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Studies on high-strength slag and fly ash compound cement

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Abstract

High-strength composite portland cement blending blast furnace slag (BFS) and fly ash was obtained by using activators. The influence of the activators on the composite portland cement has been studied. Hydration phases and hydration mechanism were investigated by means of XRD, SEM, and DTA tests. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fly ash; BFS; Activator; High strength; Hydration

1. Introduction

Composite portland cement is a kind of cement that has just been developed in recent years. It consists of more than two kinds of mixed materials that are mainly derived from industrial waste slag or natural minerals. Reasonable dosage with the above two mixed materials can supply mutual advantage, help to improve properties, and increase its quality. Therefore, exploiting, investigating, producing composite portland cement, and studying its behaviors if of great importance.

Some mixed materials blended in the cement have potential activity, some are inert. By increasing the proportion of mixed materials by a large degree in cement, some side effects would occur, such as a reduction in cement strength, especially at early stages, and setting time lengthens. Therefore, this paper aims to investigate and obtain by using activators high-strength composite portland cement with large amounts of BFS and fly ash, and to explore for preliminary hydration mechanism.

2. Experimental methods

2.1. Raw materials

Raw materials were clinker from a cement plant in Jinan City, granulated blast furnace slag (BFS) from the Jinan Steel–Iron Plant and fly ash from the Jinan Huangtai Electricity Power Plant, and their chemical compositions are shown in Table 1. Activators were sodium salt, alunite, calcined gypsum, burned bauxite that were signified by N, A, G, E, respectively, their chemical compositions were also listed in Table 1.

2.2. Methods

Requiring water, setting time were performed according to GB1346-89 (Standard Test Method For Water Requirement of Normal Consistency, Setting Time and Soundness of the Portland Cement, The State Standards of the P.R. China). Mortar strength was performed according to GB177-85 (Test Method of Strength of Hydraulic Cement Mortar, The State Standards of P.R. China). The Blaine's

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

Raw materials	Loss	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	SO_3
Clinker	–	19.68	5.48	5.08	60.66	1.92	–	1.45
BFS	2.49	32.58	1.43	11.10	41.56	4.18	–	2.21
Fly ash	5.95	57.95	7.10	25.18	2.70	1.33	–	0.40
Gypsum	–	2.96	0.38	0.41	29.38	1.43	–	37.24
Alunite (A)	8.93	47.5	2.30	13.1	0.85	0.40	–	15.74
Sodium salt (N)	–	–	–	–	–	–	42.0	53.49
Calcined gypsum (G)	–	–	–	–	38.7	–	–	45.1
Burned bauxite (E)	–	12.25	5.39	71.01	1.71	2.21	–	–

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

	Dosages (wt.%)			Compressive			Flexural		
No.	Clinker	Fly ash	Gypsum	3 days	7 days	28 days	3 days	7 days	28 days
F1	96	0	4	29.10	36.30	55.25	5.33	6.03	7.92
F2	76	20	4	24.75	30.65	52.00	4.82	5.47	8.03
F3	56	40	4	14.65	20.70	42.25	3.22	4.38	7.18
F4	54	40	6	13.25	21.95	41.80	2.48	4.35	6.67
F5	52	40	8	9.35	17.45	42.70	1.97	3.35	7.72
F6	50	40	10	7.56	11.40	37.8	1.67	2.55	7.62

Table 3
Effect of BFS and G on cement strength (MPa)

	Dosages (wt.%)				Flexural			Compressive		
No.	Clinker	Slag	Fly ash	G	3 days	7 days	28 days	3 days	7 days	28 days
A0	65	30	0	5	4.86	6.43	8.24	24.2	38.5	59.1
A1	55	30	10	5	4.26	5.55	8.94	19.8	32.3	58.5
A2	45	30	20	5	3.92	6.13	8.72	19.2	33.3	52.1
A3	45	40	10	5	3.65	5.56	8.55	18.0	30.8	50.2
A4	35	50	10	5	3.56	5.90	7.72	17.69	35.0	51.3

specific surface area of each formula composite cement was 340–360 m^2/kg. Matter phase analysis of hydrates was conducted on X-ray diffractometer, type D/MAX-RA, 12 kW, made by Japan, S-2500 SEM made by HITACHI, Japan, and on DTA instrument, type LCT-2, by Beijing Optics Instrument Plant, China.

3. Results and discussion

3.1. *Effect of fly ash*

Table 2 was the effect of mixing amount of fly ash on cement strength. F1, F2 and F3 showed that mortar strength of cement decreased obviously with the increasing amount of fly ash. When fly ash ratio was 40%, compressive strength decreased 50% at 3 days and 23% at 28 days. F3–F6 indicated that with the increasing amount of gypsum, the strength at all stages was also reduced. Therefore, high-strength cement with large amounts of fly ash could not be obtained by means of increasing the amount of gypsum. So, BFS and G were added to improve the strength of composite cement.

3.2. *Effect of BFS and G*

The set of experiments was carried out in order to overcome lower strength of cement. The formulas and the results of the strength were shown in Table 3. Comparing A1–A4 in Table 3 with F4–F6 in Table 2, the conclusions were obvious that the compressive strength of A1 was higher than F3–F6 although they contained 40% of total

Table 4
Effect of activators on cement strength (MPa)

	Dosage (wt.%)					Flexural			Compressive		
No.	Clinker	BFS	Fly ash	G	Activators	3 days	7 days	28 days	3 days	7 days	28 days
B1	53	30	10	5	2(N)	5.89	7.25	10.00	32.4	44.4	62.3
B2	43	30	20	5	2(N)	5.71	7.30	9.08	26.3	40.2	52.4
B3	43	40	10	5	2(N)	5.18	7.97	8.99	21.8	43.2	56.2
B4	33	50	10	5	2(N)	5.55	7.63	10.56	28.3	44.0	61.5
C1	52	30	10	5	3(A)	4.08	5.76	8.51	21.4	38.1	53.2
C2	42	30	20	5	3(A)	3.69	6.44	8.26	17.3	33.7	53.1
C3	42	40	10	5	3(A)	3.97	6.33	7.89	20.8	35.5	54.3
C4	32	50	10	5	3(A)	3.98	6.42	7.91	16.4	35.3	51.5
D1	50	30	10	5	2N+3A	6.39	7.85	9.84	35.7	47.8	58.4
D2	40	30	20	5	2N+3A	5.54	7.48	8.73	27.5	41.2	55.5
D3	40	40	10	5	2N+3A	5.78	8.20	9.02	28.3	45.5	58.5
D4	30	50	10	5	2N+3A	6.17	7.94	9.70	29.6	45.7	57.4
E1	29	50	10	5	2N+4E	5.94	8.37	9.75	27.4	42.3	57.0
E2	24	50	10	5	2N+9B	6.16	8.13	8.94	32.9	44.9	56.5

mixed materials of BFS and fly ash. The strengths of A2, A3 or A4 were also higher than F3–F6 not only in flexural strength but also in compressive strength. These results indicated that G and BFS really improved the properties of cement. It also might be seen from A1, A3, and A4 that with the increasing amount of BFS while the content of fly ash was 10%, cement strengths were reduced, such as compressive strength was reduced about 10% at 3 days and 14% at 28 days. With the increasing amount of fly ash while the content of BFS was kept in 30%, cement strengths of A0, A1, and A3 were also reduced about 20% at 3 days and 12% at 28 days. This coincides with the Section 3.1 experimental results above, but its strength was higher than the former.

3.3. *Effect of activators*

Roy et al. [1–4] had confirmed that alkali could activate cementious materials, aluminate also accelerates the hydration of cement [5,6]. Thus, a small amount of N, A, E activators were added in composite cement with different dosage ratios, and the results are shown in Table 4.

Comparing the samples of groups B, C, D or E (in Table 4) with the samples of groups A (in Table 3), respectively and correspondingly, composite cement strengths increased greatly. For example, the mortar compressive strength of B2 with 2% N increased about 30% in the early curing age. The results proved clearly that activators N, A, and E improved the structure of cement. The result of group B (B1–B4) and C (C1–C4) showed that activator A had less effect on strength than N. While, when N and A were used in composite, the strengths of Nos. D1–D4 were higher than that of B1–B4 or C1–C4 with the same amount of mixed materials. High-strength composite cement with large amounts of BFS and fly ash could be obtained by using 2% N and 3% A. The strengths of samples E1 and E2 were also higher than that of A4 and C4. Thus, when N and E were used in composite, the effect was better, and higher strength cements were also obtained.

Based on the above analysis, activators N and A (or E) used jointly, not alone, could cause composite cement to have higher strength. The formulas of composite cements with high-strength could be obtained: clinker 30–50%, BFS 30–50%, fly ash 10–20%, G 5%, N 2%, and A (or E) 3–4%. The question about whether the 2% N alkali (in above formulas) would cause alkali aggregate reaction or not will be discussed in another paper.

Fig. 1. SEM photo of A_0 hydrates at 3 days.

Table 5
Setting time of composite cement

	Dosages (wt.%)				Setting time (h:min)	
No.	Clinker	BFS	Fly ash	Activators	Initial	Final
H1	56	–	40	4 gypsum	8:27	15:32
H2	45	40	10	5G	5:56	8:37
H3	43	40	10	5G+2N	3:57	6:38
H4	40	40	10	5G+2N+3A	2:48	5:20
H5	35	50	10	5G	6:08	8:56
H6	33	50	10	5G+2N	4:32	7:13
H7	30	50	10	5G+2N+3A	3:29	5:58

3.4. *Setting time*

The setting time of composite cement was shown in Table 5. The results of the tests showed that the setting time of H1 was very long without activator. H2, H3, and H4 indicated that the setting time had been shortened with the kinds of activator increasing. H5, H6, and H7 also demonstrated the same pattern. Therefore, compounds using activators G, N, and A could obtain the short setting time.

4. Hydration mechanism

The high-strength composite cement containing large amounts of BFS and fly ash was obtained by using all kinds of activators. Thus, these activators were certain to have an effect on hydrates and the structure of cement stone.

Fig. 2. SEM photo of B_4 hydrates at 3 days.

Fig. 3. SEM photo of D_4 hydrates at 3 days.

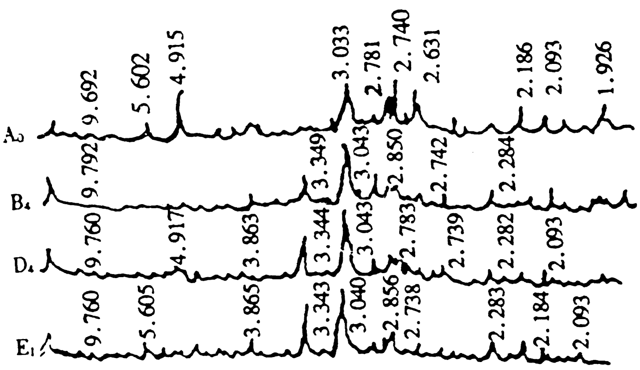

Fig. 5. XRD patterns of pastes at 3 days.

4.1. Hydrates

Samples A0, B4, D4, and E1 were made as paste specimens and cured at 3 days and analyses were performed by XRD, SEM, and DTA.

In Fig. 1, fly ash particles in A0 reacted [7] only in the surface and formed C–S–H gel. Bigger empty cavities existed and the whole structure was not dense enough. A large amount of needle-column AFt had filled up the cavities between particles in the other three samples hydrated at 3 days. Floccular C–S–H gel and needle-column AFt linked with each other to densify the structure of cement stone (Figs. 2–4).

The XRD patterns of pastes in Fig. 5 showed that diffraction peaks of calcium hydroxide crystallites were lower in samples B4, D4, and E1 than in A0, which indicated that the amount of Ca $(OH)_2$ in the pastes was less than in A0. But the clear peaks of AFt indicated that the amount of each AFt was higher than that in A0.

The thermograms of pastes in Fig. 6 showed that the dehydration peaks of C–S–H gel and AFt in pastes of B4, D4, and E1 were higher and endothermic peaks of calcium were lower than A0.

Based upon the analysis, C–S–H gel, AFt, Ca $(OH)_2$, hydro-grossularite, and unhydrated particles exist in cement stone. With the existence of activators, more hydrate products and less $Ca(OH)_2$ were produced in B4, D4, and E1, compared with that in A0.

4.2. Hydration mechanism

When high-strength BFS and fly ash composite cement were mixed with water, clinker minerals hydrated first and released calcium hydroxide. Water phase was saturated by calcium hydroxide. Then the glass phase of BFS and fly ash reacted with alkalis, and led to Si–O–Si, Al–O–Al links, etc. ruptured. It depolymerized to produce SiO_4^{4-}, AlO_4^{5-}, Ca^{2+}, etc., which went into the solution and formed new hydrated calcium silicate and hydrated calcium aluminate. The latter went on to react with SO_4^{2-} dissolved from gypsum, and derived AFt. In addition, hydro-grossularite, etc., hydrates were produced. The more amounts of mixed materials, the lower the clinker content, and the lower the alkalinity would be reduced to. The decomposing reaction of the glass phase network for BFS and fly ash would be

Fig. 4. SEM photo of E_1 hydrates at 3 days.

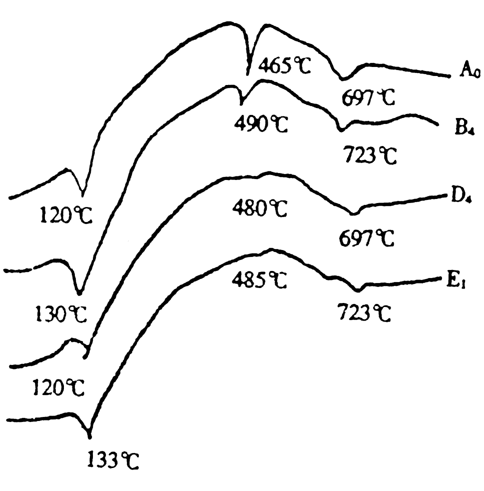

Fig. 6. Thermograms of pastes at 3 days.

slowed down. And these factors made the defect of the structure of cement stone so large that its strength was very low. Activator N increased the alkalinity of the solution [8] and induced the glass phase network to decompose. The dissolution of activators A and E introduced Al $(OH)_3$, AlO_4^{5-}, and SiO_4^{4-}, which reacted with Ca^{2+} to produce C–S–H gel and AFt of lower solubility. Hence, the structure of cement stone was greatly improved and the strength was increased, especially at early stages. So, activators not only dissolved itself to take part in the hydration reaction and increased the hydrates at the early stages, but also increased the alkalinity of the solution to promote the hydration of BFS and fly ash. Thus, the desired cement stone with dense structure and increased strength was achieved with the help of suitable activators.

5. Conclusions

By using activators, high-strength composite cement was obtained which contained a large amount of BFS and fly ash. The proper proportion for composite cement are detailed as following: clinker 30–50%, BFS 30–50%, fly ash 10–20%, G 5%, N2%, and A (or E) 3–4%.

The effect of compound activators N and A (or E) together was found to be better than that of a single one. N increased the alkalinity of solution and promoted the depolymerization of BFS and fly ash. A (or E) dissolved and took part in hydration.

The main hydrate products were C–S–H gel AFt and Ca $(OH)_2$ crystallites, though little amount of the last in high-strength cement. Under the influence of activators, Ca $(OH)_2$ went on to react with AlO_4^{5-} and SiO_4^{4-} depolymerized from BFS and fly ash, to form more products and, therefore, strengthen the structure of the cement stone.

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