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Research on optimizing components of microfine high-performance composite cementitious materials

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Abstract

The relationship between material components and mechanical properties was studied in terms of composite material principles and orthogonal experimental design. Moreover, the microstructure of microfine high-performance composite cementitious material (MHPCC) paste was investigated by means of scanning electron microscopy (SEM) methods. The results showed that the composite material consisting of blast furnace slag (BFS), gypsum (G_2) and expansive agent (EA) could obviously improve the strength of the cementitious material containing 40% fly ash (FA). Although microfine cement (MC) was merely 45% percent of the MHPCC, the compressive strength of MHPCC paste was higher than that of neat MC paste. BFS played an important role in MHPCC. The optimum-added quantity of BFS was 15%. The needle-shaped ettringite obtained from the EA reacting with $Ca(OH)_2$ forms a three-dimensional network structure, which not only improved the early strength of MHPCC paste but also increased its late strength. The reason was that the network structure, which was similar to a fiber-reinforced composite, was formed in the late period of hydration with the progress of hydration and the deposition of hydration products into the network structure.

Keywords: Microfine cement; Blended cement; SEM

1. Introduction

Owing to the development of grinding technology, microfine cement (MC) is now widely used for repairing buildings and reinforcing foundations in hydroelectric engineering, mining and tunnel engineering, etc. Because of its smaller particle size, MC can penetrate microcracks and can even compete with chemical grouting materials [1,2]. But along with the reduction of the particle size of cement, the rheological properties of cement paste become poor. In addition, both the shrinkage and heat of hydration of the cement paste also increase. The above shortcomings badly hinder further the application of MC [3,4]. Based on design methods for high-performance concrete (HPC) [5], the composite materials, which were made of fly ash (FA), slag and an expansive agent (EA), were added to MC in order to improve its properties [6–8]. The utilization of FA not only protects the environment and decreases the cost of MC, but also markedly improves the properties of MC [9]. At present, research on microfine high-performance composite cementitious material (MHPCC) is deficient. In this paper, the relationship and mechanism between components and mechanical properties of MHPCC are studied.

2. Raw materials and methods

2.1. Raw materials

The raw materials used in this experiment are listed in Table 1. MC consisted of 95% clinker and 5% gypsum (G_2). FA was collected from an electrical dust collector of a power plant. Blast furnace slag (BFS) was produced by superfine grinding of slag. The EA was made of alunite and G_2. The particle size distribution of the fine material was measured by a Malvern laser granulometer from England. Their chemical composition and particle size distribution are shown in Tables 1 and 2, respectively.

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Table 1
Chemical composition of raw materials (%)

	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Loss	SO_3
Clinker	21.49	64.39	5.53	3.37	2.28	1.46	–
Gypsum	6.99	28.61	2.67	0.96	2.18	21.42	36.91
FA	50.00	4.91	32.85	4.21	1.58	3.22	–
BFS	33.49	34.84	15.61	0.74	9.91	1.06	–
EA	29.5	17.93	7.76	2.82	1.83	20.67	24.79

2.2. Methods

The compressive strength of cement paste specimens was tested at 3, 7 and 28 days. The size of the specimens was 20×20×20 mm. The specimens were demoulded after 24 h of casting, and then cured in standard condition (20 °C, underwater).

3. Results and discussion

3.1. Influence of material components on compressive strength of cement paste

The material components and test results are listed in Table 3. BFS, G_2 and EA were added to the samples on the basis of the M_2 composition.

Table 3 shows that both the 3-day compressive strength (R_3) and the 28-day compressive strength (R_{28}) of M_1 (net MC paste) were high, whereas the increasing rate of strength from 3 to 28 days was the lowest among all samples. When 40 wt.% FA was substituted for MC, the R_3 and R_{28} of the sample (M_2) decreased to 44.25 and 54.15 MPa, respectively, which were about 34% lower than those of M_1. As other samples in Table 3 were admixed with BFS, G_2 and EA on the basis of M_2, the R_3 and R_{28} from samples M_3 to M_5 gradually increased. Comparing M_5 with M_2, it seems that R_3 and R_{28} obviously increased and reached 63.75 and 84.67 MPa, respectively, with the increases being 44.08% and 56.36%, respectively. Moreover, for M_5 paste, R_3 was close to that of M_1 and R_{28} was higher than that of M_1. Therefore, the strength of the cementitious material containing 40% FA can be improved according to the principle of multicomponent composite materials, and MHPCC could be prepared.

3.2. Orthogonal tests and analysis

The above test results showed that the compressive strength of the sample M_5, which only contained 45% MC, was higher than that of MC. It indicated that material components significantly affect the strength of MHPCC. Thus, material components should be optimized. The test results of the relationship between compressive strength and material components, according to the orthogonal experimental principle, are shown in Tables 4 and 5. The control sample was made of 60% MC and 40% FA. BFS, G_2 and EA were added on the basis of the control sample.

Table 2
Particle size distributions of raw materials (%)

Diameters (μm)	0.5	1	3	5	10	15	20	30	40
MC	0.00	0.61	15.96	38.87	76.80	90.76	95.00	98.90	100
FA	2.85	19.77	64.09	82.01	96.79	99.43	100	100	100
BFS	14.90	27.97	51.26	67.65	91.64	98.30	99.00	99.47	100

Table 3
Component proportion and compressive strength of the materials

Sample	Material component (%)					R_3 (MPa)	R_{28} (MPa)	Strength increasing ratio from 3 to 28 days (%)
	MC	FA	BFS	G_2	EA			
M_1	100	–	–	–	–	67.56	81.5	20.63
M_2	60	40	–	–	–	44.25	54.15	22.37
M_3	60	40	10	–	–	46.06	60.42	31.37
M_4	60	40	10	7	–	52.75	77.33	46.6
M_5	60	40	15	3	15	63.75	84.67	32.82

For 3-day compressive strengths of cement pastes, their difference values for EA, BFS and G_2 were in the order: EA>BFS>G_2 (Table 5). R_3 was 63.75 MPa when EA quantity added was at Level 1 (5%), and that decreased to 58.52 MPa at Level 2 (10%) and to 53.31 MPa at Level 3 (20%), respectively. This indicated that EA brought down the R_3 values of the samples. The effect of BFS on 7- and 28-day compressive strength was the largest among EA, BFS and G_2. The R_7 and R_{28} values were 68.0 and 80.06 MPa, respectively, when slag quantity was added at Level 1 (10%) and those increased to 78.15 and 90.39 MPa, respectively, at Level 2 (15%). But at Level 3 (20%), they, respectively, decreased to 71.5 and 79.47 MPa. BFS had the same effect on R_3. The above test results showed that the optimum quantity of the slag added was at Level 2 (15%). For EA, the compressive strength of cement paste decreased from Levels 1 to 3. G_2 hardly affected compressive strength at the various levels. The measured strength of K_1, K_2, K_5, K_7, K_8 and K_9 were better than the other samples in Table 4.

It was shown from Table 4 that the samples K_3, K_4 and K_8 were all admixed with 20% EA, but their strength was different; the compressive strength of K_8 was the highest and those of K_3 and K_4 were low in the nine samples. This

Table 4
Orthogonal design and compressive strength of the materials

Sample	Level of MHPCC quantity added (%)			R_3 (MPa)	R_7 (MPa)	R_{28} (MPa)
	BFS	G_2	EA			
K_1	1 (10)	1 (3)	1 (5)	60.13	67.69	81.75
K_2	2 (15)	2 (7)	2 (10)	57.31	77.19	87.5
K_3	3 (20)	3 (10)	3 (20)	49.25	65.31	75.75
K_4	1	2	3	46.44	63.06	75.42
K_5	2	3	1	65.44	81.44	88.83
K_6	3	1	2	58.25	69.13	73.92
K_7	1	3	2	60.00	73.25	83.00
K_8	2	1	3	63.63	75.81	94.83
K_9	3	2	1	65.69	80.06	88.75

Table 5
Analysis of the orthogonal experiment data

Factor level	R_3 (MPa)			R_7 (MPa)			R_{28} (MPa)		
	BFS	G_2	EA	BFS	G_2	EA	BFS	G_2	EA
1	55.52	60.67	63.75	68.00	70.88	76.40	80.06	83.50	86.44
2	62.13	56.48	58.52	78.15	73.44	73.19	90.39	83.89	81.47
3	57.73	58.23	53.31	71.50	73.33	68.06	79.47	82.53	82.00
Difference value	6.61	4.19	10.44	10.15	2.56	8.34	10.92	1.36	4.44

was because the proportions of the other components in the samples were different. It indicated that the quantity of EA added should match with BFS and G_2 to get the highest compressive strengths.

3.3. Analysis of microstructure

The hydration progress and microstructure of MHPCC were further investigated by means of scanning electron microscopy (SEM) methods. Figs. 1–4, respectively, show the microstructures of M_1, M_2, M_3 and M_5 paste.

It was seen from Fig. 1 that the C–S–H gel of M_1 (neat MC paste) formed a dense network structure after 3 days. This showed that the hydration reaction of MC was fast and a lot of hydration products was formed. Thus, the paste structure tissue became dense; moreover, the early compressive strength was high. Comparing Fig. 1a with Fig. 1b, we find that the density and appearance of cement paste structure tissue cured for 28 days were similar to that for 3 days. This kind of microstructure also explains why the increasing ratio of compressive strength of M_1 paste from 3 to 28 days was the lowest among the five samples (Table 3). Fig. 2a and b shows SEM photographs of M_2 paste cured for 3 and 28 days, respectively. The FA beads were enrobed by C–S–H gel and $Ca(OH)_2$. FA beads surface were still smooth after 3 days. The C–S–H gel did not form a fibriform network structure in this cement paste. After 28 days, some bead surfaces of FA became coarse because of the hydration reaction between $Ca(OH)_2$ and FA. This kind of reaction easily occurs in FA pores and defects.

Fig. 3 shows the SEM photographs of M_3 paste that was admixed with FA and slag. Slag had hydrated after 3 days, which was because the activity of slag was higher than that of FA. The quantities of the early hydration products of M_3 were larger than that of M_2 and formed a network structure.

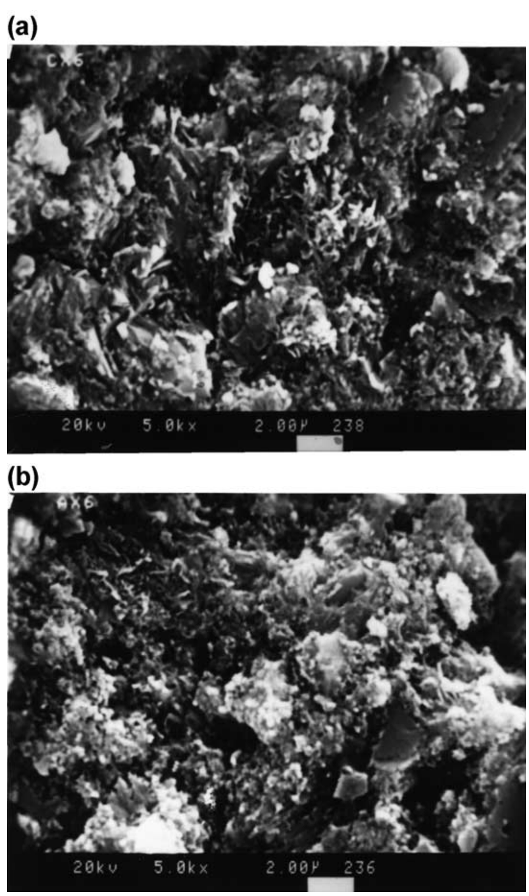

Fig. 1. SEM of the hardened paste of the sample M_1. (a) Hydrated for 3 days. (b) Hydrated for 28 days.

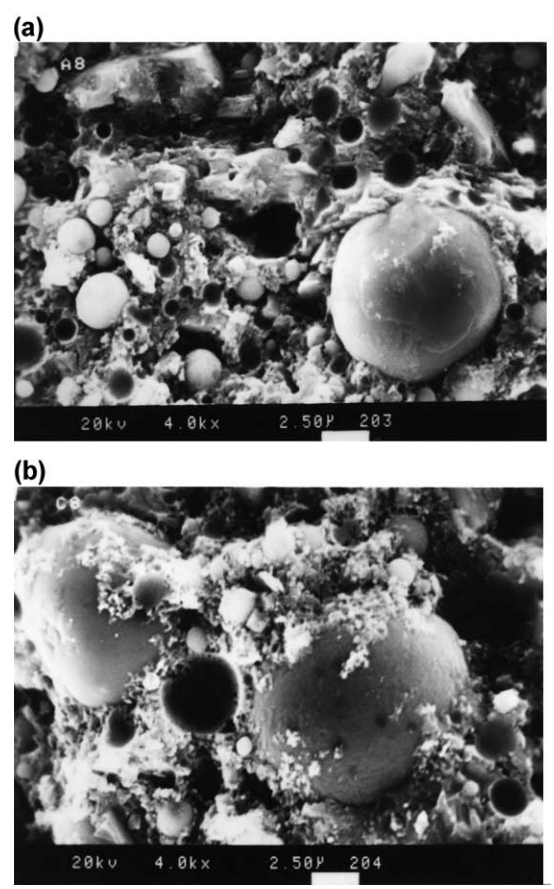

Fig. 2. SEM of hardened paste of the sample M_2. (a) Hydrated for 3 days. (b) Hydrated for 28 days.

In the latter age of hydration, the surface of FA in M_3 paste was coarser than that in M_2 paste. It indicated that the activity of FA could be improved with the addition of BFS. Fig. 4 is the microstructure of the M_5 paste admixed with FA, slag and EA. A lot of needle-shaped ettringite formed a network structure at the early stage of hydration. FA filled the network structure. As hydration progressed, other hydration products gradually filled the network structure. The cement paste structure became tight at the latter stage of hydration. Thus, we can conclude that ettringite formed a three-dimensional network structure in the early stages of hydration. As hydration proceeded, other hydration products filled in the three-dimensional network structure and formed the structure that is similar to fiber-reinforced composite materials. Fig. 4b shows that there were some microcracks in the M_5 paste with the addition of 15% EA, which might be due to forming too much ettringite in the latter stages of hydration. The ettringite expansion caused the cement paste to crack. The orthogonal tests also demonstrated that excessive EA added would bring on the decrease of compressive strength of cement paste. Thus, the ratio of EA added should be optimized to ensure that ettringite can form a three-dimensional network structure in the early stage of hydration and avoid cement paste cracking from ettringite expansion in the latter stages.

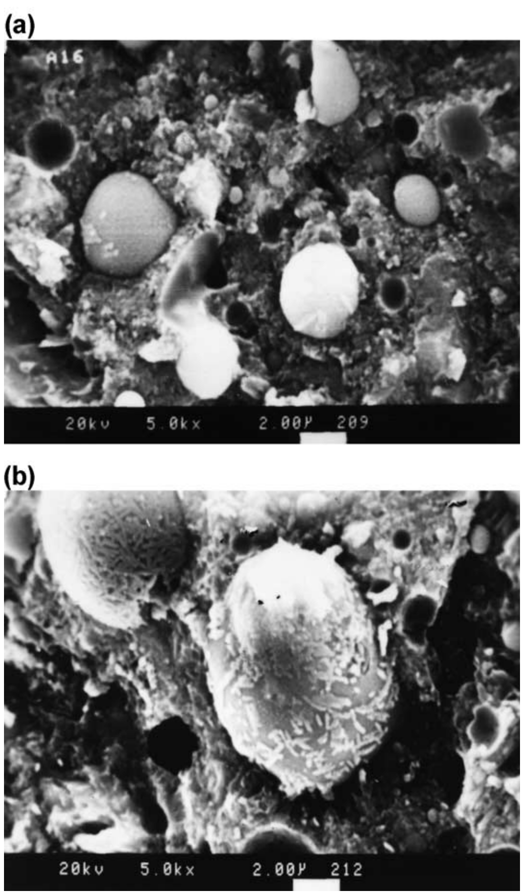

Fig. 3. SEM of hardened paste of the sample M_3. (a) Hydrated for 3 days. (b) Hydrated for 28 days.

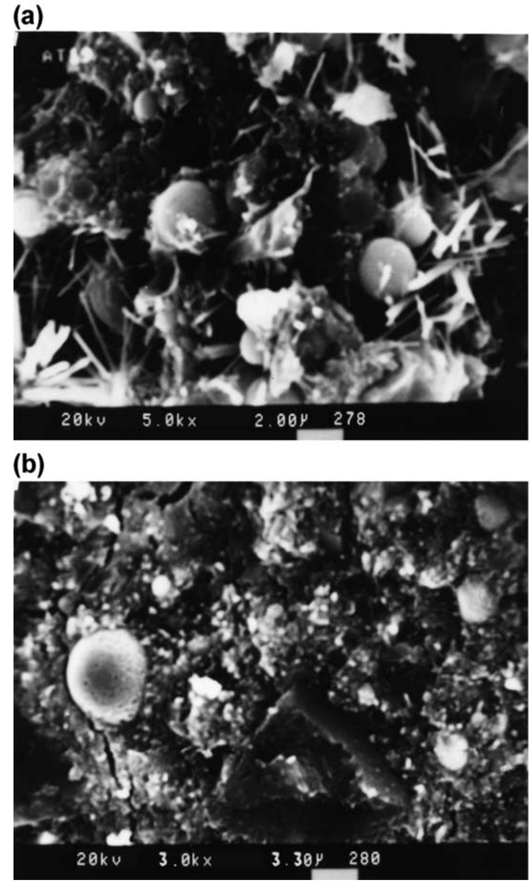

Fig. 4. SEM of the hardened paste of the sample M_5. (a) Hydrated for 3 days. (b) Hydrated for 28 days.

4. Conclusions

(1) The composite material consisting of BFS, G_2 and EA can obviously improve the strength of cementitious material containing 40% FA. Although MC was merely 45% of the MHPCC, the compressive strength of MHPCC paste was higher than that of neat MC paste. The results demonstrate that MHPCC can be prepared on the basis of composite material theory.

(2) BFS played an important role in MHPCC. It was observed that at optimum BFS content, strength is maximized. The test results showed that the optimum quantity of slag added was at Level 2 (15%).

(3) When EA was added to MHPCC, needle-shaped ettringite obtained by the EA reacting with $Ca(OH)_2$ formed a three-dimensional network structure, which not only improved the early strength of MHPCC paste but also increased its late strength. The reason was that the network structure, which was similar to a fiber-reinforced composite, was formed in the late stage of hydration along with

hydration progressing and hydration products filling in the network structure. However, the ratio of EA added should be optimized to avoid causing cement paste to crack due to ettringite expansion.

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