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HYDRATION OF SHRINKAGE-COMPENSATING BINDERS WITH DIFFERENT COMPOSITIONS AND WATER–BINDER RATIOS

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Abstract

The calorimetric data of blended shrinkage-compensating binders with different compositions were measured at 25°C at different water–binder ratios using an isothermal calorimeter. The hydration characteristics of shrinkage-compensating binders were evaluated and their influence on the expansive properties of blended shrinkage-compensating binders was determined. Composition and *w/b* ratio significantly affect the hydration rate and degree of shrinkage-compensating binders, as well as their expansive and mechanical properties. The total heat of hydration of binders decreases with *w*/*c* ratios. Its final hydration degree also decreases with *w*/*c* ratio. The ternary binders composed with Portland cement, mineral admixture and expansive agent show low hydration heat and rate of heat evolution, but their total heat of hydration increases continuously and surpasses that of binary binder in later period at low *w*/*b* ratio.

Keywords: calorimetric study, composition, hydration, shrinkage-compensating binder, *w*/*b* ratio

Introduction

Utilization of shrinkage-compensating concrete is one of important measures to minimize cracks in concrete structures [1]. Nowadays, sulfoaluminate-based expansive agent is widely used in China to prepare shrinkage-compensating concrete that is mainly for the constructions of massive reinforced concrete foundation of high-rising buildings [2]. Besides Portland cement and expansive agent, mineral admixture is also a key ingredient for producing shrinkage-compensating concrete [3]. The *w*/*b* ratio of shrinkage-compensating concrete varies according to the required strength class. These factors significantly influence the hydration mechanism of complex shrinkage-compensating binders and its properties [4].

The hydration mechanism of blended binder of Portland cement and mineral admixtures was studied intensively using calorimetry [5–7]. The rate of heat release and heat of hydration is proportionally lowered with the decrease of Portland cement con-

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tent in the cementitious system of Portland cement-fly ash [8]. This conclusion was confirmed by Atis using a concrete sample [9]. In contrast, no more than 15% of replacement of Portland cement by silica fume or metakaolin which possess high hydration reactivity enhances the hydration of blended binders to increase the rate of heat release and total heat of hydration [10, 11]. When silica fume and fly ash are added together with Portland cement, the reactivity of silica fume is hampered and the hydration of blended binder is significantly retarded [12]. The reactivity of ground granulated blast-furnace slag substituting for Portland cement in blended binder increases with the hydration temperature and *w*/*b* ratio [13].

The hydration reaction of calcium sulfoaluminate, one of the important clinker minerals of expansive agent, differs from the main hydration reaction of Portland cement and the pozzolanic reaction of mineral admixtures. Calcium sulfoaluminate reacts with SO_4^{2-} containing products and the $Ca(OH)_2$ formed during the hydration of Portland cement to form expansive hydration product, ettringite [14]. Mineral admixture also needs $Ca(OH)_2$ to trigger its pozzolanic reaction. Therefore, there are two competing reactions taking place simultaneously in the hydration process of blended ternary binders. The hydration mechanism of complex shrinkage-compensating binder is more complicated than that of plain Portland cement. In order to accurately understand the behavior and efficiency of complex shrinkage-compensating binder in real concrete structure, the hydration characteristics of complex shrinkage-compensating binder with different compositions was investigated using calorimetry under the condition of different water-binder ratios.

Experiment

The used materials in this study included PO-42.5 ordinary Portland cement complying with Chinese National Standard GB 175-99 and a sulfoaluminate-based expansive agent complying with Chinese National Standard JC476-1998. A fly ash complying the quality requirement of Chinese National Standard GB 1596-91 for the second class and a ground granulated blast-furnace slag (GGBS) with specific surface of 458 m^2 kg^{-1} were used. Their chemical compositions are shown in Table 1. The mineral composition calculated by Bogue Equation and physical properties of used Portland cement are shown in Table 2.

Four samples were prepared. PC: plain Portland cement; PC-EX: binary binder of 92% Portland cement and 8% expansive agent; FA-EX: ternary binder of 62% Portland cement, 8% expansive agent and 30% fly ash; SL-EX: ternary binder of 62% Portland cement, 8% expansive agent and 30% GGBS. Rate of heat release and total heat of hydration of samples were recorded isothermally at 25°C respectively at three water-binder (*w*/*b*) ratios of 0.3, 0.4 and 0.5 using a ToniCal differential calorimeter made by Toni Technik. The mass of the samples was 10 g and the continuous measuring time 96 h.

Table 1 Chemical composition of raw materials/%

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss of ignition
Cement clinker	22.71	4.57	2.85	66.10	1.90	0.68	0.15	0.37	0.50
Expansive agent	23.93	12.55	1.65	19.59	2.40	0.73	0.11	31.75	6.15
Fly ash	49.88	31.76	3.36	4.30	0.73	0.018	1.11	0.88	4.51
GGBS	34.03	9.26	2.88	39.03	10.11				0.58

Table 2 The mineral composition and physical properties of used Portland cement

Mineral composition of Portland cement/%					Setting time/h:min		Flex. strength/MPa		Compr. strength/MPa	
C_3S	C_2S	C_3A	C_4AF	SO_3	Initial	Final	3 d	28 d	3 d	28 d
60.59	19.49	7.29	8.66	3.02	2:46	3:31	5.2	9.2	26.2	52.8

Results and discussion

Effect of the w/b ratio on hydration

The curves of the rate of heat release and the total heat of hydration of 4 samples at different water-binder ratios are shown in Figs 1 to 4. The hydration characteristics of binders with different compositions vary, as well as those of the same binder at different *w*/*b* ratios. All binders show typical hydration characteristics with two peaks of heat release. The first peak emerging immediately after the introduction of water is attributable to a combination of exothermic wetting and the early-stage reactions of cement. The second peak emerging after a short induction period corresponds to the main hydration reaction of the binders.

The hydration of plain Portland cement (Sample PC) goes on quickly and acutely (Fig. 1). It possesses the largest second peak among the 4 binders. There is only small alternation of the rate of heat release and almost same heat of hydration in the first hydrating day for PC hydrating at different water–cement (*w*/*c*) ratio. The hydration processes of PC at different water cement ratio alter little in this stage. The rate of heat release falls quickly and the heat of hydration increases little in the later period of hydration in the sample with low *w*/*c* ratio. The heat of hydration of PC at *w*/*c* of 0.3 differs much from which at *w*/*c* of 0.4 and 0.5. There is not enough water for hydration in the sample at *w*/*c* of 0.3. The migration of water in the dense hardened paste with low *w*/*c* ratio is more and more difficult with the prolongation of hydrating time, which hinders the continuous advancement of hydration. Therefore, the total heat of hydration of PC decreases with its *w*/*c* ratio.

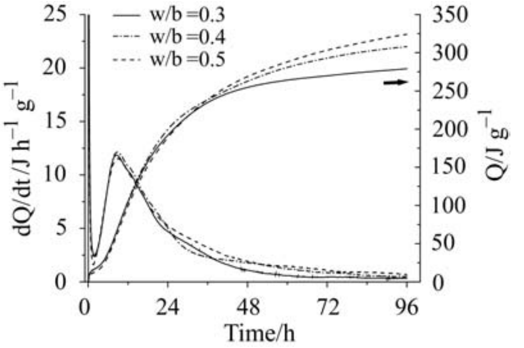

Fig. 1 Heat evolution rate and total hydration heat of paste PC at different values of *w*/*b*

The initial hydration process of PC-EX substituting 8% of expansive agent for Portland cement (Fig. 2) is similar to that of PC at *w/b* of 0.4 and 0.5. The rate of heat release is larger and continuing time of reaction is shorter for the hydration of calcium sulfoaluminate, which is a main clinker mineral of expansive agent than that of Portland cement [1]. It induces a greater rate of heat release and a shorter continuing time of reaction for the hydration of PC-EX than PC. Hydration of expansive agent to form ettringite, which contains 32 molecules of H_2O consumes a huge amount of wa-

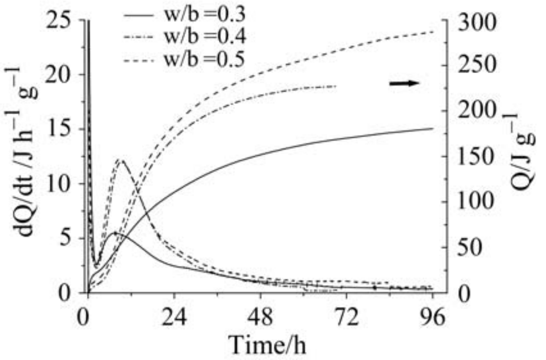

Fig. 2 Heat evolution rate and total hydration heat of paste PC-EX at different values of *w*/*b*

ter and forms a dense hydrate film deposited on anhydrous binder particles. Along with the progress of hydration, the effect of *w/b* ratio on the hydration reaction emerges gradually. The curves of heat of hydration for PC and PC-EX are nearly the same at *w/b* of 0.5 (Figs 1 and 2). At *w/b* ratio of 0.4, the rate of heat release falls rapidly and the heat of hydration increases little for PC-EX in the later period of hydration. Remarkably suppressed hydration reaction of PC-EX results in a much lower total heat release than PC-EX at *w/b* ratio of 0.5. The lack of water in the PC-EX paste at *w/b* of 0.3 results in an insufficient hydration reaction because there is not enough water supply for simultaneous hydration of Portland cement and expansive agent. Its peak rate of heat release of the second peak falls to 5 J h^{-1} g^{-1}, smaller than half of that at *w/b* ratio of 0.4. The total heat of hydration of PC-EX decreases significantly with its *w*/*c* ratio. Its final hydration degree also decreases significantly with its *w*/*c* ratio. The low expansive efficiency of ettringite formed in the loose paste of PC-EX at *w*/*b* ratio of 0.5 with a low strength results in a small expansion. The paste of PC-EX at *w*/*b* ratio of 0.4 is denser and has higher strength than PC-EX at *w*/*b* ratio of 0.5. Its huge expansion destroys the glass tube containing paste in the calorimeter on the 60th measuring hour to interrupt the test. Absence of ettringite in the paste of PC-EX at *w*/*b* ratio of 0.3 because of its low hydration degree results in a little expansion. A high expansive efficiency of shrinkage-compensating concrete can be obtained only under the condition of appropriate *w*/*b* ratio.

The rate of hydration reaction of ternary binders replacing Portland cement by 8% of expansive agent and 30% of fly ash or GGBS (Figs 3 and 4) is reduced to about the half of that of PC or PC-EX cases. The second main peak shifts to later period and the total heat of hydration in the first day decreases. There is a step on the declining side of the second peak for SL-EX. It is due to the pozzolanic reaction of GGBS. Less water is consumed because of slower reaction rate and lower degree of hydration in the ternary binder pastes than in PC and PC-EX. Thus, the variation of *w*/*b* ratio has less influence on the reaction rate and hydration degree of the pastes. The difference of the reaction rate and hydration degree in FA-EX and SL-EX at different *w*/*b* ratios is much lesser than in PC-EX, although there is a little decrease in FA-EX and SL-EX at *w*/*b* ratio of 0.3. The reactivity of GGBS is higher than fly ash. Thus, total heat re-

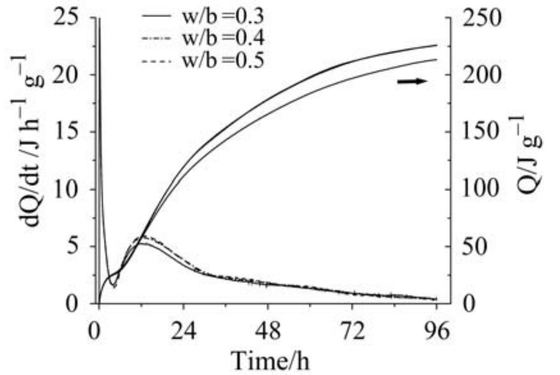

Fig. 3 Heat evolution rate and total hydration heat of paste FA-EX at different values of *w*/*b*

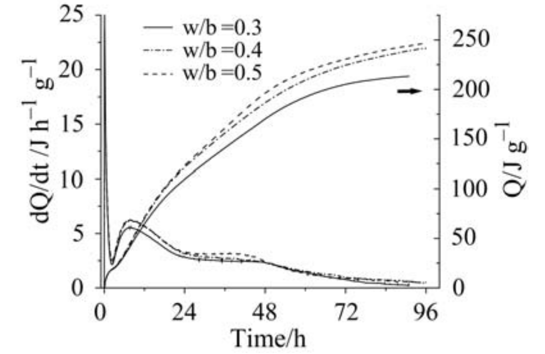

Fig. 4 Heat evolution rate and total hydration heat of paste SL-EX at different values of *w*/*b*

lease is higher and the effect of *w*/*b* ratio on the hydration reaction is greater for SL-EX than for FA-EX.

Effect of binder composition on hydration

The time-dependent changes of total heat of hydration of binders with different compositions are shown in Figs 5 to 7. The heat release in 3 days is determined by real measurement. The one after 7 days is extrapolated using a linear regression method according to its developing tendency on the end of measuring. The difference between extrapolated values and real values measured till 7th day is less than 5% in the cases of the rate of heat release on 96th measuring hour less than 0.5 J h^{-1} g^{-1}. The used commercial software was developed by Toni Technik.

Under the condition of *w*/*b* ratio of 0.5, the total heat release of PC-EX is slightly higher in 12 h and lower in later period than that of PC. The hydration reaction of expansive agent needs the participation of $Ca(OH)_2$ formed during the hydration of Portland cement; the consumption of $Ca(OH)_2$ also enhances the hydration of Portland cement. The hydration reaction of both Portland cement and expansive agent is accelerated each other to increase the hydration degree of PC-EX in the initial period

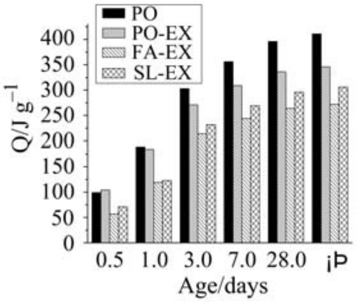

Fig. 5 Measured and estimated heat evolution of pastes prepared with *w/b*=0.5

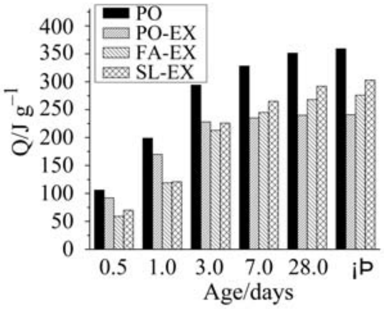

Fig. 6 Measured and estimated heat evolution of pastes prepared with *w/b*=0.4

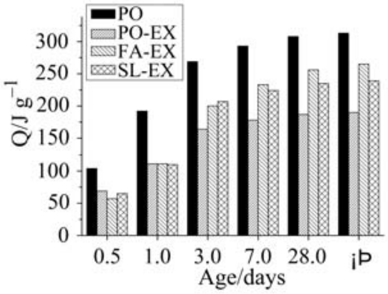

Fig. 7 Measured and estimated heat evolution of pastes prepared with *w/b*=0.3

when there is enough water supply in loose paste structure. The heat release in the first day of PC is less than 50% of its total heat release, but one of PC-EX is more than 60% of its total heat release. The heat release in the first day of ternary binders, FA-EX and SL-EX, is significantly smaller than that of PC and PC-EX due to the slow pozzolanic reaction of mineral admixtures. The slower hydration rate in early period results in less hydrates, looser paste structure and lower strength for FA-EX and SL-EX pastes than for PC and PC-EX ones. The forming rate of ettringite is not harmonious with the strength development of pastes. It results in a low expansion of ternary pastes in the early period [4]. The slow reaction rate of mineral admixtures and its small participation on hydration in the initial period, increases the available *w*/*c* ratio of Portland cement involved in the ternary binders, which accelerates its hydration reaction [4]. The enhanced hydration of Portland cement and the continuous pozzolanic reaction of mineral admixtures increase the total heat release of ternary binders in later periods. The total heat release of FA-EX reaches 80% of that of PC-EX; the one of SL-EX containing GGBS, whose reactivity is higher than fly ash, reaches even 90% of that of PC-EX. Along with the increase of hydration degree of ternary binders, the quantity of C–S–H gel and ettringite increases simultaneously. A little expansion appears in the dense hardened pastes [4].

Hydration reaction of PC-EX is suppressed in a short time after the beginning of the accelerating stage of hydration at *w*/*b* ratio of 0.3 because the hydration of Portland cement and the formation of ettringite quickly result in the lack of water in the paste at this low *w*/*b* ratio. The hydration rate of PC-EX decays firstly and it has lowest total heat of hydration at *w*/*b* ratio of 0.3 because it needs largest water supply in 4 binders. Especially total heat of hydration increases little after 3 days of hydration. Portland cement is replaced partly by fly ash or GGBS with slow hydration rate in the ternary binders FA-EX and SL-EX. Therefore, their water demand correspondingly reduces and their hydration time is prolonged comparing to PC-EX. The total heat of hydration of ternary binders increases continuously and surpasses that of PC-EX in 7 days at *w*/*b* ratio of 0.4 and in 3 days at *w*/*b* ratio of 0.3.

Conclusions

Composition and *w/b* ratio affect significantly the hydration rate and degree of shrinkage-compensating binders, as well as their expansive and mechanical properties. Hydration is limited at low *w/b* ratios. The lower is the *w*/*c* ratio, the lower are the total heat of hydration of binders and their final hydration degree. The rate of heat release and total heat of hydration of ternary binders composed by Portland cement, expansive agent and mineral admixtures are lower than that of binary binder composed by Portland cement and expansive agent for the highest *w*/*c* ratio Their water demand correspondingly reduces the hydration of the other components and their hydration time is prolonged comparing to the binary binder. At low *w/b* ratio the total heat of hydration of ternary binders increases continuously and surpasses that of binary binder for higher hydration times.

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References

1 D. He, B. K. You and R. L. Fang, Chinese Building Waterproof, 6 (1999) 12.
2 Z. H. Wang, Constr. Technol., 28 (1999) 8.
3 B. K. You, D. M. Wang, G. M. Li and L. L. Han, Constr. Technol., 29 (2000) 41.
4 Z. Q. Xu, P. Y. Yan and J. Peng, Proceeding of 5th International Congress of Cement and Concrete, Oct. 28–31, 2002. Shanghai China.

5 J. Brandstetr, J. Polcer, J. Kratky, R. Holesinsky and J. Havlica, Cement and Concrete Res., 31 (2001) 941.
6 H. Kada-Benameur, E. Wirquin and B. Duthoit, Cement and Concrete Res., 30 (2000) 301.
7 A. Usherov-Marshak, L. Pershina and P. Krivenko, J. Therm. Anal. Cal., 54 (1998) 57.
8 W. Nocun-Wczelik, J. Therm. Anal. Cal., 65 (2001) 613.
9 C. D. Atis, Cement and Concrete Res., 22 (2002) 751.
10 R. C. A. Pinto and K. C. Hover, ACI Materials Journal, 96 (1999) 600.
11 J. Bai and S. Wild, Cement and Concrete Res., 32 (2002) 201.
12 B. W. Langan, K. Wenig and M. A. Ward, Cement and Concrete Res., 32 (2002) 1045.
13 J. I. Escalante, L.Y. Gomez, K. K. Johal, Cement and Concrete Res., 31 (2001) 1403.
14 H. F. W. Taylor, Cement Chemistry, 2nd Edition, Thomas Telford, 1997.