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The influences of siliceous waste on blended cement properties

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Abstract

The influences of siliceous waste on the properties of fly ash and blast furnace slag cement were studied, and its optimum mixing amount in blended cement was determined. The strength, setting time, resistance to chemical attack, dry shrinkage, and impermeability of blended cement mixed with siliceous waste were also investigated by different experiments. The measurement of pore size distribution for hardened cement pastes made by Poremaster-60 was recorded and analyzed in this article.

Keywords: Blended cement; Physical properties; Hydration; Pore size distribution; Siliceous waste

1. Introduction

The siliceous waste is an infusible residue in the process of preparation of aluminum sulfate, and it is separated by filtration after the calcined alumite reacts with sulfuric acid at 800–1000 °C to form $Al_2(SO_4)_3$ in solution. Its chemical composition is 65–85% SiO_2, 10–15% Al_2O_3, 1–5% SO_3, with 5–8% loss on ignition. Its structure is like an amorphous glass and there exists a little $Al_2(SO_4)_3$ mineral. The average diameter of the residue particles is about several micrometers and it presents a state of coacervate, in which the physical and chemical properties are similar to silicate fume, such as higher SiO_2 content, lower loss on ignition, more fine particle size and amorphous glass structure, etc. The silicate fume used in concrete, especially in manufacturing high-property concrete, has been investigated, and achievements have been obtained for the elaboration of high-performance concrete using silicate fume [1], but the studies of siliceous waste on performances of cement or concrete are just a little [2–5]. This article studies the effect of siliceous waste on the properties of blended cement, such as its strength, setting time, dry shrinkage, and pore size distribution of hardened cement paste.

2. Materials and methods

2.1. Raw materials

Raw materials were clinker from Zhangshan Cement Plant and Shandong Cement Plant. Siliceous waste was from Jucheng City, fly ash was from Thermal Power Factory of Jining, and blast furnace slag from the Jinan Steel–Iron Plant. Gypsum was from Pingyi and calcined gypsum (G) was from the Laboratory. The calcined gypsum was used in this study because of its good dissolving property in alkaline or water solution and higher activity for improving the performances of blended cement. These properties were examined by our previous study work [6,7]. For example, shortened setting time and increased the compressive strength at 3 and 28 days are excitation requirements for blended cement with a large amount of slag and fly ash, and these requirements could be achieved by using calcined gypsum. The calcined gypsum is a surplus product after gypsum was calcined at 750 °C for 2 h in experimental electric oven. In addition, the calcined gypsum has been used in many cement plants to enhance the properties of blended cement. The chemical compositions of main raw materials are listed in Table 1.

2.2. Methods

The proportional mixture of clinker, fly ash, siliceous waste, gypsum, and limestone was ground in an experi-

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

Name	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Siliceous waste	9.98	67.1	15.38	0.77	0.81	0.39	5.06
Clinker (Shandong)	1.21	22.18	3.61	3.18	63.70	1.61	0.02
Clinker (Zhangshan)	0.48	19.76	6.75	4.64	64.14	2.78	0.70
Fly ash	1.08	56.92	27.43	6.02	5.64	2.28	–
Blast furnace slag		32.90	11.39	5.29	38.47	6.62	0.35
Gypsum		2.96	0.41	0.38	39.38	1.43	39.00

mental mill. The blended cement was derived after 30-min grind.

The Blaine's specific surface area of each composite cement was about 340 m^2/kg. The process requires water, the setting time was performed according to GB1346-89 [8], the strength of hydraulic cement mortar was according to GB177-85 [9], and the drying contraction of cement mortar was to GB751-81 [10]. The pore size distribution of hardened cement paste was determined by a mercury porosimeter (Poremaster-60).

3. Results and discussion

3.1. Effects on fly ash cement

In order to investigate the influence of siliceous waste on properties of fly ash cement, orthogonal experiments ($L_9(3^4)$) were conducted, which are an effective experimental method. From only a few experimental data, the influence of each factor on the properties of blended cement was observed precisely and comprehensively. The optimum compositions of various raw materials for fly ash cement and the compressive strength could be predicted through orthogonal experimental analysis. In the experiments, three factors and three variables of each factor were selected and listed as follows: the weight content of siliceous waste was 5%, 10%, 15%, calcined gypsum (G) 3%, 5%, 7%, and limestone 3%, 5%, 7%. The weight content of clinker from Zhangshan was fixed at 50% and the fly ash was the rest of the content. Tables 2 and 3 list the series of the orthogonal experimental percentage of each factor and the results of each test. Samples A_{10} (95% clinker + 5% gypsum) and A_{11} (75% clinker + 20% fly ash + 5% gypsum) were used as controls.

It was observed from Tables 2 and 3 that when the same amount of calcined gypsum was used, normal water requirements for the pastes of blended cement increased with the amounts of siliceous waste increasing from 5% to 15%. For example, the normal water requirement of sample A_1 was 27.5%; comparatively, it was 30.5% in sample A_3. The setting time was shortened, for instance, the initial setting time was 52 min in sample A_1 compared with 23 min in sample A_3 and final setting time was shortened to 53 min from 2 h and 30 min. Thus, the siliceous waste presented higher normal water requirement and shortened setting time. This indicated that the siliceous waste enhanced the hydration of blended cement. The mortar compressive strengths for blended cements (the ratios of water to cement was 0.46) at 3 and 7 days also increased, apparently with the increase of siliceous waste, and reach the top value when the amount of siliceous waste was 15% with 3% calcined gypsum, such that the mortar compressive strengths of sample A_6 were increased 7.5, 11.4, and 7.3 MPa at 3, 7, and 28 days, respectively, compared to A_4. Similarly, the mortar compressive strengths of sample A_9, which has 15% siliceous waste, was higher than that of control A_{11} at 7 and 28 days. It also indicated that the hydration of siliceous waste improved the properties of fly ash cement. By orthogonal analysis [11] of the compressive strength at 3, 7, and 28 days, the optimal formula cement and best strengths at every age were obtained, that is, 50% clinker, 29% fly ash, 15% siliceous waste, 3% calcined gypsum, and 3% limestone, and compressive strengths predicated are 27.6, 42.1, and 50.7 MPa at 3, 7, and 28 days, respectively. This optimal formula was verified by Section 3.3.

3.2. Effect on blast furnace slag cement

Table 4 shows the effects of siliceous waste on the properties of blast furnace slag cement. Compared with H_2, the strengths of every age of sample H_3 had been improved greatly when siliceous waste replaced blast furnace slag by 8.5% and calcined gypsum replaced gypsum by 5%. For example, the compressive strength increased from 53.5 to 59 MPa at 28 days. The mortar compressive strength of H_4, H_5, and H_6 were reduced with the increase in blast furnace slag and siliceous waste, but they were higher than that of H_1 and H_2 at all ages. H_4 has optimal compressive strength at every age. It implied that the best realignment of various components was 55% clinker, 31.5% blast furnace slag, 8.5% siliceous waste, and 5% calcined gypsum, and the hydration products, such as calcium silicate

Table 2
$L_9(3^4)$ orthogonal experimental dosages (wt.%) (clinker from Zhangshan Cement Plant)

Number	Fly ash	Siliceous waste	Calcined gypsum	Limestone	Gypsum
A_1	31	5	7	7	–
A_2	30	10	7	3	–
A_3	23	15	7	5	–
A_4	35	5	5	5	–
A_5	28	10	5	7	–
A_6	27	15	5	3	–
A_7	39	5	3	3	–
A_8	32	10	3	5	–
A_9	25	15	3	7	–
A_{10}	–	–	–	–	5
A_{11}	20	–	–	–	5

Table 3
Data of the orthogonal experiments (w/c = 0.46)

Number	Normal water requirements (%)	Setting time (h:min)		3 days (MPa)		7 days (MPa)		28 days (MPa)	
		Initial	Final	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
A_1	27.50	0:52	2:31	2.82	15.8	4.71	26.6	7.62	37.8
A_2	29.75	0:37	1:51	3.32	17.2	6.49	29.1	8.26	38.1
A_3	30.50	0:23	0:53	3.75	19.0	6.21	30.5	8.28	37.8
A_4	27.75	1:54	3:14	3.47	15.5	5.22	24.5	7.97	35.3
A_5	28.25	1:09	2:52	4.32	19.5	6.44	25.8	8.28	40.8
A_6	29.50	0:41	1:03	4.95	23.0	6.84	35.9	8.69	42.6
A_7	28.75	2:17	3:19	5.22	20.7	6.54	35.7	9.11	46.7
A_8	28.75	1:44	2:58	4.98	21.5	7.06	33.8	9.17	43.9
A_9	30.25	0:30	1:09	5.00	24.3	7.41	38.1	8.8	46.3
A_{10}	26.0	3:06	4:21	7.64	39.6	8.65	48.4	9.27	54.4
A_{11}	26.50	2:39	3:59	5.59	28.1	7.14	37.3	8.77	45.9

Table 4
Effect on performance of blast furnace slag cement (clinker from Zhangshan Cement Plant)

Number	Dosages (wt.%)					3 days (MPa)		7 days (MPa)		28 days (MPa)	
	Clinker	Slag	Calcined gypsum	Gypsum	Siliceous waste	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
H_1	95	–	–	5	–	5.55	29.6	6.42	37.1	7.47	44.8
H_2	75	20	–	5	–	6.05	31.2	7.34	41.0	8.90	53.5
H_3	75	11.5	5	–	8.5	7.36	44.0	9.08	52.4	10.03	59.0
H_4	55	31.5	5	–	8.5	7.88	44.3	9.87	54.7	11.73	63.7
H_5	55	26.5	5	–	13.5	6.65	40.0	10.01	52.3	10.78	57.9
H_6	50	30.5	5	–	14.5	6.64	36.9	9.00	48.5	10.68	54.9

hydrates, calcium aluminate hydrates, were formed from the hydration of blast furnace slag and siliceous waste.

3.3. Verification of best formulas

Based on the analysis above, the best formulas were determined as the siliceous waste was mixed with fly ash or blast furnace slag and later verified by experiments with clinker from Shandong Cement Plant. The experimental composites of raw materials and results are shown in Tables 5 and 6.

In Table 6, as the amount of siliceous waste was increased from 8.5% in sample B_2 to 13.5% in sample B_3, the normal water requirement of B_3 was increased to 30.75% from 29.60%, and initial setting time was shortened to 29 min from 59 min, and final setting time to 1 h from 2 h and 1 min. The experimental results are similar to that in Section 3.1.

Although the performance of clinker from Shandong Cement Plant was distinguished from that in Zhangshan Cement Plant, the strengths of B_2 and B_3 caught up with H_4 at 28 days, which are also higher than that of B_0 and B_1 at every age, in spite of the content of 50% clinker, which was lower than that in H_4, B_0, and B_1. Similarly, the mortar compressive strengths of B_4 and B_5 exceeded the predicted data at 3 and 28 days, confirming the predicted value through orthogonal analysis. Thus, the best siliceous waste content ranging from 8.5% to 15% were determined. Besides, the compressive strength of B_2, B_3, and B_4 were higher than that of B_0 and B_1 although the content of clinker in B_2, B_3, and B_4 were only 50%. It expressed that the blended cements with higher properties were prepared by mixing siliceous waste with blast furnace slag or fly ash and a small amount of clinker. The fact that the strengths of samples B_2 and B_3 were higher than that of B_4 and B_5 shows that the higher effectiveness of siliceous waste was achieved by mixing it with blast furnace slag rather than with fly ash.

Table 5
Best formulas of blended cement (wt.%) (clinker from Shandong Cement Plant)

Number	Clinker	Slag	Fly ash	Limestone	Calcined gypsum	Siliceous waste	Gypsum
B_0	95	–	–	–	–	–	5
B_1	75	20.0	–	–	–	–	5
B_2	50	33.5	–	3	5	8.5	–
B_3	50	28.5	–	3	5	13.5	–
B_4	50	–	29	3	3	15	–
B_5	50	–	28.5	3	5	13.5	–

3.4. Effect on permeability of mortars

The samples for impermeation of water were made with frustum of a cone (bottom surface diameter, top diameter,

Table 6
Performance of best formulas cement

Number	Normal water requirement (%)	Setting time (h:min)		3 days (MPa)		7 days (MPa)		28 days (MPa)	
		Initial	Final	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
B_0	26.40	1:34	2:50	5.77	27.82	6.96	35.48	7.18	50.08
B_1	25.50	2:03	3:03	7.42	31.17	7.35	41.18	8.59	51.71
B_2	29.60	0:59	2:01	6.73	38.47	9.00	48.97	12.17	62.16
B_3	30.75	0:29	1:00	7.29	38.25	9.52	51.14	11.49	61.65
B_4	31.25	0:25	0:42	6.62	30.80	9.19	41.64	10.65	53.85
B_5	31.25	0:19	0:48	6.53	30.40	8.21	39.94	10.31	51.98

and height were 80, 70, and 30 mm, respectively). They were taken from mould after 1 day, then cured for 2 days under of temperature at 20 ± 3 °C and relative humidity of >90%. Table 7 lists the height and percentage of permeation of samples under hydraulic pressure of 1 MPa on the permeameter for 14 h.

It could be seen from Table 7 that the permeation height and permeation percentage of samples B_3, B_4 and B_5 were higher than that of sample B_1, and many large pores were bigger that 1000 Å in diameter (see Fig. 1) in their hardened pastes. Thus, they had lower impermeability water than that of B_1, whereas they should have had higher impermeability water because the total volume of the large pore is small (see Fig. 2) at 28 days.

3.5. Effect on dry shrinkage rate of mortar

The dry shrinkage experiments of mortar samples B_1, B_3, and B_4 were made according to GB751-81[10], and the shrinkage rates were listed in Table 8. Table 8 shows that the rate of dry shrinkage for B_3 and B_4 were about half of that of B_1, which explained that the siliceous waste could decrease the dry shrinkage of blended cement. It was also found that the dry shrinkage was higher during days 7–14 and lower after 28 days. This corresponds with lower porosity for hardened pastes, and higher amounts of hydration products formed from the hydration of siliceous waste at later ages.

3.6. Effect on chemical resistance

The main SO_4^{2-}, Mg^{2+}, and Cl^- ions could first diffuse through the capillary pore into the inner concrete and then react with the hydration products of the cement, such as the hydrated aluminate and C-S-H gel, to form the expanding sulfoaluminate AFt or products without binding property. Thus, the structure of cement stone is destroyed and the building could be broken down. To measure the effect of this attack on strength of blended cements with siliceous waste, three kinds of solutions with high ionic concentration were made up, as listed in Table 9. B_1 and mortar samples B_3 and B_4 were $40 \times 40 \times 160$ mm in size, cured in fresh water for 14 days, and immersed in three kinds corrosive solutions for another 90 days. Then they were subjected to strength tests. The results are shown in Table 10. Taking the strength of specimens cured in fresh water at the same age as the control, we can determine the chemical resistance ability of cement by its strength ratio. In Table

Table 7
Permeability of mortars

Number	Sample height (mm)	Permeation height (mm)	Permeation percentage (%)
B_1	30	22.67	76
B_3	30	27	90
B_4	30	28	93
B_5	30	28	93

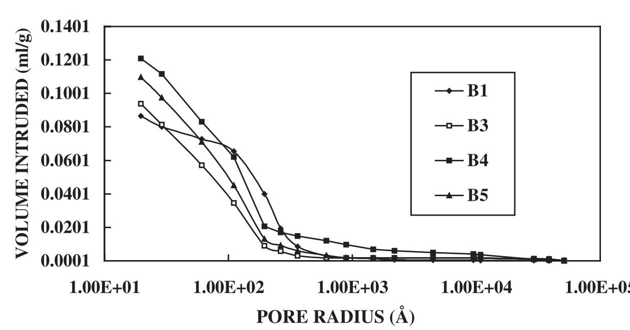

Fig. 1. Pore size distributions at 3 days.

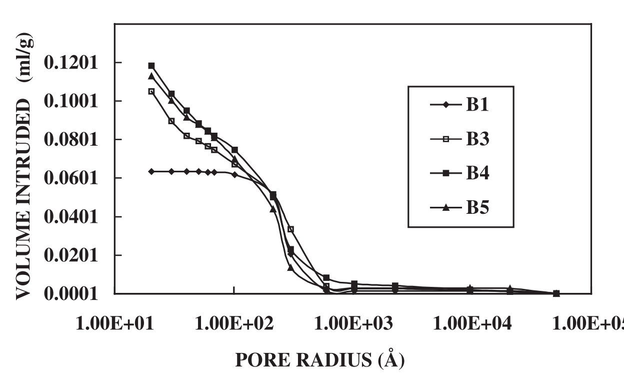

Fig. 2. Pore size distributions at 28 days.

Table 8
Dry shrinkage rate of mortar (10^{-4})

Number	Shrinkage rates					
	7 days	14 days	28 days	2 months	3 months	6 months
B_1	−4.32	−11.7	−8.75	−8.88	−8.78	−8.89
B_3	−0.373	−5.68	−4.37	−4.37	−4.36	−4.39
B_4	−0.467	−5.97	−4.24	−4.61	−4.58	−4.60

Table 9
Ions concentrations of corrosion solution (mg/l)

Number	SO_4^{2-}	Mg^{2+}	Cl^-
A	5000	8100	20,000
B	10,000	12,800	30,000
C	20,000	18,700	40,000

10, the numerator was strength (MPa) and the denominator was strength ratio (%).

The experimental results in Table 10 show that the flexure strength of B_1, B_3, and B_4 increased by different degrees in three kinds of solutions, while the compressive strength ratios of B_3 and B_4 specimens were higher than that of B_1. For example, the compressive strength ratio of B_3 was 106% in chemical corrosion solution A; it increased by 6% as compared to fresh water. Yet, the value of sample B_1 was 83% in solution A; it decreased by 17% as compared to fresh water. Therefore, the chemical resistance ability of blended cement with siliceous waste was higher than that of control B_1. The siliceous waste made the structure of hardened blended cement pastes dense, the corrosion ions' penetrating into the inner part of the cement paste was difficult, thus, the ability of chemical resistance attack improved.

3.7. Pore structure

The volume of pore in the hardened cement pastes reduced gradually during the hydration of clinker mineral. In the course of the experiment, the structure of the pastes became denser and the strength improved in varying degrees. However, pores of various sizes existed at all hydration ages, such as large spherical pore, capillary pore, micropore, and gel pore, whose size in diameter ranged from 10 to 100 μm, from 500 Å to 10 μm, from 100 to 500 Å, and from 5 to 100 Å, respectively. The large spherical pore were formed by air bubbles, while the capillary pore, micropore, and gel pore were formed by evaporating water, and their volume relies on the ratios of water to cement. The effects of large spherical pore, capillary pore, and micropore on the performance of hardened cement pastes, such as impermeability, dry shrinkage, and chemical resistance attack, are more serious than that of gel pore. The pore size distribution of hardened cement pastes is given in Figs. 1 and 2.

Fig. 1 shows that the total volume of large spherical pore, capillary pore, and micropore bigger 100 Å in sample B_1 was the smallest, leading to its higher strength and low permeability at 3 days. The pore volume of the pores bigger than 100 Å and the total pore volume were both higher in B_3, B_4, and B_5, thus the properties were lower at 3 days than that of sample B_1.

In Fig. 2, the pore volume of the pore bigger than 100 Å in B_3, B_4, and B_5 is smaller than that in B_1, therefore the higher properties, such as compressive strength at 28 days, were obtained although the total pore volume was higher than that of B_1.

Based on the analysis above, the siliceous waste can improve the properties of blended cements due to its reaction with calcium hydroxide. Active SiO_2 and Al_2O_3, which were the main chemical compositions of siliceous waste, were gradually deploymerized and release the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ ions under the activity of $Ca(OH)_2$, which was derived from the cement clinker minerals hydration. Then, they reacted with Ca^{2+} to form calcium silicate hydrates of lower Ca/Si and calcium aluminate hydrates. The latter reacted with gypsum to form the calcium sulfoaluminate hydrate. These products could have effects on binding the cement particles, on packing pore, and on reducing pore volume of the pore bigger than 100 Å. On the other hand, the fine grains of siliceous waste filled up holes between the particles, decreasing the pore volume and improving the structure of hardened cement paste. Thus, the strength and ability of resistance to chemical corrosion have been improved with the increment of amount of siliceous waste within the range of 5–15%. If more siliceous wastes (more than 15 wt.%) were mixed with blended cement, the normal water requirement would be increased and the structure of hardened cement pastes would present more pore volume of large spherical pore, capillary pore, and micropore, resulting in poor properties.

Table 10
Resistance to chemical corrosion (MPa/%)

Number	Fresh water		Solution A		Solution B		Solution C	
	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
B_1	9.18/100	62.80/100	10.29/112	51.86/83	10.80/117	48.96/79	10.83/118	53.45/85
B_3	10.10/100	51.68/100	12.06/119	54.91/106	12.26/121	51.12/99	12.08/120	53.60/104
B_4	10.47/100	50.82/100	10.57/101	50.72/100	11.80/113	49.76/98	10.69/102	47.16/93

4. Conclusion

1. By studying the effect of siliceous waste on the properties of fly ash and blast furnace slag cement, the optimum mixing amount of siliceous waste in blended cement was determined and the optimum content range was from 8% to 15%. The experimental result was the same as the predicated data through orthogonal analysis.
2. Siliceous waste could improve the strength and the ability of resistance to chemical attack of the cement and reduce the dry shrinkage rate of mortar, but increase the normal consistency water requirement and shorten its setting time.
3. The total pore volumes of hardened cement paste that is mixed with siliceous waste are higher, but those of the large spherical pores, capillary pores, and micropores bigger than 100 Å are lesser at 28 days, leading to better properties, such as higher ability of resistance to chemical attack and lower dry shrinkage rate.

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