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Hydration properties of cement pastes containing high-volume mineral admixtures

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Abstract This research aimed to investigate the influence of high-volume mineral admixtures (MAs), i.e., fly ash and slag, on the hydration characteristics and microstructures of cement pastes. Degree of cement hydration was quantified by the loss-on-ignition technique and degree of pozzolanic reaction was determined by a selective dissolution method. The influence of MAs on the pore structure of paste was measured by mercury intrusion porosimetry. The results showed that the hydration properties of the blended pastes were a function of water to binder ratio, cement replacement level by MAs, and curing age. Pastes containing fly ash exhibited strongly reduced early strength, especially for mix with 45% fly ash. Moreover, at a similar cement replacement level, slag incorporated cement paste showed higher degrees of cement hydration and pozzolanic reaction than that of fly ash incorporated cement paste. Thus, the present study demonstrates that high substitution rates of slag for cement result in better effects on the short- and long-term hydration properties of cement pastes.

Keywords: cement paste; mineral admixtures; hydration; microstructures.

1. Introduction

Mineral admixtures (MAs) can be used individually with Portland cement or blended cement or in different combinations (Kosmatka *et al.* 2002). It is well recognized that a proper use of MAs offers certain beneficial effects to concrete (Metha and Monteiro 2006, Uzal and Turanli 2003, Turanli *et al.* 2004). This is because MAs, when used in conjunction with Portland or blended cement, contribute to the properties of the hardened concrete through hydraulic or pozzolanic activity or both. As a result, they make concrete mixtures more economical, reduce permeability, increase strength, and improve other concrete properties. Furthermore, increased use of industrial by-products, such as fly ash or ground granulated blast furnace slag (hereafter referred to as slag), leads to an equivalent reduction of green house gases emissions and represents a technically proven and effective approach of reducing cement industry emissions.

In fact, with today's higher quality requirements for a high performance concrete (HPC) or a low heat concrete for massive structures, mix proportions containing fly ash or slag in addition to Portland cement are used more commonly. Nevertheless, it is generally recognized that the maximum cement content for an ordinary HPC or a low heat concrete is exceeded by either the cement content needed for concrete strength or the minimum cement content required for durability.

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For instance, currently in commercial practice, the percentage of fly ash as part of the total cementing materials in structural concrete normally ranges from 15% to 25%, despite the fact that it can go up to 30-70% in some applications (Berry *et al.* 1994, Malhotra 2002, Bilodeau and Malhorta 2000, Bouzoubaa *et al*. 2002, Reiner and Rens 2006, Wu *et al*. 2006). As far as slag is concerned, it has cementitious properties by itself but these are enhanced when it is used with Portland cement. Practically, the amount of slag in concrete can vary from 20% to 80% by mass of the cementitious materials, depending on the source and composition of the slag and the performance requirements of the concrete (Hussin *et al*. 2007, Burak *et al*. 2007).

From a practical viewpoint, concrete can be regarded as a two-phase material composed of a matrix phase and a particle phase. Usually, the matrix phase is composed of water and Portland cement, which consists of some compounds. Once water is added to cement, each of the compounds undergoes hydration reaction that ultimately converts the water-cement suspension into a rigid porous material. When a cement paste is incorporating with MAs, a chemical reaction called pozzolanic reaction happens between some of the hydration products of cement and the admixtures. Some MAs enhance cement hydration (Maltais and Marchand 1997, Taylor 1990), whereas others decrease the hydration rate (Taylor 1990, Fajun *et al.* 1985). Therefore, there have been many studies concerning the hydration and microstructure of Portland cement incorporating MAs (Feldman *et al.* 1990, Berry *et al.* 1990, Richardson and Groves 1992, Cao and Detwiler 1995, Lam *et al.* 2000, Hwang and Hsieh 2007, Rukzon and Chindaprasirt 2008, Ge and Wang 2009, Chen *et al.* 2009). Most of the results found in the literature cover groups of parameters for hydration conditions, including water-cementitious ratio, percentage of MAs replacement, etc. It is generally accepted that the proper substitution rate of MAs for Portland cement will vary depending upon the chemical composition of both the MAs and the Portland cement. However, the hydration characteristics of the cement pastes blended with high volume of MAs is not yet fully understood and further research is needed to provide the information on their short- and long-term performance.

The main aspects of the concrete performance that will be improved by the use of MAs are increased long-term strength and reduced permeability of the concrete resulting in potentially better durability. However, during the initial stages of hydration, cement is normally the only component of a concrete mixture that is chemically reacting. Thus the effects of MAs on the early age properties of concrete, including setting time and early strength gain, should also be taken into account when proportioning concrete mixtures. Especially, a few additional precautions have to be taken to insure that concrete containing high-volume MAs in addition to cement will meet all the performance criteria. In addition, fly ash is classified as a pozzolan while slag is classified as a latent hydraulic material. There are major differences in the physical and chemical characteristics of these replacement materials. For this reason, the present study aimed to investigate the influence of high substitution rates of fly ash and slag for cement on the hydration characteristics and microstructures in cement pastes and to make comparisons between the hydration properties of fly ash and slag systems with different levels of replacement.

2. Experimental details

2.1. Experimental program

A high replacement of cement by MAs would affect the hydration evolution and microstructure development of the cement paste within concrete, and thus altering the performance properties of the hardened concrete. In view of this, a more quantitative understanding of the hydration process of fly ash and slag systems with different levels of replacement is needed. In this study, three series of pastes (i.e., plain Portland cement (PC), fly ash/cement (FC), and blast-furnace slag/cement (SC) pastes) were prepared. Among them, plain PC pastes without MAs were prepared at the same water to binder ratio (*w/b*) as the reference. Experiments were designed to evaluate performance of paste with respect to compressive strength, non-evaporable water content, calcium hydroxide content, reactivity of pozzolan, and porosity and pore size distribution. The experimental variables included *w/b* ratio, cement replacement level by MAs, and curing age. Water/binder ratios used were 0.30, 0.45, and 0.60. Cement replacement levels (by mass) by fly ash were 15, 30, and 45 percents in FC paste and by slag were 30, 50, and 70 percents in SC paste. Curing ages were 7, 28, and 91 days.

2.2. Materials and mixture proportioning

The cement used was an ordinary Portland cement. A low calcium fly ash equivalent to ASTM Class F and a ground blast furnace slag were used as MAs. The chemical composition and physical properties of these materials are shown in Table 1. Mixture proportions of the three series of pastes are given in Table 2. For example, mix number P30 denotes the PC mixture with a *w/b* of 0.30, while F30-15 denotes the FC mixture with a *w/b* of 0.30 and containing 15% fly ash.

The pastes were mixed in a mechanical mixer with 5-liter capacity. After mixing, a number of specimens were produced for each mixture proportion. All the specimens were cast in 50×50×50 mm steel molds. Following casting, all the specimens were covered with wet burlap and de-molded after 24 hours. Then all specimens were cured in a saturated calcium hydroxide solution bath at 23±2°C until 24 hours before testing.

2.3. Compressive strength test

At the designed ages, the compressive strength of paste specimens was measured according to the specification of ASTM C109. Compression testing of cubic specimens was performed using a servo-hydraulic material testing system. After the compression test the fracture pieces of the cubes were preserved for other tests. In order to stop the hydration reactions, the samples were soaked in methanol for 5 minutes and placed in a vacuum desiccator overnight to remove the methanol. Then these samples were further dried in an oven at 105°C for 24 hours and ground in a mortar to pass through a 150 μm sieve.

Table 1 Chemical composition and physical properties of cement and MAs

Item	Cement	Fly ash	Slag
SiO_2 (%)	20.21	50.40	33.05
Fe_2O_3 (%)	2.97	12.50	0.33
Al_2O_3 (%)	5.35	25.70	15.59
CaO (%)	60.55	4.50	40.73
MgO (%)	3.94	1.42	7.68
SO_3 (%)	2.51	0.61	0.07
Loss on ignition (%)	1.30	4.10	0.12
Specific gravity	3.15	2.13	2.86
Specific surface area (cm^2/g)	3440	3931	4270

Table 2 Mixture proportions of pastes

Paste type	Mix number	w/b*	Replacement ratio (%)	Water (kg/m^3)	Cement (kg/m^3)	Fly ash (kg/m^3)	Slag (kg/m^3)
PC	P30	0.30	-	486	1620	-	-
	P45	0.45	-	586	1303	-	-
	P60	0.60	-	654	1090	-	-
FC	F30-15	0.30	15	469	1328	234	-
	F30-30	0.30	30	452	1056	452	-
	F30-45	0.30	45	437	802	656	-
	F45-15	0.45	15	569	1076	190	-
	F45-30	0.45	30	554	861	369	-
	F45-45	0.45	45	538	658	538	-
	F60-15	0.60	15	638	904	160	-
	F60-30	0.60	30	623	727	312	-
	F60-45	0.60	45	609	558	456	-
SC	S30-30	0.30	30	481	1123	-	481
	S30-50	0.30	50	478	797	-	797
	S30-70	0.30	70	475	475	-	1108
	S45-30	0.45	30	582	905	-	388
	S45-50	0.45	50	579	643	-	643
	S45-70	0.45	70	576	384	-	896
	S60-30	0.60	30	650	758	-	325
	S60-50	0.60	50	647	539	-	539
	S60-70	0.60	70	644	322	-	751

Note: *: w/b=Water-to-binder ratio

2.4. Calculations of non-evaporable water and calcium hydroxide content

Samples of 1 g powder of the hydrated pastes were first dried in an oven at 105°C for 3 hours and then heated in an electric furnace at 10°C/min to 950°C for 1 hour. The weight loss due to the evaporation of the free water and the decomposition of the chemically combined water was measured. But the amount of the non-evaporable water need to be corrected by the loss of ignition of the dry binder powder at 950°C with respect to its mass at 105°C. A precision of 0.0001 was used in all weighing operations. According to the law of conservation of mass, the equation, modified from the equation derived by Powers and Brownyard (1948), for calculating the amount of the non-evaporable water per gram of original binder can be easily derived, as shown in Eq. (1):

$$\frac{w_n}{b} = \frac{W_{105}}{W_{950}}(1-L_b)-1 \tag{1}$$

where w_n/b=non-evaporable water per gram original binder; W_{105}=sample weight after heating for 3 hours at 105°C; W_{950}=sample weight after heating for 1 hour at 950°C; and L_b=loss on ignition of original binder (i.e., L_b=yoriginal fractions of cement×ignition loss of original cement+original fractions of MAs + ignition loss of original MAs).

On the other hand, the amount of calcium hydroxide (CH) was estimated from the step of weight loss occurring at 450-550°C (Escalante *et al.* 2001). The modified equation for calculating the CH content per gram of original binder can be derived using the law of conservation of mass, as shown in Eq. (2) (Escalante-Garcia and Sharp 1998):

$$\frac{W_{n,450}}{b}-\frac{W_{n,550}}{b}=\frac{W_{450}-W_{550}}{W_{950}}(1-L_b)-\left(\frac{b_{450}}{b}-\frac{b_{550}}{b}\right) \tag{2}$$

where $w_{n,450}/b$=non-evaporable water content per gram original binder at 450°C; $w_{n,550}/b$=non-evaporable water content per gram original binder at 550°C; W_{450}=sample weight after heating for 1 hours at 450°C; W_{550}=sample weight after heating for 1 hours at 550°C; b_{450}/b=weight of binder per gram original binder at 450°C; and b_{550}/b=weight of binder per gram original binder at 550°C; and all other variables are as defined previously.

2.5. Calculations of reactivity of pozzolan

The reactivity of pozzolan in the pastes blended with MAs was estimated by a selective dissolution procedure using a particular solution and water. The principle of the procedure is that in a blended cement paste, pozzolan reacts with CH to form acid-soluble hydration products. It is possible to dissolve the hydration products of cement and pozzolan, and the unreacted cement components, leaving the remaining unreacted pozzolan undissolved (Ohsawa *et al.* 1985, Li *et al.* 1985). The solutions used in the experiment were picric acid and ethylene diamine tetraacetic acid (EDTA) for the FC pastes and the SC pastes, respectively. The determinations of the degree of reaction of the pozzolans in FC and SC pastes were carried out following a procedure described by Lam *et al.* (2000) and by Luke and Glasser (1987), respectively. The equation for calculating the degree of pozzolanic reaction per gram of original pozzolan can be given by:

$$\alpha_p = 1-\frac{R/W_p-(c_r/c)p_c+(p_d/p)p_p}{p_p} \tag{3}$$

where α_p=degree of pozzolanic reaction (g/g of original pozzolan); W_p=weight of paste sample; R =weight of undissolved residue of binders (g); c=weight of original cement (g); p=weight of original pozzolan (g); c_r/c=undissolved cement (g/g of original cement); p_d/p=dissolved pozzolan (g/g of original pozzolan); p_c=original fractions of cement (%); and p_p=original fractions of pozzolan (%).

2.6. Measurements of porosity and pore size distribution

The porosity and pore size distribution in the pastes was measured by mercury intrusion porosimetry (MIP). The 5 mm thick samples used were obtained from the fracture pieces of the cubes after the compression test. The fragments were dipped into methanol for 5 minutes to stop the hydration, and then dried in the vacuum desiccators for 2 days. The pressure of mercury intrusion porosimeter ranges from 1.4 MPa to 414 MPa. The pressure required is a function of the pore size and can be converted to equivalent pore width using the Washburn equation, as in Eq. (4) (Galle 2001):

$$D=\frac{-4\gamma\cos\theta}{P_a} \tag{4}$$

where D=equivalent pore width (m); P_a=absolute pressure exerted (Pa); γ=surface tension of mercury (N/m); and θ=contact angle (wetting angle) between solid and mercury (^{o}). The relationship is commonly known as the Washburn equation. A surface tension of 480 mN/m and a contact angle of 140^o were used in the Washburn equation to convert applied pressure to pore diameter.

3. Experimental results

3.1. Compressive strength

Fig. 1 presents the plots of strength versus age for paste with different *w/b* ratios. Each value for compressive strength, f_c', at 7, 28, and 91 days is the average of three test results. Fig. 1 demonstrates that the values of f_c' generally increased from the age of 7 days to 91 days for all types of paste specimens. But in early age pastes containing fly ash or slag as a cement replacement developed strengths more slowly than the reference PC pastes. The degree of decline in early strength is a function of *w/b* ratio and MAs content. For FC pastes, it can be observed from Fig. 1(a) that the replacement of cement by fly ash caused a reduction in the 7- and 28-day strengths, as compared with the reference PC pastes. In addition, the higher the replacement was, the lower was

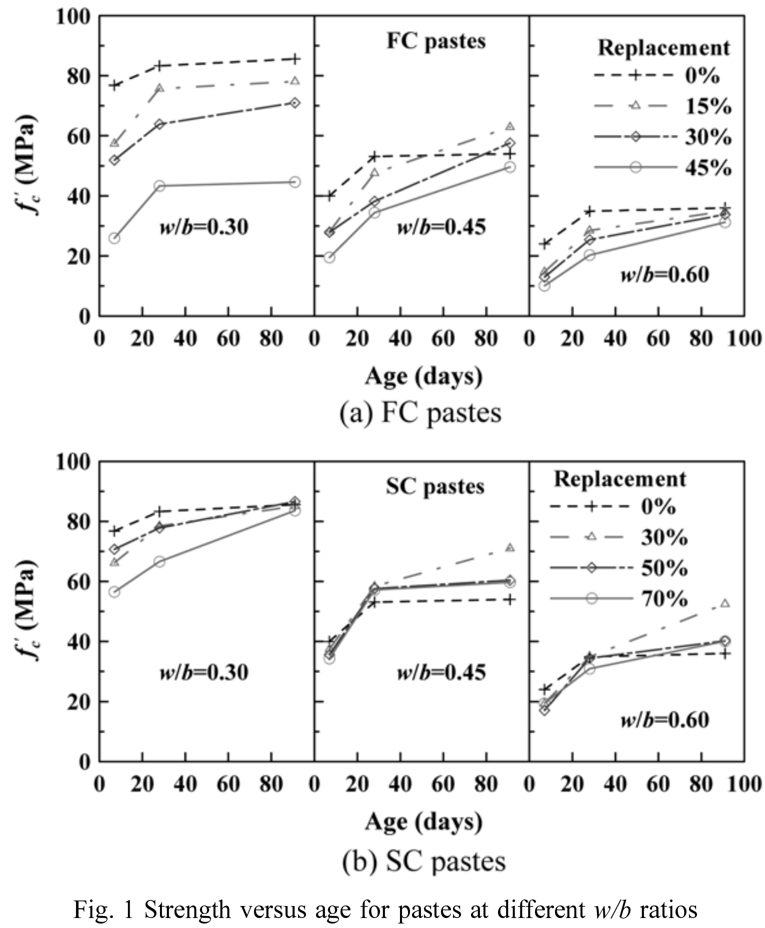


Fig. 1 Strength versus age for pastes at different *w/b* ratios

the strength. This is because in a fly ash-admixed paste, strength up to 28 days is mainly contributes by hydration of cement. But at 91 days the strength development of FC pastes is depending on *w/b* ratio. Fig. 1(a) shows that the 91-day strength of FC pastes having a *w/b* ratio of 0.30 and 0.60 was still lower than PC pastes. However, some of FC pastes having a *w/b* ratio of 0.45 showed higher compressive strength than PC pastes. This different behavior indicates that the later strength development of fly ash incorporated cement pastes is a function of water to binder ratio and cement replacement level by fly ash.

For SC pastes, the effect of slag content on compressive strength is shown in Fig. 1(b). It can be observed from Fig. 1(b) that at a lower *w/b* ratio, the replacement of cement by slag also caused a reduction in the 7- and 28-day compressive strengths, as compared with the reference PC pastes. But at a *w/b* ratio of 0.45, all SC pastes showed higher strength than the reference PC pastes at the age of 28- and 91-day. Even at a *w/b* ratio of 0.60, all SC pastes developed higher strength than the reference PC pastes at the age of 91-day.

3.2. Non-evaporable water and calcium hydroxide content

In the study the amounts of non-evaporable water, w_n, of the pastes at different ages are reported in terms of w_n per gram cement, w_n/c, in Table 3, in which each value is the average of two test results. For PC pastes, the results clearly show that the value of w_n/c increased with the increase of

Table 3 Non-evaporable water content of pastes

Mix number	w_n/c (gram per gram of cement)		
	7-day	28-day	91-day
P30	0.122	0.150	0.152
P45	0.156	0.194	0.195
P60	0.164	0.205	0.211
F30-15	0.160	0.166	0.184
F30-30	0.164	0.180	0.201
F30-45	0.176	0.204	0.205
F45-15	0.176	0.198	0.224
F45-30	0.187	0.231	0.244
F45-45	0.225	0.227	0.269
F60-15	0.174	0.212	0.247
F60-30	0.169	0.220	0.246
F60-45	0.211	0.265	0.284
S30-30	0.223	0.229	0.236
S30-50	0.282	0.304	0.322
S30-70	0.373	0.427	0.447
S45-30	0.239	0.260	0.270
S45-50	0.350	0.382	0.412
S45-70	0.430	0.567	0.583
S60-30	0.229	0.339	0.363
S60-50	0.326	0.428	0.456
S60-70	0.477	0.560	0.617

w/b ratio. At each age, the value of w_n/c of the paste with a *w/b* ratio of 0.60 was substantially higher than that of the paste having a *w/b* ratio of 0.30 and 0.45.

Table 3 shows that the value of w_n/c for the FC pastes was higher than that for the reference PC paste, and the higher the fly ash content was, the higher was the value of w_n/c. In other words, the presence of the fly ash increases the reactivity of the cement fraction. This is consistent with the results of Feldman *et al.* (1990) and Berry *et al.* (1990). The higher value of w_n/c in FC pastes can be attributed to the contribution of fly ash reaction, on one hand, and the 'enhanced' hydration of the cement in FC pastes due to the relatively higher effective *w/c* ratio, on other hand, as proposed by Berry *et al.* (1994). The latter is because when part of cement was replaced by fly ash, the concentration of cement in the system was diluted, and the effective *w/c* ratio controlling the rate of cement hydration was relatively increased. Moreover, the removal of cement hydration product CH could be an important factor of higher hydration degree of cement paste. On the other hand, Fig. 2(a) illustrates that for FC paste with a *w/b* ratio of 0.30, the value of w_n/c increased from the age of 7 days to 28 days but finally became blunted after 28 days because of the lower content of water than that necessary to continue the hydration. Whereas FC paste with a *w/b* ratio of 0.60 seemed to

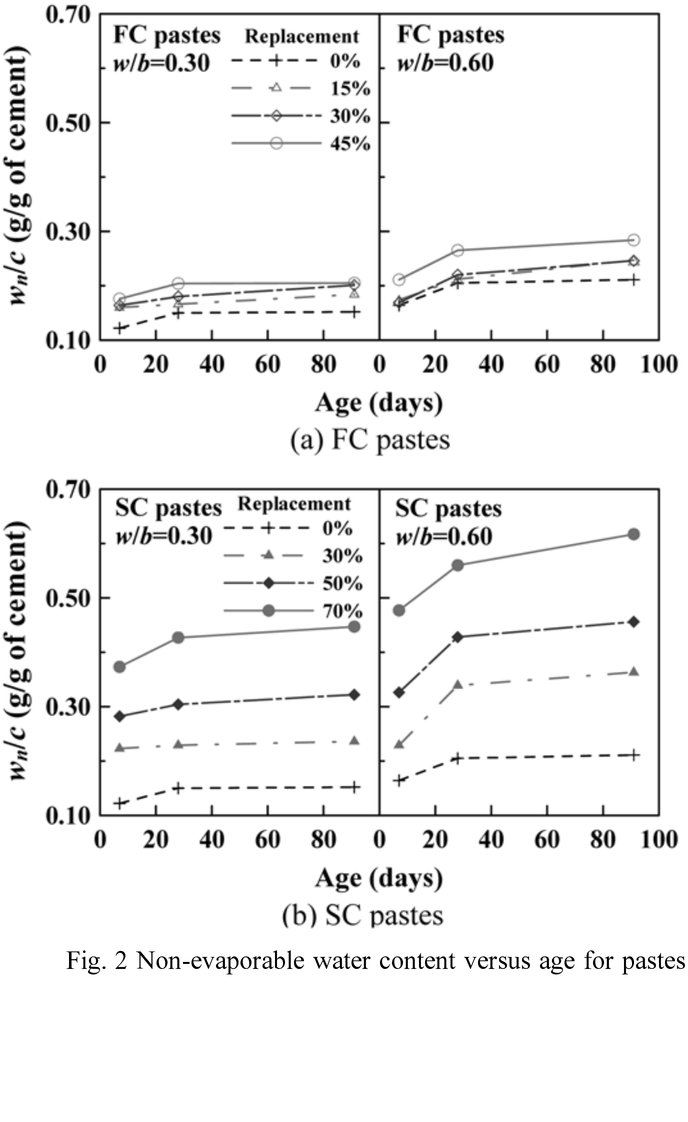


Fig. 2 Non-evaporable water content versus age for pastes

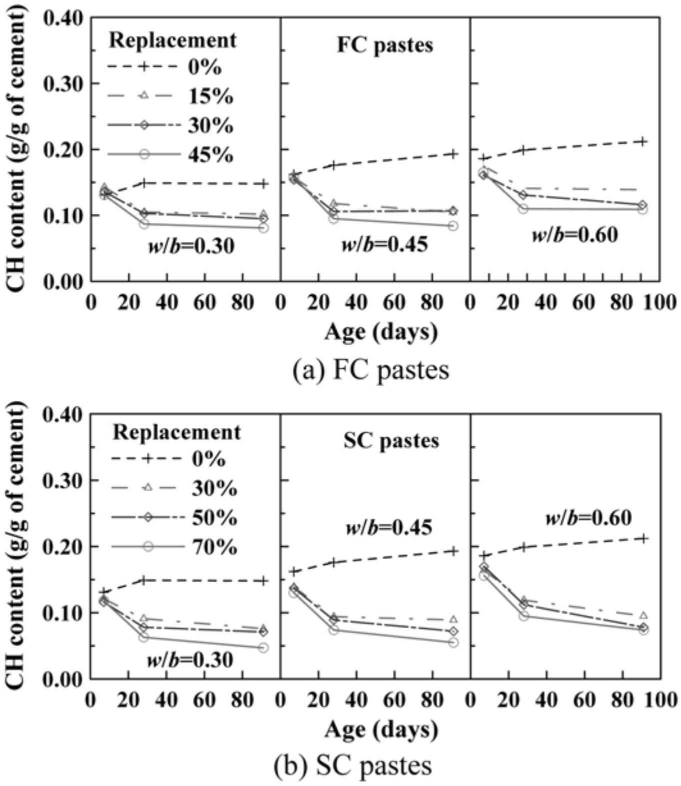


Fig. 3 $Ca(OH)_2$ content versus age for pastes at different *w/b* ratios

have enough water to continue the hydration reaction even after 28 days.

In the case of SC pastes, Table 3 also shows that the value of w_n/c was higher than that of its corresponding PC paste. Moreover, for a fixed *w/b* ratio, the effect was more noticeable because the value of w_n/c for the SC paste was higher than that for the FC paste. For example, a comparison between Figs. 2(a) and 2(b) shows that at a similar mass replacement ratio of 30%, the values of w_n/c in the SC pastes were obviously higher than those of the FC pastes.

The CH content per gram of original binder was calculated by Eq. (2). Then the calculated value was further divided by the original fractions of cement in the binders. Fig. 3 presents the plots of CH content (g/g of cement) versus age for pastes with different *w/b* ratios. For PC pastes, at each *w/b* ratio, the results of CH content are consistent with the results of w_n content with an increasing trend with age. As for FC and SC pastes, the obtained results show that CH content depended on the *w/b* ratio and age of the sample. For the first 7days, the cement produced CH, while the fly ash seemed to consume an insignificant amount of CH. Therefore, the amounts of CH content in the FC pastes and the reference PC pastes were similar at the age of 7 days, as shown in Fig. 3(a). During the period of 7 day to 28 days, however, with the increase of curing age, the progress of pozzolanic reaction consumed a part of the CH in the FC and SC pastes. Then CH content obviously dropped at the age of 28 days. But the amount of CH content in the FC and SC pastes changed very little from 28 days of hydration onwards. On the other hand, Figs. 3(a)-3(b) reveal that for a fixed *w/b* ratio, the amount of CH content decreased as the pozzolan replacement level and curing age increased. The reason is with the increase of curing age the cement has reduced its rate of reaction and the pozzolan, which is still reacting, is consuming small amounts of CH for the formation of calcium silicate hydrates (C-S-H) products. As a result, the amount of CH content decreased, and the higher the replacement was, the less was the CH content.

3.3. Reactivity of pozzolan

The degree of reaction of the pozzolan in blended pastes was calculated by Eq. (3) and listed in Table 4. Overall, it can be observed that at a higher *w/b* ratio, the reactivity of the pozzolan increased. This is attributed to the fact that the cement reactivity increases with the increase of *w/b* ratio, as there is more space available for hydration product to form, and thus bringing an enhancement of the cement-activating environment for the pozzolanic reaction in the blended pastes. It can also be observed that with a few insignificant exceptions in Table 4, a consistent decrease in reactivity with increased content of pozzolan.

For FC pastes, the analysis results show that at the age of 7 days, a measurable amount of pozzolanic reaction had taken place already. The measured degree of fly ash reaction ranged from 3.1% to 8.2%. However, this amount of fly ash reaction seemed to have little effect on the relative CH content in the FC pastes. As mentioned previously, therefore, at the age of 7 days, the FC pastes had the relative CH content similar to the reference PC pastes. Then at the age of 28 days, the measured degree of fly ash reaction increased to 6.3-16.1%. Essentially, this increasing tendency in the degree of fly ash reaction corresponded to the decreased amount of CH content in the FC

Table 4 Degree of pozzolanic reaction of pastes

Mix number	Degree of pozzolanic reaction (%)		
	7-day	28-day	91-day
F30-15	8.1	13.0	21.9
F30-30	6.5	13.4	17.6
F30-45	3.1	6.3	11.2
F45-15	7.4	15.3	24.7
F45-30	7.1	16.1	22.9
F45-45	4.2	8.4	16.6
F60-15	8.2	15.4	28.3
F60-30	7.4	14.2	24.6
F60-45	5.0	9.8	13.6
S30-30	23.2	26.8	27.3
S30-50	21.8	23.3	24.2
S30-70	14.7	16.0	18.6
S45-30	26.9	31.1	34.7
S45-50	27.3	33.0	33.2
S45-70	22.4	26.1	29.8
S60-30	25.8	33.7	39.5
S60-50	30.3	36.5	40.3
S60-70	27.0	31.5	34.8

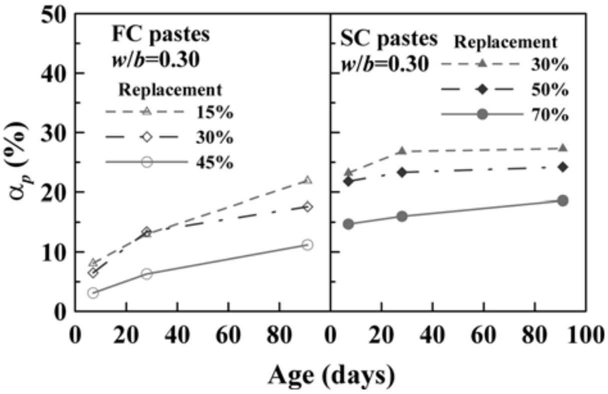


Fig. 4 Degree of pozzolanic reaction versus age for pastes with *w/b* ratio=0.30

pastes, and thus indicating active pozzolanic reaction. Further, at the age of 91 days, the measured degree of fly ash reaction ranged from 11.2% to 28.3%, about 2.7 to 3.9 times of that at 7 days. The results of fly ash reaction are consistent with the results of w_n content with an increasing trend with curing age.

As for SC pastes, Table 4 shows that for a fixed *w/b* ratio, slag reacts much faster than fly ash at all ages due to its inherent hydraulic and higher pozzolanic reactivity. For example, Fig. 4 demonstrates that at a *w/b* ratio of 0.30, the slag in the SC pastes with the percentage of slag in the blend over the range of 30-70% displayed much higher reactivity than the fly ash in the FC pastes with the percentage of fly ash in the blend over the range of 15-45%. On the other hand, the analysis results show that at 7 days, the measured degree of slag reaction reached from 14.7% to 30.3%, whereas degree of fly ash reaction was only from 3.1% to 8.2%. These results are consistent with the results of CH content in the SC pastes at the age of 7 days. Further, with the increase of curing age, the reactivity of slag became more significant and the measured degree of slag reaction reached from 16.0% to 36.5% at the age of 28 days. However, the increase of the reactivity of slag became less significant at later ages and the measured degree of slag reaction reached from 18.6% to 40.3% at the age of 91 days.

3.4. Porosity and pore size distribution

Fig. 5 shows the plots of total intrusion volume of mercury versus age for FC pastes with different *w/b* ratios. It can be seen that intruded pore volume, V_I, decreased with increasing curing age, while increased with increasing *w/b* ratio. In addition, as compared with the reference PC pastes, FC pastes developed higher V_I, but FC paste with a *w/b* ratio of 0.30 and with 15% fly ash was an exception at the age of 28 days. Moreover, at a constant *w/b* ratio, V_I increased with increasing fly ash content, especially for 45% fly ash mix. This is an indication that FC paste with high fly ash content possesses a larger total porosity. The reason is the FC paste sample with a higher fly ash replacement had a lower degree of pozzolanic reaction, as shown in Table 4. On the other hand, Fig. 6 shows the data pairs of V_I and *w/b* ratio for FC and PC pastes, along with the corresponding regression equations and coefficients of determination, R^2. It can be seen from Fig. 6 that a well linear relationship exists between the V_I and the *w/b* ratio since the values of R^2 for the FC and PC paste are all greater than 0.93.

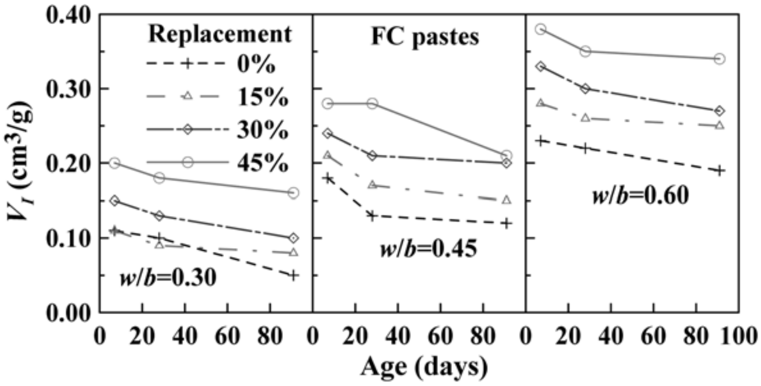


Fig. 5 Intruded pore volume versus age for FC pastes at different *w/b* ratios

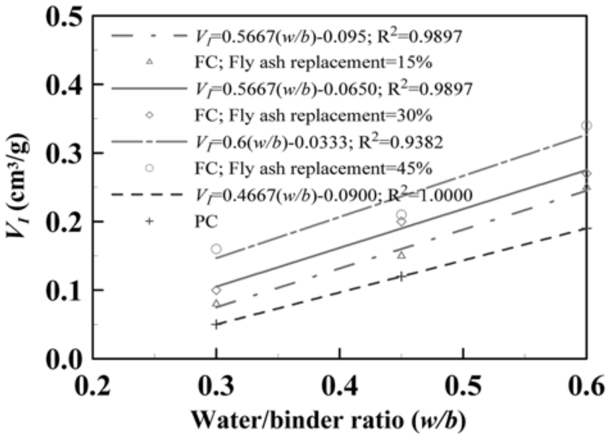


Fig. 6 Correlation between intruded pore volume and *w/b* for FC pastes at 91 days

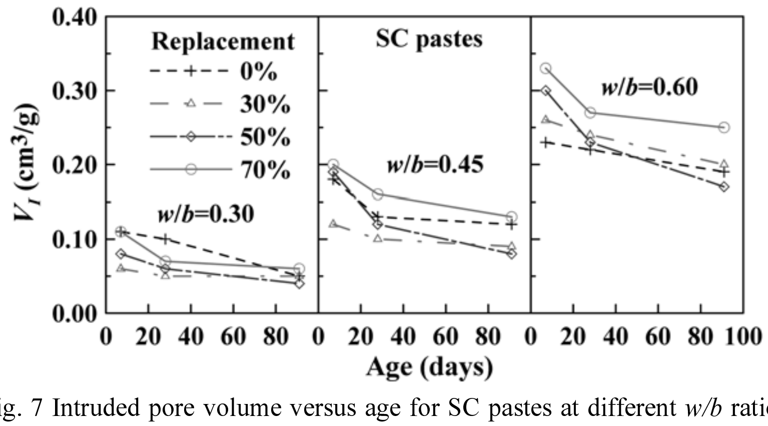
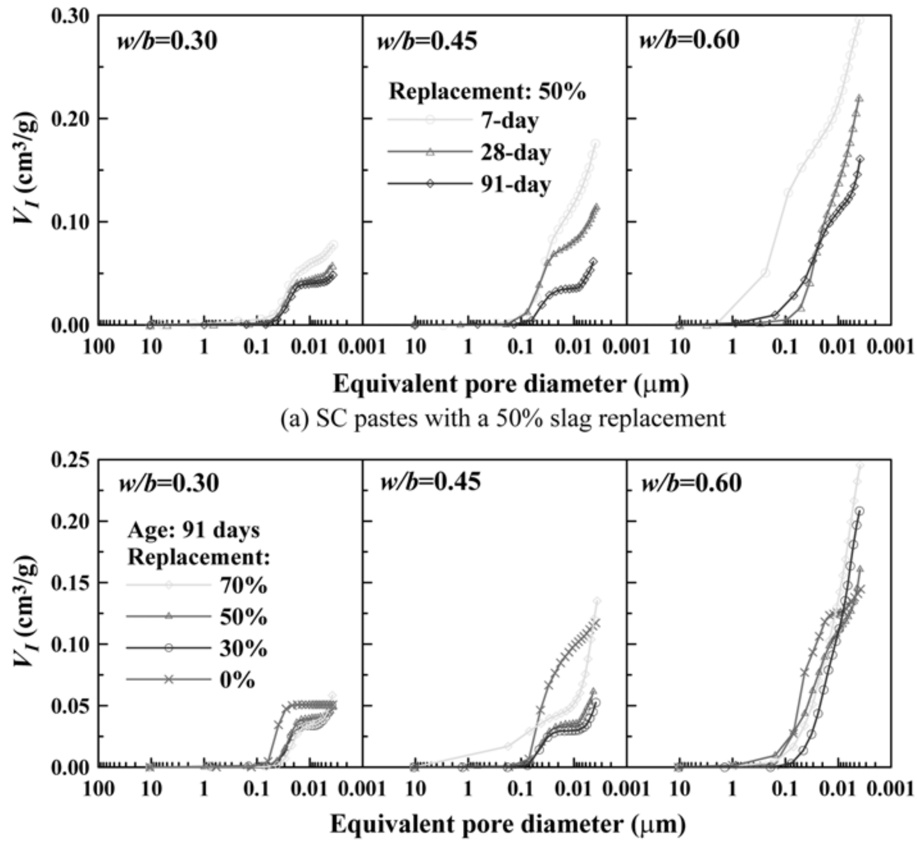


Fig. 7 Intruded pore volume versus age for SC pastes at different *w/b* ratios

Concerning SC pastes, Fig. 7 also reveals that V_I decreased with increasing curing age and increased with increasing *w/b* ratio. Basically, SC pastes developed less V_I than the reference PC pastes at a lower *w/b* ratio. But with increasing *w/b* ratio the V_I in the SC pastes became higher than



(a) SC pastes with a 50% slag replacement

(b) SC pastes with different *w/b* ratios at age of 91 days

Fig. 8 Cumulative intruded pore volume versus equivalent pore diameter for SC pastes

in the reference PC pastes, especially for SC pastes with a 70% slag substitution for cement. On the other hand, Fig. 8 shows the cumulative intruded pore volume versus equivalent pore diameter curves of some SC pastes, in which the equivalent pore diameter was calculated by using the Washburn equation, as in Eq. (4). It can be observed from Fig. 8(a) that for 50% slag mix, the average size and total intrusion volume of mercury decreased with the increase of curing age for each *w/b* ratio. This hints that the pore structure of SC pastes became finer with the increase of curing age. The refinement of pore structure with curing age is a result of Portland cement hydration and continuing pozzolanic activity. In addition, Fig. 8(b) shows that for SC pastes with different *w/b* ratios, at the age of 91 days, the average pore diameters decreased with increasing slag, while the measured porosity increased. This indicates that the SC paste had higher gel porosity, of which the pore diameter was considered less than 0.03 μm, as compared with the reference PC paste with more capillary porosity, of which the pore diameter was considered between 0.03 and 10 μm. The reduction in capillary porosity may be attributed to the size of the slag particles and their role in densifying the microstructure (Tixier *et al.* 1997).

4. Discussion

4.1. Degree of cement hydration

In a plain cement paste, by relating the content of non-evaporable water at a certain age to that for complete hydration, the degree of cement hydration at this age can be calculated by:

$$\alpha_c(t) = \frac{w_n(t)}{w_{n,com}} \times 100\% \tag{5}$$

where α_c(t)=degree of cement hydration at age t days; w_n(t)=content of non-evaporable water at age t days; and $w_{n,come}$=content of non-evaporable water for complete hydration that can be obtained from the potential Bogue composition of the cement (Bogue 1929).

In the case of a blended paste, it becomes more complicated to calculate the degree of cement hydration. The reasons for the difficulties in determining the degree of cement hydration in a blended paste are due to the fact that the amount of water bound in pozzolanic reaction products is uncertain, and the pozzolanic reaction consumes CH. In other words, non-evaporable water in a cement paste blended with MAs can only provide a semi-quantitative indicator of the degree of cement hydration; it contains the contribution of the cement and pozzolans fractions, which cannot be easily separated. Nevertheless, it is well recognized that the degree of cement hydration strongly depends on water-to-cement ratio. For this reason, following the analysis technique described by Lam *et al.* (2000), in the study an equation describing the relationship between the degree of cement hydration and the *w/c* ratio is given by:

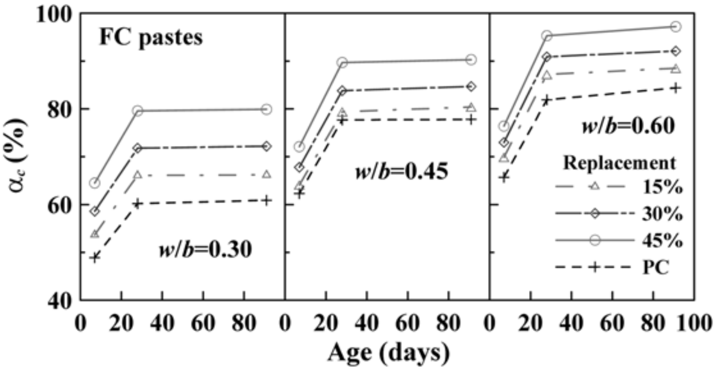
$$\alpha_c = a_1 \cdot e^{-a_2/(w/c)} \tag{6}$$

where α_c=degree of cement hydration in weight percent; *w/c*=water-to-cement ratio; and a_1 and a_2 =empirical constants. By means of statistical techniques, the data obtained in present study can be fitted into Eq. (6). The determined regression constants (i.e., a_1 and a_2) and the corresponding R^2 of the fitting are given in Table 5. From Table 5, it can be seen that the experimental data have a pretty good correlation with the model. Then the degree of cement hydration in the blended pastes can be estimated by using Eq. (6).

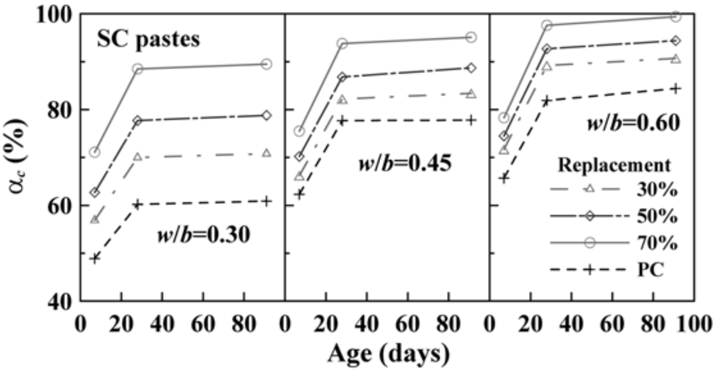
Since pozzolan is partially reactive, the reactive part of pozzolan should be taken into account in the effective *w/c* ratio of the blended pastes. The reactivity of pozzolan can be quantified by a well-known cementing efficiency factor, *k*, which depends on several conditions such as *w/c* ratio, curing age, and the type of pozzolan (Babu and Rao 1996). Thus, the *w/c* variable in Eq. (6) was substituted by $w/(c+kp)$, where c and p are the original fractions of cement and pozzolan in a blended paste based on ignited weight, and k is the cementing efficiency factor of the pozzolan. In this study, data on k values are not available, but the degrees of pozzolanic reaction, α_p, at different

Table 5 Regression analysis of hydration degree of cement in PC pastes

Regression equation	Curing age (day)	Constants		Coefficients of determination (R^2)
		a_1	a_2	
$\alpha_c = a \cdot e^{-a_2/(w/c)}$	7	0.9094	0.1831	0.9734
	28	1.1524	0.1918	0.9708
	91	1.192	0.1999	0.9912



(a) FC pastes



(b) SC pastes

Fig. 9 Degree of cement hydration versus age for pastes at different *w/b* ratios

ages have been determined. Accordingly, using α_p to replace the k value, the degrees of cement hydration in the blended pastes can be calculated.

The relationship between the degree of cement hydration and the curing age for the blended pastes is shown in Fig. 9. As can be clearly seen in the figure, for each *w/b* ratio, the degree of cement hydration in the blended pastes increased with the increasing curing age and replacement ratio of MAs. Moreover, the degree of cement hydration in the blended pastes was higher than that of the reference PC paste. One possible reason is that, although the *w/b* ratio is constant, the *w/c* ratio increases with the increase in the replacement ratio of MAs. The other reason is that MAs provides a site for the hydration of cement. The overall results presented here confirm the enhancement effect of MAs on the hydration of cement. Furthermore, in Fig. 9, it can be seen that at a *w/b* ratio of 0.30, the degree of cement hydration in FC paste with a 45% fly ash substitution for cement was about 65% at the age of 7 days. This value increased by 15% at the age of 91 days. However, at a *w/b* ratio of 0.60, the degrees of cement hydration in FC paste were 76% and 97% at the ages of 7 and 91days, respectively. One possible reason for the lower degrees of cement hydration for the pastes at lower *w/b* ratios can be attributed to the insufficient space available to accommodate more hydration products (Neville 1995). Another reason could be the lower amount of water available to hydrate cement particles.

4.2. Gel/space ratio of pastes

The gel/space ratio is a representation of the capillary porosity of the paste in terms of its measurable parameters. It is defined as the ratio of the solid products of hydration to the space available for these hydration products (Feldman *et al.* 1990). For PC pastes, assuming that 1 ml of hydrated cement occupies 2.06 ml, the gel/space ratio is given by (Neville 1995):

$$X_c = \frac{2.06\, v_c \alpha_c}{v_c \alpha_c + w/c} \tag{7}$$

where X_c=gel/space ratio of PC paste; v_c=specific volume of anhydrous cement; and all other variables are as defined previously. As far as a blended paste is concerned, volume stoichiometry for pozzolanic reaction is not well established because the relevant data for blended systems are too scanty and too uncertain (Taylor 1990). For this reason, following the analysis technique described by Lam *et al.* (2000), Eq. (7) is modified to calculate gel/space ratio of the blended paste, as shown in Eq. (8):

$$X_p = \frac{2.06\, v_c \alpha_c p_c + 2.52\, v_p \alpha_p p_p}{v_c \alpha_c p_c + v_p \alpha_p p_p + w/b} \tag{8}$$

where X_p=gel/space ratio of blended paste; v_p=specific volume of pozzolan; and all other variables

Table 6 Calculated gel/space ratios of pastes

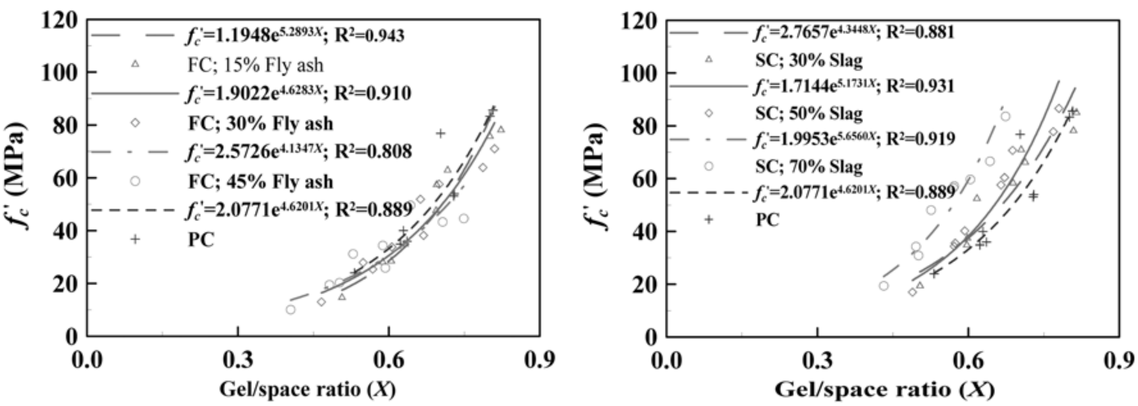
Mix number	X_c or X_p		
	7-day	28-day	91-day
P30	0.703	0.801	0.807
P45	0.629	0.729	0.730
P60	0.532	0.623	0.636
F30-15	0.695	0.801	0.823
F30-30	0.663	0.787	0.810
F30-45	0.593	0.707	0.749
F45-15	0.588	0.694	0.717
F45-30	0.549	0.669	0.700
F45-45	0.482	0.588	0.643
F60-15	0.507	0.605	0.632
F60-30	0.466	0.568	0.606
F60-45	0.405	0.502	0.529
S30-30	0.713	0.809	0.815
S30-50	0.688	0.769	0.780
S30-70	0.570	0.643	0.674
S45-30	0.598	0.689	0.705
S45-50	0.574	0.665	0.672
S45-70	0.496	0.572	0.604
S60-30	0.504	0.597	0.617
S60-50	0.489	0.572	0.593
S60-70	0.432	0.501	0.526

are as defined previously.

In the present study the gel/space ratios of the reference PC pastes and the blended pastes were calculated by Eq. (7) and Eq. (8), respectively. Table 6 summarizes the calculated results. For PC pastes, it can be observed from Table 6 that the value of X_c decreased with the increase of *w/c* ratio, while increased with the increase of curing age. For FC pastes, Table 6 reveals that the value of X_p was dependent on *w/b* ratio and percentage of cement replacement. Overall, FC pastes have lower values of gel/space ratio than the reference PC paste with the same *w/b* ratio. Moreover, at each *w/b* ratio, the pastes with a higher fly ash replacement possess lower values of gel/space ratio. On the other hand, similar phenomena were also observed for SC pastes. It is noted that according to Eq. (8), the volume change of the reacted slag is larger than the anhydrous cement (2.52 versus 2.06). This indicates that the products of the reacted slag are more effective in filling pores. The effect of pore filling will be better if the degree of reaction of the slag in pastes is higher. However, the degree of slag reaction not only depends on *w/b* ratio but on cement replacement level of slag. Based on the experimental results, the degree of slag reaction increased with increasing *w/b* ratio and with decreasing cement replacement level of slag. Although SC pastes with a *w/b* ratio of 0.60 had a higher degree of slag reaction, they contained more capillary pores. As a result, they had lower gel/space ratio than the reference PC paste with the same *w/b* ratio. On the contrary, at *w/b* ratio of 0.30, the SC paste with a 30% slag substitution for cement contained less capillary pores and thus resulting in a higher gel/space ratio than the reference PC paste with the same *w/b* ratio.

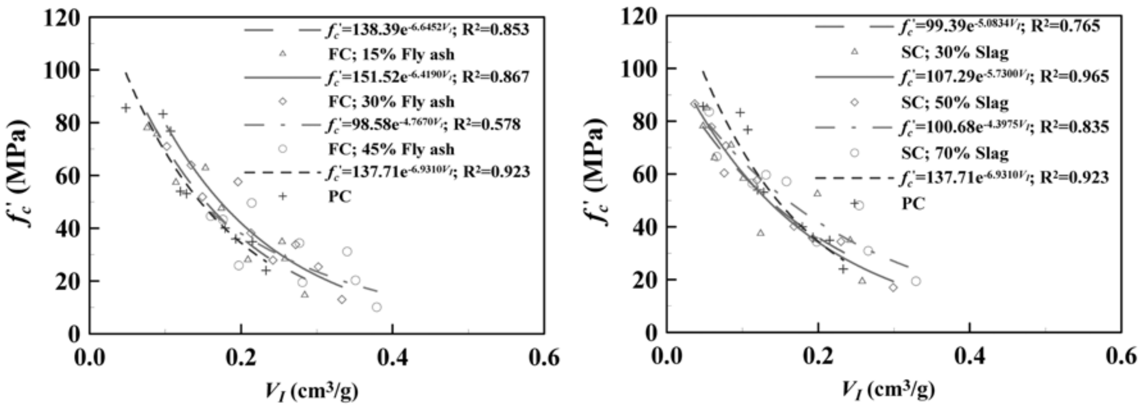
4.3. Relationship between compressive strength, gel/space ratio, and intruded pore volume

The experimental data of f_c' and gel/space ratio obtained from the previous sections are used to establish the relationship equations between f_c' and gel/space ratio of pastes. Fig. 10 shows the data pairs of f_c' and gel/space ratio along with the best-fit curves of exponential functions for different pastes and the corresponding R^2. It can be found from Fig. 10(a) that in despite of the percentage of cement replacement, the trend for FC pastes and that for PC pastes almost coincided. In the case of SC pastes, Fig. 10(b) reveals that the relationship between f_c' and gel/space ratio of 70% slag mix



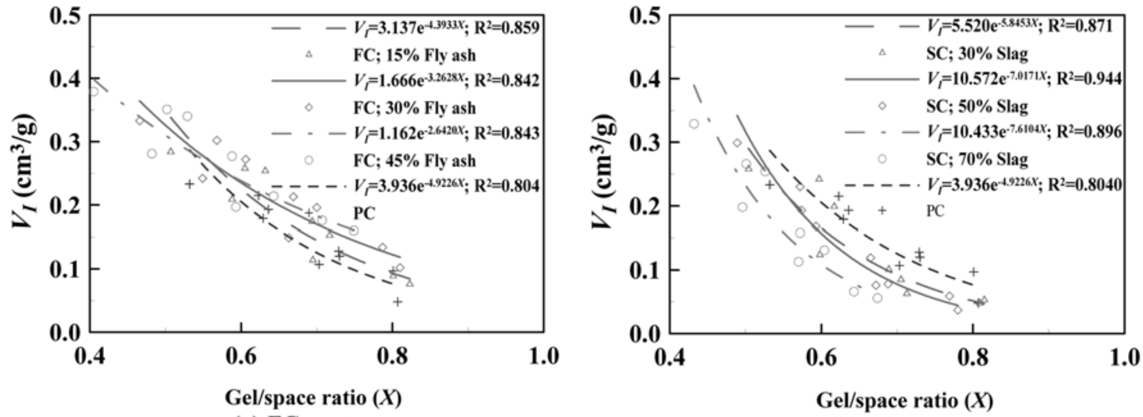
(a) FC pastes (b) SC pastes

Fig. 10 Relationship between compressive strength and gel/space ratio of pastes



(a) FC pastes (b) SC pastes

Fig. 11 Relationship between compressive strength and intruded pore volume of pastes



(a) FC pastes (b) SC pastes

Fig. 12 Relationship between intruded pore volume and gel/space ratio of pastes

was obviously different from that of PC pastes. For instance, at the same strength, SC pastes with a 70% slag substitution for cement had a smaller gel/space ratio.

Fig. 11 reveals the relationship between f_c' and V_I of pastes. A comparison between Figs. 10(a) and 11(a) shows that for FC pastes, strength was better correlated with gel/space ratio than with V_I. On the other hand, a comparison between Figs. 10(b) and 11(b) shows that similar phenomenon was also observed for SC pastes. These results indicate that it is a better method to describe the strength of a blended paste as a function of gel/space ratio.

Fig. 12 demonstrates the data pairs of V_I and the gel/space ratio of pastes along with the best-fit curves of exponential functions for different pastes and the corresponding R^2 obtained from regression analysis. It is can be observed from Fig. 12 that the data of V_I well correlated inversely with the data of gel/space ratio since the values of R^2 for the FC and SC paste are all greater than 0.84. The obtained exponential equations can be used to estimate the value of V_I in the FC and SC systems once the gel/space ratio, which is a function of the hydration degree of cement and pozzolan and the mixed proportions, has been calculated by Eq. (8).

5. Summary and conclusions

In the present research, the effects of high substitution rates of fly ash and slag for cement on the short- and long-term hydration properties of cement pastes were investigated. The results demonstrate that the hydration properties of blended pastes are a function of water to binder ratio, cement replacement level by MAs, and curing age. To compensate for slow strength gain, it would be better to adopt a lower *w/b* ratio in the FC pastes if high early strength is a must. However, pastes with very large amounts of MAs showed a relevant hydration after the 28th day due to the fact that pozzolan forms additional C-S-H products with the CH from cement hydration and thereby increases the denseness of the matrix through pore refinement. Even the later strength of the blended pastes made with a high replacement ratio of fly ash or slag was far higher than those of the reference PC pastes. This indicates that to further improve the engineering property of concrete, it still has ample room to reduce the cement content and to increase the MAs content in a typical concrete mixture, provided water to binder ratio and curing age are properly designed. The results would be useful to concrete technology to decide a reasonable cement replacement level by MAs and to produce concrete with optimum properties. Based on the above results and discussion, the following conclusions can be drawn:

1. For blended pastes containing MAs, the degree of decline in early compressive strength is a function of *w/b* ratio and MAs content. FC pastes exhibit strongly reduced early strength, especially for fly ash mix (45%). As compared with the FC pastes, the replacement of cement by slag caused a minor reduction in the 7- and 28-day compressive strengths since slag is most like Portland cement and least like a pozzolan. In contrast with early strength, the later strength development of the blended paste is substantially better than the reference PC paste.

2. Degrees of fly ash and slag reaction depend on *w/b* ratio and curing age. Higher *w/b* ratios and longer curing age result in greater degrees of reaction of pozzolan. At different curing ages, the degree of pozzolanic reaction depends on not only the *w/b* ratio of the paste, but also the MAs content in the mix. The paste with high volumes of MAs exhibited a lower degree of pozzolanic reaction than a paste with fewer MAs. Slag reacts much faster than fly ash at all ages. At 7 days, the measured degree of slag reaction increased from 14.7% to 30.3%, whereas degree of fly ash reaction was only from 3.1% to 8.2%.

3. Porosity (i.e., intruded pore volume of mercury) depends on *w/b* ratio and curing age. Lower *w/b* ratios and longer curing age result in lower values of porosity. At a constant *w/b* ratio, porosity increases with increasing fly ash content, especially for mix with 45% fly ash. SC pastes develop less porosity than the reference PC pastes at a lower *w/b* ratio. But with increasing *w/b* ratio the porosity in the SC pastes becomes higher than in the reference PC pastes, especially for SC pastes with a 70% slag substitution for cement.

4. The degree of cement hydration in the blended pastes increases with the increasing curing age and replacement ratio of MAs. At a *w/b* ratio of 0.30, the degree of cement hydration in FC paste with a 45% fly ash substitution for cement was about 65% at the age of 7 days. This value increased by 15 percent at the age of 91 days. However, at a *w/b* ratio of 0.60, the degrees of cement hydration in FC paste were 76% and 97% at the ages of 7 and 91days, respectively.

5. Gel/space ratio depends on *w/b* ratio and cement replacement level by MAs. Lower *w/b* ratios and cement replacement levels by MAs result in greater values of gel/space ratio. In addition, the experimental data of compressive strength and intruded pore volume correlate well with the calculated data of gel/space ratio.

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Notation

a_1 = empirical constant
a_2 = empirical constant
b_{450}/b = weight of binder per gram original binder at 450°C
b_{550}/b = weight of binder per gram original binder at 550°C
c = weight of original cement
c_r/c = undissolved cement (g/g of original cement)
D = equivalent pore width
f_c' = compressive strength
k = cementing efficiency factor
L_b = loss on ignition of original binder
P_a = absolute pressure exerted
p = weight of original pozzolan
p_c = original fractions of cement (%)
p_d/p = dissolved pozzolan (g/g of original pozzolan)
p_p = original fractions of pozzolan (%)
R = weight of undissolved residue of binders

V_I = intruded pore volume
v_c = specific volume of anhydrous cement
v_p = specific volume of pozzolan
W_{105} = sample weight after heating for 3 hours at 105°C
W_{550} = sample weight after heating for 1 hours at 550°C
W_{950} = sample weight after heating for 1 hour at 950°C
w_n = non-evaporable water
$w_n(t)$ = content of non-evaporable water at age t days
$w_{n,com}$ = content of non-evaporable water for complete hydration
$w_{n,450}/b$ = non-evaporable water content per gram original binder at 450°C
$w_{n,550}/b$ = non-evaporable water content per gram original binder at 550°C
w/b = water to binder ratio
w/c = water to cement ratio
X_c = gel/space ratio of PC paste
X_p = gel/space ratio of blended paste
α_c = degree of cement hydration
$\alpha_c(t)$ = degree of cement hydration at age t days
α_p = degree of pozzolanic reaction
γ = surface tension of mercury
θ = contact angle (wetting angle) between solid and mercury