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Communication

Studies on Portland cement with large amount of slag

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Abstract

It is necessary to make some technological measures to improve the characteristics of the cement in which a large amount of granulated blast furnace slag (BFS) is added. A few kinds of activators were adopted to develop activity of the cement in this paper. The influence of the additives on the high amount slag cement has been studied. The effect of the compound activators being better than that of an individual one was confirmed by a lot of test data. The optimum ingredient of this blended cement and its powder fineness had been found. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Activator; Cement; Granulated blast furnace slag; Hydration; Compressive strength

1. Introduction

The furnace slag is the by-product released from blast furnace. The main chemical composition includes CaO, SiO_2, and Al_2O_3. In addition, it contains very little MgO, FeO, and a little sulfide, such asCaS, MnS, and FeS. High proportions of CaO, Al_2O_3, and MgO are advantageous to the activity of slag while the viscosity increases with high content of SiO_2. It is easy to form $CaSiO_3$ and the high silicate glass that decreases the activity of slag. The activity of granulated blast furnace slag (BFS) is determined by the quantities and the properties of amorphous glass, as well as the chemical compositions. Facts have been proved that the higher the proportion of glass, the greater is the activity of slag at the same chemical composition. Thus, slag has been widely used as an active additive in China. Since 60% of cement is produced by mechanical shaft kiln factories, the blending quantity of slag is 25–30% in normal cement. So, this paper discusses the increase of amount of BFS added to the present clinker and the influence of activators on its properties.

2. Experimental methods

2.1. Raw materials

1. The chemical composition, the ratio value, and the physical properties of the clinker presented by the Cement Factory of Railway Station in Jinan are shown in Tables 1 and 2.
2. The slag composition presented by the steel manufacturer in Jinan is shown in Table 1.
3. The chemical composition of gypsum presented by a mineral factory in Pingyi is shown in Table 1.

Alunite, mirabilite, and calcined gypsum are signified by A, N, and G, respectively, their chemical compositions are shown in Table 1.

2.2. Methods

The strength of the cement is tested according to GB177-85 (Test Method of Strength of Hydraulic Cement Mortar, The State Standards of People's Republic of China). The fineness of cement is determined by Blaine's specific surface area equipment. The standard consistency water requirement, setting time, and soundness are examined by the method of GB1346-89 (Standard Test Method For Water Requirement of Normal Consistency, Setting Time, and

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

Name	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	f-CaO	CaF_2	Loss	Others
Clinker	21.02	4.08	5.16	62.58	2.24	1.14	2.91	0.99	2.03	1.08
Slag	32.90	5.28	11.39	38.47	6.62	0.35	–	–	–	4.99
Gypsum	2.96	0.38	0.41	29.38	1.43	37.24	–	–	–	28.2
Alunite (A)	47.5	2.30	13.1	0.85	0.40	15.74	–	–	8.93	11.18
Mirabilite (N)	–	–	–	–	–	53.49	–	–	–	–
Calcined gypsum (G)	–	–	–	38.7	–	45.1	–	–	–	–

Soundness of The Portland Cement, The State Standards of People's Republic of China).

3. Results and discussion

3.1. The selection of the activator

The mineral contents of clinker decrease relatively when both slag and clinker are mixed to form slag cement which cause the initial setting slower and the strength decrease, thus, we use the activators such as N, A, and G according to the principle of alkali slag cement to improve the disadvantage. The strength results obtained are shown in Table 3 (the cement used contained 50% slag).

It shows in Table 3 that the compressive strength at 28 days reaches 49.1 MPa when the amount of slag is increased by 50% with 2% A (No. A_1). The initial strength increases greatly when adding to 2% N (No. A_2), but the strength at 28 days is only 9.8/43.3 MPa. The strength at both 7 and 28 days is higher when adding 4% G (No. A_3). This kind of activator not only improves the early properties, but also reinforces the later stage properties, therefore, the activators used separately caused different influences on the cement. We designed the formula of using the mixed activator and observed the regulation of the cement property in order to make full use of all kinds of activators.

The numbers of A_4, A_{10}, and A_{11} showed that better value of the flexural strength can be obtained when the activators N and A were both 2%, but the value diminished with the increasing amount of A at all ages. When the blending quantity of A was 3%, the compressive strength reached the optimum value and the higher early strength was obtained in this formula. The numbers A_5, A_8 and A_9 indicated that the flexural strength at all ages would go up with the increase in G and the compressive strength reached optimum value when G and A contents were 6% and 2%, respectively. The compressive strength of blended cements showed that the active effect of mixed A and G occurs in late ages. Numbers of A_5, A_{12}, and A_{13} indicated that higher strength could be obtained not only early but also at late ages with the mixture of N and G.

Based upon the analysis of all the results, the cement obtained a higher early strength by using the mixture of N and A, while the higher later strength was obtained when using the mixture of A and G. When both N and G were blended, higher early and later strength could be obtained and make full use of N and G. The activator N plays an early active role while the activator G prompts the development of the later strength. The mixture of N and G is correlates with the balance of all the ions' reaction during hydration. It can prompt the formation of hydration product and improve the properties of the cement.

3.2. The definiteness of the best formula

It is well known that activator N is an early strengthening agent which prompts the hardening of concrete, but it can slow the development of later strength of the cement. Some investigators reached different conclusions after extensive research. The idea that alkali can accelerate the hydration and the formation of hydraulic products in early ages as well as prevent the hydration development in later ages has been accepted by more and more people [1–4]. The second set of experiments was carried out in order to diminish the alkali quantity in the cement, to minimize the prevention of the later hydration, and improve the later properties. The formulas and the results of the experiments are shown in Table 4 (the cement used 50% slag in its formulations).

The results of the tests (see Table 4) showed that early and later strength values of the cement with 50% slag were lower without activator. The early strength of the cement

Table 2
Physical properties of clinker

		Setting time (h:min)		Strength (flexural/compressive) (MPa)		
Surface area (m^2/kg)	Water requirement (%)	Initial	Final	3 days	7 days	28 days
301.6	25.2	3:14	5:18	5.5/31.1	6.5/44.1	7.8/58.0

Table 3
Influence of activator on cement strength (MPa)

			Activators			3 days		7 days		28 days	
No.	Clinker (%)	Gypsum(%)	A	N	G	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
A_1	44	4	2	–	–	3.4	14.4	5.2	20.1	8.1	49.1
A_2	44	4	–	2	–	5.6	21.9	7.5	29.2	9.8	43.3
A_3	46	–	–	–	4	4.4	18.4	6.6	28.3	8.7	53.8
A_4	42	4	2	2	–	6.0	22.0	8.0	30.3	8.9	43.4
A_5	44	–	2	–	4	4.1	17.0	6.9	28.4	9.0	50.0
A_6	42	–	2	2	4	6.5	22.5	7.6	32.2	9.1	47.1
A_7	44	–	–	2	4	5.6	20.5	7.4	35.6	9.2	49.3
A_8	42	–	2	–	6	4.2	14.1	6.8	31.4	8.5	50.0
A_9	40	–	2	–	8	4.7	16.9	7.3	30.6	9.7	48.3
A_{10}	41	4	3	2	1	6.0	22.2	7.8	36.3	9.4	46.5
A_{11}	40	4	4	2	–	5.5	19.1	7.0	30.9	8.2	41.5
A_{12}	42	–	–	2	6	6.0	24.0	8.2	40.8	10.1	52.7
A_{13}	40	–	–	2	8	5.2	21.8	9.0	39.4	9.2	51.3

(B_2, B_3, and B_4) with 1% activator N increased. The compressive strength at 28 days has been increased with the increase of A. The compressive strength reached 45.2 MPa when it is blended with 3% of A. The results of the tests (B_8, B_9, and B_{10}) showed that the compressive strength and the flexural strength at all ages developed slower with the increase of A when the activator G was kept constant, therefore, the blending quantity of A should be kept below 3%. The results also showed that the use of both A and G can activate the slag and obtain the ideal properties of the cement without alkali.

The compressive strength of B_{11}, B_{12}, and B_{13} which was mixed with 1% N respectively, at 3, 7, and 28 days goes up with the increase of G. The strength (at 28 days) is 50.6 MPa when the mixture of G is 6%. It indicated that we could also obtain cement material with high strength if we make use of G and lower the amount alkali as activator. The cement characteristic affected by the activator G was also indicated from the test results of B_5, B_6, and B_7. The flexural strength and the compressive strength (at 7 and 28 days, but not at 3 days) showed increasing values, especially at 28 days. It provided again that G has the influence of improving the later strength of the cement stones.

If we increase the amount of slag in the cement, the Al_2O_3 content in the cement must increase. It means that the aluminate content increases. The requirement of gypsum will change greatly relatively. In order to observe the effects of calcined gypsum (G) on the cement strength we carried out two group experiments. The amount of slag is 60% in experiment D while 70% in experiment E. The results are shown in Table 5.

We know from Table 5 that the early strength of cement increased when the gypsum was added from 5% to 9%. However, the strength at 28 days decreased. The reason was that the early hydration sulfoaluminate was advantageous to the structure and caused the structure to get closer, but too much sulfoaluminate in later ages is disadvantageous to the structure, therefore the content of gypsum should be controlled at 5–7%.

Table 4
Influence of the amount of activator on slag cement strength (MPa)

			Activator				3 days		7 days		28 days	
No.	Clinker	Gypsum	A	N	G	Fineness	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
B_1	45	5	–	–	–	–	2.5	12.7	4.20	22.1	7.5	41.0
B_2	42	5	2	1	–	–	2.9	15.8	4.30	25.4	7.8	41.0
B_3	41	5	3	1	–	–	3.69	17.6	5.58	28.4	8.1	45.2
B_4	40	5	4	1	–	–	3.20	15.1	5.00	25.4	7.5	42.9
B_5	46	–	–	–	4	3.2	3.24	13.8	4.87	24.0	7.8	42.3
B_6	44	–	–	–	6	3.6	3.17	13.7	4.67	24.6	8.0	44.9
B_7	42	–	–	–	8	4.1	3.05	13.4	5.55	26.5	9.3	47.1
B_8	42	–	2	–	6	1.5	3.93	18.9	5.96	32.6	7.7	52.1
B_9	41	–	3	–	6	1.9	3.60	16.4	5.23	28.6	7.6	47.7
B_{10}	40	–	4	–	6	4.0	3.10	14.2	4.98	25.9	7.3	44.4
B_{11}	45	–	–	1	4	3.8	4.08	18.2	5.78	28.2	8.4	44.6
B_{12}	43	–	–	1	6	2.7	4.38	20.7	6.51	32.7	9.3	50.6
B_{13}	41	–	–	1	8	4.0	4.33	21.0	6.95	33.1	9.0	48.7

Table 5
Influence of gypsum on the properties of cement strength (MPa)

No.	Gypsum	3 days		7 days		28 days	
		Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
D_1	5	4.88	22.4	7.68	38.7	8.90	61.6
D_2	7	5.45	26.0	7.65	41.2	8.73	58.7
D_3	9	5.18	25.1	7.77	42.1	9.45	58.1
E_1	5	5.20	23.2	7.02	36.1	9.15	53.4
E_2	7	5.03	25.2	6.47	35.7	7.90	52.8
E_3	9	5.10	24.2	7.18	37.3	8.37	48.3

Because the especial properties of the reaction between organic admixture and cement particles. It is used as water-reducing agent of concrete to improve the compressive strength of concrete. Some organic admixtures were added to the cement that the content of slag is 60% in order to observe it reacts on the cement activity. The results are listed in Table 6.

Table 6 illustrated that the compressive strength (3 and 7 days) with activator N improved 60% and it was far better than the others, the later flexural strength improved 18% and the compressive improved 5%. The early strength with activity A improved 15–23% in program F_3, the compressive strength in 28 days improved 12% and reached 61.6 MPa, which was the best effect. Comparing the additives in Table 6, the effect of FDN, NC, and RNC were better, while the effect of NF was not very evident.

Cement particle size is an important factor in affecting the properties of large amount of slag cement. The 20% clinker, 70% slag, 7% gypsum, and 3% A were ground to reach different specific surface areas, changes of properties shown in Table 7.

The strengths at all ages improved with the increase of fineness. Its particle fineness increased, the activity, and effectiveness was increased. Because the thickness of CSH gel surrounding the cement particles during hydration reaches 25 μm, the reaction rate is controlled by diffusion, the diffusion rate is very slow, in fact, the hydration has essentially stopped. Part of the core may be unhydrated if the dimension is very large. Thus, efficient fineness is needed to improve the activity of particles fully. The proper fineness of the large amount slag cement was 340–360 m^2/kg.

Based on the above analysis, activator without alkali A and G caused slag cement to have higher later strength. The activator with little alkali ($Na_2O + 0.658K_2O < 0.55$) could generate higher strength properties in the cement.

4. Discussion about the mechanism of hydration

The slag is vitreous and the potential activity is determined by the structure of the glass. The structure of slag glass consists of some different oxides (such as Al_2O_3 and SiO_2) forming a three-dimensional network. In contrast to crystalline phases, there is an order in the near distance but no order in far distance, thus, the ions such as Na^+, Mg^{2+}, and Ca^{2+} distribute in a disorderly and irregular manner in the inter-space network. The network structure of the glasses is stabilized when the slag solution is quenched. But the $[AlO_4]^{5-}$ formed from $[SiO_4]^{4-}$ is replaced by Al^{3+} and $[SiO_4]^{4-}$. The SiO breaks in the aluminate silicate network is not stable, but can change automatically from the non-stable condition to stable condition; the hydration takes place as it is activated by the activator. The paper [5] shows that the slag has hardly any activity in water while in alkali, hydration and hardening action are pronounced. The SiO layer of the slag structure is destroyed by an alkali activator, and hydration products, such as CSH gel and hydro-calcium aluminate are formed by rearrangement of SiO_4^{4-} and AlO_4^{5-} and produced gelling.

The slag cement reacts with water, producing hydrous calcium silicate, hydrous calcium aluminate, hydrous C_4AF, and $Ca(OH)_2$. Those products have the same properties as in

Table 6
Influence of some organic admixtures on the properties of cement strength (MPa)

No.	Additives	3 days		7 days		28 days	
		Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
F_1	–	4.3	19.4	6.40	31.5	8.31	55.0
F_2	2N	6.73	31.2	9.87	42.7	9.82	57.5
F_3	3A	4.88	22.4	7.68	38.7	8.9	61.6
F_4	0.5FDN	4.67	21.4	7.03	38.0	8.77	59.6
F_5	1NC	5.47	25.1	7.97	38.8	9.75	60.2
F_6	1NF	5.2	22.3	7.40	35.1	8.60	55.6
F_7	0.5RNC	4.03	18.8	6.52	35.9	8.38	59.3

Table 7
Influence of fineness on the properties of cement strength (MPa)

No.	Specific surface area (m^2/kg)	3 days		7 days		28 days	
		Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
H_1	272	3.22	15.5	5.07	25.4	7.15	43.5
H_2	309	4.25	21.7	5.92	31.5	6.80	45.9
H_3	345	5.03	25.2	6.47	35.7	7.90	52.8
H_4	360	5.07	25.0	6.83	25.3	5.53	53.4

the hydration of pure Portland cement. In the alkali $Ca(OH)_2$ solution, Ca^{2+}, AlO_4^{5-}, and SiO_4^{4-} ions of the glass enter the solution and form new hydrate (such as the hydrated silicate and the hydrated aluminate). The quantity of $Ca(OH)_2$ which, being produced in the slag cement, decreases relatively because of the lesser amount of clinker. It causes the alkali concentration to decrease in the solution and the depolymerization of the slag glass is not complete. According to the mechanism of cement with alkali and slag, the network of slag separates completely in the alkali and forms more hydration products. The existence of sodium salt can improve the relative alkalinity, prompt the slag glass to depolymerize, and accelerate the speed of the hydration as well as the formation of the ettringite through solution. The influence of SO_3 on slag cement is not only to react with C_3A of the clinker but also to react with AlO_4^{5-} from the dissolution glass to form calcium trisulfoaluminate to prompt the hydration of slag. This action lasts until the complete hydration of slag occurs in the presence of enough SO_4^{2-} solution. Therefore, it is very important for the complete depolymerization of glass and subsequent hydration to keep enough SO_4^{2-} in the solution. The activator G in slag cement solution can cause the amount of SO_4^{2-} in later solution to increase and react with AlO_4^{5-} to create the difficult dissolution and redistribution of hydrates which plays an important part in the structure density of cement stone.

Based on the analysis above, the hydration and hardening step of slag cement can be described as follows: Firstly, CSH gel and ettringite form from hydration of clinker minerals and release $Ca(OH)_2$. This $Ca(OH)_2$ not only maintains a certain value of P/H in the solution to activate the hydration of slag but also reacts with all ions of slag separation to form the new hydration products. Sodium dissolves immediately and greatly increases the amount of alkali in solution. It can accelerate the depolymerization of glass and increase the early hydration products, but too much alkali is disadvantageous to negative ion polymerization and affects the late hydration product. The activator G affords SO_3 to form ettringite that is advantageous to the structure density. It should not form too much ettringite because it would cause the structure of cement stone to be destroyed in the long term. Therefore, in order to obtain the better cement properties and the ideal activation effect, the influences detailed in this paper should be followed.

5. Conclusion

1. The effective measure of adding activator was used to optimize the properties of cement containing a large amount slag. The effect of a double activator was found to be better than a single one, causing "the complementary advantage for each other." Higher early strength was obtained when A was mixed with N, higher long term strength was achieved when A was mixed with G, while the mixture of N and G evidently improved both the early and late structure and the ideal properties were obtained.

2. The proper formula for mixtures with high amount of slag are detailed as follows: clinker 30–50%, slag 45–65%, activator 6–8%, fineness 340–360 m^2/kg.

3. The hydration process was as follows: the hydration products were formed from the slag glass depolymerization and separation. $Ca(OH)_2$ produced from the clinker hydration and alkali activator N together afforded the alkali which was required for the glass deploymerization and G afforded the SO_3 to form ettringite. The influence among the three prompted the hydration reaction of glass and the development of density of the structure of the cement stone.

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