Preparing High Performance Composite Cement and Exploring the Properties

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Abstract: In the paper, 70%, 60%, 50% (mass percent) clinker and 30%, 40%, 50% admixture (including micro powder of slag, activated fly ash, activated coal gangue) were used to prepared high performance composite cement. The hydrates and mechanism of hydration were studied by means of mortar strength measurement, SEM analysis and Pore structure. The result show that the high performance composite cement can be prepared with clinker and admixture which is included all waste slag mentioned above. The highest strength of the sample can be reached 65MPa. And all of them were higher than 50MPa. By micro test methods, the hydrating product phases of the cement were C-S-H gel, $Ca(OH)_2$ and AFt. And higher gel pores and lower total porosities were found in samples. The prepared cement can be used for industrial production. It's good for saving clinker and using waste slag fully.

Key words: high performance composite cement; slag; coal gangue; fly ash; SEM; MIP

In China, blast furnace slag (BFS) has been widely used as an additive to cement and it was studied more [1-6]. And it is almost completely utilized. But the cost of slag is higher, so the cement expense is going to increase. Therefore, it is necessary to synthetically other industrial by-products, such as fly ash, coal gangue. Fly ash is a powdered waste solid discharged from coal-burning electric-generating plants. Its major chemical compositions are SiO_2, Al_2O_3, Fe_2O_3, CaO and unburned carbon granule [7-8]. Fly ash contains stable mullite crystal and high polymerization degree, its activation is low. Coal gangue is industrial solid residues that are discharged when coal is excavated and washed in the production course of coal mine [9]. Fresh coal gangue has stable crystal structure. All particles in lattice arrange rigidly, so that its chemical composition is fixed and the activity is poor. Comparing with slag, fly ash and coal gangue have much lower hydration activities, which are mainly showed as the slowly generating of early strength and the lower strength.

It is reported [10] that the potential activation of fly ash and coal gangue can be excited through some specifically conditions. Activated fly ash and coal gangue can become quality mixtures of cement. This paper, activated fly ash was prepared by mixing fly ash, soluble salts and water together, than dried at low temperature. Activated coal gangue was prepared by calcining coal gangue with given limestone, than mingled with a bit calcined lime.

In this paper, slag, activated fly ash, coal gangue were blended with clinker in designed proportion to prepare high performance composite cement. And the relationships between the high performance of the composite cement and its microstructure are discussed.

1 Experimental

1.1 Raw materials

Main raw materials in experiment are clinker, slag, activated fly ash, activated coal gangue. Activator is gypsum. The clinker, activated fly ash and coal gangue come from Beijing. Slag comes from Meishan Iron and Steel Co., and gypsum (containing SO_3 29.20% by weight) comes from Nanjing Qinglongshan Cement Plant. In this experiment, main materials were milled with 0.08mm sieve residue 2.0%.

The chemical composition of main materials is listed in Table 1.

Table 1 Chemical composition of raw materials w/%

	loss*	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	MnO	K_2O	R_2O**	SO_3
clinker	-	21.74	3.56	5.06	66.60	0.88	-	-	0.55	0.41	0.81
slag	-	32.23	0.81	15.65	38.97	9.02	0.60	0.20	-	-	0.27
fly ash	2.61	46.28	3.76	34.99	5.88	1.48	-	-	0.76	-	1.45
coal gangue	2.02	57.00	4.12	17.38	14.63	1.56	-	-	2.12	-	0.45

loss*: loss on ignition
R_2O**: alkali oxide

1.2 Specimen preparation and testing conditions

1.2.1 Preparation of hardened cement paste

(1) Preparing the hardened cement paste specimens for strength

Tests on strength development were carried out according to China Standard GB17671-1999. Cement mortar specimens were made with 40×40×160mm in size according to standard method. Hardened cement paste specimens were prepared from both clinker and admixture in water/cement ratio 0.5 and curing in fog room at 20±3°C first for 24h, then curing in water at 20±2°C until the prescribed curing age.

(2) Preparing the hardened cement paste specimens for SEM and pore structure test

Selecting some samples of paste, the ratio of water to cement of all samples is 0.30. Samples were put into water at 20±2°C after hydration 1d and taken out at 3d, 28d and 90d of hydration. Hydration of the samples were ceased by putting into alcohol and then dried when testing.

1.2.2 Testing conditions

(1) Compressive strength was measured in the universal compression-testing machine made in China. Bending strength was measured in the electric bending resistance machine made in China.

(2) SEM observation was carried out on scanning electron microscope JSM-5900 made in Japan, for morphology observation of hardened cement paste.

(3) The pore structure test was carried out on an Auto-60 mercury scanning porosimeter made in the USA.

2 Results and discussion

2.1 Strength properties

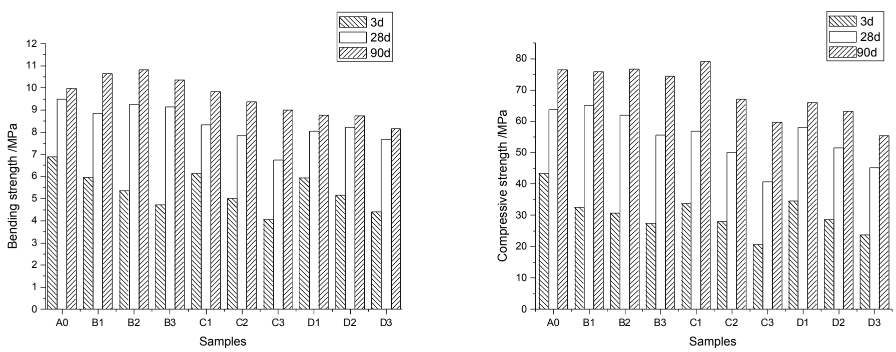
2.1.1 Strengths of clinker with admixtures blended respectively

First, the experiments of 70%, 60%, 50% clinker with three admixtures blended respectively were studied. The proportions are listed in Table 2. It can be shown the mechanic properties of these admixtures elementary.

Fig.1 shows that strength results of A0 are great. After curing 28d, the bending strength and compressive strength of A0 were come to 9.5MPa and 63.7MPa respectively. With reducing the content of clinker, it is obvious that the strengths results of samples were decreased. From Fig.1, the strengths results of the samples blending with slag (series B) were greater than that of others (series C and D). The strength results of B1 are approach to that of A0. And after curing 28d, the compressive strength of B1 was even higher than that of A0. Curing for 28d, the bending strengths and compressive strengths of the samples blending with activated fly ash (C1, C2, C3) were almost equal to that of the samples blending with activated coal gangue (D1, D2, D3). 90d, the strengths results of series of C and D were increased.

Table 2 Proportions of clinker with admixtures blended respectively w/%

	clinker	slag	fly ash	coal gangue	gypsum
A0	95				5
B1	70	25			5
B2	60	35			5
B3	50	45			5
C1	70		25		5
C2	60		35		5
C3	50		45		5
D1	70			25	5
D2	60			35	5
D3	50			45	5



(a) Bending strength (b) Compressive strength

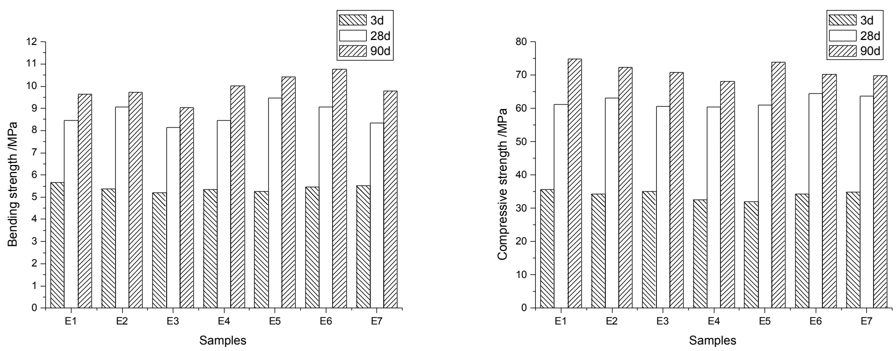
Fig.1 The strength results of clinker with admixtures blended respectively

2.1.2 Strengths of composite cement

70% clinker and admixtures (slag, activated coal gangue and fly ash) were blended in designed proportion (Table 3). The results of the bending strengths and compressive strengths were shown in Fig.2. In early-stage of hydration (3d), the strengths results of each sample were approximate. The bending strengths of the samples were about 5.4MPa and the compressive strengths were about 34MPa. Hydrating for 28d, the bending strengths of E2, E5 and E6 were above 9MPa and the compressive strengths of E2, E6 and E7 were come to 63MPa. From these results, it can be concluded that the higher the content of slag blended, the greater the mechanic properties of cement samples. In long-stage of hydration (90d), the bending strengths and compressive strengths of all samples were increased.

Table 3 Proportions of composite cement with 70% clinker w/%

	clinker	slag	fly ash	coal gangue	gypsum
E1	70	25/3	25/3	25/3	5
E2	70	25/2	25/4	25/4	5
E3	70	25/4	25/2	25/4	5
E4	70	25/4	25/4	25/2	5
E5	70	10	10	5	5
E6	70	10	5	10	5
E7	70	5	10	10	5

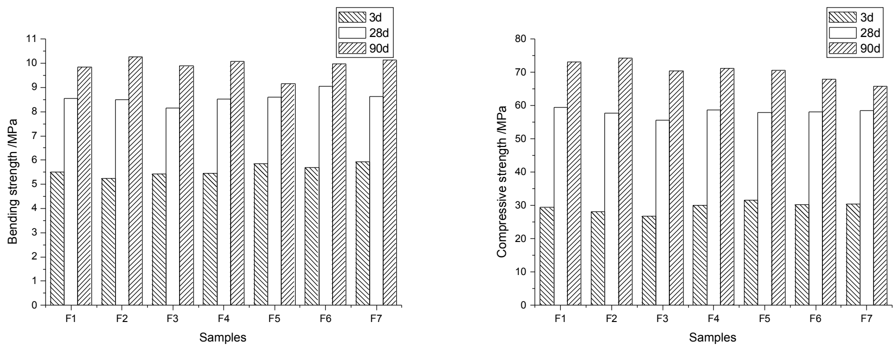


(a) Bending strength (b) Compressive strength

Fig.2 The strength results of composite cement with 70% clinker

Table 4 Proportions of composite cement with 60% clinker w/%

	clinker	slag	fly ash	coal gangue	gypsum
F1	60	35/3	35/3	35/3	5
F2	60	35/2	35/4	35/4	5
F3	60	35/4	35/2	35/4	5
F4	60	35/4	35/4	35/2	5
F5	60	14	14	7	5
F6	60	14	7	14	5
F7	60	7	14	14	5



(a) Bending strength (b) Compressive strength

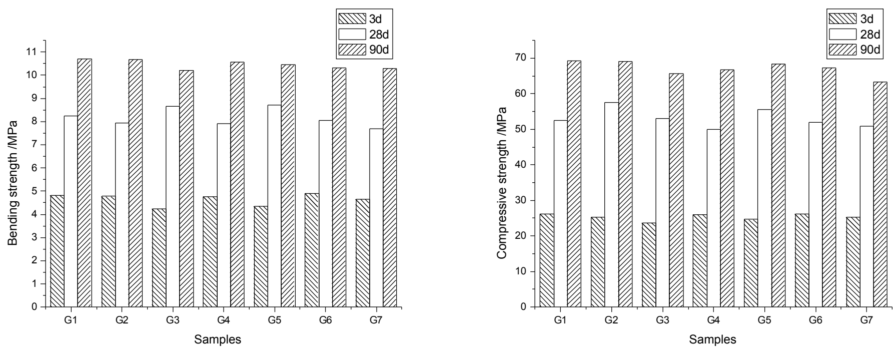
Fg.3 The strength results of composite cement with 60% clinker

60% clinker and admixtures (slag, activated coal gangue and fly ash) were blended in designed proportion (Table 4). The results of the bending strengths and compressive strengths were shown in Fig.3. As a whole, the strengths results of series F were a bit lower than that of series E. In early-stage of hydration (3d), the compressive strengths of the samples were above 5.2MPa and the bending strengths were about 30MPa. Hydrating for 28d, the bending strengths and compressive strengths of all samples were increased obviously. The bending strengths of samples were about 8.5MPa, and the compressive strengths of samples were about 55MPa. And in long-stage of hydration (90d), with the process of hydration reactions, the strengths results of all samples were created more.

Table 5 Proportions of composite cement with 50% clinker *w*/%

	clinker	slag	fly ash	coal gangue	gypsum
G1	50	15	15	15	5
G2	50	45/2	45/4	45/4	5
G3	50	45/4	45/2	45/4	5
G4	50	45/4	45/4	45/2	5
G5	50	18	18	9	5
G6	50	18	9	18	5
G7	50	9	18	18	5

50% clinker and admixtures (slag, activated coal gangue and fly ash) were blended in designed proportion (Table 5). The results of the bending strengths and compressive strengths were shown in Fig.4. In early-stage of hydration, the bending strengths results of series G samples were all above 4.2MPa, the compressive strengths results of each sample were approximate, about 25MPa. Curing for 28d, the bending strengths of samples were about 8MPa, while the compressive strengths of samples were more than 50MPa. The bending strength of G2 was even come to 57.5MPa. In long-stage of hydration, the bending strengths of each sample were increased greatly, more than 10.2MPa. And the compressive strengths were raised in a large degree.



(a) Bending strength (b) Compressive strength

Fg.4 The strength results of composite cement with 50% clinker

Comparing with three admixtures blended respectively in clinker, the composite cement (Series E, F and G) had superiority in strength properties. In this paper, composite technology was used, than proper proportions with materials having different performances were designed. These mixed materials supply mutual advantage to create the superimposed effect, which help to improve properties and increase its quality. The activities of cement clinker, slag, activated coal gangue and fly ash were lower in turn. Preparing composite cement with these materials in designed proportions, ordinal hydration effect was come out. Because hydration of the composite cement was ordinal, the structures were denser and the mechanic properties of the composite cement were improved.

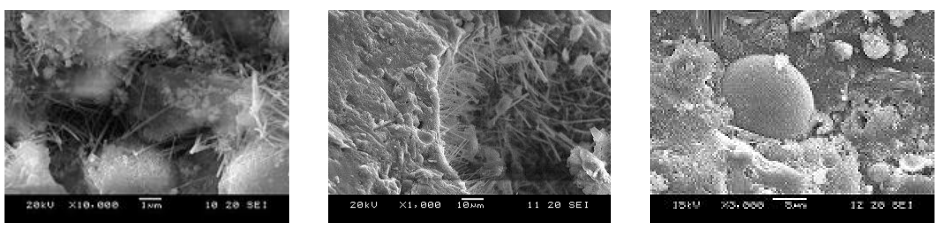
2.2 Microstructure of the hardened cement paste

2.2.1 SEM test

Two samples were chosen: E2, G2. In E2 and G2, both the weight ratios of slag, fly ash and coal gangue were 2: 1: 1. Curing time is 3d or 28d or 90d. The SEM photographs for the two samples are shown in Fig.5 to Fig.6.

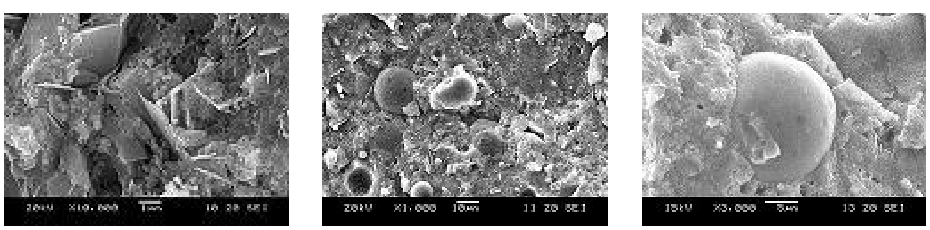
Fig.5 (a) shows the microstructure of E2 cured for 3d. Some C-S-H gel and a few needle-like AFt are found. And the surface of particles was coated by these hydration products, but the edge was clear. The degree of hydration was low and the structure was incompact. In Fig.5 (b), after curing 28d, the speeds of hydration reactions were running up. A lot of hydration products were formed and clusters of needle-like AFt were existed in some big empty cavities. Continuing hydration to 90d, Fig.5 (c) shows that the structure of E2 was denser than ever before. Few unhydrated particles, such as fly ash, were covered thick-bedded with hydration products, and the edge was blurry.

Fig.6 (a) shows the microstructure of G2 cured for 3d. A lot of plate-like $Ca(OH)_2$ was existed in the cement stone with a few C-S-H gel. The hydration reactions were processed slowly. It can be seen obviously that the structure was incompact. In Fig.6 (b), after curing 28d, the speeds of hydration reactions were still slow. Many unhydrated particles were existed. It is because that the contents of coal gangue and fly ash were increased, and they hydrate in long-stage mainly. In Fig.6 (c), after curing 90d, the situation was similar to that of E2, and the degrees of hydration were high. A lot of hydration products were formed, hydration products filled in pores more, and the structure was denser.



(a) E2-3d (b) E2-28d (c) E2-90d

Fig.5 SEM photographs of E2

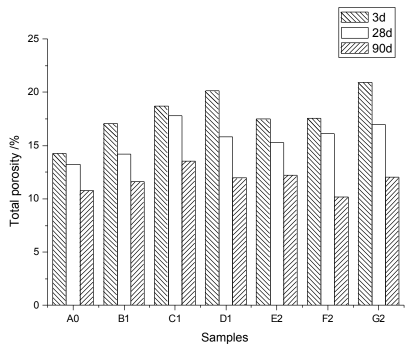


(a) G2-3d (b) G2-28d (c) G2-90d

Fig.6 SEM photographs of G2

2.2.2 Characterization of pore structure

It emphasizes the importance of pore structure of cement more than ever before, because an excellent pore structure indicates a denser structure which provides cement with good performances. It is a good method to study pore distribution, such as gas pore, capillary pore and gel pore. Ordinarily the more the ratio of gel pore is, the better the properties of cement are [11].



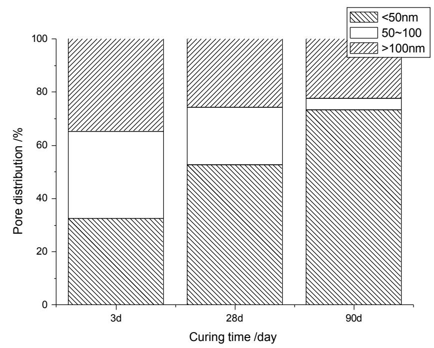
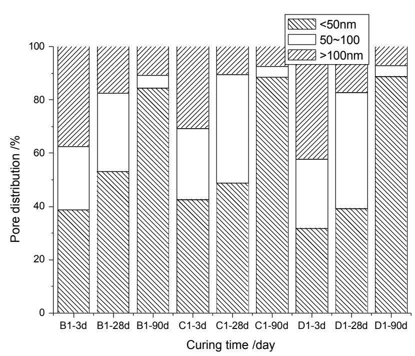


Fig.7 The total porosity of selected samples

Fig.8 Pore distribution of A0

It is showed from Fig.7, with the increase of hydration time, descending tendency was present of the total porosities of all selected samples. About cement clinker sample A0, after curing for 28d, the total porosity is 1.03% lower than that curing for 3d. And to 90d, the total porosity of A0 was fall down to 10.97%. Meanwhile, the ratio of gel pore (Aperture size is less than 50nm.) of A0 was ascended from 32.48% (curing for 3d) to 52.73% (curing for 28d), and that was 73.33% curing for 90d. The ratio of gas pore (Aperture size is more than 100nm.) of A0 was descended from 34.77% (curing for 3d) to 25.66% (curing for 28d), and that was 22.28% curing for 90d (Fig.8). Taking Fig.1 as a comparison, in the process of curing, the strength results of A0 were improved in a large degree. From results mentioned above, it can be concluded that the relation between pore structure and strength was tight.



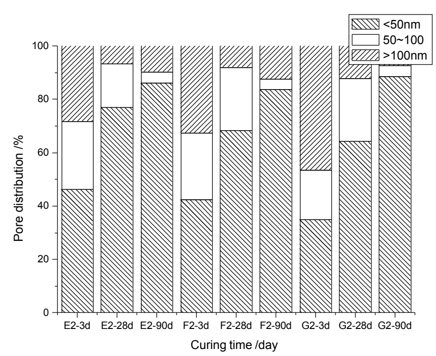


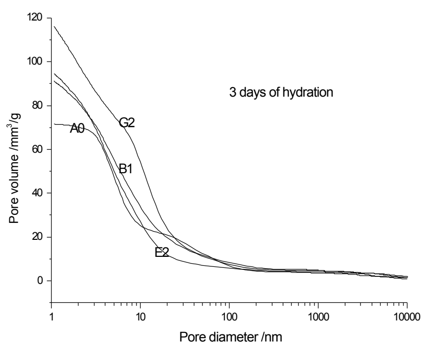
Fig.9 Pore distribution of B1, C1, D1

Fig.10 Pore distribution of E2, F2, G2

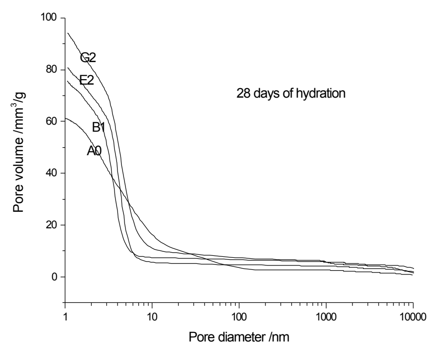
From Fig.7 and Fig.9, both in early-stage and long-stage of hydration, the porosity parameters of the sample blending slag (B1) were superior to those of samples blending fly ash (C1) and coal gangue (D1). The total porosity of B1 was lower, the ratio of gel pore was larger and the ratio of gas pore was smaller. It is because slag has more hydration activity than fly ash and coal gangue. Comparing C1 with D1, in early-stage of hydration, the total porosity of D1 was higher, and the porosity parameters of D1 were inferior to that of C1. But after 28d, the pore structure property of D1 was improved much more. The porosity parameters of D1 were superior to that of C1, and the compressive strength is 1.3MPa higher than that of C1 (Fig.1).

Fig.10 describes the pore distributions of E2, F2 and G2. In the 3 samples, the weight ratios of slag, fly ash and coal gangue were 2: 1: 1. Fig.11 describes the relations between pore diameter and pore volume in different stage.

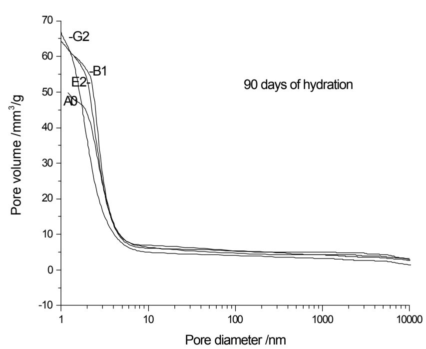
Comparing E2 with G2, in early-stage of hydration, the total porosity of G2 was 20.92%, which is about 3.5% higher than that of E2. The ratio of gel pore of E2 was higher (Fig.10). And from Fig.11(a), the pore volume of G2 was larger than that of E2. Taking SEM photographs (Fig.6(a)) as a comparison, the structure of G2 was looser. It is because that cement clinker plays an important role in early-stage of hydration, it creates early strength of cement.



(a) 3d



(b) 28d



(c) 90d

Fig.11 The influence of pore volume on pore diameter of samples

Hydrating for 28d, both porosity parameters of E2 and G2 were improved in a certain degree. The total porosity of G2 was approach to those of E2. About pore volume, though the pore volume of G2 was larger, the difference was shrunken (Fig.11(b)). It shows that admixtures hydrate in long-stage mainly. When curing for 90d, the ratios of gel pore of E2 and G2 were up to 85%. From Fig.11(c), the pore volumes of samples were smaller than before. The pore volume of G2 was even smaller than that of E2. This stage, the degrees of hydration were high. Hydration products filled in pores more, and the structure was denser, which matched to SEM test.

3 Conclusion

(1) 70%, 60%, 50% (mass percent) clinker and 30%, 40%, 50% admixture (including micro powder of slag, activated fly ash, activated coal gangue) were used to prepared high performance composite cement. The prepared cement can be used for industrial production. It’s good for saving clinker and using waste slag fully.

(2) Comparing with three admixtures blended respectively in clinker, the composite cement (three admixtures blended in designed proportions) had superiority in strength properties. The hydration of the composite cement was ordinal, the structures were denser and the mechanic properties of the composite cement were improved.

(3) The denser microstructure and the better pore structure are the physical reasons contributing to the good strength performance.

References

[1] Manjit Singh, Influence of blended gypsum on the properties of Portland cement and Portland slag cement, Cem. Concr. Res. 30 (2000) 1185-1188.
[2] L.Bagel, Strength and pore structure of ternary blended cement mortars containing blast furnace slag and silica fume, Cem. Concr. Res. 28 (7) (1998) 1011-1020.
[3] D. Li, X. Fu, X. Wu et al, Durability study of steel slag cement, Cem. Concr. Res. 27 (1997) 983-987.
[4] D. Li, X. Wu, J. Shen et al, The influence of compound admixtures on the properties of high-content slag cement, Cem. Concr. Res. 30 (2000) 45-50.
[5] B. Xu, X. Pu, Study on the relationship between the phase separation of slag glass and the latent hydraulic activity of BFS, J. Chin. Ceram. Soc. 25 (6) (1997) 729-733.
[6] D. Li, Z. Xu, Z. Luo et al, The activation and hydration of glassy cementitious materials , Cem. Concr. Res. 32 (2002) 1145-1152.
[7] A. L. A. Fraay, J. M. Bijen, Y. M. Dehaan, The reaction of fly ash in

concrete, a critical examination, Cem. Concr. Res. 19 (1989) 235-246
[8] A.Katz, Microscopic study of alkali-activated fly ash, Cem. Concr. Res. 28(2) (1998) 197-208.
[9] X. Song, C. Gong, D. Li, Research on cementitious behavior and mechanism of composite cement with coal gangue, J. Chin. Ceram. Soc. 32 (3) (2004) 358-363.
[10] C. Gong, X. Wang, D. Li, Evaluation of activation and its action mechanism of calcined coal gangue with calcium, J. Chin. Ceram. Soc. 33 (7) (2005) 842-845.
[11] H. Lian, L. Tong, E. Chen, The foundation of the research on building materials, The press of Tsinghua university, Beijing, 1996.