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# Studies on blended cement with a large amount of fly ash

Xinghua Fu[a,*], Zhi Wang[a], Wenhong Tao[a], Chunxia Yang[a], Wenping Hou[a], Youjun Dong[a], Xuequan Wu[b]

[a]Department of Materials Science and Engineering, Jinan University, Jinan, Shandong 250022, People's Republic of China
[b]Nanjing Institute of Chemistry Technology, Nanjing 210009, People's Republic of China

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**Abstract**

The influence of the contents of the clinker, activators and fly ash on the properties of blended cement with high fly ash content was studied. Experimental data from X-ray diffraction and pore size distribution indicated that the main hydration product of the fly ash blended cement was C–S–H gel, ettringite and a small amount of $Ca(OH)_2$. The volume porosity of the pores with diameter bigger than 0.1 μm was lower than that of the micro pores and gel pores with diameter lower than 0.05 μm. The amount of chemical combined water has increased with the curing age duration, while the content of $Ca(OH)_2$ has reduced after 7 days. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Hydration; Pore size distribution; Physical properties; Fly ash; Chemical binding of water

## 1. Introduction

The fly ash is the waste residue that is released from the coal combustion process in thermal power plants. The main chemical composition includes $SiO_2$ and $Al_2O_3$, which are regarded as pozzolanic addition. There is a small amount of crystalline minerals, such as quartz, mullite, mica, etc., in the fly ash, but the amorphous glass is the main component. The crystalline mineral has no properties such as hydration and hardening under normal temperature. The amorphous glass reacts with the $Ca(OH)_2$ which is released from the hydration of clinker to form calcium silicate hydrate and calcium aluminate hydrate, etc. Therefore, the activity of fly ash depends on the proportion of vitreous and crystalline mineral. The higher the proportion of vitreous matter, the greater the activity of fly ash is at the same chemical composition.

In the Jining District in Shandong Province, large amounts of fly ash are available. Local specifications require the use of large quantity of fly ash in blended cement for use in road-beds. The present study investigates the properties of such type of blended cements. The effects of the contents of clinker, activators, gypsum on the properties of blended cement were studied. The hydration product, pore structure and hydration mechanism were also investigated by XRD, pore size distribution and chemical binding of water.

* Corresponding author. Tel.: +86-531-797-4453.

## 2. Scope

Seventeen mortar mixtures with blended cements, designated as $A_1$–$A_7$, $B_1$–$B_7$ and $C_1$–$C_3$, in which the fly ash content ranged from 40% to 70%, were tested to evaluate the effect of the fly ash content, the compound activators (CA) and the fineness of the blended cement on the compressive and flexural strengths of mortars. Three blended cements with fly ash content ranging from 44% to 65% were then chosen. The workability, compressive and flexural strengths of the mortars made with these blended cements were determined and compared with those of the mortar made with the control blended cement $F_0$ that incorporates 20% of fly ash. The normal consistency, hydration product and pore structure of the cement pasts made with the above blended cements were also determined and compared with those of the cement paste made with the control blended cement.

## 3. Experimental methods

### 3.1. Raw materials

Raw materials were clinker from Lunan Cement Plant, fly ash from Thermal Power Factory of Jining, gypsum from Zaozhuang City. Their chemical compositions are listed in Table 1. $Na_2CO_3$ and molasses were used as CA. The fly

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Table 1
Chemical compositions of raw materials (wt.%)

| Name | $SiO_2$ | $FeO_3$ | $SO_3$ | CaO | $Al_2O_3$ | MgO | $Na_2O$ | $K_2O$ | Loss |
|---|---|---|---|---|---|---|---|---|---|
| Fly ash | 53.6 | 6.1 | 0.4 | 4.0 | 30.6 | 1.5 | 0.6 | 0.9 | 0.7 |
| Clinker | 21.8 | 3.1 | 0.6 | 63.5 | 5.1 | 3.8 | – | – | – |
| Gypsum | 4.5 | 0.6 | 41.5 | 30.7 | 1.8 | 0.4 | – | – | 19.3 |

ash Portland cement was from Jining Cement Factory, designated as $F_0$, which contained 20% weight of fly ash, 69% clinker, 6% gypsum and 5% limestone.

### 3.2. Methods

Mortar samples of blended cement were cast with $40 \times 40 \times 160$ mm in size and cured for 48 h in the curing box at $20 \pm 2$ °C and 90% RH. Then, the samples were separated from mould plate and cured at $20 \pm 2$ °C and 100% RH to several ages. Finally, the samples were subjected to strength test.

The fineness of cement was examined by Blaine's Specific Surface Area Equipment. The normal consistency water requirement and setting time were examined by the method of GB1346-89 [8]. The flow of cement mortar was performed according to GB2419-81 [9].

When the specimens of blended cement pastes (the ratios of water to cement were according to the water requirement of normal consistency) were cured for 3, 7, 28 and 90 days, they were taken out from fresh water and washed by the anhydrous ethanol and acetone to stop their hydration and dried at the temperature of 60–70 °C. Phase analysis of these specimen hydrates was conducted on D/MAX-RA (radiation source, Cu K$\alpha$) X-ray diffractometer, and the pore size distribution of cement pastes was determined by Autopore III 9420 mercury porosimeter.

## 4. Results and discussion

### 4.1. Effect of fly ash content

The strength of the mortars made with the blended cements decreased with increased fly ash content in the blended cement, especially at an early age. Table 2 shows the effect of fly ash content on the strength of mortars made with blended cements designated as $A_1$–$A_7$ that were ground for the same period of time in order to obtain similar specific surface area.

Table 2
Effect of fly ash on blended cement strength (MPa)

| | Dosage (wt.%) | | | | Flexural | | | Compressive | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Clinker | Fly ash | Slag | Gypsum | 7 days | 28 days | 90 days | 7 days | 28 days | 90 days |
| $A_1$ | 15 | 69.3 | 7.7 | 8 | 0.9 | 2.8 | 3.4 | 5.5 | 13.5 | 18.3 |
| $A_2$ | 20 | 64.8 | 7.2 | 8 | 1.4 | 3.7 | 4.6 | 7.3 | 16.3 | 23.9 |
| $A_3$ | 25 | 60.3 | 6.7 | 8 | 1.9 | 4.1 | 5.0 | 9.8 | 20.1 | 25.8 |
| $A_4$ | 30 | 55.8 | 6.2 | 8 | 2.3 | 4.7 | 5.6 | 11.3 | 24.8 | 31.7 |
| $A_5$ | 35 | 51.0 | 6.0 | 8 | 2.8 | 5.1 | 6.0 | 13.0 | 28.3 | 35.8 |
| $A_6$ | 40 | 46.5 | 5.5 | 8 | 3.3 | 5.6 | 6.5 | 14.9 | 32.5 | 39.3 |
| $A_7$ | 45 | 42.0 | 5 | 8 | 3.6 | 6.1 | 7.0 | 16.7 | 36.0 | 43.8 |

Table 3
Effect of compound activators on strength of blended cement (MPa)

| | Dosages (wt.%) | | | | | Flexural | | | Compressive | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Clinker | Fly ash | Slag | Gypsum | CA | 7 days | 28 days | 90 days | 7 days | 28 days | 90 days |
| $B_1$ | 15 | 69.3 | 7.7 | 8 | 1.15 | 2.1 | 6.7 | 7.5 | 5.5 | 22.8 | 36.8 |
| $B_2$ | 20 | 64.8 | 7.2 | 8 | 1.15 | 2.2 | 6.9 | 8.3 | 7.3 | 24.6 | 38.3 |
| $B_3$ | 25 | 60.3 | 6.7 | 8 | 1.15 | 2.2 | 7.1 | 8.6 | 10.1 | 25.0 | 38.6 |
| $B_4$ | 30 | 55.8 | 6.2 | 8 | 1.15 | 2.3 | 7.3 | 8.6 | 10.4 | 26.0 | 39.1 |
| $B_5$ | 35 | 51.0 | 6.0 | 8 | 1.15 | 2.8 | 7.6 | 8.8 | 13.2 | 34.1 | 44.0 |
| $B_6$ | 40 | 46.5 | 5.5 | 8 | 1.15 | 3.1 | 7.8 | 8.7 | 14.7 | 39.0 | 47.6 |
| $B_7$ | 45 | 42.0 | 5.0 | 8 | 1.15 | 3.7 | 8.1 | 9.0 | 17.0 | 41.4 | 52.6 |

It is shown in Table 2 that the compressive or flexural strength at all ages decreased with the increase of fly ash content. When the fly ash content increased from 42% to 69.3%, the compressive strength of the mortars decreased from 16.7 to 5.5 MPa at 7 days, and from 43.8 to 18.3 MPa at 90 days. This implied that fly ash hydrated slowly and the products resulting in the course of hydration were decreased with the increase of fly ash content.

### 4.2. Effect of CA

The experimental results of Table 2 shows that when the contents of fly ash were higher in blended cement, the strength of the mortar was relatively lower. In order to overcome this phenomenon, the CA were introduced in the experiment. The experimental results are shown in Table 3.

When comparing the results of Tables 2 and 3, it is observed that the strengths were significantly improved at 28 and 90 days when 1.15% CA was added to the blended cement. For example, the 28 and 90 days compressive strengths of $B_1$ and $B_2$ were 50% higher than that of $A_1$ and $A_2$, respectively. The compressive strength of $B_3$ was 25% and 50% higher than that of $A_3$ at 28 and 90 days, respectively. The 28 and 90 days compressive strengths of $B_5$, $B_6$ and $B_7$ were 10–25 % higher than those of $A_5$, $A_6$ and $A_7$. But the increase of strengths was lower at 7 days, indicating that the activation was poor at this age. However, after 7 days, the vitreous matter of fly ash reacted with $OH^-$ and $Na^+$ ions under CA function, and the bonds of O–Al and

Table 4
Influence of fineness on strength of blended cement (MPa)

| | Formulas (wt.%) | | | | Specific surface area | Flexural | | | Compressive | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Fly ash | Slag | Gypsum | CA | ($m^2$/kg) | 7 days | 28 days | 90 days | 7 days | 28 days | 90 days |
| $C_1$ | 64.8 | 7.2 | 8 | 1.15 | 322 | 2.0 | 6.3 | 8.2 | 6.5 | 21.7 | 36.0 |
| $C_2$ | 64.8 | 7.2 | 8 | 1.15 | 386 | 2.3 | 7.2 | 8.7 | 7.6 | 24.9 | 38.9 |
| $C_3$ | 64.8 | 7.2 | 8 | 1.15 | 461 | 2.6 | 7.9 | 9.1 | 8.3 | 28.6 | 40.8 |

Table 5
Best formulas of blended cement (wt.%)

| No. | Clinker | Gypsum | Fly Ash | Slag | CA |
|---|---|---|---|---|---|
| $F_{13}$ | 23 | 8 | 65 | 4 | 1.7 |
| $F_{14}$ | 38 | 7 | 51 | 4 | 1.45 |
| $F_{15}$ | 45 | 7 | 44 | 4 | 1.45 |

Table 7
Cement standard consistency and setting time

| No. | $F_0$ | $F_{13}$ | $F_{14}$ | $F_{15}$ |
|---|---|---|---|---|
| Standard consistency (%) | 0.255 | 0.330 | 0.315 | 0.310 |
| Initial setting time (h:min) | 2:42 | 5:44 | 4:42 | 6:22 |
| Final setting time (h:min) | 4:32 | 15:54 | 11:52 | 13:41 |

O–Si were destroyed to form $[SiO_4]^{4-}$, $[AlO_4]^{5-}$ anion mass, resulting in the reduced degree of polymerization of the aluminosilicate vitreous matter of fly ash. Then, the anion mass reacted with $Ca(OH)_2$ to produce calcium aluminate hydrate and calcium silicate hydrate and resulted in improvement of the strength of the mortars at 28 and 90 days.

### 4.3. Effect of the fineness

By increasing the specific surface area of the blended cement to increase the surface energy of the cement particles, the activity of the grain improved. On the other hand, enlarging the contact surface between clinker grain and fly ash promoted the hydration between the calcium hydroxide and silicon oxide or aluminum oxide in the fly ash, thus increased the activity of the fly ash. In order to investigate the effect of the fineness on the strength of the mortars made with blended cements with high fly ash content, the blended cements were ground for different durations to achieve different finenesses. Table 4 shows that the strengths of the mortars increased at all ages with increased specific surface area.

### 4.4. Best formulations and performances of blended cement

Based on the above analyses, three blended cements with high fly ash content were chosen and their formulations are shown in Table 5. The blended cements are designated as $F_{13}$, $F_{14}$ and $F_{15}$ and they were ground for the same period of time. The blended cement $F_0$ that incorporates 20% fly ash was used as control in this part of the study.

#### 4.4.1. Flowability and strength of mortars

The values of flow and mortar strength of $F_{13}$, $F_{14}$ and $F_{15}$ are listed in Table 6. Table 6 shows that the strengths of the mortars made with blended cements with high fly ash content were lower than that of $F_0$ at ages of 3 and 7 days, except for $F_{15}$, but from 7 to 28 days, the incremental quantity, which was from 18 to 19 MPa, for blended cements $F_{13}$, $F_{14}$ and $F_{15}$ was higher than that of $F_0$, which was 12.7 MPa. This indicated that the mortars made blended cement with high fly ash content developed faster strength at later stage. Although the content of clinker in $F_{14}$ was smaller than that in $F_{15}$, the strengths of $F_{14}$ were almost the same as that of $F_{15}$ at 28 days. This is because the amount of particles smaller than 30 μm in $F_{14}$ were more than that in $F_{15}$ (see Table 8). The fact that the strengths of $F_{14}$, $F_{15}$ all exceeded the strength of $F_0$ after 7 days indicated that the CA had activated the fly ash to form much more C–S–H gel and AFt in the hydration course at later ages.

The experimental results in Table 6 also show that for similar w/c ration, the flow values of $F_{13}$, $F_{14}$ and $F_{15}$ were higher than that of $F_0$ (w/c = 0.46). It resulted from the tiny particles of fly ash which increased the flowability of mortars made blended cement with high fly ash content.

#### 4.4.2. Normal consistency and setting time of cement paste

Table 7 shows the experimental results of normal consistency and setting time of cement pastes. The standard consistency and setting time of $F_0$ were normal, but the standard consistency of $F_{13}$, $F_{14}$ and $F_{15}$ were relatively higher, and the setting times were relatively longer. This is probably due to the fact that the fly ash was porous and had lower pozzolanic activity.

#### 4.4.3. Particle sizes distribution of blended cement

The grain size distribution for fine particles that passes through the sieve with 0.077-$mm^2$ mesh size is tested by using FAM type laser hondrometer made in Shanghai, and the data are listed in Table 8.

In Table 8, the weight percentages of particles of $F_{14}$ and $F_{15}$, which were smaller than 10.0 μm in diameter or that were within the range of 3.0–30.0 μm, were higher than $F_0$, $F_{13}$. Thus, the rate of hydration and the strengths of $F_{14}$ and $F_{15}$ were higher, and the work ability was higher. While the weight percentage of particles of $F_0$, which were more than 60.0 μm in diameter, was higher, the hydration only appeared

Table 6
Flowability (mm) and strength (MPa) of cement mortars

| | | Flexural | | | Compressive | | |
|---|---|---|---|---|---|---|---|
| No. | Flow | 3 days | 7 days | 28 days | 3 days | 7 days | 28 days |
| $F_0$ | 117.0 | 3.7 | 4.0 | 6.8 | 16.4 | 21.3 | 35.0 |
| $F_{13}$ | 135.0 | 1.3 | 2.1 | 5.2 | 3.5 | 7.5 | 26.3 |
| $F_{14}$ | 124.7 | 3.5 | 4.6 | 7.5 | 13.4 | 19.4 | 38.1 |
| $F_{15}$ | 127.3 | 4.2 | 5.0 | 7.3 | 16.9 | 22.1 | 40.4 |

Table 8
Particle size–weight distribution and characteristic sizes

| | Diameters (μm) (accumulative weight (wt.%)) | | | | | Characteristic |
|---|---|---|---|---|---|---|
| No. | ≦ 90.0 | ≦ 60.0 | ≦ 30.0 | ≦ 10.0 | ≦ 3.0 | size (μm) |
| $F_0$ | 98.9 | 94.8 | 76.0 | 36.3 | 9.9 | 22.7 |
| $F_{13}$ | 98.4 | 93.4 | 73.1 | 33.9 | 9.1 | 23.1 |
| $F_{14}$ | 99.8 | 97.8 | 84.1 | 44.0 | 12.5 | 16.8 |
| $F_{15}$ | 99.2 | 95.8 | 78.3 | 38.2 | 10.5 | 20.1 |

Table 9
Chemical binding of water in blended cement (wt.%)

| Ages (days) | $F_0$ | $F_{13}$ | $F_{14}$ | $F_{15}$ |
|---|---|---|---|---|
| 3 | 9.8 | 3.3 | 7.1 | 7.9 |
| 7 | 13.2 | 6.4 | 8.7 | 9.7 |
| 28 | 12.6 | 9.5 | 11.1 | 12.7 |

on the external surfaces of bulky grains and the internal section was only used as fine aggregate.

## 5. Hydration product and pore structure

### 5.1. Chemical combined water in cement paste

The chemical combined water in blended cements was determined by method of weightlessness on ignition at 800 °C, and the data are shown in Table 9.

In Table 9, the amount of chemical combined water in all specimens increased with age. The amounts of chemical combined water of $F_{13}$, $F_{14}$ and $F_{15}$ samples were lower than that of $F_0$ at 3 and 7 days, while the amounts of chemical combined water in blended cements reached or exceeded the amounts of that in specimen $F_0$ at 28 days. This indicated that the rate of fly ash hydration was accelerated after 7 days.

### 5.2. The contents of $Ca(OH)_2$ in cement paste

The contents of $Ca(OH)_2$ in cement paste were determined by extraction, reaction and titration in the glycol and ethanol blending solution. The experimental results were illustrated in Table 10.

As shown in Table 10, the $Ca(OH)_2$ contents of $F_0$ and $F_{15}$ increased with the increase in hydration ages, which was associated with the higher amount of $C_3S$ and $C_2S$ in the blended cement, which contained much more clinker, while the $Ca(OH)_2$ contents of $F_{13}$ and $F_{14}$ were lower, and they decreased in the period from 7 to 28 days. There are two reasons for this: one is the lower contents of $C_3S$ and $C_2S$ in samples, and the other is the consumption of large amounts of $Ca(OH)_2$ in the fly ash hydration to form more hydraulic products. It indicated again that the hydration of fly ash began after 7 days under the active action of activators. This is not in line with previous investigation [1].

### 5.3. XRD analysis

Figs. 1 and 2 present the XRD patterns of specimens hydrated at 7 and 90 days, respectively. In Fig. 1, the diffraction peaks of AFt, C–S–H, $Ca(OH)_2$, $\alpha$-$SiO_2$ crystallized phases appeared in every samples hydrating at 7 days, while the diffraction peaks of dolomite also appeared in sample $F_0$. In Fig. 2, the peaks of AFt and C–S–H were higher in specimen $F_{14}$ and $F_{15}$, but the peaks of $Ca(OH)_2$ crystallites were lower than that of $F_0$ when hydrated for 90 days. These indicated that the AFt, C–S–H gel were the main hydrates and the amount of $Ca(OH)_2$ was less in the cement paste of $F_{13}$, $F_{14}$ and $F_{15}$, hydrating at 90 days.

Table 10
Contents of Ca $(OH)_2$ in cement paste

| Ages (days) | $F_0$ | $F_{13}$ | $F_{14}$ | $F_{15}$ |
|---|---|---|---|---|
| 3 | 5.7 | 2.0 | 3.0 | 4.9 |
| 7 | 6.2 | 1.9 | 4.7 | 4.9 |
| 28 | 8.3 | 1.2 | 4.1 | 5.8 |

### 5.4. Pore structure

The volume of pores in the hardened cement paste decreased gradually with the hydration of clinker. During the course, the structure of the paste becomes more and more dense, and the strength has improved in varying degrees too; however, the various sizes of pores exist at all hydration ages, such as large spherical pores, capillary pores, micro pores and gel pores. The effects of large spherical pores and capillary pores on the strength and permeability of hardened cement paste is higher [2]. The pore structure of blended cement and controlled cement $F_0$ are given in Table 11 and in Figs. 3–6 (the median pore diameter and average pore diameter were designated as MPD and APD, respectively). The relationship

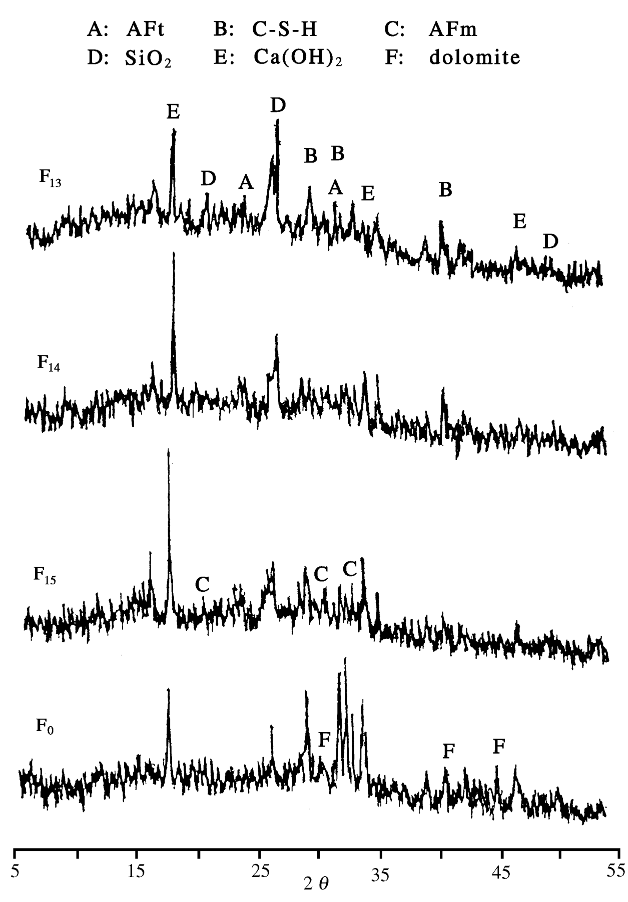


Fig. 1. XRD patterns of the cement pastes at 7 days.

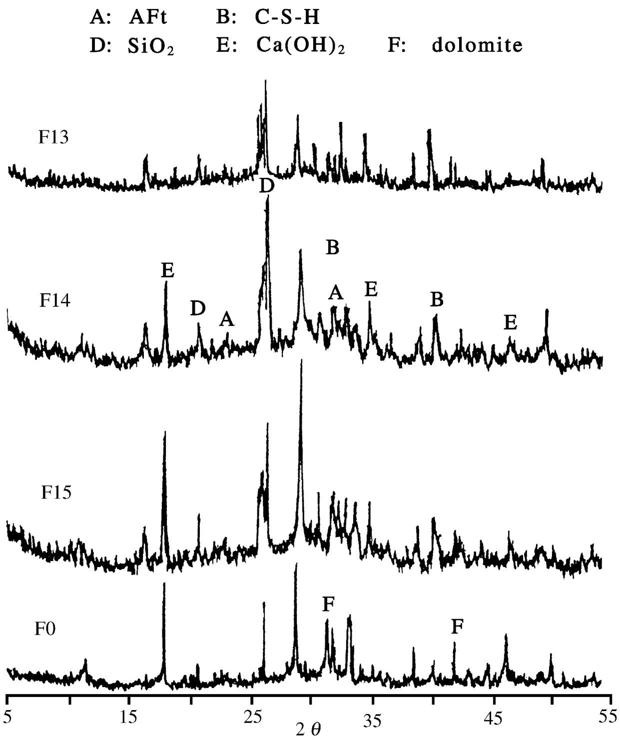


Fig. 2. XRD patterns of the cement pastes at 90 days.

between pore structure and properties of cements could be described as follows.

(1) In Table 11, the total porosity, MPD and APD in $F_{13}$, $F_{14}$ and $F_{15}$ hardened cement pastes decreased with increasing hydration time, which corresponded with the increase of compressive strength.

(2) In Figs. 3 and 4 and in Table 11, the porosities, MPD and APD of blended cement pastes were higher than that of $F_0$ when hydrated for 3 and 7 days, resulting in the lower early strength, yet the volume porosities of capillaries having diameters more than 0.1 μm were lower than $F_0$.

(3) In Figs. 5 and 6 and in Table 11, although the total porosities of blended cement pastes were higher than that of $F_0$, generally the data were lower, such as MPD, APD and the volume porosities of capillaries, but the volume porosities of gel pores were higher. All these results implied that the blended cements possessed higher permeability resistance and durability. Besides, it indicated that the rate of fly ash hydration accelerated after 7 days, and more calcium silicate hydrate and calcium trisulphoaluminate hydrate were produced. Therefore, the connecting pores were obstructed and filled up by hydrates, leading to the decrease of porosity, MPD and APD in blended cement.

Based on the analysis of all the results, the total porosities of blended cement pastes was higher than that of sample $F_0$. Nevertheless, because of hydration of fly ash, the volume porosities of capillaries, MPD and APD were much lower, and the volume porosities of gel pores were much higher, especially after 7 days, which signified the higher permeability resistance and higher later age strength.

## 6. The mechanism analysis of hydration

When fly ashes cement is mixed with water [3,7], cement clinker minerals hydrate first, to release $Ca(OH)_2$ crystal, producing the alkalinity solution. Then the active compound of fly ash reacts with $Ca(OH)_2$ to produce the calcium silicate hydrate and calcium aluminate hydrate, resulting in the content of $Ca(OH)_2$ in the solution to be reduced, thus the hydration of cement clinker is accelerated. The later hydration reaction equation is shown as:

$$x\,Ca(OH)_2 + SiO_2 + nH_2O = x\,CaO \cdot SiO_2 \times (n+x)H_2O \quad (1)$$

$$x\,Ca(OH)_2 + Al_2O_3 + mH_2O = x\,CaO \cdot Al_2O_3 \cdot (m+x)H_2O \quad (2)$$

In the formula: $x \leq 3$,

$$3Ca(OH)_2 + Al_2O_3 + 2SiO_2 + mH_2O = 3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot (m+3)H_2O \quad (3)$$

In the condition of existing gypsum, the calcium aluminate hydrate reacts further ahead to produce AFt or AFm (Eqs. (4) and (5)):

$$Al_2O_3 + 3Ca(OH)_2 + 3CaSO_4 + 29H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (4)$$

$$Al_2O_3 + 3Ca(OH)_2 + CaSO_4 + 9H_2O = 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \quad (5)$$

However, the porous vitreous sphere of fly ash is relatively stable, the depolymerization speed of the structure

Table 11
The porosity (%), MPD (Å) and APD (Å) of cement paste

| | 3 days | | | 7 days | | | 28 days | | | 90 days | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Porosity | MPD | APD | Porosity | MPD | APD | Porosity | MPD | APD | Porosity | MPD | APD |
| $F_0$ | 24.5 | 89 | 232 | 23.4 | 130 | 258 | 21.3 | 135 | 230 | 15.0 | 352 | 327 |
| $F_{13}$ | 37.8 | 330 | 564 | 35.2 | 225 | 358 | 33.6 | 96 | 154 | 31.7 | 86 | 123 |
| $F_{14}$ | 33.2 | 159 | 290 | 31.0 | 170 | 264 | 26.0 | 72 | 127 | 27.0 | 73 | 118 |
| $F_{15}$ | 32.5 | 142 | 260 | 29.2 | 141 | 231 | 24.0 | 66 | 123 | 23.1 | 65 | 109 |

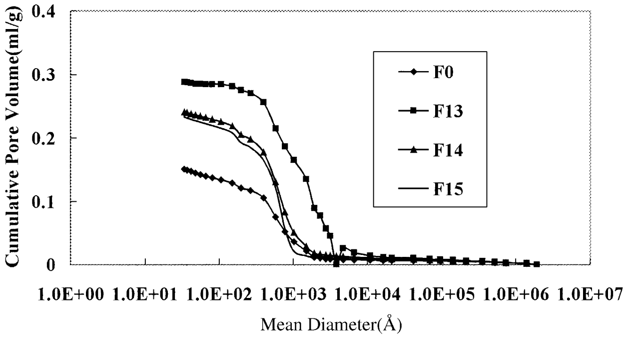


Fig. 3. Pore size distribution at 3 days.

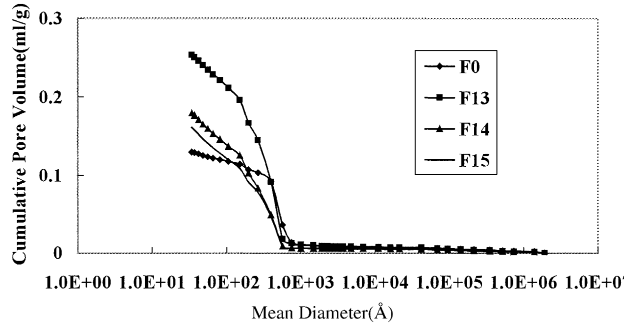


Fig. 5. Pore size distribution at 28 days.

is relatively slow under the action of $Ca(OH)_2$. If the amount of fly ash is relatively higher, the strength of the cement is relatively lower and the setting of the cement is very slow.

When the sizes of most grains of fly ash are smaller than 30 μm through the fineness grinding, its surface structure is broken to promote its activity. By using $Na_2CO_3$ as activator, the alkalinity of solution is increased [4,5], the surface structure of fly ash grain is gradually depolymerized to release the ion masses of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, which acts later with $Ca^{2+}$ to form calcium silicate hydrates of lower Ca/Si ratio and calcium aluminate hydrate according to the reactions (1)–(3). Then the latter hydrates react with gypsum to form the calcium sulphoaluminate hydrate. These products have a very important effect on sticking of cement particles, packing pores and slight expansion of the hardened cement paste. After 7 days, the surface of fly ash grain was covered with a thin layer of C–S–H gel, and ettringite (AFt) and AFm filled in pores, resulting in the increasing amount of chemical combined water, and the total amount of $Ca(OH)_2$ in the system was small. Correspondingly, the volume porosities connecting large pores which were bigger than 0.1 μm in diameter also reduced, while the gel pores and micro pores which were smaller than 0.05 μm in diameter increased, leading to the improvement properties of blended cement [6]. Constantly producing AFt at 7 days, even at 28 days also resulted in the further increment of densification and slight expansion of the structure.

The molasses is a surfactant, as it is absorbed on the surface of $C_3A$, a film forms, and the reaction rate with water molecule is reduced. Thus, the hydration rate of cement grains drops, and the setting is slowed down, the early-strength improvement of cement paste is not significant. This is confirmed by experimental results.

Based on the above analysis, the grains of fly ash depolymerize constantly to release the ion mass of $[SiO_4]^{4-}$, $[AlO_4]^{5-}$, which react with $Ca^{2+}$ and $SO_4^{2-}$ to form the hydration products of C–S–H gel and AFt, with the presence of $Ca(OH)_2$, $Na_2CO_3$ and gypsum. The C–S–H gel has a lower ratio of Ca/Si in the surface of fly ash, and draws all kinds of species in the system together tightly. Meanwhile the ettringite packs the hole, making the pores smaller and total porosity of the hardened cement paste is getting lower and lower. Thus, the hardened cement paste has a more dense structure and its performance is improved.

## 7. Conclusions

(1) The influences of the amount of fly ash on properties of blended cement is greater with the increasing amount of fly ash. The early strength of the blended cement with high fly ash content decreases significantly and its setting is relatively slow. Nevertheless, the CA improve the strength of cement at 28 days and 90 days considerably. Activators destroy the glass pearl surface structure of fly ash to dissolve the $[SiO_4]^{4-}$, $[AlO_4]^{5-}$ ion mass, and accelerate the hydration of fly ash grain. Meanwhile, the accumulated weight percentage of particles that was smaller than 30 μm in

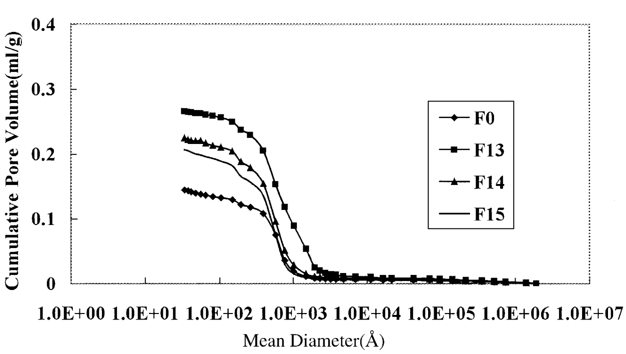


Fig. 4. Pore size distribution at 7 days.

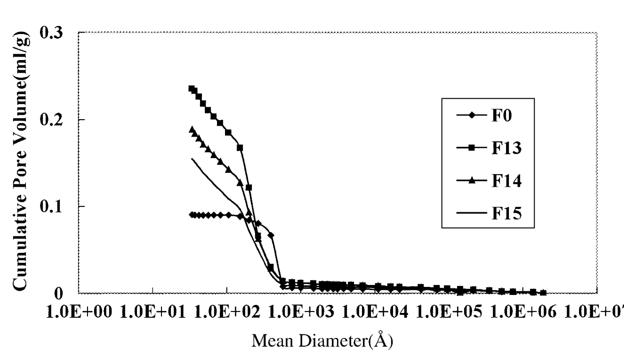


Fig. 6. Pore size distribution at 90 days.

diameter is more than 70%. These factors enhance the properties of blended cement.

(2) The amount of chemical combined water for the blended cement with high fly ash content is relatively small at initial stage, but with the increase of hydration age, a large amount of fly ash begins to hydrate and more hydration products are produced. The amount of chemical binding of water reaches or exceeds the amount for the blended cement $F_0$ (blended cement incorporating 20% of fly ash)at 28 days, while the content of $Ca(OH)_2$ is relatively small for the blended cement with high fly ash content, which shows a tendency to decrease in quantity after 7 days.

(3) The XRD patterns indicate that the main hydration products for the blended cement are C–S–H gel, ettringite and a small amount of $Ca(OH)_2$.

(4) Total porosity, MPD and APD for the blended cement with high fly ash content is higher than that for the blended cement $F_0$ at early stage. But after 7 days, the MPD, APD and the volume porosities of capillaries, which are more than 0.1 μm in diameter, are lower, and the volume porosities of gel pores are higher than that for $F_0$.

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