.65 and decreases with the addition of silica fume and fly ash when compared with the specimen without the addition. The water absorption decreases with an increasing silica fume addition and increases with an increasing fly ash addition at both the w/c ratios. In addition, the water absorption of specimen with silica fume mixed fly ash replacement was higher than that of specimens with silica fume addition and lower than that of specimen with fly ash addition. The decrease of water absorption of the specimen with silica fume and fly ash replacement results from filler effect and pozzolanic reaction.

Multiple regression analysis of the water absorption was conducted using SPSS. The independent variables include the w/c ratio ( $w$ ), silica fume content ( $S$ ,%), and fly ash content ( $F$ ,%). The linear regression equation correlating the water absorption ( $W_a$ ,%) with w/c ratio, silica fume content, and fly ash content is obtained as follows:

$$W_a(\%)=2.50+10.57w-0.10S(\%)-0.01F(\%); R^2=0.97 \quad (6)$$

The effect on water absorption is related to the coefficient of the independent variables. The coefficient of silica fume content is higher than that of fly ash content and the ratio is about 10 (0.10/0.01). The significance of the above correlation is that the water absorption is primarily reduced by the decrease of the w/c

**Table 6** Water absorption.

Mixture no	Water absorption (%)	Relative reduction percentage (%)
A	7.5	100.0
AS5	6.4	85.3
AS10	6.0	80.0
AF15	6.7	89.3
AF25	6.9	92.0
AS5F10	6.2	82.7
AS5F20	6.4	85.3
B	9.6	100.0
BS5	8.5	88.5
BS10	8.0	83.3
BF15	8.7	90.6
BF25	8.9	92.7
BS5F10	8.4	87.5
BS5F20	8.6	89.6

ratio, and secondarily increased by the silica fume and fly ash replacement level. It indicates that the w/c ratio is still a control variable on water absorption of cement-based composites and silica fume contents have more pronounced effect than fly ash contents. The effects of silica fume contents on water absorption are 10 times (0.10/0.01=10) as many as the fly ash contents.

### 3.4. Rapid chloride penetration test and diffusion coefficient

Rapid chloride penetration test is a convenient test for evaluating concrete permeability. The total charge passed and chloride diffusion coefficients for specimens are given in Table 7. The relative charge passed defines the percentage of total charge passed of specimens with addition of silica fume/fly ash to total charge passed of specimens without silica fume/fly ash. Specimens with a w/c ratio of 0.45 have lower total charge passed than those of with a w/c ratio of 0.65 and the total charge passed of specimen containing any replacement of silica fume and fly ash decreased compared with the specimen without silica fume or fly ash. The total charge passed decreases with an increasing silica fume addition. At the w/c of 0.45, specimens with addition of silica fume result in significantly reducing the total charge passed when compared with the fly ash results. At the w/c of 0.65, specimens with addition of silica fume or fly ash decrease the total charge passed compared with the control specimen; however, the relative charge passed is not significantly different. The decrease of total charge passed of specimen with silica fume and fly ash replacement results from filler effect and pozzolanic reaction. Furthermore, it can be pointed out that silica fume is a very fine particle and has higher chemical reactivity compared to fly ash.

As expected, lowering the w/c ratio resulted in smaller diffusion coefficient for specimens. The diffusion coefficient of control specimen (A) with a w/c of 0.45 is  $3.71 \times 10^{-12} \text{ m}^2/\text{s}$ , which had a decrease of 7% compared to specimen (B) with a w/c of 0.65. The diffusion coefficient decreases with the

**Table 7** Total charge passed and diffusion coefficient of cement-based composites.

Mixture no	Total charge passed (C)	Relative charge passed (%)	Diffusion coefficient ( $\times 10^{-12} \text{ m}^2/\text{s}$ )
A	2632	100.0	3.71
AS5	1355	51.5	1.92
AS10	980	37.2	1.67
AF15	2043	77.6	2.45
AF25	1863	70.8	2.99
AS5F10	1213	47.1	1.84
AS5F20	1152	43.8	1.89
B	4764	100.0	3.99
BS5	2075	43.6	2.14
BS10	1601	33.6	1.82
BF15	2109	44.3	2.97
BF25	1933	39.1	3.37
BS5F10	1868	40.6	2.08
BS5F20	1722	36.1	2.15

increase of silica fume replacement for the specimens. At the w/c of 0.45, the diffusion coefficient of specimens (AS5, AS10) with 5% and 10% silica fume replacement compared with the control specimen (A) shows a decrease of 48% and 55%, respectively. At the w/c of 0.65, the diffusion coefficient of specimens (BS5, BS10) with 5% and 10% silica fume replacement compared with the control specimen (B) shows a decrease of 46% and 54%, respectively. At the w/c of 0.45 or 0.65, the diffusion coefficients of specimens (AF15, AF25 or BF15, BF25) with 15% and 25% fly ash replacement compared with control specimens (A or B) shows a decrease of 34%, 19% and 26%, 15%, respectively. In addition, the specimens with silica fume mixed fly ash also have the lower diffusion coefficient compared with control specimens. The diffusion coefficient of specimen with silica fume mixed fly ash is lower than those of only fly ash addition. It can be summarized that the addition of silica fume and fly ash results in reducing diffusion coefficient and silica fume when compared with fly ash is beneficial.

On the basis of the analysis of the diffusion coefficient, it was shown that both the silica fume and fly ash content and the w/c ratio had a significant effect on the diffusion coefficient. The multiple regression analysis of diffusion coefficient was conducted using SPSS. The independent variables include w/c ratio ( $w$ ), silica fume content ( $S, %$ ), and fly ash content ( $F, %$ ). The linear regression equation correlating the diffusion coefficient ( $D, \times 10^{-12} \text{ m}^2/\text{s}$ ) with the w/c ratio, silica fume content, and fly ash content is obtained as follows:

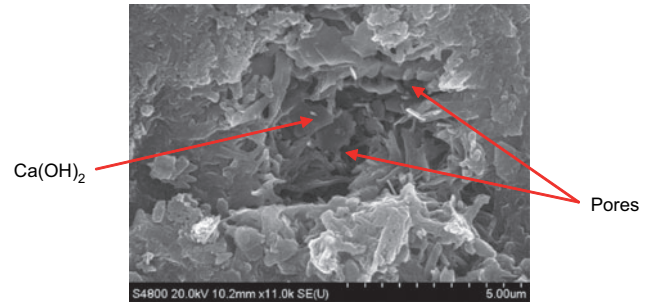
$$D(\times 10^{-12} \text{ m}^2/\text{s}) = 2.53 + 1.60w - 0.15S(\%) - 0.03F(\%);$$

$$R^2 = 0.81 \quad (7)$$

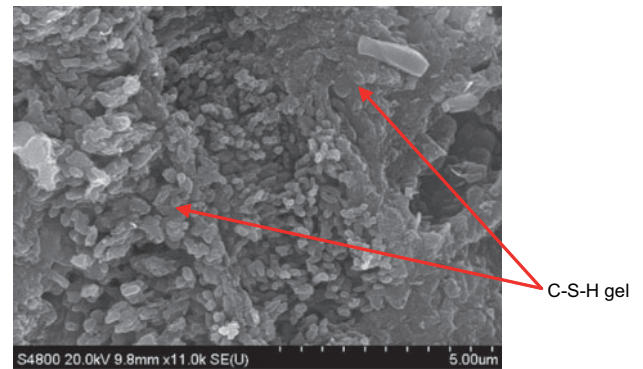
The effect on diffusion coefficient is related to the coefficient of the independent variables. The coefficient of silica fume content is higher than that of fly ash content and the ratio is about 5 (-0.15/-0.03). The significance of the above correlation is that the diffusion coefficient is primarily reduced by the decrease of the w/c ratio, and secondarily increased by the silica fume and fly ash replacement level. It indicates that the w/c ratio is still a control variable on diffusion coefficient of cement-based composites and silica fume contents have more pronounced effect than fly ash contents. The effects of silica fume contents on diffusion coefficient are about 5 times (-0.15/-0.03=5) as many as the fly ash contents.

### 3.5. SEM analysis

The microstructure of specimen without and with the addition of silica fume and fly ash was investigated by means of SEM methods and shown in Figures 3–5. Observations revealed more differences in the microstructural features between the control specimens and those produced with silica fume and fly ash replacement. Figure 3 shows the SEM photograph of the control specimen (A) at the w/c of 0.45. It can be seen that the surfaces had more capillary pores and  $\text{Ca}(\text{OH})_2$ , which resulted in lower compressive strength and higher water absorption. Figure 4 shows the SEM photographs obtained for the specimen (AS10) with 10% silica fume replacement at the w/c of 0.45. It was observed that a large amount of C-S-H gel

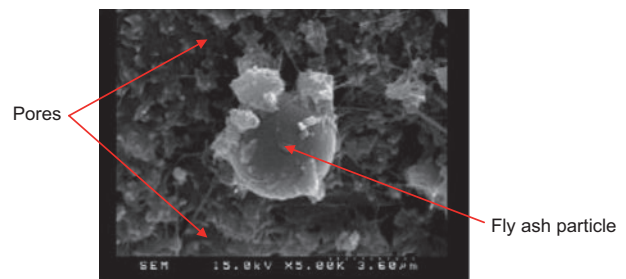


**Figure 3** SEM micrograph of the control specimen at the w/c of 0.45 at 11,000  $\times$ .



**Figure 4** SEM micrograph of specimen with 10% silica fume at the w/c of 0.45 at 11,000  $\times$ .

with a dense structure is discerned. With the addition of silica fume to the mix, there takes place a reaction of the portlandite produced by the hydration of the calcium silicates in the cement and the silica and alumina reactivates in the pozzolanic material. This reaction produces C-S-H gel, which grows into the capillary spaces. Hence, the paste structure tissue became dense. Figure 5 shows the SEM photograph of the specimen (BF15) with 15% fly ash replacement at the w/c of 0.65. It can be seen that there exist a few relatively large pores and fly ash particles that have not reacted with  $\text{Ca}(\text{OH})_2$  yet. The fly ash particles in the cement-based composites react slowly with CH to form C-S-H and the process goes on for years [21, 22].



**Figure 5** SEM micrograph of specimen with 15% fly ash at the w/c of 0.65 at 5000 $\times$ .

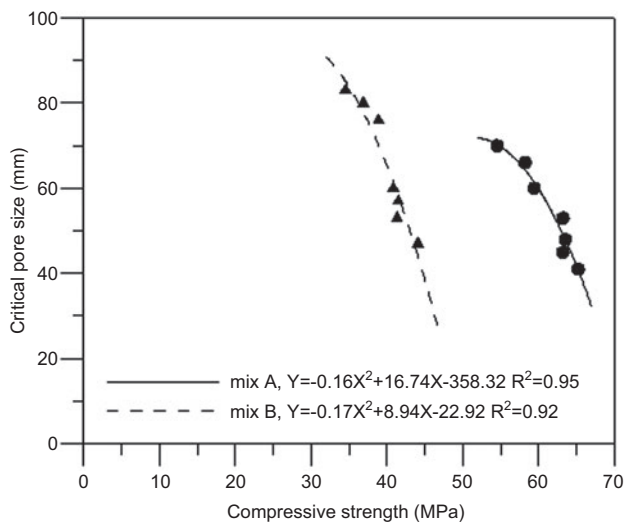
### 3.6. Relations among compressive strength, critical pore size, and water absorption

In this study, ordinary least squares linear multiple regressions was carried out on the basis of the experimental data of compressive strength, critical pore size, and water absorption of cement-based composites with the w/c of 0.45 and 0.65 at the ages of 91 days, respectively. Figure 6 shows the relation between compressive strength and critical pore size of the cement-based composites. It indicates that the higher compressive strength seems to have the smaller critical pore size at the same w/c ratio. It can be attributed to the reason that the compressive strength is related to the pore structure and porosity of concrete matrix. The relation between compressive strength and water absorption of cement-based composites is shown in Figure 7. It shows a linearly correlated trend between compressive strength and water absorption for all mixes. The higher compressive strength seems to have the lower water absorption. The relation between critical pore size and water absorption of cement-based composites is shown in Figure 8. It can be seen that the relation between critical pore size and water absorption is strongly affected by the w/c ratio. The correlation coefficient values  $R^2$  are 0.92 at the w/c ratio of 0.45 and 0.77 at the w/c ratio of 0.65. The higher water absorption seems to have the larger critical pore size at the same w/c ratio.

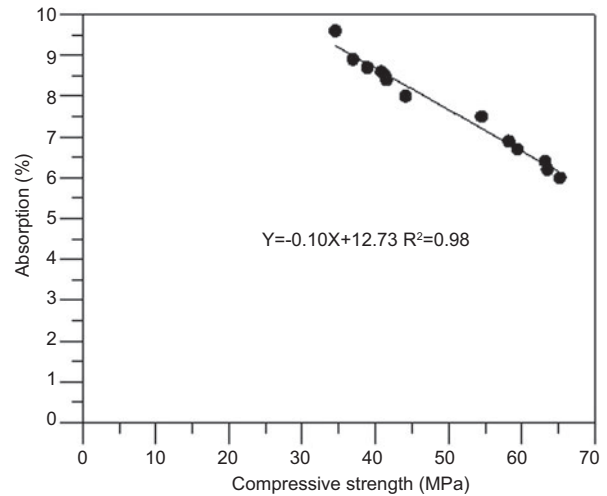
## 4. Conclusions

On the basis of experimental results and discussions above, the following conclusions were drawn:

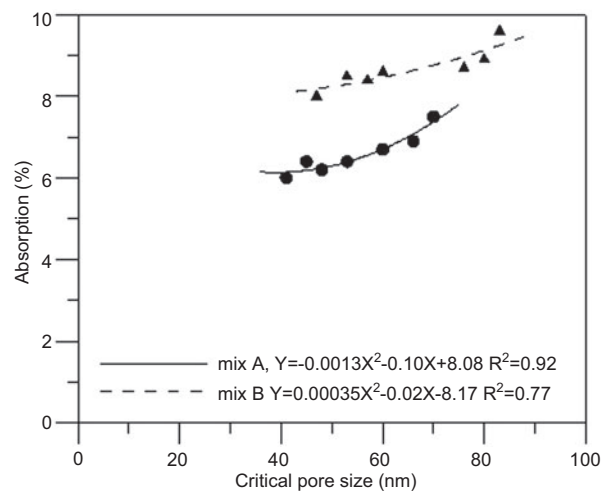
1. The compressive strength of specimens with the addition of silica fume and fly ash showed an increase of 6.8–27.8% at the age of 91 days. Meanwhile, replacing the Portland cement with 5% silica fume and 10% fly ash lowered the



**Figure 6** Compressive strength vs. critical pore size for all specimens.



**Figure 7** Compressive strength vs. water absorption for all specimens.



**Figure 8** Critical pore size vs. water absorption for all specimens.

critical pore size, water absorption, total charge passed, and diffusion coefficient. The effect of silica fume was better than that of fly ash.

2. Composites with 10% silica fume replacement of cement indicated the best mechanical performance and durability. In addition, replacing the Portland cement with 5% silica fume and 10% fly ash showed the optimum combined effects and interaction on the properties, pore structure, and durability of cement-based composites.
3. SEM observations revealed that a large amount of C-S-H gel forms on cement-based composites with the addition of silica fume.
4. By comparing the results of multiple regression analyses of testing data, the coefficient of silica fume is about 5–10 times as many as that of fly ash.

The above conclusions show that the addition of silica fume and fly ash or a lower w/c ratio would more effectively improve mechanical properties, pore structure, and durability of cement-based composites, and that silica fume is more beneficial than fly ash. However, this conclusion needs further research to be properly confirmed.

## References

- [1] Holt E, Raivio P. *Cement Concrete Res.* 2006, 36, 441–448.
- [2] Lam L, Wong YL, Poon CS. *Cement Concrete Res.* 1998, 28, 271–283.
- [3] Bilodeau A, Sivasundaram V, Painter KE, Malhotra VM. *ACI Mater. J.* 1994, 91, 3–12.
- [4] Berndt ML. *Constr. Build. Mater.* 2009, 23, 2606–2613.
- [5] Babu KG, Rao GSN. *Cement Concrete Res.* 1994, 24, 277–284.
- [6] Poon CS, Lam L, Wong YL. *Cement Concrete Res.* 2000, 30, 447–455.
- [7] Carette GG, Malhotra VM. *Cement Concrete Aggr. CCAGDP* 1983, 5, 3–13.
- [8] Cohen MD, Bentur A. *ACI Mater. J.* 1988, 85, 148–157.
- [9] Xie J, Elwi AE, MacGregor JG. *ACI Mater. J.* 1995, 92, 135–145.
- [10] Toutanji HA, Liu L, El-Korchi T. *Mater. Struct.* 1999, 32, 203–209.
- [11] Cong X, Gong S, Darwin D, McCable S. *ACI Mater. J.* 1992, 89, 375–382.
- [12] Kumar R, Bhattacharjee B. *Cement Concrete Res.* 2003, 33, 417–424.
- [13] Barbhuiya SA, Gbagbo JK, Russell MI, Basheer PAM. *Constr. Build. Mater.* 2009, 23, 3233–3239.
- [14] Carette G, Malhotra VM. *ACI Mater. J.* 1983, 79, 765–784.
- [15] Mehta PK, Gjrv OE. *Cement Concrete Res.* 1982, 12, 587–595.
- [16] Bhanjaa S, Sengupta B. *Cement Concrete Res.* 2002, 32, 1391–1394.
- [17] Bouzoubaa N, Fournier B. *Cement Concrete Res.* 2003, 33, 1029–1037.
- [18] Tanyildizi H. *Mater. Des.* 2009, 30, 3252–3258.
- [19] Fedrizzi L, Azzolini F, Bonora PL. *Cement Concrete Res.* 2005, 35, 551–561.
- [20] Yang CC, Cho SW. *Cement Concrete Res.* 2003, 81, 116–125.
- [21] Taylor HFW. *Cement Chemistry*, 2nd ed., Thomas Telford: London, 1997.
- [22] Menetrier D, Jawed I, Sun TS, Skalny J. *Cement Concrete Res.* 1979, 9, 473–482.