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Activation of fly ash and its effects on cement properties[1]

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Abstract

A new method of fly ash activation with addition of $Ca(OH)_2$ and a small quantity of Na_2SiO_3 is presented. Scanning electron microscopy, differential thermal analysis, x-ray diffraction analysis, alkali-absorption test, and strength measurement show that the activity of activated fly ash by this method is obviously increased, which can accelerate cement early hydration and promote setting and hardening.

Keywords: Alkali activated cement; Fly ash; Alkalis; $Ca(OH)_2$

The discharge of fly ash (FA) is rapidly increasing in China; the amount will be more than 160 million tons by the year 2000 [1]. Some classified high-quality FA has the effect of water reduction and characteristics of fine aggregate, which obviously can improve concrete properties; thus, it has been applied as concrete fine aggregate. Many other kinds of FA, however, can be used neither as fine aggregate due to their low quality, such as high water absorption, nor as cement admixture due to their lower activity and high ignition loss. At present, the utilization rate of FA in cement and concrete in China is only 2.3% [2]. Therefore, enhancing the activity of FA is the critical key to large-scale application. In this paper a new method of activating FA is presented. Treated by this method, FA can accelerate cement early hydration and improve setting property and strength. Therefore, it shows a broad future for application.

1. Experimental materials and methods

FA for activation was obtained from Huang Pu Power Plant, Guangzhou, China. The ash was mixed with $Ca(OH)_2$ in certain proportion by weight, Na_2SiO_3 addition = 3.91%, W/S = 3:1. After being homogeneously mixed, the mixture was held at a constant temperature of 55°C until $Ca(OH)_2$ disappeared by optical microscopy observation [3], then kept at this temperature for another 8 hours. The sample was then wet ground for 40 min and dried at a temperature of 120°C; activated fly ash (AFA) was so obtained. The chemical compositions of FA and AFA are listed in Table 1. The experimental cements were 525(II) (Chinese specification) PC from Zhu Jiang Cement Plant (rotary kiln), 425 (R) OPC from Shi Jin, and Ren Hua Cement Plants (shaft kiln).

The reaction degree of FA was measured according to [4], in which β is the soluble constituent content (%) of the mixture, α is the reaction degree of FA (%) [$\alpha = (\beta_t - \beta_{4h})/F$, where F is the FA proportion in the mixture]. An alkali-absorption test was conducted as follows: 10 g of sample was weighed and put into a plastic bottle containing 100 mL standard mixed liquid of NaOH and $Ca(OH)_2$, nitrogen was poured in the bottle to prevent carbonation, and the sample was vibrated for 4 hours, then filtered. The mmol figures of Na_2O and CaO absorbed were calculated by the titration results of the filtered liquid. Strengths were measured according to [5]: ratio of insoluble material $(100 - \beta)$ of AFA to $Ca(OH)_2$ = 3:1, W/S = 0.66.

2. Results and discussion

2.1. Activation of FA

The reasons for lower activity of FA arise from two factors. (1) The glassy surface layer of glass beads is dense and chemically stable. This layer protects the inside constituents, which were porous, spongy, amorphous, and therefore with higher activity [6]. (2) Its silica-alumina glassy chain of high Si, Al, and low Ca is firm; the chain must be disintegrated if activity is to take place. With $Ca(OH)_2$ addition and higher basicity, the densified outer layer is corroded and the active core is exposed. In normal cement paste pore solution, the pH is relatively lower, so the speed of corrosion

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[1] This article is being published without the benefit of the authors' review of the proofs, which was not available at press time.

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Table 1
Chemical compositions of FA and AFA (%)

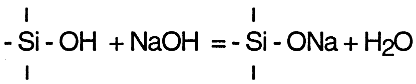
Kind	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
FA	47.98	32.48	5.23	3.51	0.72	0.14	5.82
AFA	40.11	30.12	4.75	15.77	0.93	—	6.33

on the glassy surface is quite slow. If the concentration of OH^- is high enough, the silica-alumina glassy chain will be rapidly disintegrated and will produce a large number of active groups. Obviously, the pH value of liquid environment possesses a significant determinant for FA activation [7].

2.1.1. Stimulation effect of Na_2SiO_3

With a small addition of Na_2SiO_3 to the mixture of FA and $Ca(OH)_2$, Na_2SiO_3 hydrolyzes and forms NaOH, increasing OH^-, the pH value being obviously higher (13.10) than that (12.63) of $Ca(OH)_2$ saturated liquid, thus greatly facilitating silica-alumina glassy chain corrosion. The course of NaOH effect can be concluded by the following overlapping reactions:

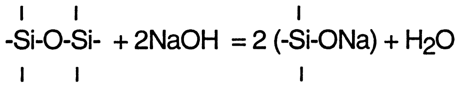
(a) Neutralization of surface silanol groups:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{NaOH} = -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{ONa} + \mathrm{H_2O}$$

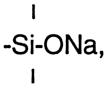
This neutralization repeats on new surfaces, known as corrosion of FA.

(b) Gradual destroying of inside silane chain, resulting in $[(Si,A1)O_4]_n$ disintegration:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + 2\mathrm{NaOH} = 2\,(-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{ONa}) + \mathrm{H_2O}$$

Owing to solubility of



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{ONa},$$

Na^+ is replaced by Ca^{2+}, forming sedimentary calcium silicate hydrate. Repeating the above reaction, Na_2SiO_3 can accelerate FA activation [8].

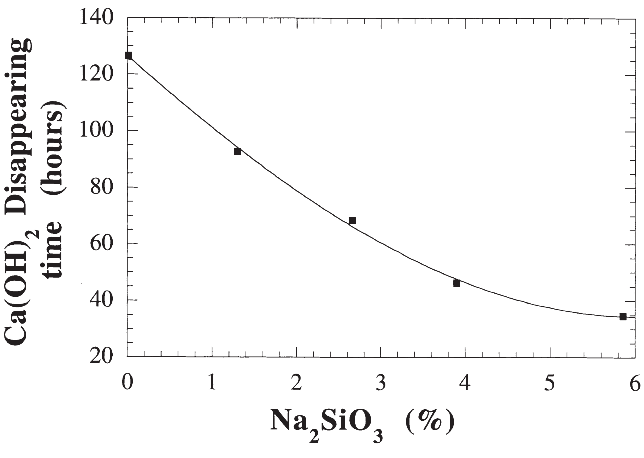


Fig. 1. Relationship between Na_2SiO_3 addition and time of $Ca(OH)_2$ disappearance.

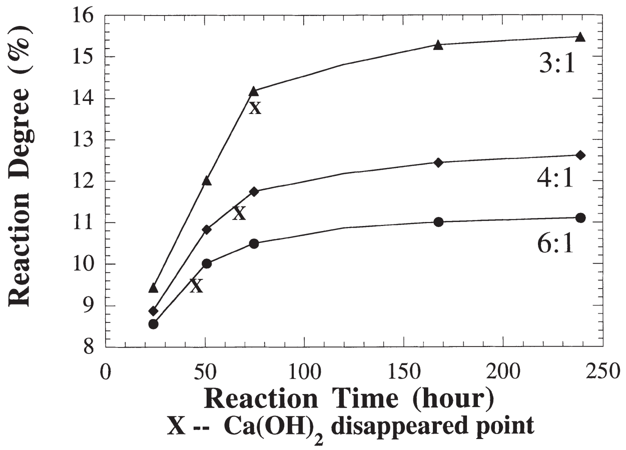


Fig. 2. Effect of $Ca(OH)_2$ addition on α (a:b = weight ratio of FA to $Ca(OH)_2$).

2.1.2. Effect of different conditions on reaction degree (α) of FA

Effects of additions of Na_2SiO_3, $Ca(OH)_2$, and temperature on α are shown in Figs. 1 and 2 and Table 2.

Fig. 1 illustrates that, as Na_2SiO_3 addition increases, the $Ca(OH)_2$ disappearing time shortens much, and reaction between FA and $Ca(OH)_2$ speeds up because of the augmentation of pH value as Na_2SiO_3 addition increased. Fig. 2 demonstrates the gradual consumption of $Ca(OH)_2$ as α increases slowly. When $Ca(OH)_2$ disappears, pH value drops (from 12.63 to 11.77), and α increases slowly (the same as in Table 2). When $Ca(OH)_2$ addition increases (from 14.3% to 25%), $Ca(OH)_2$ disappearing time slightly increases, but the extent is far less than that of addition increase. This indicates that reaction speed increases rapidly as addition increases. Data in Table 2 show $Ca(OH)_2$ disappearing time shortening as temperaure rises. By electron

Table 2
Effect of temperature on α

Temp. (°C)	CaO disappearing time (h)	Reaction time and reaction degree (α)	
		Hours	(%)
55	45	24	8.53
		48	10.05
		72	10.50
		120	10.89
70	30	24	7.95
		35	9.24
		48	9.80
		96	10.12
90	12	12	6.73
		20	8.47
		30	9.17
		48	9.67

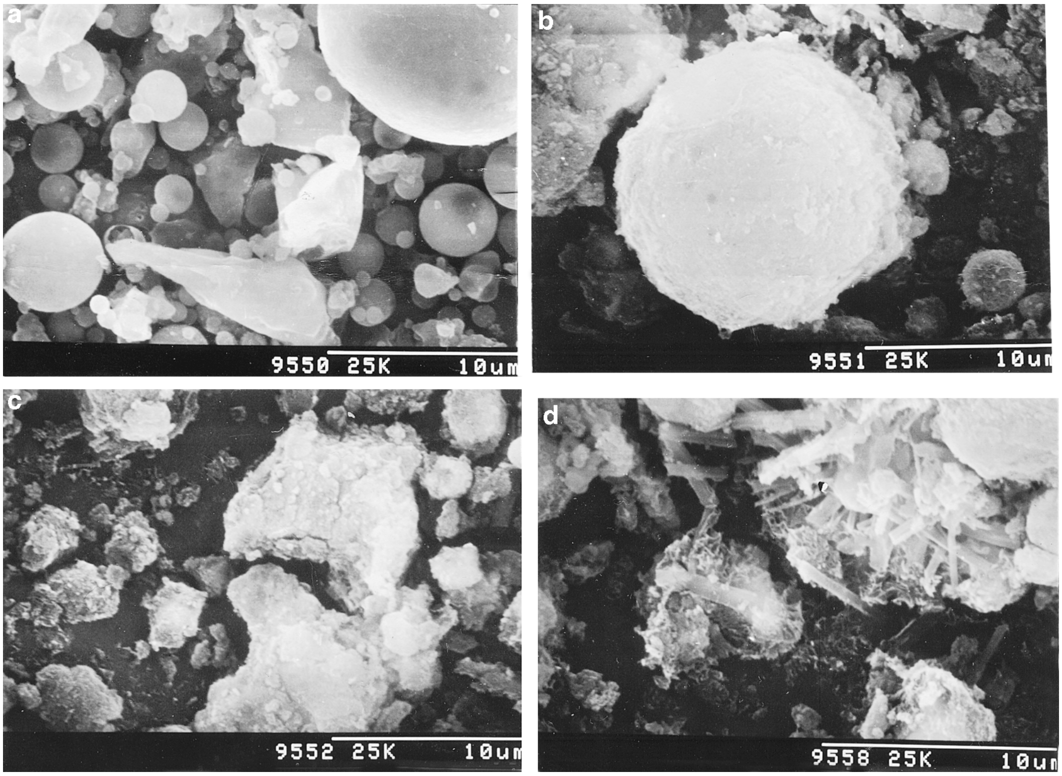


Fig. 3. Scanning electron microscopic observations of FA (*a*) and AFA (*b,c,d*).

probe it has been shown that the Ca/Si ratio of hydrate is higher as temperature rises; thus, α drops.

2.2. Structure and properties of FA

2.2.1. Structure of FA

Scanning electron microscopy shows that FA is composed mainly of smooth-surface glass beads of different sizes and a minor quantity of spongy glass, mullite, and quartz (shown in Fig. 3a). Fig. 4 shows the x-ray diffraction (XRD) dispersed peaks ($2\vartheta = 17^\circ$–30°) of silica-alumina glass, distinctive peaks of α-quartz (ds: 3.34, 4.26, 1.82), and mullite (ds: 3.40, 3.43, 2.21). On the other hand, glass beads in AFA (Fig. 3b), spongy glass, and mullite (Fig. 3c) have been severely corroded and covered by a large quan-

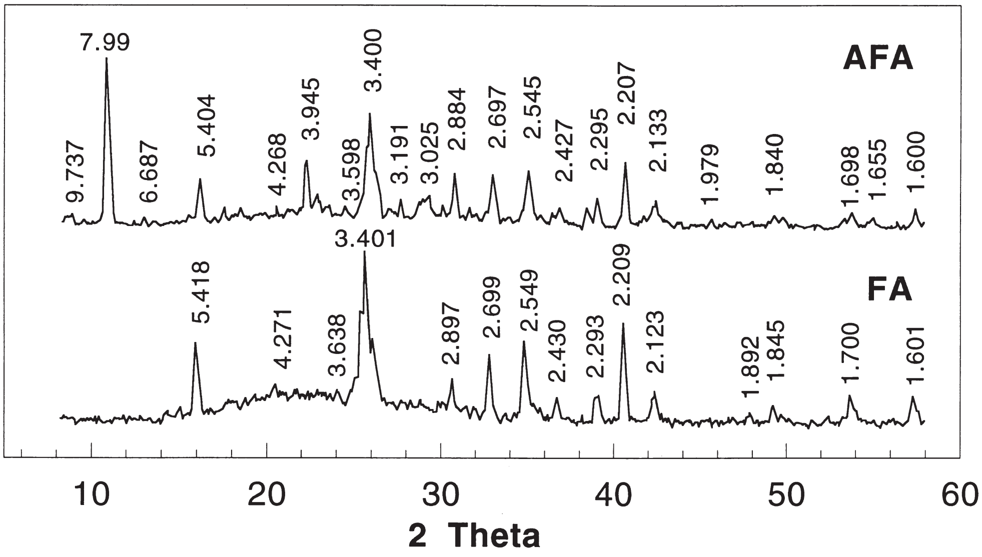


Fig. 4. XRDs of FA and AFA.

Table 3
Alkali-absorption test results

Kind	pH in filtered liquid	CaO absorbed (mmol/kg)	Na_2O absorbed (mmol/kg)
FA	12.70	40.55	0
AFA	12.34	93.81	−15.14

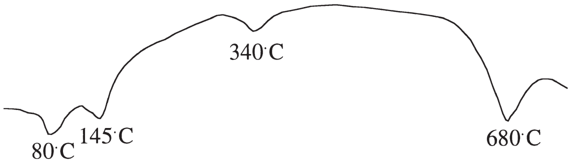


Fig. 5. DTA of AFA.

tity of gelatinous hydrates on surface, among which fibrous hydrates are seen (Fig. 3d). Granulometric analysis shows that the particle size of AFA obviously has been reduced, 87.8% of which is smaller than 20 μm; specific area reaches 639 m^2/g.

XRD (Fig. 4) also shows that diffractions of glass, α-quartz, and mullite in AFA are all weaker than those in FA (influence of $Ca(OH)_2$ addition has been deducted). This means that AFA has been corroded, forming lower Ca/Si calcium silicate hydrates (ds: 3.03, 9.80, 1.83 being weaker and slope-shape; differential thermal analysis [DTA]: 80°C, 150°C, and 680°C in Fig. 5) and calcium aluminate hydrates (ds: 7.99,2.88,1.66; DTA: 340°C in Fig. 5).

2.2.2. Alkali-absorption test

Table 3 shows the results of alkali-absorption test. From Table 3 it is implied that (a) in AFA the amount of active groups is increased, active cores are exposed, specific area is greater, thus the reaction between $Ca(OH)_2$ and these active groups is accelerated; (b) lower Ca/Si hydrates from AFA can also absorb some $Ca(OH)_2$; (c) with 3.91% Na_2SiO_3 addition, AFA possesses 320.5 mmol Na_2O/kg (19.87g Na_2O /kg). If Ca^{2+} in liquid is sufficient, the absorbed Na+ can all be replaced, showing stronger capability of absorbing $Ca(OH)_2$ and explaining why Na_2O absorption of AFA is negative.

2.2.3. Strength of paste with AFA

To investigate the reaction speed between $Ca(OH)_2$ and FA as well as AFA in older age, reaction degree and strength of ash-$Ca(OH)_2$ paste are measured in certain curing periods. The results are listed in Table 4.

Note in Table 4 that reaction degree $\alpha = (\beta_t - \beta_0$ soluble content when molding)/insoluble content when molding.

The following can be seen. (a) For FA the early α is lower, resulting in quite lower strengths of 3 to 28 days, but its α and strength in periods longer than 28 days are constantly increasing. (b) For AFA without Na_2SiO_3 (which is prepared by mixing FA with $Ca(OH)_2$ in a weight proportion of 6:1, reacting at a temperature of 55°C until $Ca(OH)_2$ disappears), the activating time increases by three times compared with that containing Na_2SiO_3 (Fig. 1). Its structure and hydrates are similar to those of AFA with Na_2SiO_3. Compared with FA, its α and strength in the same ages are obviously higher. (c) For AFA with small Na_2SiO_3 addition, early α is higher, strength of 3 to 28 days increases rapidly, where 28 days has reached 70% of final strength. α and strengths of 28 to 56 days are continually increasing until $Ca(OH)_2$ runs out. Because AFA with Na_2SiO_3 addition has higher CaO absorption capability and more residual Na^+, which promotes further hydration, its pozzolanic reactivity is the highest.

2.3. Effects of AFA on paste properties

2.3.1. On cement setting property

With fluorite mineralizing technique, the Al_2O_3 in clinker is more solid solution into alite and aluminoferrite, resulting in lower C_3A content, alite-bearing F^- shows higher reactivity, which produces supersaturated liquid with higher basicity during early hydration, and C-S-H and $Ca(OH)_2$ crystals are finer, difficult to form setting structure. Meanwhile, alite hydration is slowed down because there a layer of coverage forms on its surface owing to inner absorption. These all prolong cement setting [9]. Setting properties of normal and retarded setting cement were tested; some results are listed in Table 5.

Table 5 shows the following. (a) For setting-retarded cement produced with fluorite mineralizer, addition of AFA can shorten setting time at least 40 min, and the time can be adjusted to near that without mineralizer. The effect is more obvious as AFA addition appropriately increases. (b) The more retarded setting is, the more acceleration of setting would arise with AFA addition. For normal setting cement, this effect is less, but will not result in rapid setting.

Table 4
Reaction degree and compressive strength of FA and AFA pastes

Kind	Reaction degree (α)						Compressive strength (MPa)					
	3 days	14 days	28 days	56 days	90 days	120 days	3 days	14 days	28 days	56 days	90 days	120 days
FA	1.05	5.19	7.32	9.29	10.66	13.60	0	0	0.13	0.34	1.00	2.75
AFA without Na_2SiO_3	1.83	9.86	12.42	27.13	29.31	30.43	0.13	1.58	4.70	10.81	14.19	14.19
AFA with Na_2SiO_3	2.10	10.00	14.87	24.70	24.74	24.74	0.75	4.43	7.00	10.60	10.69	10.69

Note: Reaction degree ($\alpha = (\beta_t - \beta_{0\ \text{soluble content when molding}})$/insoluble content when molding.

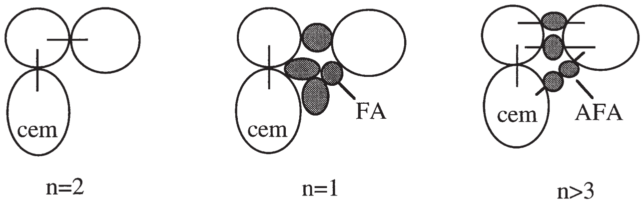


Fig. 6. FA and AFA effects on cement particles connection (n = number of connecting points).

There are two main reasons for setting acceleration. (1) The setting structure formation has close relation with the numbers of connecting points among cement hydration particles. The AFA particle is smaller than that of cement particles, which can increase the degree of connection (Fig. 6) and form inhomogeneous coagulation among cement particles [10], promoting cement setting. For FA, which is inert in the early period, its connection with cement particles is weaker. (2) The strong capability of CaO absorption by AFA reduces the supersaturation degree in liquid resulting from early hydration of alite-bearing F^-. This can speed up alite hydration, so that hydrates of AFA can behave as "crystal seeds," promoting the growth of C-S-H and $Ca(OH)_2$, which is advantageous to coagulative structure formation. From XRD patterns of Shi Jin 425R OPC of retarded setting (A) and with 5% AFA addition (B) shown in Fig. 7, it is shown that $Ca(OH)_2$ (ds: 4.909, 1.791) and ettringite (ds: 9.60, 5.59, 3.87) show stronger diffraction, and C-S-H shows sharper diffraction pattern near 1.82 Å for sample B. Dehydration peaks, as DTA shows in Fig. 8, of C-S-H (about 90°C and 680°C) and calcium aluminate hydrate (about 260°C) are both stronger in sample B than A.

2.3.2. *On strength of cement mortar*

Mortar strength of Shi Jin 425R OPC with 5% AFA addition is higher on day 1, similar to 3 and 28 days to those of reference. With increasing addition to 10% and 15%, strength on day 1 is still higher, but slightly lower in 28 days (Table 6) than the reference. Many kinds of cement and AFA were tested, and this trend was still proved.

Table 5
Setting time of cement with and without AFA

Sample	Water usage for standard consistancy (%)	Initial setting time (h:min)	Final setting time (h:min)
Shi Jin 425R OPC	26.2	3:58	5:12
5% AFA	26.6	3:17	4:19
10% AFA	27.2	2:52	3:38
15% AFA	27.8	2:28	3:16
Retarded 425R OPC	26.0	4:09	6:39
10% AFA	26.8	2:08	3:51
Ren Hua 425R OPC	25.8	2:07	4:35
5% AFA	26.1	2:04	4:17

With 5% AFA addition, cement content is reduced by the same percentage, but 1-day strength is increased by 10%. By repeating experiments with many kinds of cement, it was found that the slower setting speed and lower early strength the cement has, the more obvious the effect is. XRD and DTA indicate that this effect is mainly due to acceleration of cement hydration by AFA. During a long period of hydration, the strength can be maintained at a level similar to the reference because of the greater activity of AFA. With increasing AFA addition to 10% to 15%, promotion of hydration in early stage can still be seen, but, because cement percentage is reduced in mortar, a decreasing trend of strength in 3 and 28 days is shown.

Effects of FA and AFA mixture on mortar strength have been tested based on Zhu Jiang 525(II) PC. The results are shown in Table 7.

The following trends can be seen from Table 7: (a) With 15% addition the mortar strength in 3 and 28 days are all de-

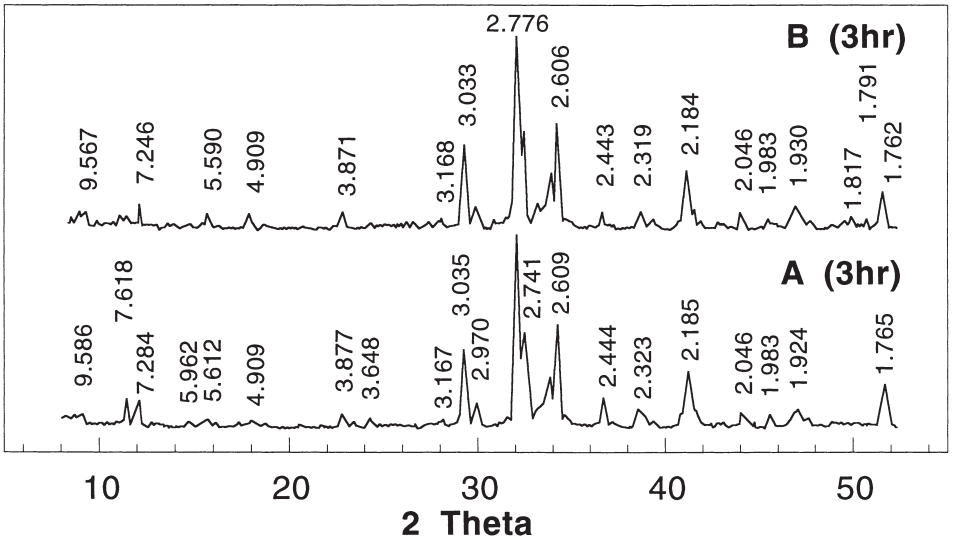


Fig. 7. XRDs of FA and AFA early hydration.

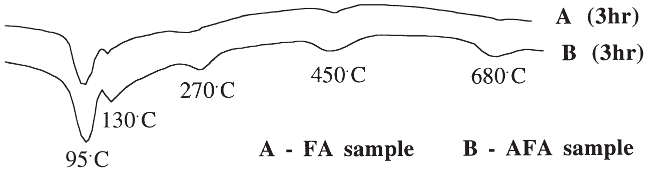


Fig. 8. Early hydration DTA of FA and AFA.

creased, strength with 15% FA addition reduced largely; 15% AFA addition, on the other hand, just reduced slightly. This situation is similar to that shown in Table 6. (b) When FA and AFA composite mixtures are used, as AFA proportion increased, strength in 3 days is increased obviously. This means that AFA substitution for FA can effectively compensate the early strength loss of cement with FA alone, of which the ratio of 5/10 proved to be the best result not only for maintaining the original cement strength, but also for saving cement and obtaining optimum economic benefit.

Table 6
Mortar strength with AFA

	Bending strength (MPa)			Compressive strength (MPa)		
Kind	1 day	3 days	28 days	1 day	3 days	28 days
425R OPC	2.9	4.7	7.5	14.3	26.4	53.7
5% AFA	3.2	4.7	7.4	15.6	26.6	54.3
10% AFA	3.0	4.5	7.1	15.4	26.1	53.2
15% AFA	3.0	4.1	6.8	15.0	25.3	52.4

Table 7
Mortar strengths with FA and AFA admixtures

Addition (%)	Bending strength (MPa)		Compressive strength (MPa)	
FA/AFA	3 days	28 days	3 days	28 days
0/0	7.3	8.9	46.4	67.4
15/0	6.5	8.8	39.2	58.3
10/5	6.6	8.9	41.6	67.3
5/10	6.8	8.9	42.6	66.7
0/15	6.6	8.7	43.3	62.5
0/5	7.1	9.0	48.0	66.9

3. Conclusion

1. A new method of AFA preparation is presented. With a small addition of Na_2SiO_3, the reaction between FA and $Ca(OH)_2$ can be accelerated obviously because of the higher pH value in hydration liquid and circulating formation of NaOH.
2. In early hydration the AFA surface is severely corroded, the amount of active groups is increased, more active cores are exposed, lower Ca/Si ratio calcium silicate hydrates as well as calcium aluminate hydrate are formed, and CaO absorption capability of AFA is strengthened.
3. AFA can act as setting and hardening accelerator. Hydrates from AFA can behave as “crystal seeds,” which accelerate cement early hydration and hydrate crystallization, normalizing the setting property.
4. Pozzolanic reactivity of AFA in both earlier and longer hydration periods is higher than that of FA. With 5% to 10% AFA addition, mortar strength is higher at 1 day, and maintains the same level as that of reference in 3 and 28 days. Therefore, composite utilization of AFA and FA as cement admixtures should be recommended.

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