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The influence of alkalinity on activation and microstructure of fly ash

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Abstract

With the wide use of fly ash in cement and concrete construction, the function and hydration of fly ash, and the influence on the concrete properties are studied and emphasized more and more. The active mechanism, hydrates and microstructure of fly ash were studied by thermal gravity analysis (TGA), X-ray and SEM analysis. Results show that the reaction of fly ash was very low in the fly ash–cement, because $Ca(OH)_2$ had less activation capability on fly ash at room temperature. Only if the curing temperature is enhanced or the blended alkalinity and sulfate is added, does the breaking of glass structure of fly ash and the formation of stable hydrates occur. Results also show that in the action of NaOH, C-S-H and zeolite were present. When the gypsum is added, ettringite formation is related with the pH of the hydration system. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Activation; Microstructure; Fly ash; Thermal gravity analysis

1. Introduction

The production of Portland cement consumes a lot of resources and energy and emits CO_2, SO_2 and NO_x. It causes the acid rain and greenhouse effect. Therefore, it is very important to synthetically utilize resources, especially industrial by-products. From the reports, there were about 750 million tons of industrial waste slag in 1995. At present, about 6 billion tons have not been used. Especially, the utilization of fly ash is low. In China, about 100 million tons of fly ash are discharged annually from coal-burning electric-generating plants, and only about a fourth of this fly ash is utilized [1].

Since fly ash is widely applied in concrete construction, the study of fly ash properties has been undertaken. Studying the strength and thermodynamic properties of high volume fly ash–concrete has been more and more interesting [2] to researchers. Although the microstructure and mechanism of fly ash–cement and concrete have been studied, most of these study were about the activation mechanism of fly ash–$Ca(OH)_2$, fly ash–cement and fly ash–lime–gypsum [3–7]. There have been some reports about the study of alkalinity of fly ash–cement [8,9], but as to their activated mechanism, there have been some different views.

Generally, the fly ash has a low level of activation in lime and gypsum during room temperature curing. Huang [10] considered that in the fly ash–$Ca(OH)_2$–H_2O system, the reaction degree of fly ash was only from 1.5% to 3.0% after 7 days of hydration, and was less than 20% after 180 days of hydration. This is because although the chemical composition of fly ash belongs to the $CaO–SiO_2–Al_2O_3$ system, its CaO content was less than that of slag (except high calcium fly ash). There was a higher content of aluminum, silicon, and higher degree of polymerization in the fly ash, so its hydration activation is much less than that of the slag.

The possibility of FA activation mainly lies in the breaking down of its glass phases. Fraay [11] considered that the pH value required to dissolve the alumina and silica is about 13.3 or higher. Therefore, it is impossible to make fly ash speed up activation in the system of fly ash–$Ca(OH)_2$ because its pH is less than 13. The usual way of achieving a high pH is by the addition of NaOH or other alkalinity in FA. It is well known that alkalinity in PC cement increases early strength, but it could produce a poor effect in concrete such as an alkali-aggregate reaction. Only when proper

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alkalinity is controlled in fly ash or other blended cements, are early and late strength and other properties improved.

This paper mainly studied the activation and microstructure of fly ash in its basic condition, including the system of fly ash–cement, to which $Ca(OH)_2$, lime–NaOH and lime–gypsum–Na_2SO_4 were added. The aim of this study is to describe the influence of blended alkalinity on the activation and microstructure of fly ash.

2. Experimental

2.1. Material and batch

The fly ash material in this experiment comes from the Nanjing coal power plant. Table 1 shows its chemical composition. It is well known that the calcium content of this fly ash is low. In order to study the relationship between chemical composition and degree of hydration in fly ash, except for fly ash–cement, three other batches were designed (see Table 2). The fly ash was cured at room temperature, and F_1 to F_3 were cured at 60°C and the ratio of w/c was 0.45. Because the hydration rate was much lower in the system of fly ash–lime, the batch of fly ash–lime alone was not described in the paper. It is only sample for comparison.

At the date of testing, samples were first grounded by adding alcohol to stop hydration, and then dried by vacuum pump. Finally, they were put into a dryer until they were tested.

3. Results and discussion

3.1. The system of fly ash–cement

In the system of fly ash–cement, the activation of the fly ash was actually co-function of $Ca(OH)_2$ and gypsum. The former mainly played an active part on the fly ash, and gypsum took part in the reaction. The degree of activation of the fly ash can be described by the absorption to $Ca(OH)_2$. Because of the existence of calcium aluminum in Portland cement, it is very difficult to judge the degree of reaction of the fly ash with the formation of ettringite. The fly ash–cement was cured at room temperature for 3, 28 and 90 days. Its XRD analysis curves are shown in Fig. 1.

It is well known that, from the XRD pattern of Fig. 1, the main mineral components are mullite, quartz and ferrite. The peak strength of $Ca(OH)_2$ decreased with the continued hydration of the fly ash–cement. It shows that the fly ash had partly hydrated. On the other hand, there is still $Ca(OH)_2$ at the end of 90 days of hydration. It also shows that the degree of hydration of the fly ash was lower at room temperature.

Table 1
Chemical composition of fly ash (mass%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	R_2O	SO_3	Total
Fly ash	5.83	52.64	25.42	7.56	0.56		0.8	92.90

Table 2
Test batch of fly ash hydrating (mass%)

	Fly ash	NaOH	$Ca(OH)_2$	Gypsum	Na_2SO_4	PC
FAC	35					65
F_0	100		25			
F_1	100	2				
F_2	100	2	25			
F_3	100		25	6	4	

Fig. 2 is the SEM photo of the fly ash–cement paste. In Fig. 2(a), the SEM photo of hydration at 3 days, it can been seen that the surface of the fly ash was smooth. It shows that there was almost no reaction between Portland cement and the fly ash. Fig. 2(b) is the SEM photo of hydration at 28 days, the surfaces of small particles of fly ash emerged into C-S-H gel, and that of larger ones were covered by C-S-H. In the Fig. 2(c), there is flocculent gel, which is similar to the product of the reaction between the silicate fume and $Ca(OH)_2$. This is the result of the reaction of the active silica of fly ash and $Ca(OH)_2$. After 90 days of hydration (Fig. 2(d)), although $Ca(OH)_2$ still existed and degree of reaction of fly ash was not high, the filling effect and binding function of C-S-H made cement hardened paste large pore decrease. Therefore, the fly ash–cement later showed the improved properties.

3.2. The system of alkalinity fly ash

3.2.1. XRD test

Fig. 3 shows the XRD pattern at 14 and 28 days of curing at 60°C from F_1 to F_3. Results show that when the fly ash is only activated by NaOH, except for existing zeolite peaks,

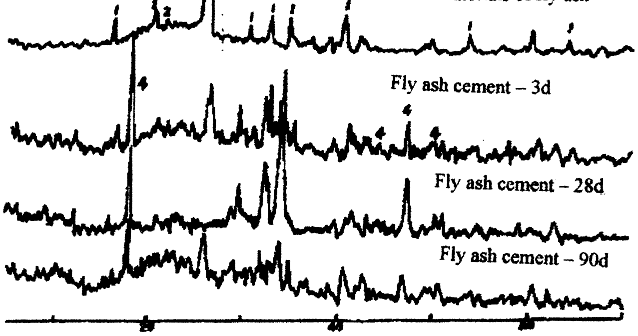
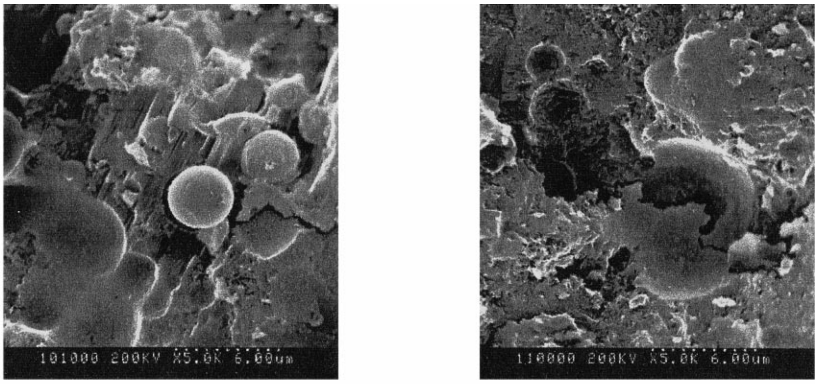
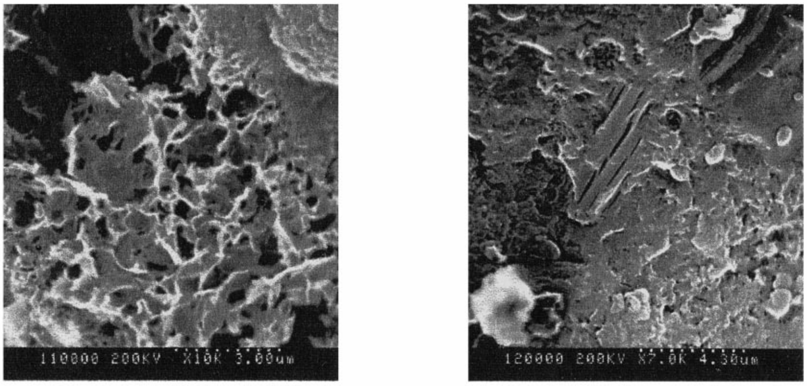


Fig. 1. XRD patterns of fly ash–cement.



(a) 3d of hydration

(b) 28d of hydration



(c) 28d of hydration

(d) 90d of hydration

Fig. 2. SEM photo of the fly ash–cement: (a) 3 days of hydration, (b) 28 days of hydration, (c) 28 days of hydration, and (d) 90 days of hydration.

the other peaks of fly ash still existed. In addition, when the fly ash was activated by NaOH and $Ca(OH)_2$, a large part of the $Ca(OH)_2$ reacted with silicate and formed C-S-H gel. Therefore, the $Ca(OH)_2$ peaks were not clear. When fly ash was activated by $Ca(OH)_2$, $CaSO_4$ and Na_2SO_4, ettringite peaks were present. It was shown that $Ca(OH)_2$ reacted with aluminum iron, which came from the breaking of glass in the fly ash and gypsum to produce ettringite. C-S-H gel was the main hydrates. Since the action of blended admixtures enhances activation capacity of the fly ash, the reaction content of the $Ca(OH)_2$ increases too. Compared with 14 days of hydration, there was a bigger difference at 28 days of hydration.

3.2.2. SEM test

Fig. 4 are SEM photos of hydration of the fly ah at 60°C for 7 and 14 days. Fig. 4(a) is an SEM photo in which the fly ash was activated by 2% NaOH at 7 days. It can be seen that the surface of the fly ash was covered with reaction products, but the edge was clear. Fig. 4(b) is an SEM photo in which the fly ash was activated by 2% NaOH at 14 days. There is breaking off at the surface of the fly ash and a rough edge. It shows that the fly ash has a large degree of erosion by NaOH. Fig. 4(c) is an SEM photo in which the fly ash was activated by NaOH and $Ca(OH)_2$ at 7 days. The surface of the fly ash was covered by C-S-H caused by the reaction of fly ash and lime.

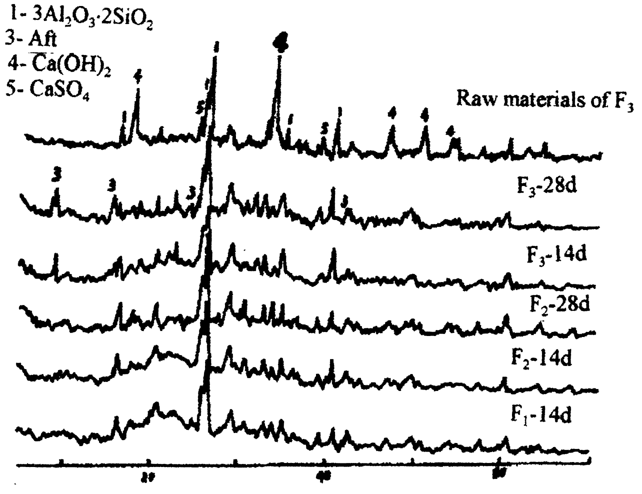


Fig. 3. XRD patterns of hydration of alkali fly ash.

Fig. 4(d) is an SEM photo in which the fly ash was activated by NaOH and $Ca(OH)_2$ at 14 days. Because the breaking and hydration of the fly ash is enhanced, the fly ash is covered with C-S-H and other hydrates and the linking force increases. When the fly ash was activated by $Ca(OH)_2$ gypsum and Na_2SO_4, the hydration of fly ash was speeded up. There was a lot of needle ettringite at 7 days (Fig. 4(e)). At 14 days of hydration, the ettringite continued increasing and developing, and needle crystal crossed each other to form a frame structure. It improves strength and other properties of cement at early stage.

3.2.3. Thermal gravity analysis (TGA)

TGA was made by TGA V5.1A DuPont 2000 from USA.

In order to describe the degree of hydration of the fly ash in the different conditions, TGA test is necessary. The aim of this study is to examine possible correlations between CH content and the amount of other hydrates as measured by water loss during dehydration.

TGA is an accurate method for the determination of crystalline CH content and other hydrates (loss of water), including C-S-H, AFt, gypsum and other hydrates. In order to simplify study system, it can generally be separated into three parts from 70°C to 900°C. At about 450°C, an abrupt weight loss occurs, which is the dehydration of CH. Between 600°C and 700°C, there is another fairly sudden decomposition of calcium carbonate; from 70°C to 400°C, weight loss was mainly calcium silicate hydrates, calcium aluminate hydrates and other hydrates, AFt, AFm, and gypsum.

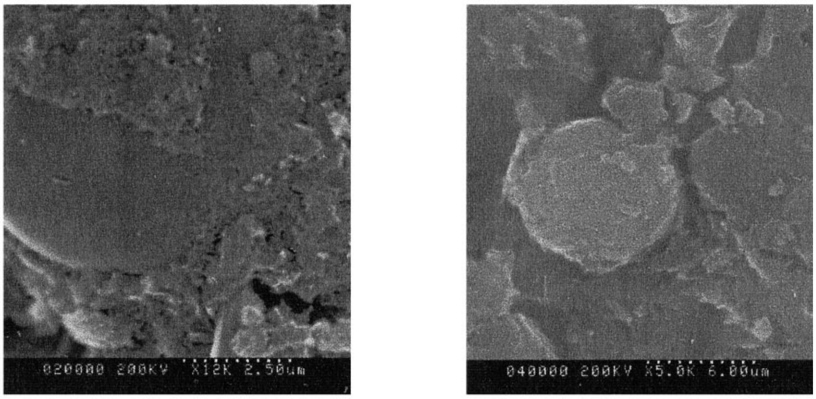
The thermal–gravity analysis testing results are in Table 3. In order to show the activation of the fly ash, it can be described by the weight loss of water and residues of $Ca(OH)_2$. Fig. 5 described the curves of water loss content at different hydration times and the degree of reaction of $Ca(OH)_2$. Results show that reaction capacity of fly ash with $Ca(OH)_2$ is very low at room temperature. It is about 10% at 28 days of curing. But in adding NaOH or Na_2SO_4 in the fly ash–$Ca(OH)_2$ system, the degree of reaction of $Ca(OH)_2$ obviously increases, especially at early stage of hydration. For example, comparing F_0 to F_2, the degree of reaction of $Ca(OH)_2$ increases to 43.67% from 1.28% at 7 days of hydration. The degree of reaction of $Ca(OH)_2$, when compared to F_3, is 16.18% at 7 days of hydration. It is shown that the effect of alkalinity on fly ash is obvious at early stage of hydration. At later stage of hydration, the effect of Na_2SO_4 on fly ash is more and more obvious, this is because the alumina of fly ash and sulfate took part in the reaction, producing ettringite.

4. Conclusions

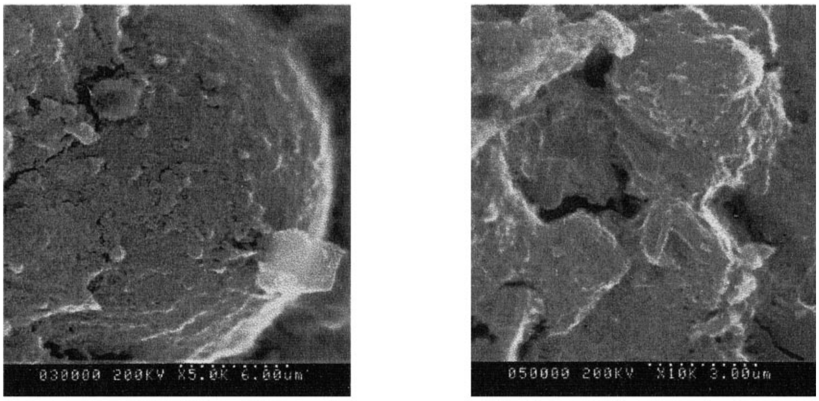
When the fly ash–cement hydrated at room temperature, because the pH of the paste solution could not meet the requirement of activation of the fly ash, the activation and hydration of fly ash was lower. At an early age of hydration, the function of the fly ash was mainly filling efficient. But the main product of later hydration of the fly ash was C-S-H gel. This played an important role in the development of strength and structure dense.

Table 3
Thermal–gravity analysis

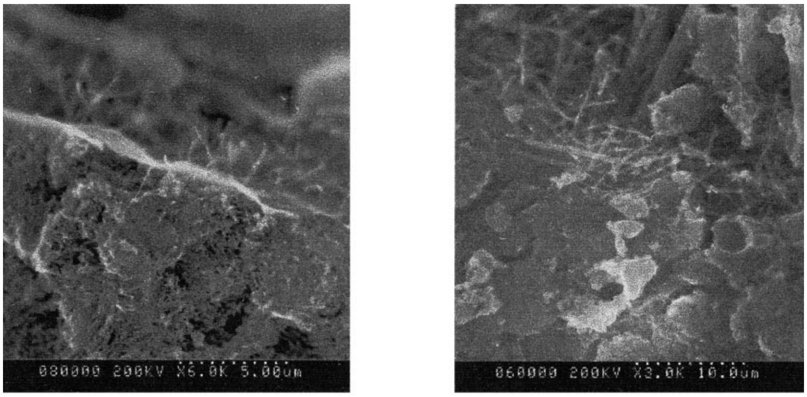
	100–400°C (%)	400–500°C (%) $H_2O/Ca(OH)_2/CaO$	500–850°C (%) $CO_2/CaCO_3/CaO$	Total $CaO/Ca(OH)_2$
$F_{0-20-8\ h}$	1.1878	5.00/20.54/15.15	2.50/5.70/3.19	18.73/24.74
$F_{0-20-7\ days}$	2.4432	4.69/19.30/14.60	3.05/6.94/3.89	18.49/24.43
$F_{0-20-14\ days}$	2.91	4.46/18.29/13.84	2.67/6.07/3.40	17.24/23.44
$F_{0-20-28\ days}$	2.50	4.48/18.42/13.94	2.15/4.90/2.74	16.68/22.04
$F_{0-20-90\ days}$	3.859	3.68/15.12/11.45	2.20/5.0/2.8	14.25/18.83
$F_{2-20-7\ days}$	7.50	2.04/8.39/6.35	3.30/7.59/4.20	10.55/13.98
$F_{2-20-14\ days}$	8.40	2.28/9.37/7.09	2.60/5.91/3.31	10.40/13.74
$F_{2-20-28\ days}$	6.46	1.37/5.64/4.27	4.36/9.91/5.55	9.82/12.98
$F_{2-20-90\ days}$	11.42	1.28/5.26/3.98	2.83/6.43/3.60	7.87/14.36
$F_{3-20-7\ days}$	2.61	4.09/14.81/12.72	2.34/5.32/2.98	15.70/20.74
$F_{3-20-14\ days}$	7.24	3.02/12.42/9.40	2.67/6.07/3.40	12.80/16.91
$F_{3-20-28\ days}$	13.01	1.96/8.06/6.10	2.84/6.45/3.61	9.71/12.83
$F_{3-20-90\ days}$	12.92	1.06/4.36/3.30	4.11/9.34/5.23	8.53/11.27



(a) F1 - 7d **(b) F1 - 14d**

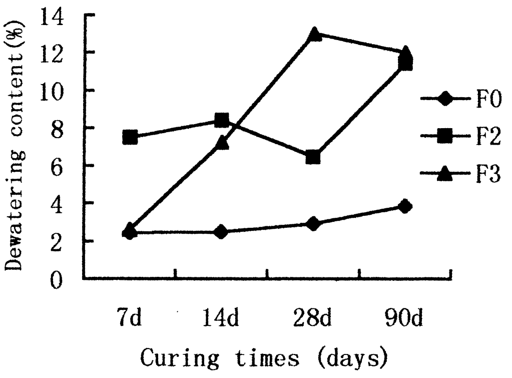


(c) F2 - 7d **(d) F2 - 14d**

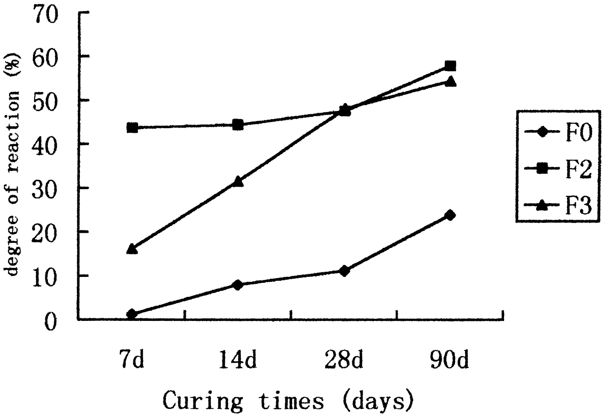


(e) F3 - 7d **(f) F3 - 14d**

Fig. 4. SEM photo of hydration of alkali fly ash: (a) $F_{1-7\text{ days}}$, (b) $F_{1-14\text{ days}}$, (c) $F_{2-7\text{ days}}$, (d) $F_{2-14\text{ days}}$, (e) $F_{3-7\text{ days}}$, and (f) $F_{3-14\text{ days}}$.



(a) Water loss vs. curing times



(b) degree of reaction vs. curing times

Fig. 5. The relation curves of watering loss and degree of reaction of Ca(OH) vs. hydration times: (a) water loss vs. curing times and (b) degree of reaction vs. curing times.

Under the higher alkalinity, the glass structure of fly ash was easily broken. Because of the lower calcium content of the fly ash, only a little C-S-H gel formed. Therefore, there were a lot of pores in the fly ash paste and it could not produce high strength.

When fly ash was activated by blended alkali (sodium hydroxide and calcium hydroxide) and gypsum, not only was the hydration of fly ash enhanced, but also more rational and relatively stable hydrates could be made. TGA testing shows that activated effect of alkalinity on fly ash at the early stage is beneficial, but the effect of Na_2SO_4 is more efficient at later stage of hydration.

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