



## Activation of fly ash/cement systems using calcium sulfate anhydrite ( $\text{CaSO}_4$ )

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### Abstract

A number of studies had been conducted on the activation of fly ash using gypsum and sodium sulfate. Anhydrite, another form of calcium sulfate, has not been used for this purpose. This paper presents an exploratory study on the effectiveness of anhydrite in activating fly ash cement systems. Anhydrite (10%) was added into cement mortars with up to 55% fly ash replacement. The prepared mortars were allowed to cure in steam at 65°C for 6 h before normal room temperature water curing. Significant strength increases (up to 70%) compared to the control mortars were observed as early as after 3 days curing. Improvements in the pore size distribution of the mortars were also observed due to the activation. The results of scanning electron microscopy (SEM) examination and quantitative X-ray diffraction (XRD) analysis show that, with accelerated curing, a large quantity of ettringite (Aft) was formed during the early stage of hydration of the anhydrite-activated fly ash cement pastes. This might be the main cause of the high early strength of the activated fly ash cement systems. A comparison was made using anhydrite and gypsum as activators. For an equivalent  $\text{SO}_3$  content, anhydrite is more effective in increasing the early-age strength of the cement/fly ash mortars, but less effective in increasing the later-age strength than gypsum. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Acceleration; Fly ash; Anhydrite; Compressive strength; Pore size distribution

### 1. Introduction

Fly ash is a by-product of coal-fired electric power stations. It lowers the heat of hydration and improves the durability when used in concrete as a cement replacement. It also contributes to concrete strength by pozzolanic and filler effects. Recently, fly ash has been increasingly used in the concrete industry. In some cases, large volume of (>40%) fly ash is used to achieve desired concrete properties and lower the cost of concrete production. However, as pozzolanic reaction is a slow process that its contribution to strength occurs only at later ages, the early strength of concrete will be significantly reduced if a large amount of fly ash is used.

Different approaches are used to accelerate the pozzolanic reaction of fly ash and therefore increase the early strength of the concrete containing fly ash. These ap-

proaches include (i) mechanical treatment (grinding) [1–3], (ii) accelerated curing and autoclaving [4,5], and (iii) chemical activating [6–11].

A number of studies had been carried out on the activation of fly ash using chemical activators. These studies involved using different activating methods including alkali activation and sulfate activation. The former involved the breaking down of the glass phases in an elevated alkaline environment to accelerate the reaction [8,12]. The latter is based on the ability of sulfates to react with aluminum oxide in the glass phase of fly ash to produce ettringite (Aft) that contributes to the strength at early ages [8,10,11]. With respect to sulfate activation, the use of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) had been well studied [8–11]. Xu and Sarkar [8] reported that the addition of 3% to 6% gypsum resulted in a distinct increase in strength for the cement pastes containing 30% to 60% low calcium fly ash. Shi [10,11] compared the effectiveness of  $\text{Na}_2\text{SO}_4$  and  $\text{CaCl}_2$  as chemical activators and found that the former increased the early strength while the latter increased the later strength of the lime–fly ash pastes. However, the

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Table 1  
Chemical composition of cement, fly ash, anhydrite and gypsum

Materials	Composition (%)						
	Loss on ignition	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>
Cement	2.97	19.61	3.32	7.33	63.15	2.54	2.13
Fly ash	3.90	56.79	5.31	28.21	<3	5.21	0.68
Anhydrite	7.53	1.88	0.02	0.04	37.94	1.57	51.0
Gypsum	–	–	–	–	–	–	>43

use of calcium sulfate anhydrite (also named anhydrite, CaSO<sub>4</sub>) for activating fly ash has not been studied.

This paper presents an exploratory study on the activation of fly ash cement systems using anhydrite with accelerated curing. The strength and microstructure developments of the fly ash mortars and pastes are investigated. A comparison is then made between anhydrite and gypsum in terms of their effectiveness in activating fly ash cured under the same curing conditions.

## 2. Experimental details

### 2.1. Materials

The cementitious materials used were Portland cement equivalent to ASTM Type I and low-calcium fly ash equivalent to ASTM Class F, both commercially available in Hong Kong. The activators were natural anhydrite and gypsum obtained from China. They were ground in a mortar to pass through a 150- $\mu$ m sieve. The sand used to prepare the mortars was natural river sand obtained from China. The chemical and physical properties of the cement, fly ash, anhydrite and gypsum are given in Tables 1 and 2.

### 2.2. Fly ash cement mortars and pastes

All cement mortars were prepared with a water-to-binder (cement + fly ash) ratio of 0.3 and a sand-to-binder ratio of 1.5. These mortars contained 0% to 55% fly ash replacements based on the total weight of cement and fly ash, with or without the addition of chemical activators. When anhydrite was added as the activator, its amount was kept

Table 2  
Physical properties of cement, fly ash and anhydrite

Properties	Materials		
	Cement	Anhydrite	Fly ash
Density	3.16	2.91	2.31
Specific surface area (cm <sup>2</sup> /g)	3519.5	12503.2	3960

at 10% of the total weight of cement and fly ash, except for the mortars with 35% fly ash, in which varied amounts of anhydrite gypsum from 6% to 14% were used. The cement mortars with the addition of 10% gypsum as the activator were also prepared for 35% and 55% fly ash replacements for comparison. The cement mortars without any activators were prepared as the control mortars. These mortars were used for compressive strength determinations and mercury intrusion porosimetry (MIP).

In addition to the mortars, two fly ash cement pastes with, respectively, 35% and 55% fly ash, and additional 10% anhydrite were prepared for scanning electron microscopy (SEM) examination and X-ray diffraction (XRD) analysis.

### 2.3. Mixing, casting, curing and compression test

The mortars and pastes were mixed in a mechanical mixer. Cube specimens 70.7  $\times$  70.7  $\times$  70.7 mm were cast in steel molds and compacted on a vibrating table. The cubes were removed from the moulds 24 h after casting. They were then subjected to either normal water curing or accelerated curing. For normal water curing, the cubes were cured at 27°C till the ages of 3, 7, 28 and 90 days. For accelerated curing, the cubes were initially cured in a steam bath at 65°C for 6 h. Additionally, for the mortars prepared with 35% fly ash and 10% anhydrite, the temperature of the initial steam curing step was varied from 45°C to 85°C, and the duration of the initial steam curing step was varied from 4 to 12 h, to explore the effects of different initial curing conditions on the strength development. After the initial steam curing and cooling down to room temperature, the cubes were allowed to be cured in water at 27°C until the ages of 3, 7, 28 and 90 days. Compressive strength test was performed on the mortar samples using a Denison compression machine.

Table 3  
Summary of experimental program

Series	Type of sample	Description			Tests
		Fly ash replacement	Activator	Curing conditions	
1	Mortar	0–55%	non	water at 27°C	compressive strength
2	Mortar	0–55%	non	steam at 65°C for 6 h and then water at 27°C	compressive strength, MIP
3	Mortar	15–55%	10% anhydrite	steam at 65°C for 6 h and then water at 27°C	compressive strength, MIP
4	Mortar	35%	0–14% anhydrite	steam at 65°C for 6 h and then water at 27°C	compressive strength
5	Mortar	35%	10% anhydrite	steam at 45–85°C for 6 h and then water at 27°C	compressive strength
6	Mortar	35%	10% anhydrite	steam at 65°C for 4–12 h and then water at 27°C	compressive strength
7	Mortar	35% and 55%	10% gypsum	steam at 65°C for 6 h and then water at 27°C	compressive strength, MIP
8	Paste	35% and 55%	10% anhydrite	steam at 65°C for 6 h and then water at 27°C	SEM, XRD

Table 4

Compressive strength of the mortars without any activator (cured in water at 27°C)

Fly ash (%)	Compressive strength (MPa)			
	3 days	7 days	28 days	90 days
0	68.3	83.1	100.1	115.0
15	65.9	77.4	99.2	116.7
25	57.2	71.2	93.9	119.9
35	49.8	60.3	81.4	106.3
45	37.4	59.3	82.0	101.2
55	25.9	36.1	66.5	88.5

#### 2.4. Mercury intrusion porosimetry

The samples for the MIP measurements were obtained from the crushed mortar cubes after compression testing. The fragments of mortars were soaked in acetone for at least 7 days to stop further hydration. They were dried in an oven at 60°C for 24 h before MIP measurements by a “Pore Sizer 9320” mercury intrusion porosimeter with a maximum mercury intrusion pressure of 210 MPa. Cylindrical pore geometry and a contact angle  $\theta$  of 140° were assumed [13,14]. The mercury intruded pore diameter  $d_p$  at an intrusion pressure of  $P_{in}$  was calculated by  $d_p = -4\gamma \cos \theta / P_{in}$ , where  $\gamma = 0.483 \text{ Nm}^{-1}$ , the surface tension of mercury [14].

#### 2.5. Scanning electron microscopy

The paste cubes at specified ages were cut into small fragments and then soaked in acetone for more than 7 days to stop the hydration of cement and fly ash. The samples were freeze-dried using a procedure described by Shi and Day [15]. The dried samples were stored in a sealed container before use. A Cambridge Stereoscan 150 Scanning Electron Microscope with a magnification ranging from  $20\times$  to  $100,000\times$  was employed to study the morphology of the cement pastes.

#### 2.6. Determination of AFt by XRD analysis

For XRD analysis, the freeze-dried paste samples, as prepared for SEM examination, were further ground in a mortar to pass through a 150- $\mu\text{m}$  sieve. XRD analysis was performed using a D/Max-III A (Japan) (35 kV and 30 mA)

Table 5

Compressive strength of the mortar mixes without any activator (cured in steam at 65°C for 6 h and then in water at 27°C)

Fly ash (%)	Compressive strength (MPa)			
	3 days	7 days	28 days	90 days
0	75.7	87.7	103.7	116.9
15	68.3	81.3	99.7	117.5
25	61.3	76.5	89.8	120.9
35	54.2	63.6	85.0	109.2
45	42.7	52.8	79.5	101.1
55	30.4	41.2	70.4	89.0

Table 6

Compressive strength of the mortar mixes with addition of 10% anhydrite (cured in steam at 65°C for 6 h and then in water at 27°C)

Fly ash (%)	Anhydrite (%)	Compressive strength (MPa)			
		3 days	7 days	28 days	90 days
15	10	79.99	89.45	109.15	123.30
25	10	72.06	85.37	104.80	122.83
35	10	66.03	78.62	103.50	114.80
45	10	54.29	69.63	92.01	106.78
55	10	51.60	64.92	80.86	99.39

on a Scintag XDS 2000 diffraction equipped with a graphite monochromator. The XRD scanner was run at a  $2\theta$  of 0.02° per step, and with a counting time of 2 s.

The AFt content in paste samples was determined using a  $K$ -value method. The  $K$  value is defined by Eq. (1)

$$K = I_{\text{CaF}_2} / I_{\text{AFt}} \quad (1)$$

where  $I_{\text{CaF}_2}$  = XRD integral intensity of  $\text{CaF}_2$ , and  $I_{\text{AFt}}$  = XRD integral intensity of pure AFt, both of which were measured from an equal weight mixture of AR grade  $\text{CaF}_2$  and AFt. The AFt was prepared by the following procedure: 1 l of saturated  $\text{Ca}(\text{OH})_2$  solution (1.2 g CaO per liter) was diluted to 1.2 l and was then mixed thoroughly with 530 ml of saturated  $\text{CaSO}_4$  solution (2.05 g  $\text{CaSO}_4$  per liter). To this mixture, a solution of 1.78 g of  $\text{Al}_2(\text{SO}_4)_3$  in 770 ml of water was added. The final mixture was shaken at 18°C until all the initially precipitated gel was replaced by crystallized materials [15].

To determine the AFt content in the sample, the ground paste sample and  $\text{CaF}_2$  were thoroughly mixed in the proportion of 9:1 by weight. The AFt content in the samples is given by Eq. (2)

$$W_i = K \times \frac{I_i}{I_s} \times \frac{W_s}{1 - W_s} \times 100\% \quad (2)$$

where  $W_i$  = AFt content of paste sample (%),  $I_i$  = XRD integral intensity of AFt of the sample/ $\text{CaF}_2$  mixture,

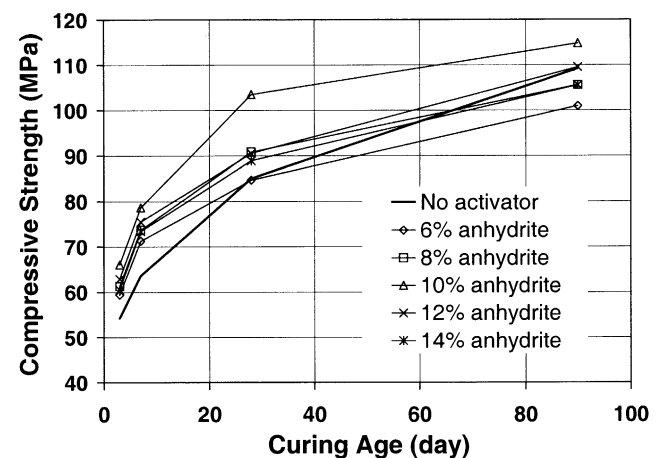


Fig. 1. Effect of different anhydrite contents on the compressive strength of the mortar mixes with a 35% fly ash replacement (cured in steam at 65°C for 6 h and then in water at 27°C).

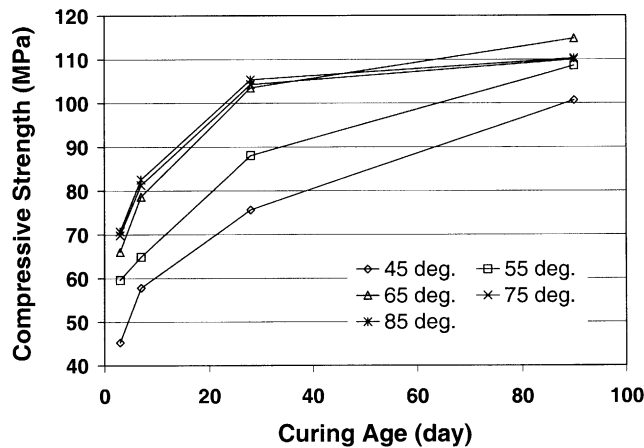


Fig. 2. Effect of initial steam curing temperature on the compressive strength of the mortar mixes with 35% fly ash and 10% anhydrite (cured in steam at different temperature for 6 h and then in water at 27°C); \* the reference mix that contained no activator was subject to normal water curing only.

$I_s$  = XRD integral intensity of  $\text{CaF}_2$  of the sample, and  $W_s$  =  $\text{CaF}_2$  content in the sample/ $\text{CaF}_2$  mixture.

A summary of the experimental program is given in Table 3.

### 3. Results and discussion

#### 3.1. Compressive strength development

To quantify the effect of initial steam curing on strength development, the results of the compressive strength test of the mortars without any activator, with or without initial steam curing are first presented in Tables 4 and 5. The compressive strength data of the mortars with the addition of anhydrite, and with an initial

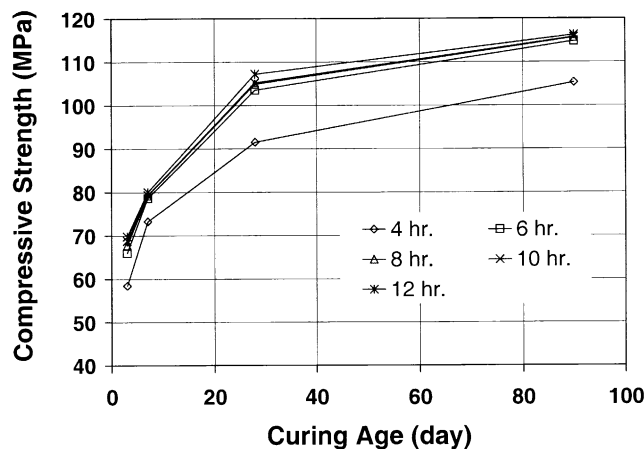


Fig. 3. Effect of different initial steam curing time on the compressive strength of the mortar mixes with 35% fly ash replacement and 10% anhydrite (cured in steam at 65°C for 6 h and then in water at 27°C).

Table 7

Average pore diameters of the fly ash cement mortars with and without anhydrite (cured in steam at 65°C for 6 h and then in water at 27°C)

Fly ash (%)	Anhydrite (%)	Average pore diameter (μm)			
		3 days	7 days	28 days	90 days
0	0	0.0413	0.0406	0.0397	0.0389
35	0	0.0369	0.0343	0.0252	0.0224
55	0	0.0349	0.0334	0.0246	0.0219
35	10	0.0358	0.0322	0.0252	0.0201
55	10	0.0293	0.0246	0.0238	0.0189

steam curing step followed by water curing are presented in Table 6. All the compressive strength data presented are the average of three measurements.

It can be observed that from Table 4 the compressive strengths of the mortars without the initial steam curing step were significantly reduced with increasing fly ash content. The 3-day compressive strength of the mortar with 55% fly ash was only 38% of the mortar without fly ash. An initial steam curing of 6 h at 65°C, as shown in Table 4, increased the 3-days compressive strength of the fly ash mortars by 4% to 17%, but did not significantly affect the strength of the mortars at later ages. Thus, the beneficial effect of initial elevated temperature curing on the compressive strength development of the fly ash mortars without the addition of any activator is limited.

Compared with the results of the fly ash mortars without any activator (control mortars, see Table 5), the early-age compressive strength of the fly ash mortars was significantly increased when anhydrite (the activator) was added. Table 6 shows that the addition of 10% anhydrite increased the 3-day compressive strength from 17% to 70% for the mortar with 15% to 55% fly ash. It also resulted in 11% increase in the 90-day compressive strength for the mortar with 55% fly ash. Generally, the activating effect of adding anhydrite is more significant for early-age strength and for mortars with high fly ash contents, but is relatively insignificant for later-age strength and for mortars with low fly ash content.

The effects of different anhydrite contents and different initial steam curing conditions on the compressive strength development of the mortars were also investigated. In Fig. 1, a comparison is made for the mix without any activator and the mixes with different anhydrite contents. It can be found that for the mortars with a

Table 8

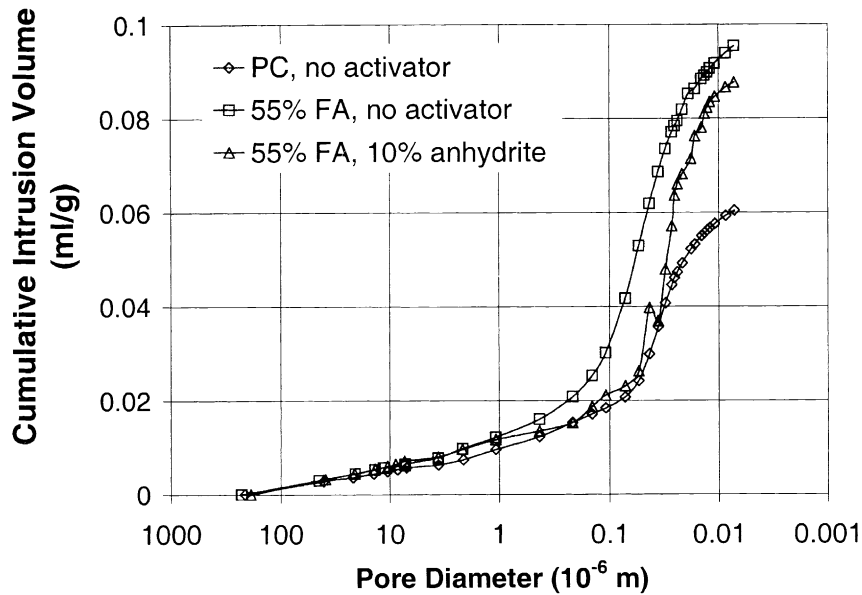
Porosity of the fly ash cement mortar mixes with and without anhydrite (cured in steam at 65°C for 6 h and then in water at 27°C)

Fly ash (%)	Anhydrite (%)	Porosity (% v/v)			
		3 days	7 days	28 days	90 days
0	0	12.44	12.32	10.61	9.15
35	0	17.04	15.04	13.15	10.76
55	0	19.92	18.14	17.58	12.92
35	10	16.44	14.64	12.34	10.31
55	10	19.10	17.58	14.25	12.31

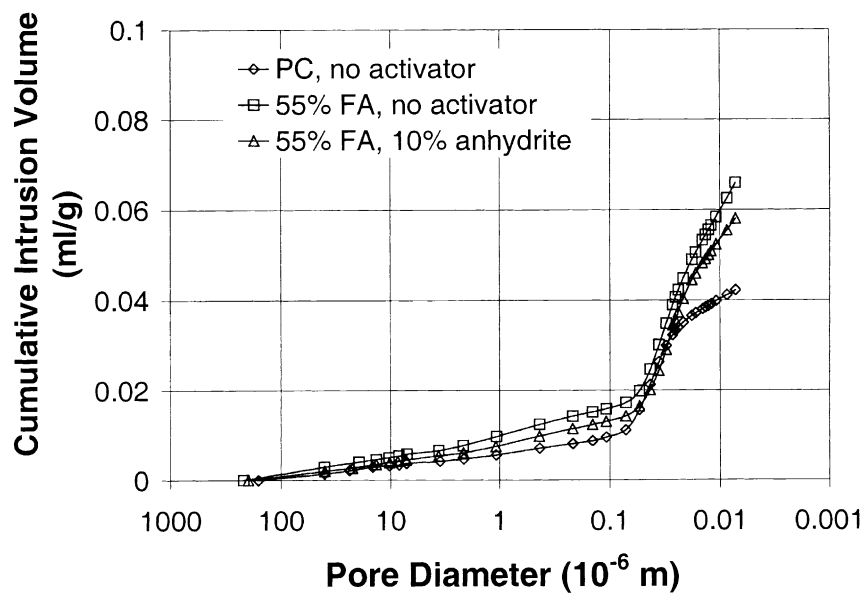
35% fly ash replacement, the optimal addition of anhydrite is 10%. Lower anhydrite contents increased the strength at 3 and 7 days, but resulted in lower strength at 90 days. When the anhydrite content was increased to 10%, both the early- and later-age strengths were increased. But further increasing the anhydrite content beyond 10% decreased the strength.

The effect of different initial curing temperatures on the compressive strength development of the mortars with

35% fly ash and 10% anhydrite is shown in Fig. 2. The duration of steam curing was 6 h. Fig. 2 shows that with an initial steam curing at 45°C, the addition of anhydrite did not result in any increase in the strength when compared with the reference mortar with the same fly ash content but without any activator under normal curing (see Table 4). The activating effect of anhydrite was observable only for curing at higher temperatures. Thus, an elevated curing temperature is necessary and essential.



(a)



(b)

Fig. 4. Pore size distribution of the cement mortar mixes with and without 10% anhydrite (cured in steam at 65°C for 6 h and then in water at 27°C): (a) at 3 and (b) 90 days.

It can be noticed that the initial curing temperature of 65°C achieved the best results in terms of the strength at both early and later ages.

The effect of initial curing time on the compressive strength was studied for the mortar with 35% fly ash and 10% anhydrite. The temperature of steam curing was 65°C. Fig. 3 shows that a 6-h initial curing was sufficient. Prolonging the initial curing did not significantly increase the compressive strength.

### 3.2. Pore size distribution

The pore size distribution of the anhydrite-activated fly ash cement mortars was determined using MIP. The results are summarized in Tables 7 and 8, which are the average of two measurements. Typical pore size distribution of the fly ash cement mortars with and without addition of anhydrite is shown in Fig. 4.

Tables 6 and 7 show that for all the samples the average pore diameters and the mercury intruded porosity decreased as the curing age increased. Fly ash replacements reduced the average pore size and increased the porosity. The observations are consistent with our previous results [16] on the pore size distribution of the fly ash cement pastes and mortars subjected to normal curing and without the addition of any activators.

It can be noticed from Tables 7 and 8 that both the porosity and the average pore diameter were smaller for the mortars prepared with 10% anhydrite than for those without the activator for all fly ash replacement levels and all curing ages. This observation also suggests that the addition of anhydrite is effective in activating fly ash cement systems.

### 3.3. SEM observations

The microstructure morphology of the anhydrite-activated fly ash cement pastes was studied by SEM. The pastes

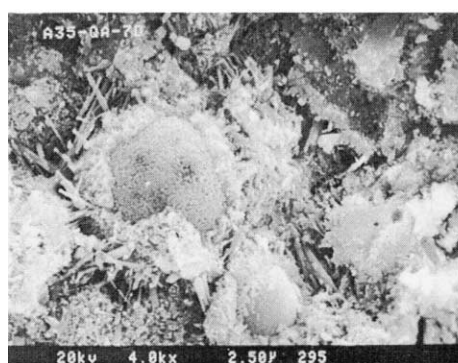
were prepared with fly ash replacement levels of 35% and 55%, with the addition of 10% anhydrite. The pastes were cured in steam at 65°C for 6 h and then in water at 27°C.

Typical morphology of the hydration products of the anhydrite-activated fly ash/cement pastes are shown in Fig. 5a and b. Fig. 5a shows that in a paste with 35% fly ash and 10% anhydrite at 7 days, the surfaces of the fly ash particles were covered with a layer of hydration products, some of which had the needle-like morphology. Fig. 5b shows that in a paste with 55% fly ash and 10% anhydrite, a large quantity of needle-like hydration products was found. Similar morphology was also observed for the anhydrite-activated fly ash/cement pastes at the later ages, except that the microstructures of the pastes were less porous and denser. According to Shi [10,11], who studied the microstructure of Na<sub>2</sub>SO<sub>4</sub>-activated lime–fly ash pastes cured at 50°C, the needle-like hydration products was identified as Aft.

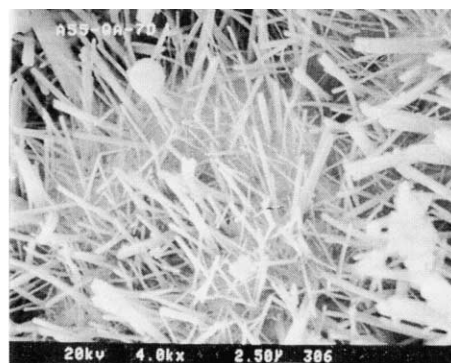
### 3.4. XRD analysis

The hydration products of the anhydrite-activated fly ash/cement pastes were also studied using XRD analysis. For the pastes without the addition of any activator, no Aft peak could be identified with accelerated curing. For the pastes with the addition of 10% anhydrite with the same curing condition, a strong Aft peak was observed.

The results of quantitative XRD analysis (Figs. 6 and 7) show that Aft was found in the pastes with 10% anhydrite, with or without fly ash replacements when subject to accelerated curing. The Aft content in the PC paste containing no fly ash was 14.6% at 3 days. The Aft contents in the fly ash pastes were higher than in the PC paste. Fig. 6 shows an increasing trend of the Aft content with increasing fly ash contents. With prolonged curing, the Aft content in the paste with a relative low fly ash content (35%) slightly increased, but that in the paste with 55% fly ash replacement reached the maximum at 7 days and decreased at 28 and 90 days (Fig. 7).



(a)



(b)

Fig. 5. Morphology of the hydration products in anhydrite-activated fly ash/cement pastes (cured in steam at 65°C for 6 h and then in water at 27°C): (a) with 35% fly ash at 7 days and (b) with 55% fly ash at 7 days.

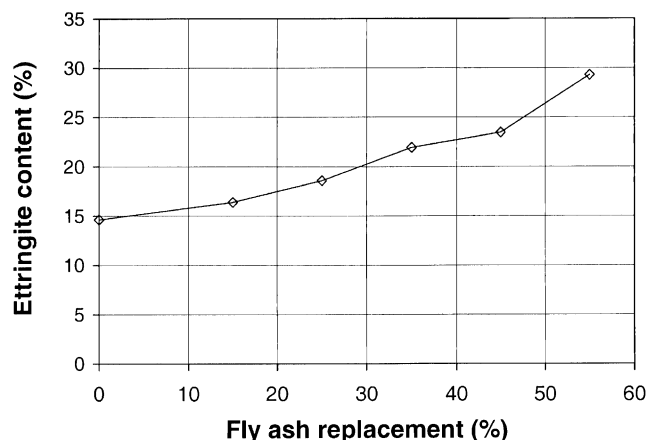


Fig. 6. AFt content of the fly ash cement pastes with 10% anhydrite and with different fly ash contents at the age of 3 days (cured in steam at 65°C for 6 h and then in water at 27°C).

Xu and Sarkar [8] reported that with the addition of 6% gypsum and subjection to normal water curing, AFt was formed at a rather slow rate in a cement paste with 60% fly ash replacement. They indicated that AFt only became distinguishable in both XRD and SEM studies after 90 days of curing. However, according to Shi [10,11], AFt was observed in 1-day-old  $\text{Na}_2\text{SO}_4$ -activated lime–fly ash pastes with accelerated curing at 50°C. In the present study, with an initial curing at 60°C, the majority of the AFt in the anhydrite-activated fly ash/cement pastes had been formed in the first 3 days. Thus, accelerated curing at elevated temperature is important for AFt crystals to be formed in sulfate-activated fly ash/cement (or lime) systems. This is consistent with the compressive strength test results of the present study. Shi [11] indicated that the main hydration product in the  $\text{Na}_2\text{SO}_4$ -activated lime–low calcium fly ash pastes was AFt and that the rapid consumption of  $\text{Ca}(\text{OH})_2$  and the formation of AFt contributed to the strength of the

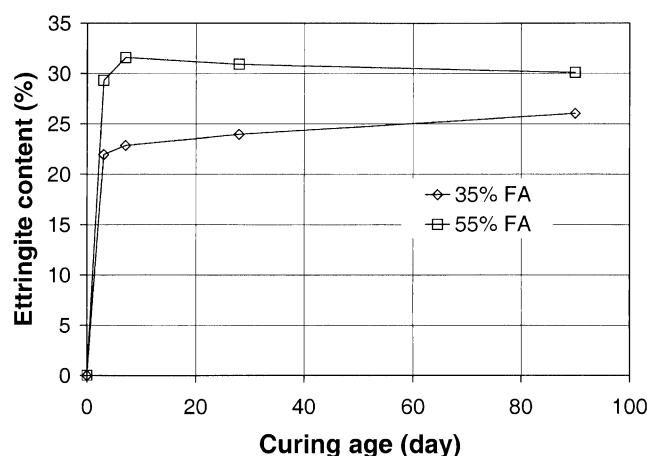
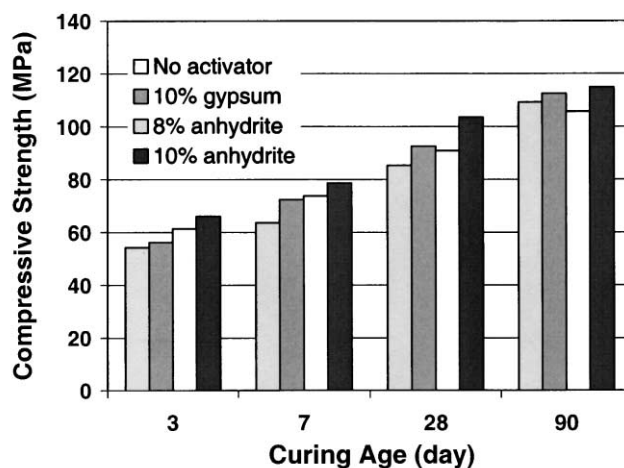


Fig. 7. AFt content of the fly ash cement pastes with 35% and 55% fly ash and with 10% anhydrite at different ages (cured in steam at 65°C for 6 h and then in water at 27°C).

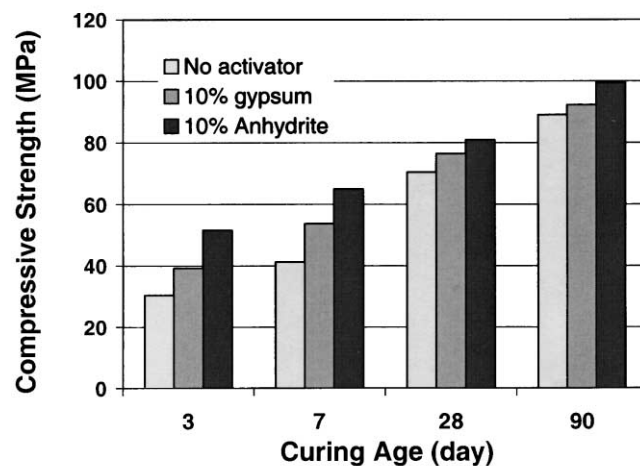
lime–fly ash pastes. This mechanism also may be applicable to the present study. The formation of large quantity of AFt during the early stage of hydration may be the main cause of the high early strength of the anhydrite-activated fly ash/cement systems.

### 3.5. Comparison with gypsum

In this study, fly ash cement mortars with an addition of 10% gypsum were also prepared. Their compressive strength and pore size distributions were compared with those prepared with the addition of anhydrite. Gypsum contains two molecules of combined water and therefore has a lower  $\text{SO}_3$  content compared to anhydrite (46.5%  $\text{SO}_3$  in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  vs. 58.8%  $\text{SO}_3$  in  $\text{CaSO}_4$ ). In terms of equivalent  $\text{SO}_3$ , a 10% addition of the gypsum is approximately equal to an 8% addition of the anhydrite.



(a)



(b)

Fig. 8. Comparison of the compressive strength of the fly ash cement mortars prepared with anhydrite and gypsum: (a) mortars with 35% fly ash and (b) mortars with 55% fly ash.

Table 9

Average pore diameters and porosity of mortar mixes with 10% gypsum (cured in steam at 65°C for 6 h and then in water at 27°C)

Fly ash (%)	Average pore diameter ( $\mu\text{m}$ )				Porosity (%)			
	3 days	7 days	28 days	90 days	3 days	7 days	28 days	90 days
35	0.0394	0.0346	0.0259	0.0224	16.78	15.07	12.76	10.42
55	0.0348	0.0329	0.0238	0.0215	19.25	17.85	14.43	12.51

Fig. 8a shows that for a 35% fly ash replacement, the compressive strength of the mortar with 8% anhydrite was higher at 3 and 7 days, but lower at 28 and 90 days than the mortar with 10% gypsum. It can be noticed from Fig. 8b that for a 55% fly ash replacement, 10% anhydrite increased the compressive strength by, respectively, 70% and 58% at the ages of 3 and 7 days. However, the addition of 10% gypsum increased the strength by only 21% and 23% at the same ages. These observations indicate that when comparison is made in terms of an equivalent  $\text{SO}_3$  content, anhydrite is more effective in increasing the early-age strength, but less effective in increasing the later-age strength than gypsum. The cause of such improvement is unclear and needs further investigation.

Table 9 shows the average pore diameter and porosity of the mortars with 10% gypsum. Both the average pore diameter and porosity of the mortars are smaller than those of the mortars without any activator but are slightly larger than those of the mortars with 10% anhydrite (Tables 7 and 8).

#### 4. Summary and conclusions

The effectiveness of anhydrite in activating fly ash cement systems has been investigated. An addition of 10% anhydrite increased the 3-day compressive strength by about 70% for the mortar with up to 55% fly ash. It also increased the strength at the later ages of these mortars. These were achieved with a short period of initial curing at an elevated temperature (65°C) before normal water curing. The activating effect of anhydrite is significant for early-age strength and for mortars prepared with high fly ash contents, but is less significant for later-age strength and for lower fly ash contents.

The addition of anhydrite also resulted in smaller pore sizes and lower porosity for the fly ash cement mortars. The formation of large quantities of AFt was the main cause of the higher early strength and finer pore structure of the activated high fly ash content mortars than those of the mortars without the activator.

A large quantity of AFt was found in the fly ash/cement pastes with the addition of anhydrite with accelerated curing by means of SEM examination and quantitative XRD analysis. Most of the AFt was formed during the early stage of hydration. This may be the main cause of the high early strength of the anhydrite-activated fly ash/cement systems.

When comparing with gypsum in terms of an equivalent  $\text{SO}_3$  content, using the same curing conditions, anhydrite is more effective in increasing the early-age strength, but less effective in increasing the later-age strength than gypsum. However, when comparison is made in terms of the same amount of addition, anhydrite is more effective in increasing the strength at both early and later ages. Thus, the use of anhydrite is advantageous.

As an initial curing at elevated temperature is necessary and essential, the technique of activating fly ash using anhydrite can be applied to precast cement and concrete products. More work is being carried out on the hydration process and microstructure development of the anhydrite-activated fly ash cement systems. Also, as other properties such as durability of the concrete containing anhydrite are not clear, further investigation is needed.

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#### References

- [1] J. Paya, J. Monzo, M.V. Bornachero, E. Peris-Mora, Mechanical treatment of fly ashes: Part I. Physical–chemical characterization of ground fly ashes, *Cem. Concr. Res.* 25 (7) (1995) 1469–1470.
- [2] J. Paya, J. Monzo, M.V. Bornachero, E. Peris-Mora, E. Gonzalez-Lopez, Mechanical treatment of fly ashes: Part II. Particle morphologies in ground fly ashes (GFA)–cement mortars, *Cem. Concr. Res.* 26 (2) (1996) 225–235.
- [3] J. Paya, J. Monzo, M.V. Bornachero, E. Peris-Mora, E. Gonzalez-Lopez, Mechanical treatment of fly ashes: Part III. Studies on strength development of ground fly ashes (GFA)–cement mortars, *Cem. Concr. Res.* 27 (9) (1997) 1365–1377.
- [4] Y.M. Maltais, J. Marchand, Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars, *Cem. Concr. Res.* 27 (7) (1997) 1009–1020.
- [5] W. Hu, R.D. Neufeld, L.E. Vallejo, C. Kell, M. Latona, Strength properties of autoclaved cellular concrete with high volume fly ash, *J. Energy Eng.* 123 (2) (1997) 44–54.
- [6] D.M. Roy, M.R. Silsbee, Alkali activated cementitious materials: An over review, *Mater. Res. Soc. Symp. Proc.* 245.
- [7] A. Katz, Microstructure study of alkali-activated fly ash, *Cem. Concr. Res.* 28 (2) (1998) 197–208.
- [8] A. Xu, S.L. Sarkar, Microstructural study of gypsum activated fly ash hydration in cement paste, *Cem. Concr. Res.* 21 (1991) 1137–1147.
- [9] W. Ma, C. Liu, P.W. Brown, S. Komarneni, Pore structures of fly ashes activated by  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , *Cem. Concr. Res.* 25 (2) (1995) 417–425.



- [10] C.J. Shi, Early microstructure development of activated lime–fly ash pastes, *Cem. Concr. Res.* 26 (9) (1996) 1351–1359.
- [11] C.J. Shi, Pozzolan reaction and microstructure of chemical activated lime–fly ash pastes, *ACI Mater. J.* 95 (5) (1998) 537–545.
- [12] A.L.A. Frany, J.M. Bijen, Y.M. de Haan, The reaction of fly ash in concrete, a critical examination, *Cem. Concr. Res.* 19 (1989) 235–246.
- [13] L. Day, B.K. Marsh, Measurement of porosity in blended cement pastes, *Cem. Concr. Res.* 18 (1988) 63–73.
- [14] H.F.W. Taylor, *Cement Chemistry*, Academic Press, London, 1990.
- [15] C. Shi, R.L. Day, *Proceedings of 5th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, Am. Concr. Inst., SP 153-61, vol. 2, 1995, pp. 1165–1177.
- [16] C.S. Poon, L. Lam, Y.L. Wong, Effects of fly ash and silica fume on interfacial porosity of concrete, *J. Mater. Civ. Eng.* 11 (1999) 197–205.