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The activation and hydration of glassy cementitious materials

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Abstract

This paper summarizes the relationship among structure, composition, and activity of glassy cementitious materials with low-calcium additions including slag and fly ash (FA). On the basis of silicate physical chemistry, silicate structure chemistry, silicate crystal chemistry, and coordination chemistry theory, five levels of glass structure have been described. Their influence on the reactivity and hydration properties of slag and FA are discussed using SEM, X-ray diffraction (XRD), thermal gravimetry analysis (TGA), DSC-TG, and pore structure analysis. On the other hand, differences in activity between slag and FA are studied. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cementitious material; Pore distribution; Coordination chemistry; Microstructure; Thermal gravity analysis

1. Introduction

The cement industry is an important part of the national economy of China. The production of Portland cement not only consumes limestone, clay, coal, and electric power, but also releases waste gases, such as CO_2, SO_3, and NO_x, which can cause the greenhouse effect and acid rain. Therefore, the development of cement industry is closely bonded up with the strategy of sustainable development. It is a valid method to use the industrial by-products as additions to cement. Blast furnace slag (BFS) cement (ordinary called slag cement) is a main cement product in our country. Except for Portland cement, it is widely used in construction engineering. Slag cement has many advantages such as higher later strength, good durability, chemical stability, and so on. With the utilization of BFS in the cement and concrete industry, the cost of BFS is continuously increasing. Therefore, it is very important to synthetically utilize resources, especially other industrial by-products.

In China, about 100 million tons of fly ash (FA) are discharged annually from coal-burning electric-generating plant and only about a fourth is utilized [1]. Generally, FA has a lower activity in the lime and gypsum surroundings during room temperature curing [2]. The reason is that there is a high content of aluminum and silicon oxide and a high degree of polymerization in it. Therefore, its hydration activity is much lower than that of the BFS.

The BFS and FA, as potential active materials, are used in cement and concrete industry. Their potential activation has been known. The main reasons for their reactivity are their glass structure and chemical composition. Because of their difference in chemical compositions, there is an obvious difference in their activity.

According to the theory of glass structure, Yuan Runzhang [3] divides the slag structure into three levels. Firstly, the slag is viewed as a whole. Its structure parameter is the ratio of glass to the amount of crystal. Usually, the glass phase is the active part and the crystal phase is the indolent part. The more the glass phase is, the more active the slag. Secondly, the level of average ionic bond is determined by considering the glassy phase of slag as the study parameter. When other conditions are unchanged, the larger this parameter is, the more active the slag is. Thirdly, the studied parameter is the tetrahedral silicate in the glassy phase of slag. The polymerization degree of tetrahedral silicate may be expressed by the average bridge oxygen number (R). Generally, if the value of R increases, the polymerization degree of tetrahedral silicate increases.

Although BFS and FA both have glass structures, there is a large difference in their hydration activities. In order to

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study the microstructure and its effects on the activation of glassy cementitious materials, admixtures were added. There are a lot of reports about the activation of slag, including gypsum, $Ca(OH)_2$, and alkali, but there are only a few reports about the study of FA activation [4–6]. Fraay et al. [7] studied the activation of FA in different pH. Results showed that the activation of FA is low when pH is less than 13.2. Results are important to state the low activation of FA in a lime system. There are some reports about alkali-activated FA [8,9].

This paper mainly studied the activation and hydration of slag and FA in the basic condition, including the $Ca(OH)_2$, NaOH, $NaSO_4$, and water glass. At the same time, the strength and hydrates properties were studied.

2. Experiment and discussion

2.1. Materials

FA came from the Nanjing coal power plant. BFS came from the Nanjing 9424 steel plant. Clinker and gypsum came from the Nanjing Nongtan cement plant. Table 1 shows their chemical composition.

2.2. Testing methods

Pore test was done using Auto-60 mercury scanning porosimeter from USA, and SEM test was done using H-800 from Japan. Thermal gravimetry analysis (TGA) was done using TGA V5.1A DuPont 2000 from USA.

2.3. SEM test

The SEM photos of BFS hydrated for 7 days at 60 °C are shown in Fig. 1. Fig. 1(a) shows that there was higher degree of hydration at the edges of the slag. Much C-S-H gel was produced in the existence of gypsum only. When gypsum and $Ca(OH)_2$ were added, the hydration of slag speeded up, so the consumed content of gypsum increased. It can be seen from Fig. 1(b) that there was much fibrous ettringite and the surface of slag was coated by-products. It also shows that AlO_2^- ions in the slag are easily soluble and reactive. Therefore, there is much ettringite and the structure of cementitious materials is strengthened.

Fig. 2 shows SEM photos of the FA hydration at 60 °C for 7 and 14 days. Fig. 2(a) corresponds to the FA activated by 2% NaOH at 7 days. It can be seen that the surface of the FA is covered with hydration products, but the edge is clear. In Fig. 2(b), the FA is activated by 2% NaOH at 14 days. The FA has a large degree of erosion by NaOH. In Fig. 2(c), the FA was activated by NaOH and $Ca(OH)_2$ at 7 days. The surface of the FA is covered by C-S-H caused by the reaction of the FA and lime.

Table 1
The chemical compositions of raw materials (mass%)

	Loss (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
Clinker		64.1	21.1	4.88	4.65		
BFS		35.2	35.5	12.4	1.79	11.3	
FA	4.8	5.83	52.7	25.4	7.56	0.56	0.80
Gypsum							34.40

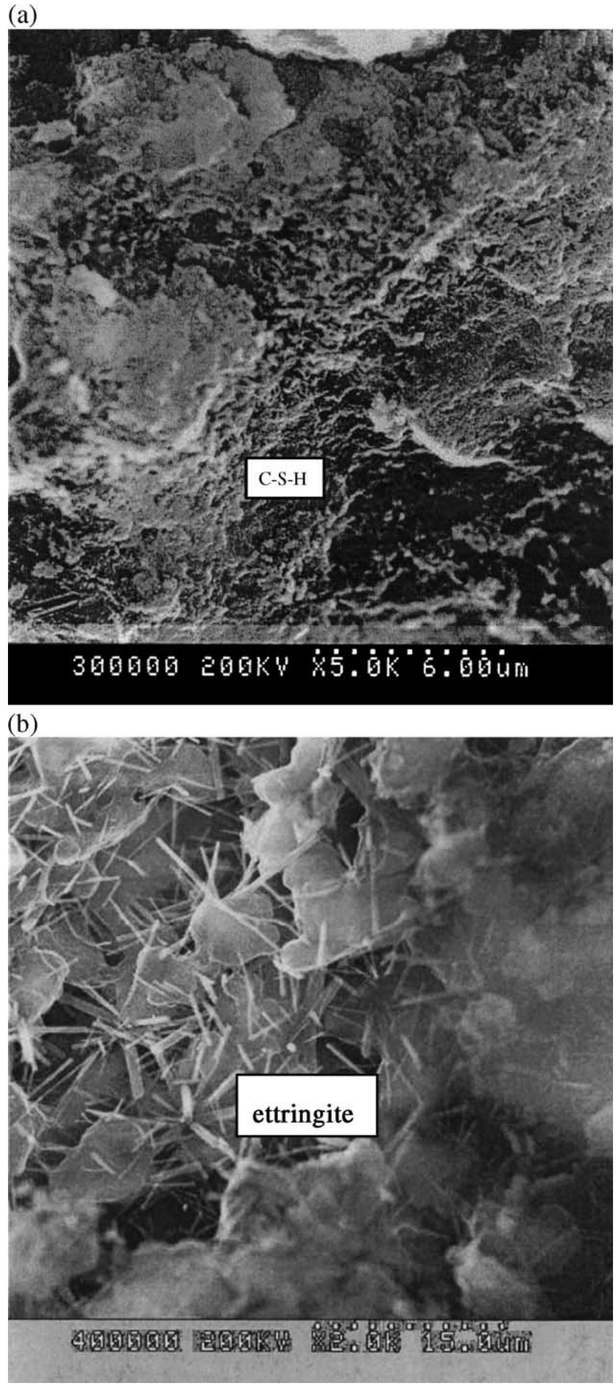

Fig. 1. SEM photo of BFS. (a) BFS + 5% gypsum, 60 °C, 7 days; (b) BFS + 5% gypsum + 2% CaO, 60 °C, 7 days.

In Fig. 2(d), the FA was activated by NaOH and $Ca(OH)_2$ for 14 days. Because the hydration is enhanced, the FA is

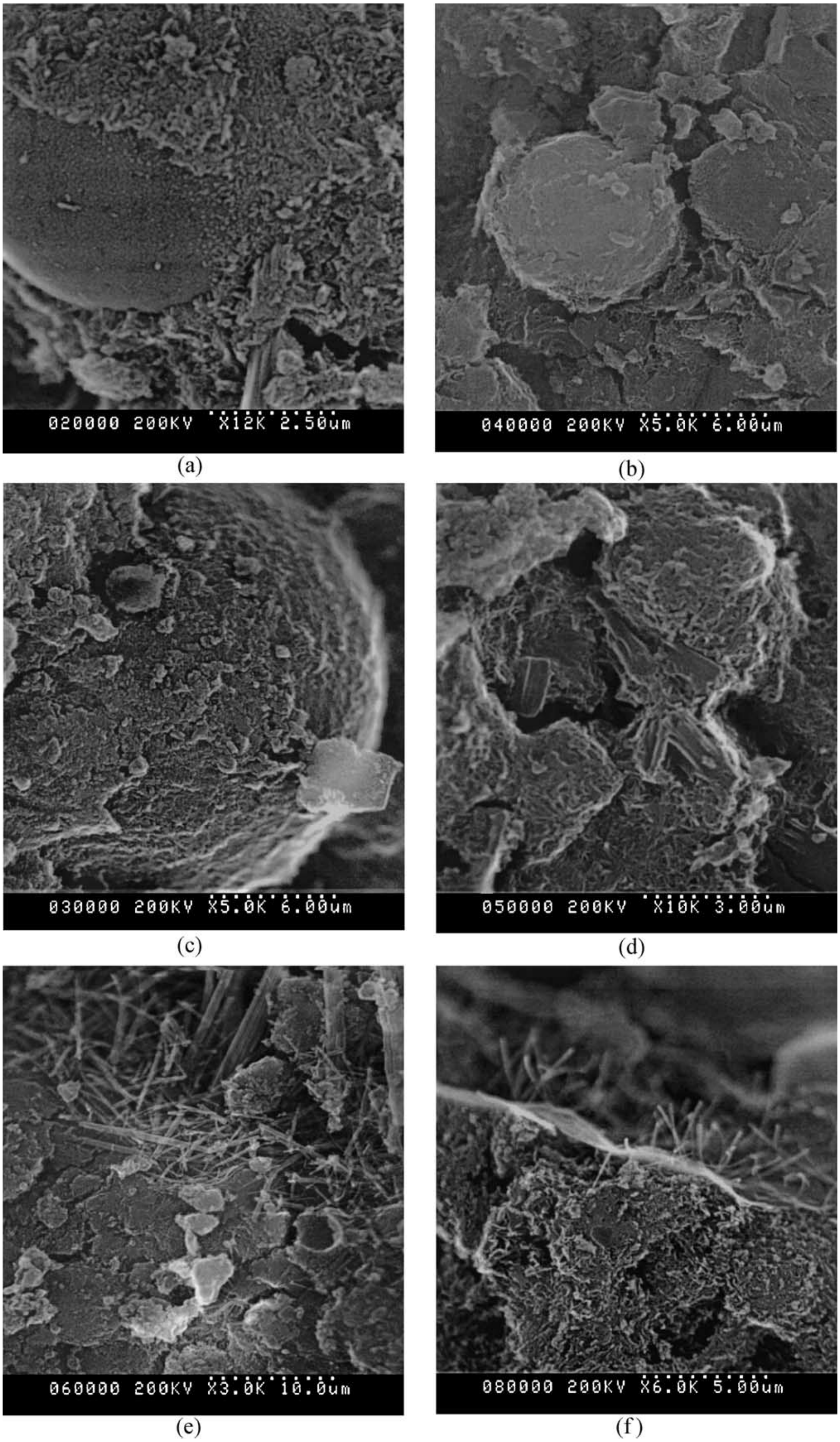

Fig. 2. SEM photo of hydration of alkali FA. (a) FA – NaOH at 7 days; (b) FA – NaOH at 14 days; (c) FA – $Ca(OH)_2$ – NaOH at 7 days; (d) FA – $Ca(OH)_2$ – NaOH at 14 days; (e) FA – $Ca(OH)_2$ – Na_2SO_4 at 7 days; (f) FA – $Ca(OH)_2$ – Na_2SO_4 at 14 days.

Table 2
Composition of test batches of FA (mass%)

Number	FA	Lime (CaO)	gypsum	NaOH	Na_2SO_4	Water glass (ml)
F1	80	20	0	0	0	
F2	75	20	5	0	0	
F3	80	20	0	4	0	
F4	80	20	0	0	0	10
F5	75	20	5	0	4	
F6	75	20	5	4		
F7	75	20	5	0	0	10

Water glass means liquid sodium silicate; the ratio of SiO_2 to Na_2O is 3.73.

covered with C-S-H and other hydration products. When the FA is activated by $Ca(OH)_2$, gypsum, and Na_2SO_4, the hydration of FA speeded up. There are a lot of ettringite needles at 7 days (Fig. 2(e)). At 14 days of hydration (Fig. 2(f)), the ettringite continues increasing and developing, and needle crystals crossed each other forming a frame structure. It improves strength and other properties of cement at early stage.

2.4. TGA test

TGA has been widely accepted as an accurate method for the determination of crystalline CH content and other hydrates (water loss), including C-S-H, AFt, gypsum, and so on. From 70 to 900 °C, the studied system can generally be separated into three parts: an abrupt weight loss near 450 °C associated with the dehydration of CH; another fairly sudden, but less distinct, weight loss between 600 and 700 °C associated with the decomposition of calcium carbonate; between 70 and 400 °C, the weight loss is mainly due to the disappearance of free water and dehydration of calcium silicate hydrates, calcium aluminate hydrates, and other hydrates, including AFt, AFm, gypsum, and so on.

Table 2 gives the composition of test batches of FA. By TGA, the activation of FA–lime and FA–lime–gypsum systems was studied in the different alkali environments. The fineness of raw materials is about 300 m^2/kg. The ratio of water to test materials is 0.47.

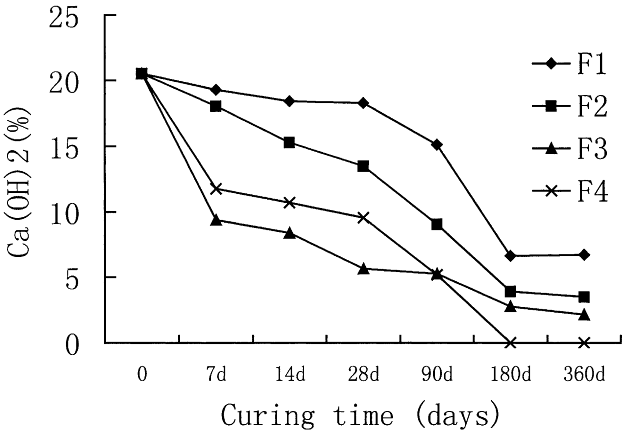

Fig. 3. Relation of curing time vs. $Ca(OH)_2$ in the system of FA–lime at 20 °C.

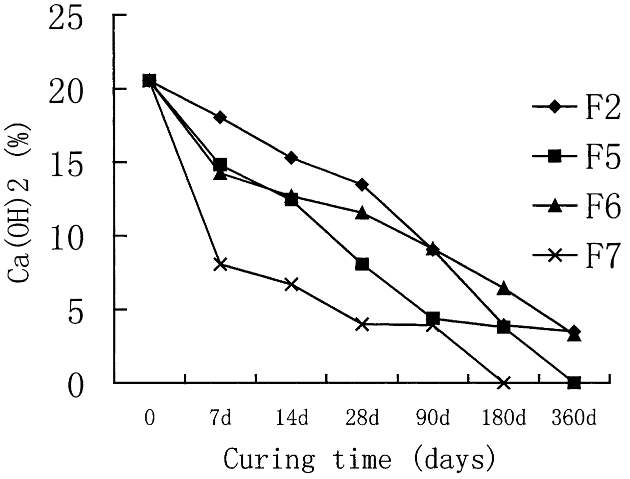

Fig. 4. Relation of curing time vs. $Ca(OH)_2$ in the system of FA–lime–gypsum at 20 °C.

In the FA–lime system, which used gypsum, NaOH, and water glass as activators, the activation of FA was studied by means of absorbing lime. Fig. 3 shows the relation between curing time and $Ca(OH)_2$ in the FA–lime system at room temperature. Results show that the hydration degree of FA is very low at 28 days in the system of FA–lime (F1) if without admixtures. With the increase of hydration time, $Ca(OH)_2$ content decreases from F2 to F4. When curing for 90 days, the reaction of FA and lime is obvious. From the function of admixtures, alkali improves the early hydration of FA, and water glass improves both early and late hydration of FA. It is because that water glass does not increase the alkalinity but reacts with lime. Therefore, there are more hydrates and the hydration rate of FA is higher.

Fig. 4 gives the TGA test results of the FA–lime gypsum system. The hydration of FA–lime gypsum system was studied by adding NaOH, Na_2SO_4, and water glass. From the results of $Ca(OH)_2$ absorption, water glass (F7) corresponds to the best rate of hydration in the FA–lime gypsum system. The early state effect of NaOH is better, while the later state effect of $Na_2SO_4$is better. It is because that addition of sulfate is beneficial to the production of ettrin-

Table 3
Composition of test batches of slag (mass%)

Number	Slag	Lime (CaO)	gypsum	NaOH	Na_2SO_4	Water glass (ml)
S1	90	10				
S2	85	10	5			
S3	90	10		4		
S4	90	10				10
S5	85	10	5		4	
S6	85	10	5		4	
S7	85	10	5			10

Table 4
TGA analysis of slag system

Number	$Ca(OH)_2$ (%)				
	7 days	28 days	90 days	180 days	360 days
S1	3.95	3.96	4.11	4.23	3.84
S2	3.08	3.60	2.92	2.92	3.45
S3	3.66	3.49	3.70	2.88	3.28
S4	3.00	1.64	0.82	0	0
S5	2.71	2.06	3.17	2.88	2.47
S6	3.29	3.54	4.93	3.45	3.49
S7	2.47	2.06	0	0	0

gite. And the production of ettringite needs the absorption of $Ca(OH)_2$.

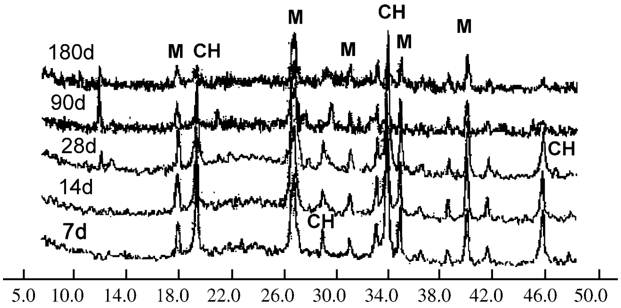

Fig. 5. XRD pattern of FA–lime system at 7, 14, 28, 90, and 180 days of hydration (F1, 20 °C). M = mullite, CH = $Ca(OH)_2$.

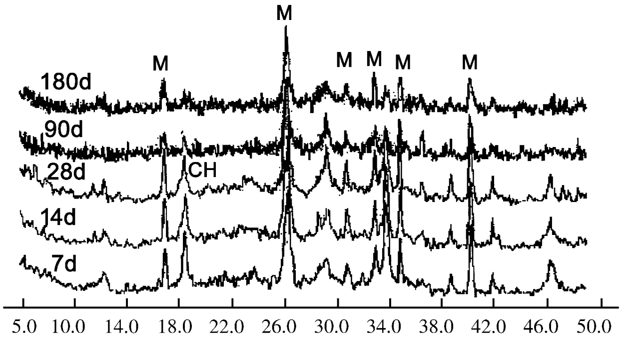

Fig. 6. XRD pattern of FA–lime–NaOH system at 7, 14, 28, 90, and 180 days of hydration (F3, 20 °C).

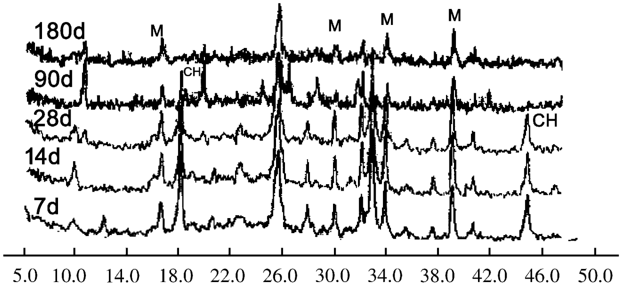

Fig. 7. XRD pattern of FA–lime–gypsum system at 7, 14, 28, 90, and 180 days of hydration (F2, 20 °C).

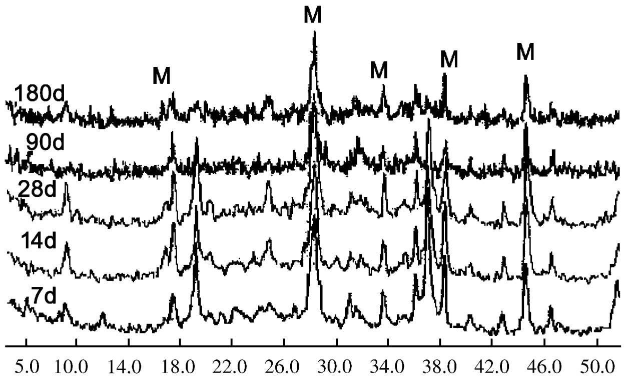

Fig. 8. XRD pattern of FA–lime–gypsum–NaOH system at 7, 14, 28, 90, and 180 days of hydration (F6, 20 °C).

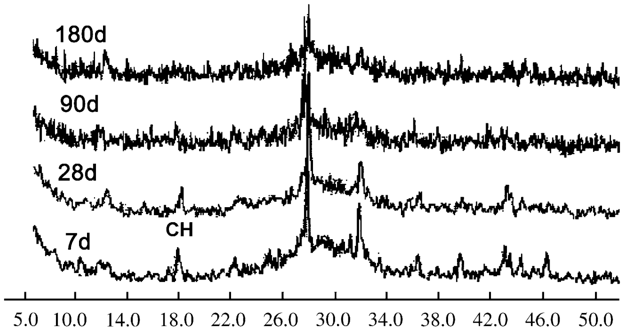

Fig. 9. XRD pattern of slag–lime system at 7, 28, 90, and 180 days of hydration (S1, 20 °C).

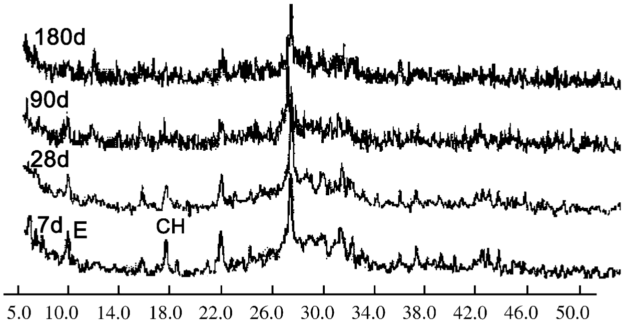

Fig. 10. XRD pattern of slag–lime–gypsum system at 7, 28, 90, and 180 days of hydration (S2, 20 °C).

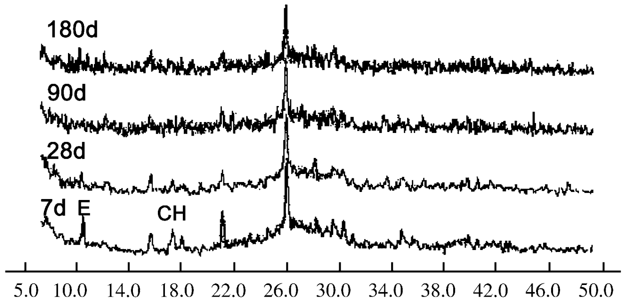

Fig. 11. XRD pattern of slag–lime–gypsum–NaOH system at 7, 28, 90, and 180 days of hydration (S6, 20 °C).

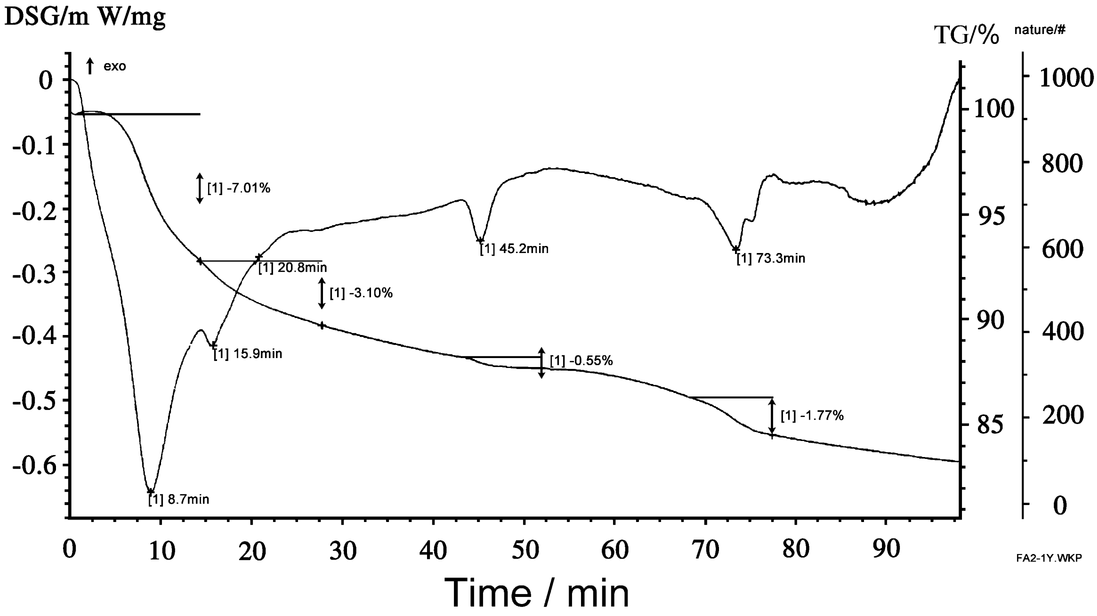

Fig. 12. DSC-TG thermal analysis pattern of F2 at 1 year of hydration.

Compared with FA, the $Ca(OH)_2$ content of slag is higher, so its activity is also higher. When the slag activation is studied, only 10% lime(CaO) is added. Table 3 gives the composition of tested slag batches. The ratio of water to test materials is 0.40.

Table 4 gives TGA analysis results of slag hydration at 7, 28, 90, 180, and 360 days. From TGA results of slag–lime system, the $Ca(OH)_2$ content of S1 decreases to 3.95% at 7 days of hydration. Thus, it is shown that the reactivity of slag with lime is much more obvious than that of FA at room temperature. Compared with S1, the effect of S3 and S4 is better. The reason is that the alkali of S3 speeds up the activation of slag, and the water glass of S4 does not play an important part in activating slag, but directly reacts with $Ca(OH)_2$ and produces C-S-H gel. Therefore, the $Ca(OH)_2$ content decreases rapidly. At 180 days of hydration, there is no more $Ca(OH)_2$ in S4. In the slag–lime–gypsum system, gypsum had sulfate-activating effect to slag, so it is useful to absorb $Ca(OH)_2$. In this system, the effect of water glass is the best. At 28 days of hydration, there is no $Ca(OH)_2$ in S7.

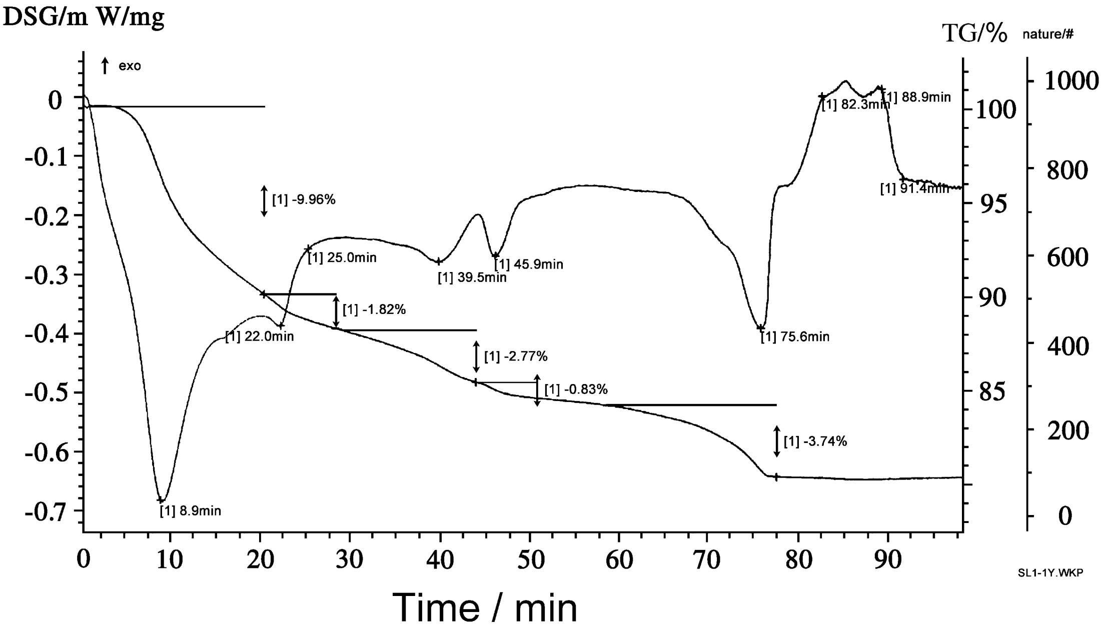

Fig. 13. DSC-TG thermal analysis pattern of S2 at 1 year of hydration.

From TGA results, the composition and activation of slag are suitable in producing hydrates only if some $Ca(OH)_2$ is added as an activator. But to activate FA, both lime and alkali are necessary.

2.5. XRD analysis

From the X-ray diffraction (XRD) pattern of FA, FA mainly contains mullite and a little quartz crystal.

Fig. 5 is the XRD pattern of the FA–lime system (F1) at 7, 14, 28, 90, and 180 days of hydration. At 180 days of hydration, two peaks of mullite ($2\theta = 16.416^\circ$, 26.215°) still exist. The $Ca(OH)_2$ peak ($2\theta = 18.001^\circ$) obviously decreases. Mullite crystals of FA are very stable at room temperature.

Fig. 6 is the XRD pattern of the FA–lime–NaOH system (F3) at 7, 14, 28, 90, and 180 days of hydration. Results show that when hydrated for 90 days, the $Ca(OH)_2$ peak is very weak. Mullite peaks still exist. Therefore, mullite crystal is still stable in the alkali surrounding.

Fig. 7 is the XRD pattern of the FA–lime–gypsum system (F2) at 7, 14, 28, 90, and 180 days of hydration. From the 7 days of hydration, the characteristic peaks of gypsum ($2\theta = 11.49^\circ$) still exist. At 14 days of hydration, there are no gypsum peaks. Therefore, gypsum has reacted and produced hydrates similar to ettringite ($2\theta = 9.0^\circ$). The production of ettringite needs the absorption of lime and aluminate.

Fig. 8 is the XRD pattern of the FA–lime–gypsum–NaOH system (F6) at 7, 14, 28, 90 and 180 days of hydration. Compared with Fig. 7, the characteristic peak of gypsum is not obvious at 7 days of hydration. The effect of alkali speeds up the breaking of glass network. Therefore, there is much CSH gel and ettringite.

Fig. 9 is the XRD pattern of the slag–lime system (S1) at 7, 28, 90, 180 days of hydration. $Ca(OH)_2$ does not exist at any way after 90 days of hydration. Fig. 10 is the XRD pattern of the slag–lime–gypsum system (S2) at 7, 28, 90, 180 days of hydration. Gypsum disappeared and ettringite appeared. $Ca(OH)_2$ does not exist after 90 days of hydration. Fig. 11 is the XRD pattern of the slag–lime–gypsum–NaOH system (S6) at 7, 28, 90, and 180 days of hydration. Compared with Fig. 10, after 7 days of hydration, the $Ca(OH)_2$ content obviously decreases.

2.6. DSC-TG thermal analysis

In order to describe hydrates and reaction temperatures, DSC-TG thermal analysis of the 1-year hydration of F2 and S2 has been made. Fig. 12 is DSC-TG results of FA system. At 87, 153, 458, and 736 °C, thermal peaks are present. They are C-S-H, $Ca(OH)_2$, and $CaCO_3$ reaction peaks. However, in the slag system (Fig. 13), besides 87, 153, 458, and 736 °C thermal peaks, 114, 216, and 384 °C peaks are also present. These peaks do not exist in the FA system. They are related with hydrates that contain aluminates. Results show that when the aluminate of FA mainly forms mullite crystal not in normal condition but in an alkali condition, it is stable. On the other hand, the aluminate of slag is more active, it easily reacts with calcium or sulfate in $Ca(OH)_2$ or in an alkali medium. Therefore, hydrate-containing aluminate in slag is much more reactive than that of FA.

2.7. Pore structure results

In order to study the relations of pore structure and strength of the low-calcium cementitious materials, selected samples of paste were put into water after 1 day of hydration and were took out at a requirement hydration time. Samples were placed in alcohol and then dried when testing.

Because of lower hydration degree of FA at room temperature, pore structure tests are made at 50 °C and cured for 7 and 28 days. Results are seen in Table 5, which shows that at 7 days of hydration, the FA–lime system (F1) has a larger porosity and median radius. At 28 days of hydration, its pore structure is obviously improved. When activators are added, the early state pore properties are obviously improved. For example, compared with F1, at 7 days of hydration, the decrease of total porosity of F5 was 11.95% and the median radius decreases to 15.40 from 487.1 nm. Results of other samples are similar to F5.

Table 5
Pore structure results of hydration in FA system (50 °C)

50 °C, 7 days

	F1	F2	F4	F5	F6	F7
Porosity (%)	45.26	43.77	42.99	33.31	44.96	40.87
Pore volume (cm^3/g)	0.4126	0.3300	0.3561	0.2486	0.3689	0.3611
Median radius (nm)	487.1	26.38	23.19	15.40	31.47	66.50
> 200 nm (%)	74.09	9.97	2.86	1.33	1.65	5.01
150–200 nm (%)	3.15	0.82	0.31	0.48	0.46	2.22
100–150 nm (%)	2.25	2.88	3.54	0.36	2.68	1.91
50–100 nm (%)	3.76	22.21	7.08	1.29	18.57	8.47
40–50 nm (%)	0.99	4.27	2.25	1.33	11.74	2.41
30–40 nm (%)	1.62	6.03	13.06	2.17	16.26	6.67
20–30 nm (%)	2.01	16.42	26.09	20.39	12.28	14.10
10–20 nm (%)	4.73	24.73	25.33	43.40	20.74	21.30
5–10 nm (%)	4.27	9.03	14.07	21.24	12.78	22.60
< 5 nm (%)	3.15	3.64	5.42	8.00	5.50	15.09

50 °C, 28 days

	Fa1	Fa2	Fa4	Fa7	Fa8	Fa10
Porosity (%)	37.21	29.76	38.00	25.39	34.91	26.75
Pore volume (cm^3/g)	0.282	0.226	0.292	0.180	0.258	0.208
Median radius (nm)	37.21	11.75	12.23	18.72	25.71	36.87
>200 nm (%)	5.56	0	0	0	0	2.88
150–200 nm (%)	0.21	2.26	0	0	0	1.11
100–150 nm (%)	0.60	6.24	0	0	0	0.38
50–100 nm (%)	3.15	2.39	0.73	0.45	2.75	12.21
40–50 nm (%)	7.22	1.37	0.89	1.40	5.58	4.47
30–40 nm (%)	36.19	1.73	2.98	7.76	19.56	13.99
20–30 nm (%)	20.75	3.80	12.45	35.94	24.71	13.46
10–20 nm (%)	17.77	45.29	46.31	30.58	26.76	14.42
5–10 nm (%)	6.41	33.11	25.56	15.51	14.45	11.15
< 5 nm (%)	2.05	3.85	11.15	8.37	6.20	6.30

3. Conclusions

1. The reaction of FA and lime is very weak at room temperature. The addition of sulfate and alkali improves the activation of FA–lime system. The effect of alkali is more outstanding than that of sulfate. The reaction of slag and lime is much more rapid than that of FA. Therefore, at room temperature, slag can react with more lime, and alkali can speeds up this reaction.

2. From the analysis of the balance system of hydrates, slag is an ideal substance in producing cementitious materials with low calcium, only adding some $Ca(OH)_2$ and a little activator to its compositions and structure. XRD, SEM, TGA, and DSC-TG results show this conclusion.

3. The difference between slag and FA is that the aluminate hydrates of the slag sample obviously increases at the same hydration time. It is because the alumina oxygen ions of the slag more easy dissolve and react. Under higher alkalinity, the glass structure of FA was easily broken. Because of the lower calcium content of the FA, only a little C–S–H gel forms. Therefore, pore structure results show that there are a lot of pores in the FA paste. Only in the higher alkalinity condition is the glass structure of FA easily broken and its activation and hydration properties are improved.

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