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Study on modification of the high-strength slag cement material

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Abstract

The influence of the slag powder's fineness, the amounts of activator, type and contents of modification addition on the dry–shrinkage and strength of the high-strength slag cement material was investigated. The experimental data showed that adding 9% Na_2SiO_3 activator and 10% Portland cement (PC) made the ratios of drying–shrinkage of high-strength slag cement material similar to the ratios of Portland cement and the compressive strengths as higher. The main hydration products are calcium alumina–silicate gels and a little CH; the gel ratio of CaO/SiO_2 is close to 1 and includes a little Na_2O and MgO for high-strength slag cement material, as shown by means of scanning electron microscope (SEM) and energy-dispersive X-ray analyzer (EDXA).

Keywords: Physical properties; Shrinkage; Alkali activate cement; Admixture; Hydration products

1. Introduction

The high strength and higher ability of resistance to sulfate corrosion for slag cement materials [1–10] is achieved as the alkali activity is added in granulated blast furnace slag. While the ratios of drying–shrinkage of this slag cement are higher than that of Portland cement (PC), the question of how to reduce the ratios of drying–shrinkage occurs and needs an answer requiring more experimental results. The influence of the granulated blast furnace slag fineness, the amount of activity, type and contents of modification additions on the ratios of drying–shrinkage and the strength of the high-strength slag cement material was investigated in this paper.

2. Materials and methods

2.1. Materials

The blast furnace slag used in this study was derived from Jinan steel plant. The chemical composition is shown in Table 1.

The Na_2SiO_3 (named as J2) was used as activator.

The modification additions used in this study were Portland cement (PC), aluminate cement (AC) and sulphoaluminate cement (SC). Their chemical compositions are shown in Table 1.

2.2. Methods

The hardened cement paste samples of slag cement material were cast with 20×20×20 mm in size, and the mortar samples with 40×40×160 mm in size were prepared according ISO method. After 24 h of curing at 20 °C with 95% humidity, these samples were placed in water at 20±3 °C and cured to several ages. Finally, the samples were subjected to strength test.

The shrinkage specimens of slag cement material were cast with 25×25×280 mm in size. After 24 h of curing at 20 °C with 95% humidity, these samples were placed in water at 20±3 °C and cured to 7 days. Then, they were placed in air in room up to 35 days.

Phase analysis of cement paste samples were observed under S2500 scanning electron microscope (SEM) made by HITACHI, Japan. The compositions of the selected hydration products were analyzed by

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Table 1
The chemical composition

	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	SO_3	TiO_2
Slag	43.44	2.95	1.18	11.54	32.89	0	0.99
PC	62.42	1.14	4.60	5.46	18.67	3.25	/
AC	34.28	0.31	1.49	54.89	7.85	1.56	2.00
SC	41.62	0.82	1.97	27.56	9.97	14.44	1.11

Table 2
Fineness and strengths of hardened slag cement paste

No	Grinding time (min)	fineness (m^2/kg)	Compressive strength (MPa)		
			3 days	7 days	28 days
T1	25	270	53.75	70.50	92.06
T2	35	310	69.06	83.87	114.75
T3	45	340	60.88	69.94	107.69

Oxford Link ISIS 300 energy-dispersive X-ray analyzer (EDXA).

3. Results and discussion

3.1. Influence of fineness of blast furnace slag

The granulation time is different, the fineness of blast furnace slag and hardened cement paste strengths of the slag cement are also different. The influence of fineness on the strength of hardened cement paste was shown in Table 2, the content of the activator J2 was 10%.

Table 2 indicates that the slag cement sample T2 which was ground for 35 min has Blaine's specific surface area of 310 m^2/kg. The compressive strength is highest of the three samples. This slag cement sample T2 is used in following test.

3.2. Influence of modification addition

Three kinds of modification addition and three contents of every addition were added in sample T2. The dosages and compressive strength were shown in Table 3.

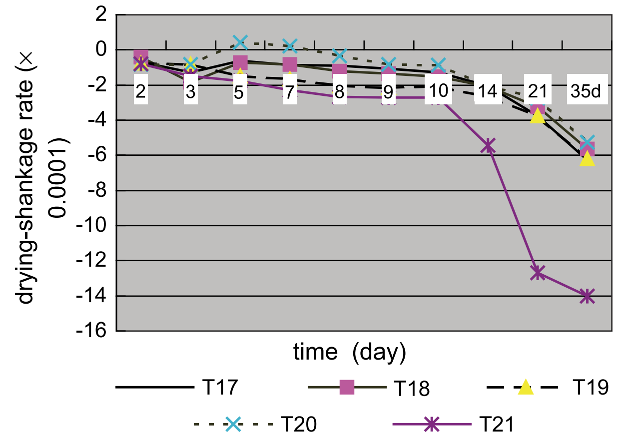

Fig. 1. The drying–shrinkage ratio of mortar ($\times 10^{-4}$). T17 Slag/PC/J2=60%:30%:10%; T18 Slag/PC/J2=70%:20%:10%; T19 Slag/PC/J2=80%:10%:10%; T20 Slag/PC/J2=0%:100%:0%; T21 Slag/PC/J2=90%:0%:10%.

Table 3 indicates that, with the content of PC of 10%, the compressive strength of sample T4 is the highest, while, with the content of PC of 20%, the strength of sample T5 is lower, and, when the content is 30%, the sample T6 is rapid setting, and the strength is lower too. When AC and SC with 10–30% amount were added in blast furnace slag cement, the compressive strengths of samples T9 to T11 and T13 to T15 were lower than that of T4 to T6, respectively. Thus, the PC addition is the best addition material, and the best amount in blast furnace slag cement is 10%.

The drying–shrinkage measurement of mortar samples with cement/sand/water=1:2.5:0.44 has been made. The drying–shrinkage ratios are shown in Fig. 1.

Fig. 1 indicates that, in the slag cement without PC, drying–shrinkage ratios of T21 are 14.7×10^{-4} at 35 days but that the ratios of samples T17 to T20 with PC replacement ratio of 10–30% show a lower drying–shrinkage. For example, at 35 days, the drying–shrinkage is 6.26×10^{-4} with PC replacement ratio of 10%, as similar

Table 3
Influence of modification addition on the strength of slag cement paste

No	Slag (%)	PC (%)	AC (%)	SC (%)	J2 (%)	Compressive strength (MPa)			Note
						1 day	3 days	28 days	
T4	80	10	0	0	10	53.38	75.06	96.31	
T5	70	20	0	0	10	48.88	63.56	83.06	
T6	60	30	0	0	10	21.00	24.75	46.75	rapid setting
T7	0	100	0	0	0	27.00	50.38	82.37	
T8	90	0	0	0	10	44.63	81.69	94.88	
T9	80	0	10	0	10	26.87	49.75	73.25	
T10	70	0	20	0	10	27.19	47.63	73.06	
T11	60	0	30	0	10	25.75	42.36	66.25	
T12	0	0	100	0	0	33.06	42.94	60.94	
T13	80	0	0	10	10	23.38	50.19	75.56	
T14	70	0	0	20	10	0.28	0.39	12.38	rapid setting
T15	60	0	0	30	10	0.15	0.10	4.81	rapid setting
T16	0	0	0	100	0	42.25	71.25	95.56	

Table 4
Influence of J2 activator content on strengths

No	Slag (%)	PC (%)	J2 (%)	Compressive strength (MPa)		
				1 day	3 days	28 days
T22	80	10	10	47.13	72.56	82.63
T23	81	10	9	50.25	85.44	98.88
T24	82	10	8	52.75	63.56	89.13
T25	83	10	7	24.06	51.25	52.87
T26	90	0	10	53.61	83.75	88.44

Table 5
Strength of slag cement mortar (MPa)

No	Slag (%)	PC (%)	J2 (%)	Compressive strength			Flexural strength		
				1 day	3 days	28 days	1 day	3 days	28 days
T27	91	0	9	6.99	29.41	57.20	1.33	3.5	6.72
T28	81	10	9	26.48	39.77	60.20	6.17	7.93	8.65

to the drying–shrinkage of the Portland cement sample (5.25×10^{-4}) at 35 days.

3.3. Influence of activator

An important find from the above experimental data was that the slag cement material with PC replacement ratio of 10% showed a lower drying–shrinkage ratio and higher compressive strength, thus the influence of J2 activator contents on the strength of slag cement material has been studied, and the results are shown in Table 4.

Table 4 indicates that the compressive strengths of T23 sample with content of 9% J2 activator had the highest values of 3 days and 28 days in the five samples. When the J2 amount is 7%, the strength was relatively lower.

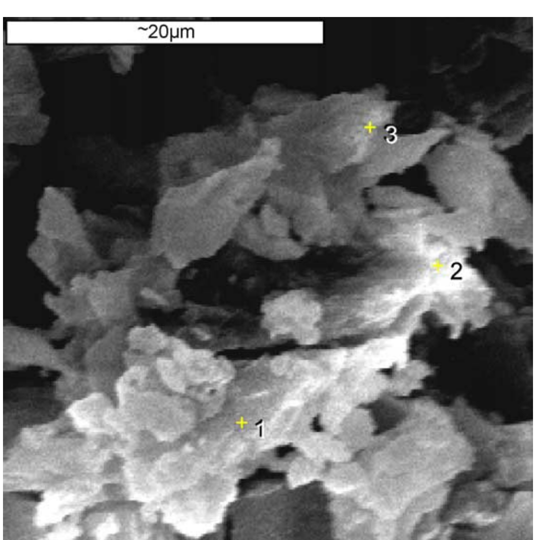

Fig. 2. The area (a) of sample A observer under SEM.

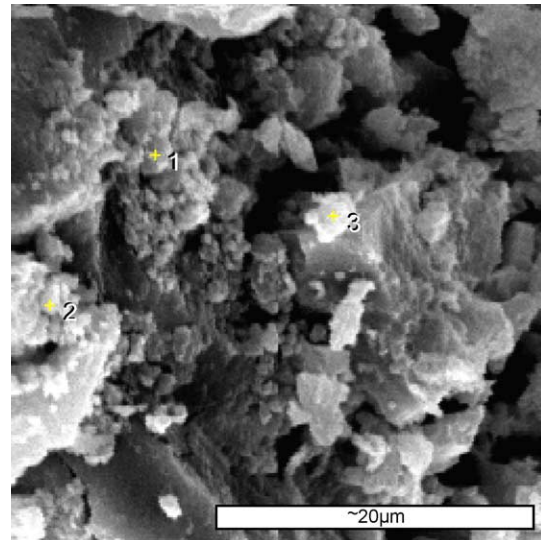

Fig. 3. The area (b) of sample A observer under SEM.

Therefore, the optimum content of activator J2 in slag cement material is 9%.

Table 4 has also shown that the best formulas of slag cement material with high strength are the following: J2 8–9%,PC 10%, blast furnace slag 81–82%.

3.4. Strength of mortar

The mortar strength and the formulas of samples T27 and T28 are shown in Table 5. The T27 is the ordinary-alkali-activated slag cement, and the T28 is the sample with the slag replacement ratio by PC 10%. In Table 5, the early strength of T28 was much higher than that of T27 at 1 day and 3 days; the strength was also higher than that of T27 at 28 days. Thus, Portland cement replacement 10% slag could reduce the drying–shrinkage ratio and enhance the early strength of the slag cement.

Table 6
Chemical compositions of the amorphous hydration products (wt.%)

Code	Na_2O	MgO	Al_2O_3	SiO_2	CaO	CaO/SiO_2
A-(a)-1	4.41	3.11	11.15	44.03	37.20	0.84
A-(a)-2	6.10	–	13.33	40.05	40.53	1.01
A-(a)-3	–	5.45	13.73	37.52	43.30	1.15
Average	5.26	4.28	12.74	40.53	40.34	1.00

m_w/m_c=0.30.

Table 7
Chemical composition of the global hydration productions (wt.%)

Code	Na_2O	MgO	Al_2O_3	SiO_2	CaO	CaO/SiO_2
A-(b)1	–	–	8.45	3.86	87.69	22.71
A-(b)-2	4.70	3.71	10.12	32.64	48.83	1.49
A-(b)-3	–	–	6.50	25.33	68.17	2.69

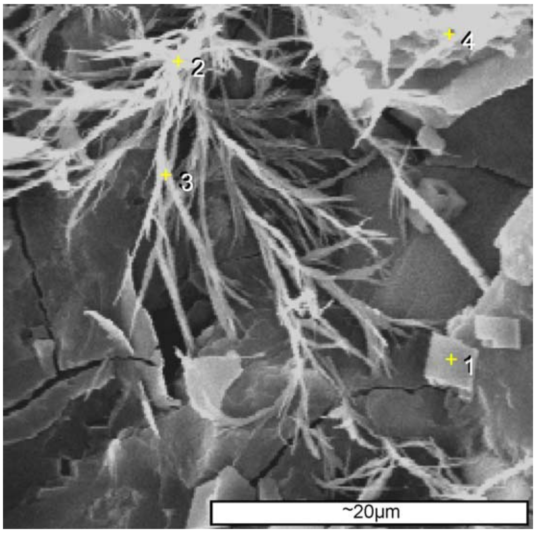

Fig. 4. The area (a) of sample B observer under SEM.

This slag cement material is a new type of high-performance cement.

4. Hydration products of slag cement

The hydration products of hardened slag cement were observed under SEM, and the compositions of the selected hydration product particles were analyzed by EDXA.

4.1. The 3-day hydration products

Figs. 2 and 3 are the different areas photos of sample A (the T23 sample hydrated for 3 days) observed under SEM; the hydration products of samples A were the amorphous gel, globoid gel and CH.

The shapes of the amorphous hydration products of sample A hydrated for 3 days are shown in Fig. 2, and the chemical compositions is shown in Table 6 as analyzed by EDXA.

From Table 6, the result could be obtained that the amorphous products are calcium alumina–silicate gels. The ratio of CaO/SiO_2 is close to 1, and a little Na_2O and MgO also appear in amorphous products.

Table 7 and Fig. 3 show that the global products are calcium alumina–silicate gels. While the ratio of CaO/SiO_2 is from 1.49 to 3.31, the hydration products include a little of Na_2O and MgO. The product of the point A-(b)-1 is the CH in which the ratio of CaO/SiO_2 is 22.71, and hydration products that include a little of Al_2O_3 exist in the point A-(b)-1.

4.2. The 28-day hydration products

Figs. 4 and 5 are the different areas photos of sample B (the T23 sample hydrated for 28 days) observed under SEM. The main hydration products are amorphous, fibroid, nubbly and lumpy products.

The forms of the fibroid and nubbly hydration products are shown in Fig. 4. The chemical compositions of the fibroid and nubbly hydration products are shown in Table 8 as analyzed by EDXA. The fibroid and nubbly products are also calcium alumina–silicate gels, with the ratio of CaO/SiO_2 close to 1; a little Na_2O and MgO are also apparent in fibroid and nubbly products.

Fig. 5 shows the forms of the sheet and lump hydration products. Table 9 shows that the chemical composition of the sheet and lump products are calcium alumina–silicate gels too. The ratio of CaO/SiO_2 is from 0.76 to 1.32, and a little Na_2O and MgO are also apparent.

Table 8
Chemical compositions of the fibroid and nubbly hydration product (wt.%)

Code	Na_2O	MgO	Al_2O_3	SiO_2	CaO	CaO/SiO_2
B-(a)-1	5.76	4.51	9.49	40.94	36.65	0.90
B-(a)-2	–	8.38	10.70	35.47	38.63	1.09
B-(a)-3	6.18	7.58	11.43	39.57	35.25	0.89
B-(a)-4	3.90	6.47	13.21	36.82	39.60	1.08
Average	5.28	6.74	11.20	38.20	37.53	0.98

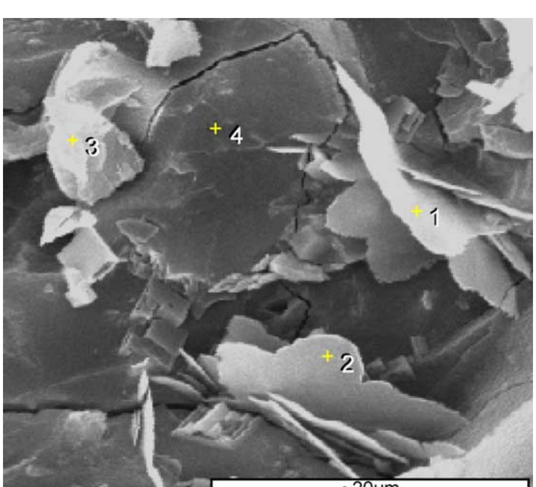

Fig. 5. The area (b) of sample B observer under SEM.

5. Conclusion

The high-strength slag cement with the PC replacement ratio 10% has a lower drying–shrinkage ratio than the

Table 9
Chemical compositions of the sheet and lump hydration products (wt.%)

Code	Na_2O	MgO	Al_2O_3	SiO_2	CaO	CaO/SiO_2
B-(b)-1	6.41	4.62	11.60	43.77	33.60	0.76
B-(b)-2	6.52	6.35	8.48	29.33	38.67	1.32
B-(b)-3	9.67	7.28	13.06	43.15	26.84	0.68
B-(b)-4	4.86	3.37	10.26	45.08	36.44	0.81
Average	6.87	5.41	10.85	40.33	33.87	0.84

ordinary-alkali-activated slag cement from 14.01×10^{-4} to 6.18×10^{-4}, as similar to the ratio of Portland cement.

The high-strength slag cement with the Portland cement ratio 10% has higher early and 28-day strength than the ordinary-alkali-activated slag cement.

The main hydration products of the slag cement with 10% Portland cement are amorphous, globoid, nubbly, sheet and lumpy; these main hydration products are calcium alumina–silicate gels which have different ratios of CaO/SiO_2, and a little of Na_2O, MgO and $Ca(OH)_2$ are also apparent in the hydration productions.

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