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Study of properties on fly ash–slag complex cement

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Abstract

In China, blast furnace slag (BFS) has been widely used as an additive to cement and concrete. So it is almost completely utilized. Therefore, the cost of BFS is higher, so the cement expense is going to increase. Therefore, it is necessary to partially replace BFS with fly ash, which has lower cost and therefore has not been used in large quantity. This paper studies the mechanical properties, hydration degree, pore distribution and hydrates of fly ash–slag complex cement (FSCC) by strength and other physical mechanical tests, XRD, TGA and pore structure analysis. Test results show that there were better properties when fly ash was added in a proper ratio. It is called an effect of mutual complement of superiority supplement. In addition to this, the admixtures speed up the hydration of complex cement and improve the strength and pore structure properties.

Keywords: Fly ash–slag complex cement; Pore structure; Median pore radius; Hydration degree

1. Introduction

Blast furnace slag (BSF) cement (ordinarily 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 and chemical stability and so on. With the utilization of BFS in the cement and concrete industry, the cost of BFS is continuing to increase. Therefore, it is very important to synthetically utilize resources, especially other industrial by-products. In many industry by-products, fly ash is more suitable. From the reports of China today, there is about 6 billion tons of the fly ash that has not been used. In China, about 100 million tons of fly ash is discharged annually from coal-burning electric-generating plant, and only about a fourth of it is utilized [1]. This is due to the fact that fly ash has lower hydration activation than slag. Since fly ash was widely applied in concrete construction, the study of the fly ash properties has become important. Even though the study of the strength and thermodynamic properties of high volume fly ash concrete has become of great interest [2] to researchers, it is not suitable to produce cement by itself. The reasons are that fly ash cement has many disadvantages such as lower strength, higher requirement water and poor resistance carbonation. So it is a good method to partially substitute for slag by fly ash in producing complex cement. Complex cement has been studied [3–7] since 1990. And made a national standard (GB12958-91).

This paper studies the properties of fly ash–slag complex cement (FSCC), including the mechanical properties, hydration degree and pore distribution. The paper also studies the influence of admixtures on complex cements.

2. Experiment

2.1. Materials

Fly ash material of experiment came from the Nanjing coal power plant. BSF was from the Nanjing 9424 steel plant. Clinker and gypsum came from the Nanjing Nongtan cement plant. Table 1 shows their chemical composition.

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

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
Clinker	64.11	21.11	4.88	4.65		
Slag	35.19	35.50	12.40	1.79	11.25	
Fly ash	5.83	52.74	25.42	7.56	0.56	
Gypsum						34.40

2.2. Testing methods

The mortar strength test was made according to GB177-85. Sample size is $40 \times 40 \times 160$ cm^3. According to some, a definition patch (Table 2) weighing 3 kg, which was then placed to a test mill and ground at the same time the cement was made. Specific surface area and sieve residues were made according to national standards. The ratio of water to cement was 0.44 in the mortar strength test. The pore structure test was done with an Auto-60 mercury scanning porosimeter from the USA. Thermogravimetric analysis (TGA) was made using TGA V5.1A DuPont 2000 from USA.

3. Test results and discussion

3.1. Test patches

In order to compare the properties of complex cement, the slag cement and fly ash cement were used as reference samples and continuously increased fly ash replacing content. The test matrix plan is seen in Table 2.

3.2. Physical properties of cements

Table 3 shows the specific surface area, water requirement and sieve residue. Because fly ash has small particle size before milling, the specific surface area of cement increased with the increase of fly ash. Similar to the special surface area results, water requirement increased with increase in fly ash content.

3.3. Strength results of cements

Strength is an important target in evaluating cement quality and property. It synthetically shows up the micro-structural properties of cement. Strength test results are shown in Figs. 1–4.

Table 2
Test matrix plan of FSCC

No.	Fly ash	Slag	Clinker	Gypsum
A0	0	0	95	5
A2	40	10	45	5
A3	30	20	45	5
A4	25	25	45	5
A5	20	30	45	5
A6	10	40	45	5
A7	0	50	45	5

Table 3
Test results of FSCC

No.	Specific surface area (m^2/kg)	Water requirement (%)	0.08 mm sieve residue (%)
A0	300	26.50	4.6
A1	450	31.25	1.4
A2	420	31.00	1.8
A3	410	29.75	2.6
A4	360	28.75	2.6
A5	370	28.50	3.1
A6	335	27.25	4.0
A7	304	26.00	6.0

Figs. 1 and 2 are compressive and flexural strength results of complex cements. From compressive strength results, it can be known that in hydration early stage, when the content of fly ash reached 25–30%, the better compressive strength can be acquired. This is because that although activity of fly ash is lower, it affects the early strength development. On the other hand, the increase of fly ash content makes the special surface area increase, so the special surface area of cement plays an important role in the early strength of cement. In the hydration later stage, because the slag activation and hydration had produced good affect on strength development, and the hydration degree of fly ash was lower, so the compressive strength of slag cement increased a little. Compared with A1, the compressive strength of A5 respectively increased by 29.5%, 46.9% and 46.5% at days 3, 7 and 28 of hydration. Results show that it is possible to partly replace slag by fly ash. Flexural strengths have also the same development rule.

In order to speed up the activation of fly ash and slag, in the basis of the A4 and A5, the admixtures were added. The aims were to enhance the hydration degree of fly ash and slag, on the basic principle of alkali slag cement. In addition to use calcine gypsum, Na_2SO_4 was also used.

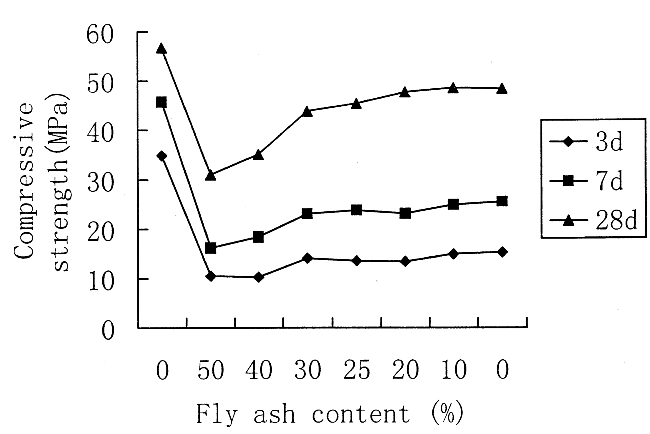

Fig. 1. Curves of fly ash content vs. compressive strength (see Table 2).

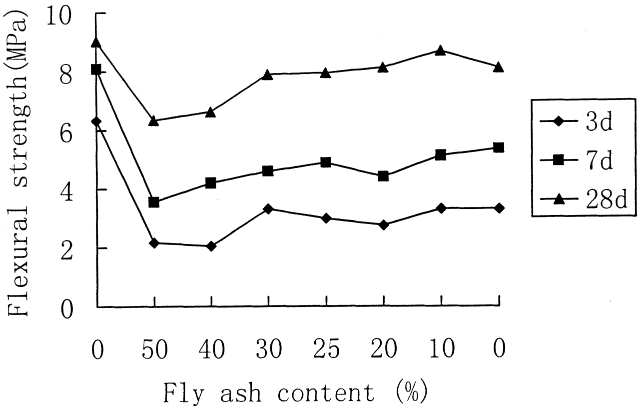

Fig. 2. Curves of fly ash content vs. flexural strength.

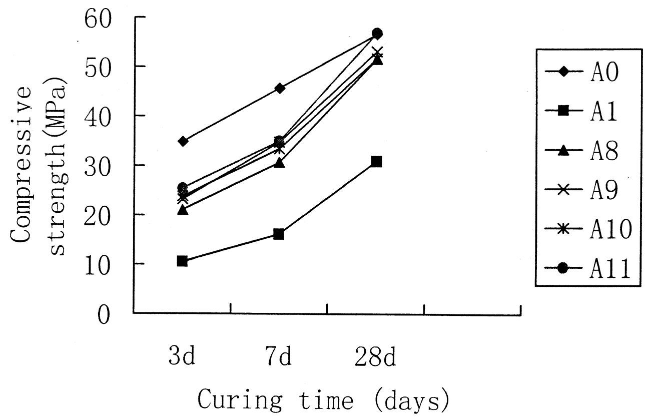

Fig. 3. Curves of curing time vs. compressive strength.

Table 4 is the test matrix of the complex cement including the action of admixtures.

Figs. 3 and 4 were test results of compressive and flexural strength. From strength results, it can be known that using calcine gypsum to replace gypsum, there were more obvious effect in enhancing compressive and flexural strength. Using complex admixtures (calcined gypsum and Na_2SO_4), the enhancing effect was the most obvious. For example, compared with A1, the compressive strength of A11 respectively increased by 139%, 116% and 83.9%, and the flexural strength increased by 141%, 97% and 51.1% at days 3, 7 and 28 of hydration. Its compressive and flexural strength at day 28 has reached the level of Portland cement. So making use of techniques of fly ash–slag complex and admixtures, it is possible to produce the higher-grade complex cement.

3.4. Pore structure results of cements

The relation between structure and properties was first established by T.C. Powers. He invented the BET and water adsorption methods, measured pore structure, and determined a series of relations such as porosity–strength, pore structure–durability. The study of pore structure is a main method in the study of hydration. The study of pore structure mainly included porosity, pore volume, pore distribution and so on. It is a good method to study different pore sizes 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.

The relation of pore structure and strength of the complex cement was studied. Selecting some samples of paste, the ratio of water to cement of all samples is 0.28. Samples were put into water after hydration day 1 and taken out at days 3, 7 and 28 of hydration. Hydration of the samples were ceased by putting into alcohol and then dried when testing. Pore structure experiment results are shown in Figs. 5–9.

Table 4
Test patch of FSCC (wt.%)

No.	Fly ash	Slag	Clinker	Calcine gypsum	$NaSO_4$
A8	25	25	45	5	
A9	20	30	45	5	
A10	25	25	45	4	1
A11	20	30	45	4	1

Fig. 5 shows the total porosity of cements at days 3, 7 and 28 of hydration. Results show that total porosity of common complex cement (A5) was lower than fly ash cement (A1) and slag cement (A7) at days 3, 7 and 28. It is because the slag of A1 has more hydration activity than fly ash that the hydration property of A5 is superior to A1. On the other hand, the particle size ratio of A5 is superior to A7, so it showed a better pore structure property. When the added content of fly ash is suitable, although the hydration activity is lower, its filling effect plays an important role in the strength development and pore structure density. When admixture was added (A11), the activation effect of the admixture on slag and fly ash made the total porosity of complex cement obviously decrease. It agrees with the strength increase.

Fig. 6 describes the median pore radius of cements at days 3, 7 and 28 of hydration. Ordinarily, with the increase of hydration time, total porosity would decrease and the median

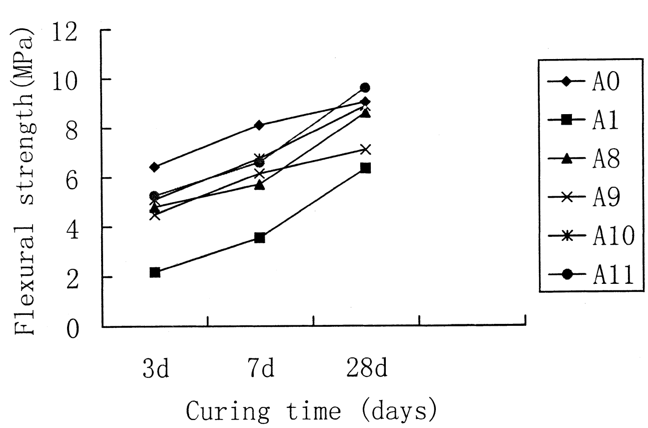

Fig. 4. Curves of curing time vs. flexural strength.

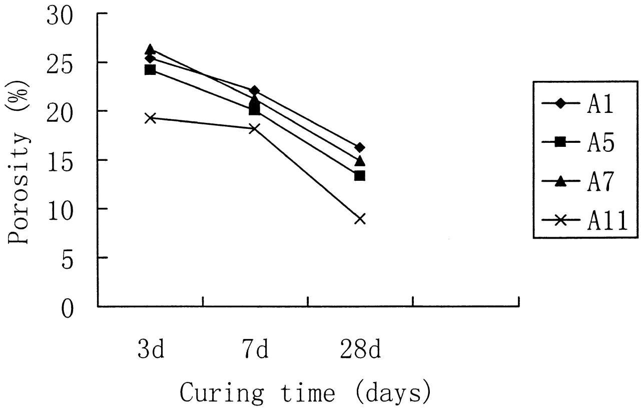

Fig. 5. Curves of hydration time vs. porosity.

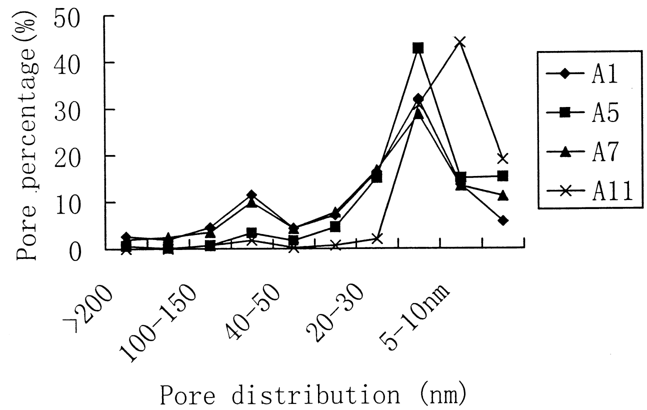

Fig. 8. Curves of pore distribution (at day 7).

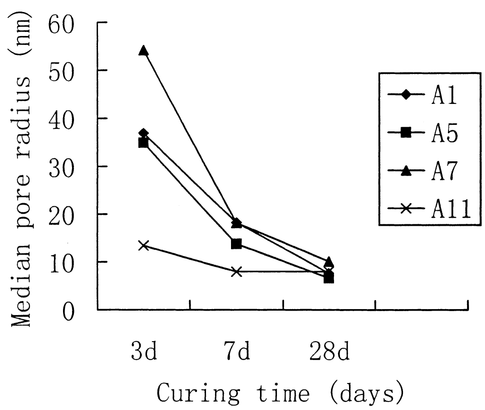

Fig. 6. Curves of hydration time vs. median pore radius.

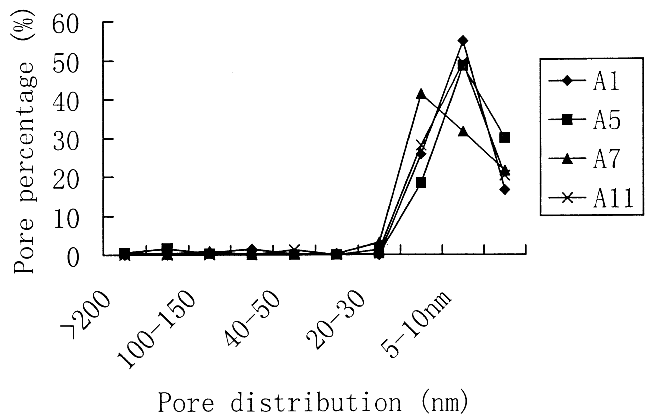

Fig. 9. Curves of pore distribution (at day 28).

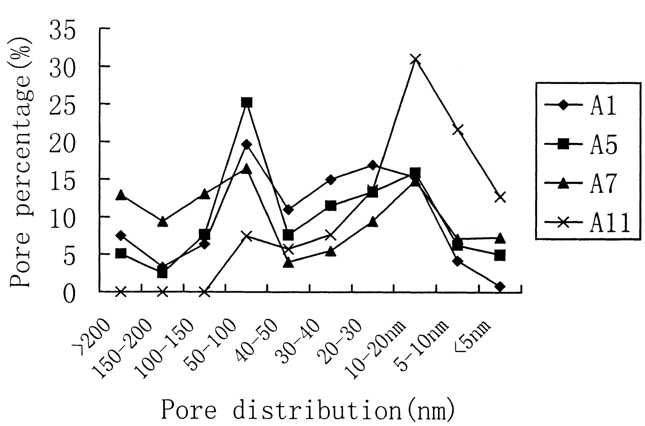

Fig. 7. Curves of pore distribution (at day 3).

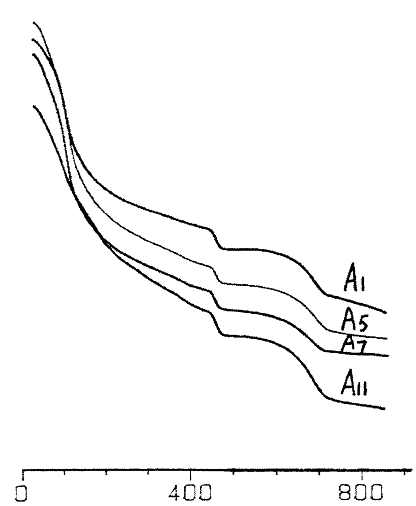

Fig. 10. Loss weight curves of hydration day 3.

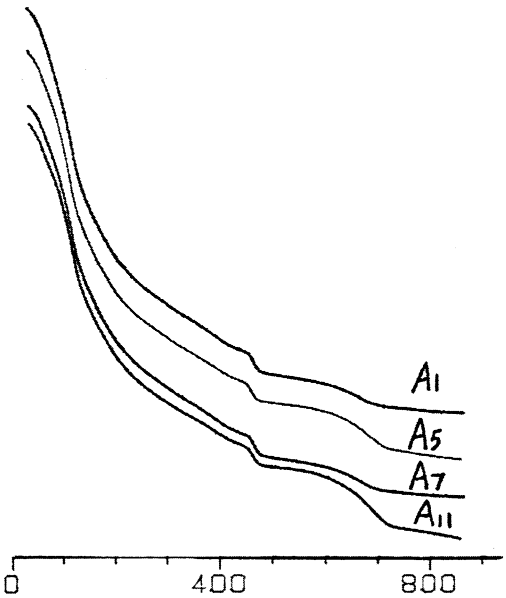

Fig. 11. Loss weight curves of hydration day 7.

pore radius would be reduced. Results are similar to those with total porosity. Early pore structure of A11 is obviously improved. Compared with A1, the median pore radius of A11, at days 3 and 7 of hydration, from 36.91 and 18.27 nm respectively reduced to 13.43 and 7.96 nm. The median pore radius of hydration day 28 shows little difference.

Figs. 7–9 are pore distribution curves of cements at days 3, 7 and 28. In order to study pore distribution condition at different pore size ranges (dividing into 10 pore radius range: >200, 150–200, 100–150, 50–100, 40–50, 30–40, 20–30, 10–20, 5–10 and 2.2–5 nm). Results show that pore distribution is more uniform at day 3 hydration, that is,

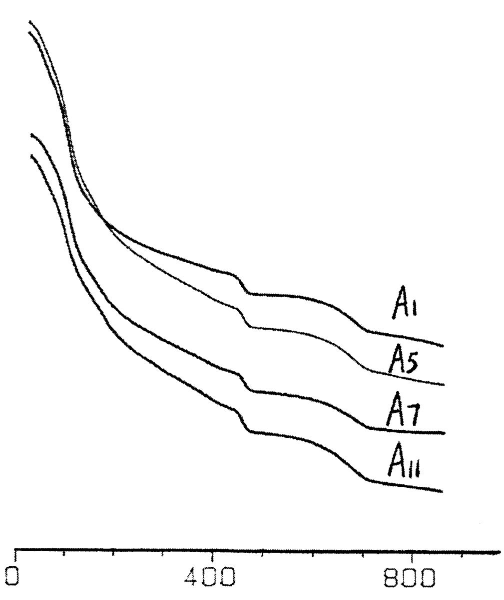

Fig. 12. Loss weight curves of hydration day 28.

Table 5
TG analysis of hydrates

	C–S–H loss water (%) (70–400°C)			$Ca(OH)_2$ loss water (%) about 450°C		
No.	Day 3	Day 7	Day 28	Day 3	Day 7	Day 28
A0	10.7	11.36	11.33	4.01	4.29	4.52
A1	7.58	10.48	14.12	0.92	1.09	1.16
A5	9.78	12.51	13.53	0.93	1.05	1.08
A7	8.55	10.40	13.53	0.90	1.00	1.14
A11	8.33	11.16	13.23	1.04	1.11	1.03

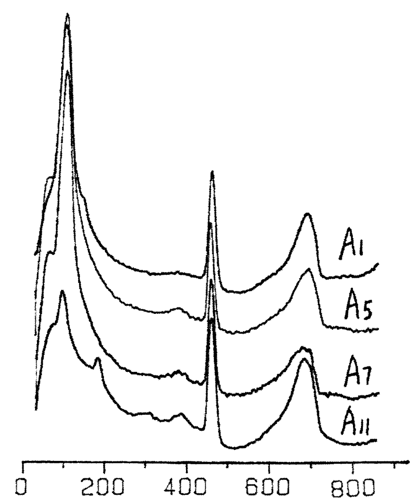

Fig. 13. Derivative curves of hydration day 3.

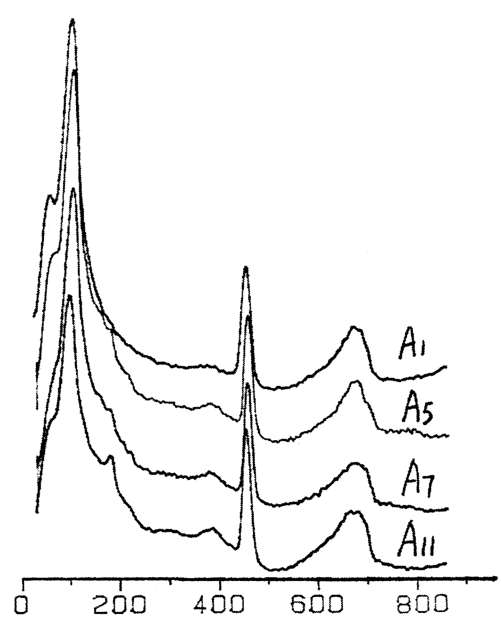

Fig. 14. Derivative curves of hydration day 7.

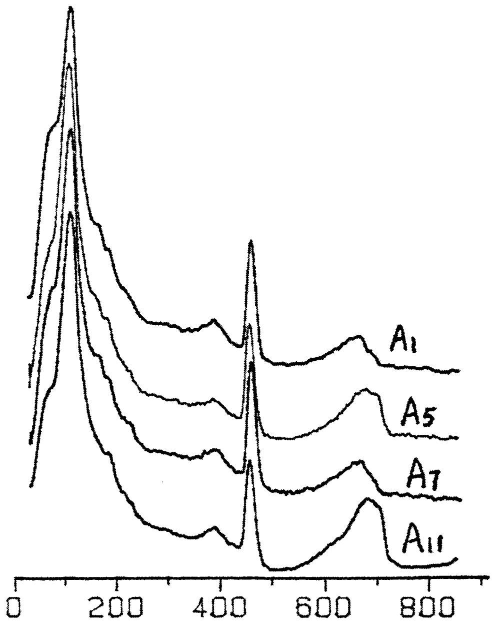

Fig. 15. Derivative curves of hydration day 28.

there are capillary and gel pores. With the increase of hydration time, capillary pore decreases and gel pore increases. So the properties of cement are improved. Compared with A1, there is no large pore of more 100 nm, to days 3 of hydration in A11. Pore percentages of less than 30 nm of A11 are, respectively, 79.15%, 95.78% and 99.17% at days 3, 7 and 28 of hydration. And that of A1 is 37.23%, 67.72% and 97.37%. It shows that admixtures obviously improved pore structure properties of early stage.

3.5. TGA tests

TGA has been widely accepted as an accurate method for the determination of crystalline CH content and other hydrates (loss water), including C–S–H, AFt, gypsum and soon from 70°C to 900°C. In the study system, it can generally be separated into three parts: (1) an abrupt weight loss near 450°C, associated with the dehydration of CH; (2) another fairly sudden, but less distinct weight loss between 600°C and 700°C, associated with decomposition of calcium carbonate; and (3) between 70°C to 400°C, a weight loss due mainly calcium silicate hydrates, calcium aluminate hydrates and other hydrates, as well as AFt, AFm, gypsum and other hydrates.

The aim of the study is to examine possible correlations between CH content and the amount of other hydrates as measured by water loss during dehydration, by means of TGA.

Figs. 10–12 are loss weight curves of hydration days 3, 7 and 28. From Figs. 10–12, dehydration of 70–400°C and $Ca(OH)_2$ dehydration content of about 450°C was calculated and listed in Table 5. From Table 5 it is well known that the loss water content of between 70°C and 400°C of A1 and A11 is more than that of A1. $Ca(OH)_2$ loss water content have large differences. It shows that except for hydration activation of complex cement, filling effect also plays an important role on cement properties.

Figs. 13–15 are derivative curves of hydration at days 3, 7 and 28. By studying curves peak at some temperature, hydrates can be determined. Fig. 3 shows that there is a peak at about 400°C to A5, A7 and A11, but A1 has none. This peak is dehydration of CSH_2. It shows that hydration property of A1 is poorer than of that of others. Another peak should noted at about 160°C. It is the dehydration of AFt. Only there is the peak in A11. From the strength and pore structure results it can be shown that admixtures obviously improve the early properties of complex cement. It is because that producing AFt at the early stage has important influence on strength and other properties.

With the increase of hydration time, the 400°C peak of A1 also increases, and that of the other samples have not changed much. To some degree, TGA tests describe hydrates and reaction degree.

4. Conclusion

1. When there is a proper ratio between fly ash and slag, and at the same mill time in mixtures containing 45% clinker, the strength and pore structure properties all exceed the slag cement. This is because of the filling effect and the effect of mutual complement of superiority supply.
2. Adapting the admixture technique, the strength, pore structure and hydration properties of complex cement are all obviously improved, especially at early stage. This because the admixtures enhance the active and reaction ability. Due to the use of admixtures, the strength of complex cement exceeds that of Portland cement.

Acknowledgments

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