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Fly ash effects
II. The active effect of fly ash

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Abstract

This paper examines the method for determining the hydration degree of cement clinker and the pozzolanic reaction degree of fly ash in the system of cement and fly ash. In the base, the active effect of fly ash is studied. The studied results show that the active effect includes two aspects: (1) Fly ash has stronger pozzolanic activity and can react with $Ca(OH)_2$, and (2) it can promote the hydration of cement. When the content of fly ash is less, its pozzolanic activity can exert well, but its promoting role to the hydration of cement is weaker. When the content of fly ash is more, it is less than its pozzolanic activity can be used, but its promoting role to the hydration of cement is stronger.

Keywords: Fly ash; Kinetics; Pore size distribution; Thermal analysis

1. Introduction

The active effect is a very important effect of fly ash, and this has been recognized by many researchers. In this aspect, a lot of research has been done [1–3]. By these researches, it is known that the hydration of fly-ash cement includes two processes: (1) the hydration of cement clinker and (2) the pozzolanic reaction between fly ash and $Ca(OH)_2$, which is released in the hydration of cement clinker. The authors [4,5] analyzed the hydration process of fly-ash cement by hydration kinetics and pointed out that both the hydration of cement clinker and the pozzolanic reaction of fly ash are accelerated each other in the hydration process of fly-ash cement. $Ca(OH)_2$ is released in the hydration of cement clinker and gives a condition for the pozzolanic reaction of fly ash. $Ca(OH)_2$ is absorbed in the pozzolanic reaction of fly ash and will promote the hydration of cement clinker. However, this is only theoretical analysis. It cannot be verified by experiment.

The most difficult thing to understand in the pozzolanic effect of fly ash is that the hydration degree of cement clinker and the pozzolanic reaction degree of fly ash in the hydration process of fly-ash cement cannot be determined. In the paper, the method will be studied. In the base, the hydration degree of cement clinker and the pozzolanic reaction degree of fly ash in the system of cement and fly ash are analyzed. The active effect of fly ash is understood further.

2. The method determining the hydration degree of cement clinker and the pozzolanic reaction degree of fly ash in the system of cement and fly ash

2.1. Theoretical analysis

There are two difficulties in determining the hydration degree of cement clinker and the pozzolanic reaction of fly ash in the system of cement and fly ash: (1) In the system, there are two reactions, and (2) these reactions are not independent—they are dependent on each other. It is because of these that dividing the hydration of cement clinker and the pozzolanic reaction of fly ash in the hydration process of fly-ash cement is not easy.

For the system of pure cement, the unknown quantity is only the hydration degree of cement. Thus, it can be determined by a characteristic index that is relative to it, for example, the quantity of combined water, etc. But, for the system of cement and fly ash, unknown quantities are both the hydration degree of cement clinker and the pozzolanic reaction degree of fly ash. They cannot be determined by a

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Table 1
The chemical composition of cement and fly ash

	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Portland cement	1.18	20.99	5.00	5.73	61.90	2.18	1.71	0.69	0.62
Pingwei fly ash	3.01	55.95	31.77	3.40	2.71	0.51	0.99	0.82	0.84

characteristic index. To determine the hydration degree of cement clinker and the pozzolanic reaction degree of fly ash, it is necessary that two characteristic indexes are taken. They may be porosity and the amount of $Ca(OH)_2$.

For hardened cement stone, the initial porosity is the percentage of the volume of mixing water. When cement clinker is hydrated and fly ash reacts with $Ca(OH)_2$, the porosity reduces because the volume of reaction produced is larger than one of the reactants. Thus,

$$P = \frac{\frac{W}{\rho_w} - 1.13\left(\frac{C}{\rho_c}\alpha_c + \frac{F}{\rho_f}\alpha_f\right)}{\frac{C}{\rho_c} + \frac{F}{\rho_f} + \frac{W}{\rho_w}} = \frac{\frac{W}{C+F}\frac{1}{\rho_w} - 1.13\left(\frac{1-x}{\rho_c}\alpha_c + \frac{F}{\rho_f}\alpha_f\right)}{\frac{1-x}{\rho_c} + \frac{x}{\rho_f} + \frac{W}{C+F}\frac{1}{\rho_w}} \quad (1)$$

Where P—the porosity of hardened cement (%); α_c—the hydration degree of cement clinker; α_f—the pozzolanic reaction degree of fly ash; W—water consumption; C—cement consumption; F—fly ash consumption; x—the content of fly ash; ρ_c—the density of cement; ρ_f—the density of fly ash; and ρ_w—the density of water.

Eq. (1) may be changed into:

$$\frac{1-x}{\rho_c}\alpha_c + \frac{x}{\rho_f}\alpha_f = \frac{1}{1.13}\left[\frac{W}{C+F}\frac{1}{\rho_w} - P\left(\frac{1-x}{\rho_c} + \frac{x}{\rho_f} + \frac{W}{C+F}\frac{1}{\rho_w}\right)\right] \quad (2)$$

For the amount of $Ca(OH)_2$, the hydration of cement clinker releases $Ca(OH)_2$ and increases the $Ca(OH)_2$ in the system. The pozzolanic reaction of fly ash absorbs $Ca(OH)_2$ and decreases the $Ca(OH)_2$ in the system. Thus, following equation can be obtained:

$$C_c(1-x)\alpha_c - C_f x\alpha_f = C_s \quad (3)$$

Where C_c is the amount of $Ca(OH)_2$ released by 1 g cement clinker when it is hydrated fully (g/g cement). It can be calculated by following equation:

$$C_c = \left[\frac{C_{CaO}}{M_{CaO}} + \frac{C_{MgO}}{M_{MgO}} - k_c\frac{C_{SiO_2}}{M_{SiO_2}} - 3\left(\frac{C_{Al_2O_3}}{M_{Al_2O_3}} + \frac{C_{Fe_2O_3}}{M_{Fe_2O_3}}\right) + \frac{C_{SO_3}}{M_{SO_3}}\right]M_{Ca(OH)_2} \quad (4)$$

Where C_f is the amount of $Ca(OH)_2$ consumed by 1 g fly ash when it reacts fully with $Ca(OH)_2$ (g/g fly ash). It can be calculated by following equation:

$$C_f = \left[k_f\frac{F_{SiO_2}}{M_{SiO_2}} + 3\left(\frac{F_{Al_2O_3}}{M_{Al_2O_3}} + \frac{F_{Fe_2O_3}}{M_{Fe_2O_3}}\right) + \frac{F_{SO_3}}{M_{SO_3}} - \frac{F_{CaO}}{M_{CaO}} - \frac{F_{MgO}}{M_{MgO}}\right]M_{Ca(OH)_2} \quad (5)$$

Where C_s is the amount of $Ca(OH)_2$ in 1 g hardened cement stone.

C_{CaO}, C_{MgO}, C_{SiO_2}, $C_{Al_2O_3}$, $C_{Fe_2O_3}$ and C_{SO_3} are the content of CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 in cement, respectively.

F_{CaO}, F_{MgO}, F_{SiO_2}, $F_{Al_2O_3}$, $F_{Fe_2O_3}$ and F_{SO_3} are the content of CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 in fly ash, respectively.

M_{CaO}, M_{MgO}, M_{SiO_2}, $M_{Al_2O_3}$, $M_{Fe_2O_3}$, M_{SO_3} and $M_{Ca(OH)_2}$ are the molecular weight of CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3, SO_3 and $Ca(OH)_2$, respectively.

k_c and k_f are the CaO/SiO_2 ratio of the reaction produce, C-S-H, of cement and fly ash, respectively.

According to the chemical compositions of cement and fly ash, C_c and C_f may be calculated by Eqs. (4) and (5). If P and C_s are known, α_c and α_f can be solved by Eqs. (2) and (3).

2.2. Experimental results and the calculation of the hydration degree of cement and the pozzolanic reaction degree of fly ash

To calculate C_c and C_f, the chemical composition of cement and fly ash and the CaO/SiO_2 ratio of the product, k_c and k_f, must be known. Table 1 shows the chemical composition of cement and fly ash. To determine k_c and k_f, X-ray spectrum analysis is made around the cement and fly ash particles in the hardened cement stone. The results are given in Table 2. It may be seen from the table that k_c is larger than k_f. In other words, the CaO/SiO_2 of C-S-H is higher around the cement particle than around the fly ash particle. With the increase of the content of fly ash, both k_c and k_f will decrease. However, the influence of age on k_c and k_f is not marked. According to k_c and k_f, C_c and C_f may be calculated by Eqs. (4) and (5). The results are given in Table 3.

To solve α_c and α_f, it is necessary to determine the porosity of cement stone and the amount of $Ca(OH)_2$ in the hardened cement stone. Paste samples with 20 × 20 × 20

Table 2
k_c and k_f

Age (days)	28				365			
Content of fly ash (%)	0	10	20	60	0	10	20	60
CaO/SiO_2 ratio around cement particle	1.50	1.44	1.38	0.89	1.50	1.44	1.38	0.90
CaO/SiO_2 ratio around fly ash particle	–	1.37	1.25	0.76	–	1.44	1.30	0.73

Table 3
C_c and C_f

Content of fly ash (%)	0	10	20	30	40	50	60
C_c	0.2658	0.2814	0.2969	0.3280	0.3590	0.3901	0.4212
C_f	–	1.6721	1.5824	1.4909	1.3995	1.3081	1.2166

mm are made and $W/(C+F)$ is 0.30. The porosity of the hardened cement stone is determined by mercury porosimeter, and the amount of $Ca(OH)_2$ in hardened cement stone is determined by thermogravimetric analysis. Tables 4 and 5 give the determined results of porosity and the amount of $Ca(OH)_2$. It can be seen from Table 4 that the porosity of cement stone increases with the content of fly ash but decreases with age. The amount of $Ca(OH)_2$ in hardened cement decreases with the content of fly ash. It is due to both the decrease of cement and the absorption of fly ash on $Ca(OH)_2$. The change of the amount of $Ca(OH)_2$ with age is complicated. If fly ash is not added, the amount of $Ca(OH)_2$ increases with age because $Ca(OH)_2$ is released further with the hydration of cement. If the content of fly ash is larger than 30%, the amount of $Ca(OH)_2$ decreases with age. This shows that the absorption of fly ash has been over the released energy of cement.

According to the data in Tables 4 and 5, the hydration degree of cement, α_c, and the pozzolanic reaction degree of fly ash, α_f, may be calculated by Eqs. (2) and (3). The results are given in Tables 6 and 7, respectively. It can be seen clearly that the hydration degree of cement increases with the increase of the content of fly ash. If fly ash is not added, only three-fourths of cement has been hydrated after one year. If 60% cement is replaced by fly ash, all of cement is hydrated almost after 90 days. The pozzolanic reaction degree of fly ash decreases with the increase of the content of fly ash, except at 7 days of age.

3. The analysis of the active effect of fly ash

The authors studied the hydration process of fly-ash cement by hydration kinetics and pointed out that in the hydration process of fly-ash cement, there are both the hydration of cement and the pozzolanic reaction of fly ash. They are relative and are promoted by each other. The hydration of cement is accelerated with the increase of the content of fly ash because the promotion of fly ash strengthens. The pozzolanic reaction of fly ash is slowed with the increase of the content of fly ash because the promotion of cement weakens. The results in Tables 6 and 7 fully prove this viewpoint.

According to above viewpoint, the active effect of fly ash should be two parts: (1) the pozzolanic activity of fly ash self and (2) the promoting role of fly ash to the hydration of cement. These two parts are of the same importance. Any part should not be neglected.

How much fly ash is active? It may be seen from Table 7 that 36.56% of fly ash has reacted at 365 days of age. It still is not full. The pozzolanic reaction will continue. It is possible that above 50% fly ash is active. However, it is uncertain that the pozzolanic reaction will occur for all active fly ash. Only under the condition that there is enough $Ca(OH)_2$ that the pozzolanic reaction can occur. When the content of fly ash is less, $Ca(OH)_2$ is enough. Thus, more active fly ash can react. For example, if the content of fly ash is 10%, there is still 13.48 g $Ca(OH)_2$/g cement at 365 days of age. In this time, the hydration degree of cement is only 77.37%. $Ca(OH)_2$ will be released further when cement continues to hydrate. Under the condition, the active fly ash will continue to react to $Ca(OH)_2$. When the content of fly ash is more, $Ca(OH)_2$ is not enough to react with the active fly ash, and a portion of fly ash cannot react. But it still is active. For example, if the content of fly ash is 60%, the pozzolanic reaction degree of fly ash is only 22.61% at 365 days of age. The pozzolanic reaction will not continue because there has been no $Ca(OH)_2$ in the system, and the hydration of cement has been finished basically too. From this viewpoint, the active effect of fly ash is a different concept with the activity of fly ash. The activity of fly ash is the potentiality that it reacts with $Ca(OH)_2$. It

Table 4
The porosity of hardened cement stone (%)

Age (days)	Content of fly ash (%)						
	0	10	20	30	40	50	60
7	20.78	22.26	24.33	24.87	26.41	28.01	29.59
28	15.31	15.29	17.26	17.80	19.11	19.51	20.85
90	10.76	9.91	11.40	10.43	11.09	12.06	15.36
365	5.28	5.64	7.58	8.51	9.43	10.56	14.55

Table 5
The amount of $Ca(OH)_2$ in hardened cement stone (%)

Age (days)	Content of fly ash (%)						
	0	10	20	30	40	50	60
7	0.1305	0.1284	0.1216	0.0959	0.0904	0.0752	0.0566
28	0.1558	0.1089	0.0918	0.0752	0.0570	0.0497	0.0397
90	0.1769	0.1212	0.0884	0.0745	0.0472	0.0309	0.0103
365	0.2022	0.1348	0.0983	0.0675	0.0418	0.0219	0.0008

Table 6
The hydration degree of cement (%)

Age (days)	Content of fly ash (%)						
	0	10	20	30	40	50	60
7	49.00	50.54	51.97	54.27	57.60	60.79	65.14
28	58.51	60.07	61.61	65.67	69.11	77.88	87.57
90	66.42	69.54	73.20	79.75	85.15	93.41	97.93
365	75.93	77.37	79.06	82.70	88.04	95.72	98.43

Table 7
The pozzolanic reaction degree of fly ash (%)

Age (days)	Content of fly ash (%)						
	0	10	20	30	40	50	60
7	–	–	0.58	6.42	6.01	6.63	7.28
28	–	25.85	17.23	16.90	16.41	15.63	14.77
90	–	32.85	25.74	24.28	24.33	23.13	21.19
365	–	36.56	28.28	27.36	26.41	25.20	22.61

is an intrinsic character and is not influenced by outside condition. The active effect of fly ash is the behavior of fly ash in the system and is different under the different conditions.

From the results in Tables 6 and 7, it may be known that the promoting role of fly ash to the hydration of cement strengthens with the increase of the content of fly ash, although the pozzolanic reaction of fly ash slows down. Thus, the active effect of fly ash still is stronger until 50% fly ash. However, the total hydration degree of the system reduces with the increase of the content of fly ash because the activity of fly ash is lower than one of cement.

4. Conclusions

This paper put forward the method by which the hydration degree of cement and the pozzolanic reaction degree of fly ash in the system of cement and fly ash are solved. In this base, the active effect of fly ash is analyzed. According to experimental results, the following conclusions can be obtained:

(1) With the increase of the content of fly ash, the hydration degree of cement increases, but the pozzolanic reaction degree of fly ash reduces.
(2) The active effect of fly ash is composed of two parts: the pozzolanic activity of fly ash self and the promoting role of fly ash to the hydration of cement.
(3) Within 0–60% of the content of fly ash, the active effect of fly ash is stronger.
(4) The total of the hydration degree of the system reduces with the increase of the content of fly ash because the activity of fly ash is lower than one of cement.

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