Pergamon

Cement and Concrete Research 32 (2002) 1341–1344

CEMENT AND CONCRETE RESEARCH

Study on high-strength composite portland cement with a larger amount of industrial wastes

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Received 29 November 2001; accepted 13 March 2002

Abstract

It is one of important measures for the sustainable development of cement industry to utilize industrial wastes. High-strength composite portland cement with a large amount of granulated blast furnace slag (GBFS), fly ash and limestone was prepared by separate grinding method, optimizing gypsum and using activators. The total amounts of blending materials are between 45% and 65% and the strength grades of cements reach 525 or even 625 according to Chinese national standard for composite portland cement. Besides setting time and strength, the hydration heat, drying shrinkage and sulfate resistance were also determined. © 2002 Published by Elsevier Science Ltd.

Keywords: GBFS; Fly ash; Blended cement; High strength; Properties

1. Introduction

Composite portland cement has been widely developed in recent years in China. Because it is characteristic of saving resources and power, utilizing industrial wastes as well as decreasing heat of hydration and improving durability of cement [1,2], composite portland cement is popular to the cement manufacturers and becomes a kind of cement for the sustainable development. However, the composite portland cement has a larger reduction in strength, especially at early ages, and a slower setting with increasing the proportion of blending materials in cement. Therefore, this composite portland cement was rarely used in key projects.

Presently, there are three problems for the development of composite portland cement in China [2–4]. Firstly, the total amounts of blending materials in composite portland cements are popularly lower than 35% and the cements only have low strength of 325 grade according to Chinese national standard. Secondly, to increase the early strength, the amounts of activators added to composite portland cement are too high, generally up to 3–7%, over the limit of 1% of processing additions for use in the manufacture of cement according Chinese national standard. Thirdly, the cement plants take no account of the difference in hardness of materials. Composite portland cements are all produced by intergrinding.

This paper aims to prepare by separate grinding method, optimizing gypsum and using compound activators high-strength composite cement with a larger amount of granulated blast furnace slag (GBFS) and fly ash.

2. Experimental materials and methods

2.1. Raw materials

Clinker was from Huaxin Cement Plant (Huangshi, P.R. China), GBFS from Wuhan Steel and Iron Group Company (Wuhan, P.R. China), fly ash from Huangshi Power Plant (Huangshi, P.R. China), limestone from Huangshi Limestone Mine (Huangshi, P.R. China), gypsum from Jingmen Gypsum Mine (Jingmen, P.R. China). Calcined gypsum was made of the above gypsum at 750 °C for 1 h. Table 1 shows the chemical composition of these materials. Activators were six chemical agents of sodium sulfate, calcium lignosulfonate, lithium carbonate, urea, triethanolamine and aluminum sulfate that were signified by A–F, respectively.

2.2. Methods

The setting time were performed according to GB1346-89 (The State Standard of P.R. China). The Blaine's specific

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0008-8846/02/$ – see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0008-8846(02)00804-9

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

Materials	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	SO_3	MnO	Loss
Clinker	21.28	3.37	5.32	63.49	3.66	–	–	–	0.74
Fly ash	55.07	6.81	29.82	4.73	1.16	–	0.48	–	0.99
GBFS	34.70	1.02	14.95	35.81	10.45	0.08	0.20	0.39	0.61
Limestone	4.09	0.41	1.22	50.22	2.03	–	–	–	41.12
Gypsum	3.61	0.51	1.45	34.91	0.64	–	48.19	–	–

surface area was performed according to GB8074-87. The mortar strength was measured as per GB177-85. Mortar bars ($4 \times 4 \times 16$ cm) were made of cement, sand and water (1:2.5:0.44), which were first cured in fog room at 20 °C for 24 h and then demoulded and cured in water 20 ± 3 °C until the desired age. The hydration heat was tested according to GB2022-80. The drying shrinkage was examined according to GB751-81. Mortar bars ($2.5 \times 2.5 \times 25$ cm) with the above proportions were cured in fog room for 1 day and in 20 °C water for 6 days and then placed in a box (20 ± 3 °C, 60 ± 5% relative humidity) for another 3, 7, 14, 28, 90 and 180 days. The length of specimen before and after drying was measured.

The sulfate resistance was tested in accordance with GB2420-81. Mortar bars ($4 \times 4 \times 16$ cm) with the above proportions were cured in 20 °C water for 28 days and then cured in 5% Na_2SO_4 solution at 20 °C for another 30 and 90 days. The compressive strengths of specimen before and after curing in sulfate solution were measured.

3. Results and discussion

3.1. Effect of grinding method

Two types of cements with the same composition were produced by both separate grinding and intergrinding. The amount of GBFS, fly ash and limestone of the cements was 30%, 20% and 5%, respectively, and the amount of gypsum was 5% by weight. Separate ground cement was produced by grinding GBFS, fly ash and the mixtures of clinker, limestone and gypsum separately to 385, 404 and 340 m^2/kg Blaine fineness and mixing them in a cone-shaped mixer. Interground cement had Blaine fineness of 372 m^2/kg. The mortar strengths of the two cements were shown in Table 2. It can be seen from Table 2 that the separate ground cement has higher strengths and more quick setting compared with the interground one, although the two cements have the same fineness and the same composition. The fly ash was softer and was more grindable and GBFS, which was harder, was less grindable than the clinker. Therefore, the separately ground and interground cements incorporated with GBFS and fly ash had appreciably different particle size distributions due to the difference in hardness of materials. The harder GBFS particle was larger in size, which led to low hydration activity and decreased strength. Cheng [5] revealed that the GBFS-incorporated cement was interground to the Blaine fineness 300–350 m^2/kg, but the Blaine fineness of GBFS is only 250–270 m^2/kg.

Table 2
Effects of grinding method on cement strength (MPa)

Grinding method	Blaine fineness (m^2/kg)	Setting time (h:min)		Compressive		Flexural	
		Initial	Final	3 days	28 days	3 days	28 days
Intergrinding	372	4:38	6:44	20.3	48.3	4.8	9.1
Separate grinding	370	4:14	6:12	24.6	53.5	5.5	9.7

3.2. Effect of gypsum

Table 3 was the difference in the mortar strengths between the gypsum-incorporated and calcined gypsum-incorporated cements. Based on previous works, the cements were produced by separate grinding and the amount of GBFS, fly ash and limestone was 30%, 20% and 5%, respectively. Specimens 1 and 6 are portland cement, which are used as a control. The results show that the appropriate amount of gypsum or calcined gypsum is 5% (by mass) and the substitution of calcined gypsum for gypsum is in favor of the development of strength, which may be related to the fact that calcined gypsum resulted in more ettringite being formed during early hydration because it possessed larger solubility and higher activity than gypsum [6].

3.3. Effect of activators

A small amount mixtures of A–F reagents were used as activators and added to Specimen 9. The best results by adding these activators with different mix proportions and amounts were chosen and are given in Table 4. It was obvious that those activators could improve the performances to a certain degree, while Specimen 13 resulted in the best improvement in both setting and strength. The results show that the addition of small amounts of compound activators used can increase the pozzolanic reactivity of both GBFS and fly ash.

Table 3
Effect of gypsum on strength of cement strength (MPa)

Specimen	Clinker (wt.%)	Gypsum (wt.%)	Calcined gypsum (wt.%)	Compressive		Flexural	
				3 days	28 days	3 days	28 days
1	95	5		34.6	64.4	7.3	8.9
2	42	3		21.7	51.5	5.0	8.9
3	41	4		22.3	51.9	5.3	9.5
4	40	5		24.6	53.5	5.5	9.7
5	39	6		23.8	54.0	5.2	9.1
6	95		5	36.5	66.7	7.8	9.2
7	42		3	24.2	53.8	5.5	9.4
8	41		4	25.4	54.4	5.8	9.7
9	40		5	26.8	56.1	6.0	10.0
10	39		6	25.9	55.7	6.2	10.3

Table 4
Effect of activators on cement strength (MPa)

Specimen	Clinker (wt.%)	Activators		Setting time (h:min)		Compressive		Flexural	
		Kind	Amount (wt.%)	initial	final	3 days	28 days	3 days	28 days
9	40	–	0	3:42	5:50	26.8	56.1	6.0	10.0
11	40	A + B + C	0.5 + 0.08 + 0.42	3:10	4:46	28.9	60.7	6.3	10.4
12	40	A + C + D	0.5 + 0.55 + 0.15	2:44	4:27	29.4	61.5	6.5	10.6
13	40	A + C + E + F	0.5 + 0.42 + 0.03 + 0.55	2:18	4:24	30.4	62.3	6.6	10.9

Table 5
Effect of amount of GBFS and fly ash on cement strength (MPa)

Specimen	Mix proportion (wt.%)					A + C + E + F (wt.%)	Compressive		Flexural	
	Clinker	Calcined gypsum	Limestone	GBFS	Fly ash		3 days	28 days	3 days	28 days
14	50	5	5	30	10	1.5	34.3	68.8	7.0	11.6
15	40	5	5	40	10	1.5	31.8	66.6	6.9	11.2
16	30	5	5	50	10	1.5	28.2	61.8	5.4	11.0
17	50	5	5	20	20	1.5	32.9	65.7	6.7	10.8
13	40	5	5	30	20	1.5	30.4	62.3	6.6	10.9
18	30	5	5	40	20	1.5	24.7	58.2	5.2	10.3
19	50	5	5	10	30	1.5	30.0	59.1	6.2	10.0
20	40	5	5	20	30	1.5	26.8	57.4	5.8	9.4
21	30	5	5	30	30	1.5	22.2	54.8	4.8	9.2

Table 6
Hydration heat of cement (kJ/kg)

Specimen	Clinker (wt.%)	Hydration time (days)								
		0.5	1	1.5	2	3	4	5	6	7
14	50	95.1	192.7	211.5	224.2	239.0	244.8	249.3	251.8	254.4
13	40	35.5	119.4	168.2	189.8	207.8	219.7	229.4	238.1	243.5
18	30	31.2	90.9	139.4	168.6	190.9	198.9	205.6	208.4	210.2
525 P·MH						⩽251				⩽293
425 P·LH						⩽197				⩽230

3.4. Effects of GBFS and fly ash

Table 5 shows the effect of mixing amount of GBFS and fly ash on cement strength. These cements were prepared by separate grinding and the Blaine fineness of each formula cement was 360–380 m^2/kg.

It might be seen from Specimens 14–16 that with the increasing amount of GBFS while the content fly ash was 10%, cement strengths were reduced. With the increasing amount of fly ash while the content of GBFS was kept in 30%, cement strengths of Specimens 13, 14 and 21 were also reduced and the cement strength decreased more obviously with the increasing amount of fly ash than with the increasing amount of GBFS. It was noted from Table 5 that all cement specimens exceeded 525 strength grade and three cements reached 625 strength grade in spite of the fact theses cements only contained 30–50% clinker, which may be related to the higher fineness of the components of the specimens and the fact that calcined gypsum and suitable activators used accelerated the hydration of cements and resulted in more C-S-H gel and ettringite being formed during hydration.

3.5. Hydration heat

The hydration heat values of Specimens 13, 14 and 18 are shown in Table 6. 525 P·MH and 425 P·LH are the hydration heat required for 525 moderate heat portland cement and 425 low heat slag portland cement, respectively,

Table 7
Drying shrinkage of cement ($\times 10^{-4}$)

Specimen	3 days	7 days	14 days	28 days	90 days	180 days
6	1.48	5.21	6.61	7.59	9.28	9.87
14	1.97	3.55	5.06	6.89	7.03	7.73
13	2.68	4.23	5.35	7.32	8.59	8.87
18	3.99	4.84	6.83	8.83	9.68	9.82

Table 8
Sulfate resistance (MPa/%)

Specimen	Water for 28 days	5% Na_2SO_4 for 30 days	5% Na_2SO_4 for 90 days
14	68.2/100	73.1/107	75.7/111
13	63.5/100	69.2/109	72.0/113
18	57.5/100	65.5/114	69.6/121
6	66.9/100	69.9/104	71.0/106

which are from GB200-89 of Chinese state standard. The results showed that the hydration heat decreased in all ages with the decreasing amount of clinker and the hydration heat for Specimens 13 and 14 accorded with the requirements for the 525 moderate heat portland cement and the hydration heat for Specimen 18 accorded with the requirements for the 425 low heat slag portland cement. Therefore, the above composite cements may be used in the constructions of mass concretes, which demand low hydration heat.

3.6. Drying shrinkage

The drying shrinkage values of Specimens 6, 13, 14 and 18 are given in Table 7. It is found that the drying shrinkage of composite cement is larger than portland cement at 3 days but becomes smaller between 7 and 180 days, which may be explained by the expansion due to the formation of ettringite for composite cement could offset higher drying shrinkage than that of portland cement.

3.7. Sulfate resistance

The compressive strength values of Specimens 6, 13, 14 and 18 cured in water and 5% Na_2SO_4 solution are listed Table 8. The ratio of strength cured in sulfate solution to that in water was represented in the denominator. Generally speaking, the sulfate resistance is lower when the cement contains higher aluminate minerals. It is evident that the sulfate resistance of composite cement is better than that of portland cement, which may be related to the fact that the incursion of Na_2SO_4 could activate the hydration of GBFS and fly ash of composite cement and increased strength.

4. Conclusions

(1) By using calcined gypsum and suitable activators and improving Blaine fineness, the preparation of high-strength composite cement with a large amount of GBFS, fly ash and limestone is possible. The total amount of GBFS, fly ash and limestone could reach 45–65% and the grade of cement could reach 525 or even 625 determined by the quality of clinker, GBFS and fly ash. The effect of compound activators of A, C, E and F is best.

(2) Separate grinding is adapted to the production of composite cement containing GBFS and fly ash and the effect of calcined gypsum on strength of the composite cement is better than gypsum.

(3) Specimens 13, 14 and 18 represent three typical formulas of high-strength composite cements in this study and show low hydration heat and smaller drying shrinkage and higher resistance to sulfate than those of portland cement (Specimen 6). The durability resistance and hydration mechanism of these composite cements needs to be studied further.

Acknowledgments

Financial support for this project was provided by Hubei Province Science and Technology Department. Authors wish to thank Huangshi City Huaxin Cement Plant for the supply and analysis of the raw materials used.

References

[1] Z.W. Wu, Environmental friendly high-effect cement-based materials, Concrete (6) (1996) 3–6.
[2] Z. Ding, D.C. Zhang, X.D. Wang, The development and actuality of composite cements in China, Cement (3) (1997) 1–5.
[3] D.X. Li, Study on properties of composites portland cement, Cem. Eng. (1) (1996) 23–26.
[4] W.P. Hou, X.H. Fu, Increasing the amount of blending materials in composite portland cement, Cem. Technol. (3) (1997) 9–12.
[5] W. Cheng, Research on the grinding technique of portland slag cement, Chin. Build. Mater. Sci. Technol. (2) (2000) 31–33.
[6] C.Z. Wu, B.R. Sun, F. Ye, Study on improving quality of 525 ordinary portland cement, Bull. Chin. Ceram. Soc. 18 (2) (1999) 19–23.