INFLUENCE OF INITIAL CASTING TEMPERATURE AND DOSAGE OF FLY ASH ON HYDRATION HEAT EVOLUTION OF CONCRETE UNDER ADIABATIC CONDITION

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The calorimetric data of binders containing pure Portland cement, 20% fly ash, 20% slag and 10% silica fume respectively are determined at different initial casting temperatures using an adiabatic calorimeter to measure the adiabatic temperature rising of concrete. The calorimetric data of binders with different dosages of fly ash at two water binder ratios (w/b) are determined, too. Elevation of initial casting temperature decreases the heat evolution of binder, enhances the heat evolution rate of binder and increases the heat evolution rate of binder at early age. The dosage of fly ash in concrete has different effects on the heat evolution of binder with different w/b. At high w/b ratio the heat evolution of binder decreases when dosage of fly ash increases. At low w/b ratio the heat evolution of binders increases when dosage of fly ash increases from 0 to 40% of total binder quantity. The heat evolution of binder decreases after the dosage of fly ash over 40%. An appropriate dosage of fly ash in binder benefits the performance of concrete at low w/b ratio.

Keywords: adiabatic condition, fly ash, hydration heat, initial casting temperature

Introduction

It is well known that the heat evolution and heat evolution rate of concrete at the early age are very important factors to influence the cracking behavior of mass concrete [1]. Mass concrete is defined by the ACI Committee 116 [2] as 'any volume of concrete with dimensions large enough to require the measures be taken to cope with generation of the heat of hydration from the cement and attendant volume change to minimise cracking'. Currently mass concrete is no longer considered only for dam construction but also for foundation and elements of various kinds of multistorey buildings and infrastructures such as large bridges and nuclear reactors. Due to heat evolution of binder at early hydrating age, the temperature in the core of concrete structure increases obviously and the hydration of composite binders containing mineral admixtures is greatly enhanced in real concrete structure. The influence of isothermal temperature on the heat evolution and heat evolution rate of binder has been investigated [3]. However there are few studies in the literature regarding evolution heat of binder in concrete is effected by initial temperature at adiabatic condition.

Mineral admixtures such as fly ash, slag and silica fume are widely used in concrete to improve concrete properties. It is known that using fly ash as supplementary cementitious material in concrete reduces the temperature rise by reducing the amount of cement. The study about the influence of fly ash on heat of hydration showed that the heat of hydration of fly ash cement was less than that of the corresponding Portland cement [4]. Bamforth [5] reported from an extensive study of mass concrete that the larger the amount of cement replaced by fly ash, the slower rate is the temperature rise and the more the reduction in temperature rise. Although the pozzolanic activity of different type fly ash is different in cementitious mixtures [6], there is an agreement that the temperature rise in concrete structure decreases when fly ash is used as partial dosage of cement because the theoretic heat evolution of binders containing fly ash is lower than Portland cement [7, 8]. Whereas, the temperature of concrete containing fly ash is still high in real structure, the heat evolution of binder containing fly ash is affected obviously by water binder ratio (w/b) and dosage of fly ash [9]. In this paper, the influences of initial temperature and the dosages of fly ash on heat evolution of concrete are investigated.

Experimental

Materials and methods

PO 42.5 ordinary Portland cement, complying with the Chinese National Standard GB 175-1999, a first class fly ash complying with the Chinese National Standard GB 1596-91, a ground granulated blast-furnace slag (GGBS) with Blaine specific surface of

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458 m^2 kg^{-1} and Elkem 920D silica fume are used. Their chemical compositions are given in Table 1. Crushed limestone with a size range of 5~20 mm and natural river sand with a fineness modulus of 3.0 are, respectively, used as coarse and fine aggregate.

Mix proportions and adiabatic temperature rising measuring of concrete

Table 2 summarizes the mix proportions of the concrete. All mixtures are prepared in a 60 L capacity rotary pan mixer. The initial temperature of fresh concrete is adjusted with the preheating of mixing water and coarse aggregate. The dry materials are premixed for 1 min. Then water is added and the mixing is continued for 3 min. The slump of fresh concrete is adjusted to 50–80 mm by the addition of superplasticizer when it is necessary.

Determination of hydration rate of binder through the measure of adiabatic temperature rise of concrete

A computer-controlled measuring system of adiabatic temperature rising of concrete was prepared in lab. Prepared concrete is cast into the container in the measuring equipment of adiabatic temperature rising. The volume of concrete sample for the adiabatic temperature rising measure is about 45 l. The peripheral temperature of concrete sample is maintained 0.05°C lower than the central temperature of ones by an electrical heater outside the container. The temperature change of concrete is recorded continuously just after it is cast into the container. The temperature rise of concrete is due to heat evolution of binder that hydrates with water. By means of the heat released, it is possible to determine the degree of hydration relative to hydration duration according to the equation.

$$\alpha(t) = \frac{Q(t)}{Q_{max}} \qquad (1)$$

where $\alpha(t)$ is hydration degree of binder at time t, $Q(t)$ is heat evolution at time t, kJ kg^{-1} and Q_{max} is theoretic heat evolution of completely hydrated binder, kJ kg^{-1}. Under adiabatic condition the hydration heat evolution completely heats up concrete. Therefore the Eq. (2) can express this process.

$$Q(t) = m_c Q_{max}\alpha(t) = \int_{T_0}^{T(t)} C_P \, dT \qquad (2)$$

Table 1 Chemical composition of used raw materials/%

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	Na$_2$Oeq	SO$_3$	Loss of ignition
Cement	22.80	4.55	2.82	65.34	2.74			0.55	2.92	3.9
Fly ash	57.6	21.9	7.7	3.87	1.68	2.51	1.54			2.9
Silica fume	>85.0							<1.5		2.2
GGBS	34.63	13.92	0.29	38.28	10.52				0.25	0.25

Table 2 Mix proportions of concrete

Mix	Cement/ kg m^{-3}	Fly ash/ kg m^{-3}	Slag/ kg m^{-3}	Silica fume/ kg m^{-3}	Sand/ kg m^{-3}	Coarse aggregate/ kg m^{-3}	Water/ kg m^{-3}	Super-plasticizer/ kg m^{-3}	w/b	Specific heat/ kJ kg^{-1} °C^{-1}
C1	368				694	1132	184		0.50	0.99
C2	294	74			683	1116	184		0.50	0.99
C3	294		74		692	1128	184		0.50	0.98
C4	332			36	690	1124	184		0.50	0.98
H0	368				681	1111	195		0.53	1.00
H2	294	74			671	1095	195		0.53	1.01
H3	258	110			666	1087	195		0.53	1.01
H4	221	147			661	1079	195		0.53	1.02
H5	184	184			656	1071	195		0.53	1.02
L0	550				712	1069	140	5.5	0.25	0.89
L2	440	110			697	1046	140	5.5	0.25	0.90
L3	385	165			689	1034	140	5.5	0.25	0.90
L4	330	220			682	1023	140	5.5	0.25	0.90
L5	275	275			674	1011	140	5.5	0.25	0.91

where m_c is binder mass of 1 kg concrete; C_P is specific heat of concrete, kJ kg^{-1} °C^{-1}; T_0 is initial temperature, °C; $T(t)$ is temperature at time t, °C. Generally C_P of concrete is thought as a constant, so heat evolution of concrete at time t.

$$Q(t) = m_c Q_{max} \alpha(t) = C_P[T(t) - T_0] \qquad (3)$$

heat evolution rate of concrete at time t.

$$\frac{dQ(t)}{dt} = C_P \frac{dT(t)}{dt} \qquad (4)$$

hydration degree of binder at time t.

$$\alpha(t) = \frac{C_P}{m_c Q_{max}}[T(t) - T_0] \qquad (5)$$

Therefore heat evolution and heat evolution rate of binder is characterized by continuous determination of adiabatic temperature rise of concrete.

Results and discussion

Influence of initial temperature on heat evolution of concrete under adiabatic condition

Figure 1a shows that the heat evolution rate of C1 without mineral admixture reaches peak value at 6 h under initial temperature 34.0°C and at 16 h under initial temperature 11.1°C, respectively. The result shows that elevation of initial temperature accelerates the hydration rate of cement. Low initial temperature slows the hydration rate of cement, but prolongs the hydration time and increases the hydration degree of cement. Heat evolution of Portland cement in the low initial temperature increases.

Figure 1b presents the characteristics of hydration heat emission of C2 of 80% Portland cement and 20% fly ash. Its hydration heat emission rate is lower, but its hydration reaction continues longer than those of pure Portland cement under the condition of high initial temperature. Therefore, its total hydration heat is similar with that of pure Portland cement. The hydration heat emission rate is similar for both C2 and C1 under the condition of low initial temperature. The hydration heat emission rate of C2 decreases more quickly than C1. Thus, the total hydration heat of C2 is less than C1. It is a commonly accepted opinion that the reaction of fly ash in concrete is only initiated after one or more weeks. During this period, fly ash serves as precipitation sites for Ca(OH)$_2$ and C–S–H gel originating from the cement hydration. Farry [10] explains that the period before the start of the pozzolanic reaction depends on the breaking down of glass phase by the alkalinity of the pore water, and the
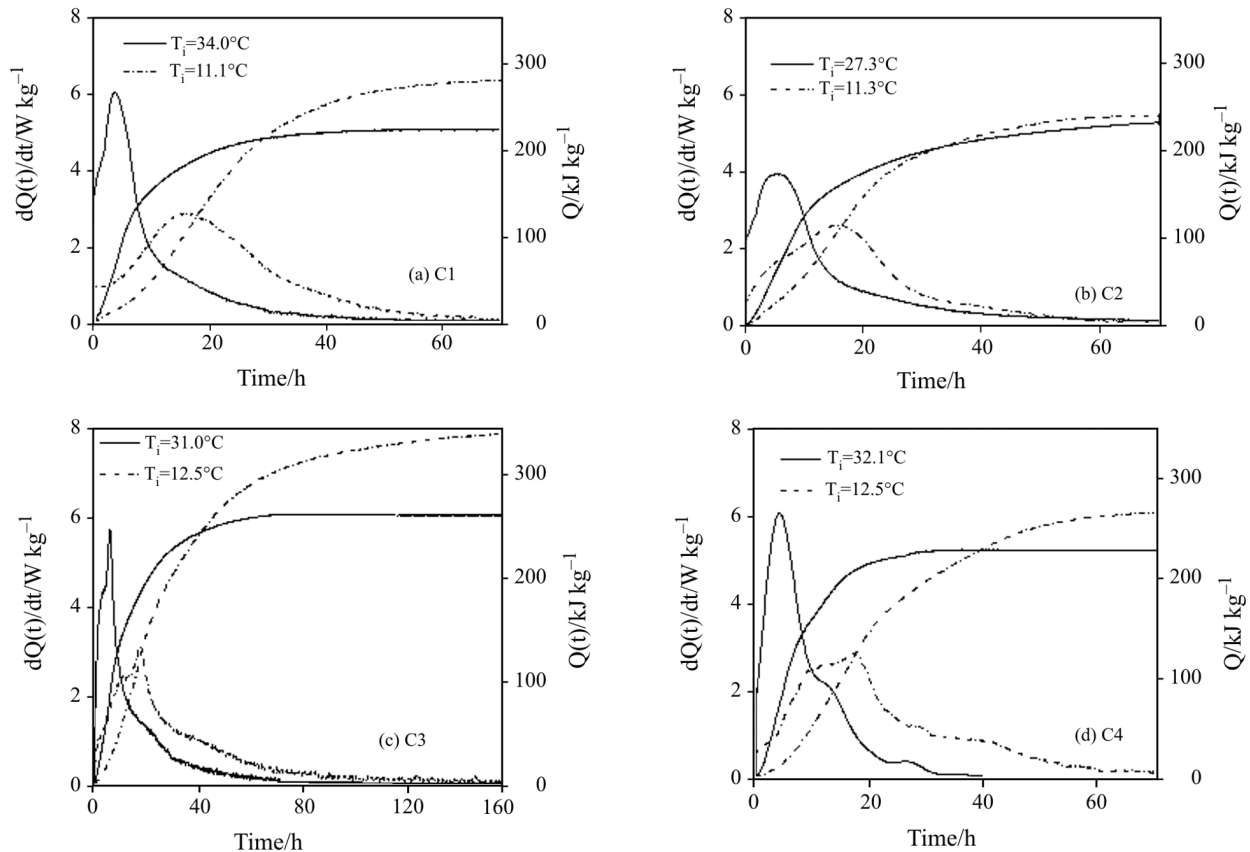

Fig. 1 Influence of initial temperature on heat evolution and heat evolution rate of binder in concrete

pore solution in the cement paste should only develop the required alkalinity after several days. The heat evolution of C2 does not reduce 20% comparing to that of C1 in this study. C2 evolves 86% of heat evolved by C1 at low initial temperature, but 106% of heat evolved by C1 at high initial temperature even though the initial temperature of C2 was lower than C1. Addition of fly ash enhances the hydration of Portland cement. This may be caused by the increase of water–cement ratio of C2 when 20% Portland cement is replaced by fly ash.

The hydration heat emission of C3 containing 20% slag is also determined at initial temperatures 12.5 and 31.0°C, respectively (Fig. 1c). Its peak value of hydration heat emission is only a little lower than that of C1. Its hydration reaction continues longer than C1. At low initial temperature the heat evolution still increases after 150 h. Therefore, the total hydration heat of C3 is higher than that of C1. The total heat of C3 evolved during the early hydration period is 116% as much as that of C1 at high initial temperature and 121% at low initial temperature.

Figure 1d presents the characteristics of hydration heat emission of C4 of 90% Portland cement and 10% silica fume. It is similar with that of pure Portland cement. The total heat evolved by C4 during early hydration period is 102% of that of C1 at high initial temperature and 96% at low initial temperature.

There are two peaks in the hydration heat emission rate curve of complex binder containing mineral admixture. The first peak emerges at about 6 h when the hydration rate of Portland cement begins to decline. The temperature of concrete rises rapidly at this time under the adiabatic condition. The potential pozzolanic activity of mineral admixture is strongly thermally triggered off. The hydration rate increases again and the second hydration heat emission peak emerges after 15 h. The intensity of the second peak is based on the pozzolanic activity of mineral admixture. C3 containing high volume of slag with a gentle activity gets the highest second peak among three samples containing different mineral admixtures.

Figure 1 shows that heat evolution rate increases and heat evolution decreases when initial temperature rises. At high initial temperature environment the hydration product shell quickly forms on the surface of unhydrating binder particles, and it can limit or even prevent the penetration of ions and water through the shell, thereby reducing the ultimate hydration degree of binder. High initial temperature does not benefit the gain of high hydration degree and an ideal paste structure.

Influence of dosage of fly ash on heat evolution of binder

The influence of supplementary rate of fly ash in complex binder on heat evolution of binder during hydration of concrete was investigated with the concrete samples series H and series L. The theoretic heat evolution of Portland cement at complete hydration Q_{max} is directly determined from the clinker composition of Portland cement. The widely used procedure to determine the Portland cement compounds is proposed by Bogue [11].

$$Q_{maxc} = 510 p_{C_3S} + 247 p_{C_2S} + 1356 p_{C_3A} + 427 p_{C_4AF} \quad (6)$$

where Q_{maxc} is theoretic heat evolution of completely hydrated Portland cement, p_i is mass ratio of compound in terms of the total cement content.

The theoretic heat evolution of Portland cement determined by Eq. (6) is 485 kJ kg^{-1} and the theoretic heat evolution of fly ash is 209 kJ kg^{-1} according to Schindler [12]. Therefore the theoretic heat evolution of Portland cement–fly ash composite binder is determined by Eq. (7).

$$Q_{maxcf} = 485 p_c + 209 p_f \quad (7)$$

where p_c is mass ratio of Portland cement and p_f is mass ratio of fly ash.

The hydration degree of binder is calculated by Eq. (1) at the time of 110 h for series H and 80 h for series L based on the measured data of adiabatic temperature rising of concrete. Figure 2a shows that the maximal hydration degree of binders with different dosage of fly ash and different w/b at determined time. When dosage of fly ash increases from 0 to 40%, the maximal hydration degree does not apparently vary at w/b=0.53, while greatly increases at w/b=0.25. When dosage of fly ash reaches 50%, the hydration degree of binder obviously decreases at both water binder ratios. Figure 2b presents that Q_{maxcf} decreases with the increase of fly ash dosage.

Since the hydrating activity of Portland cement is much higher than that of fly ash, the hydration ability of binder should decrease with the dosage of fly ash adding. At the same time the hydration degree of binder is affected obviously by w/b, too. Hydration of binder is restrained due to insufficient supply of water and its hydration degree reduces under the condition of low w/b. With increasing of dosage of fly ash, the actual water–cement ratio in concrete rises and the hydration environment of Portland cement is improved, which enhances the hydration degree of binder. There is initially enough water for hydration of Portland cement under the condition of high w/b. Dosage increase of fly ash seldom affects the hydration environment of Portland cement. Therefore, hydration degree of binder does not increase with the dosage of fly ash increasing under the condition of high w/b.
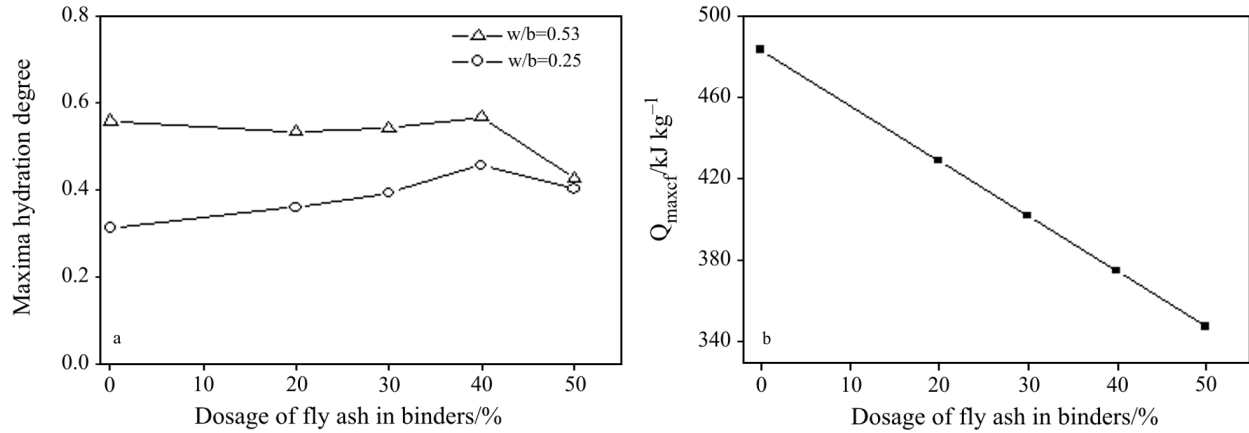
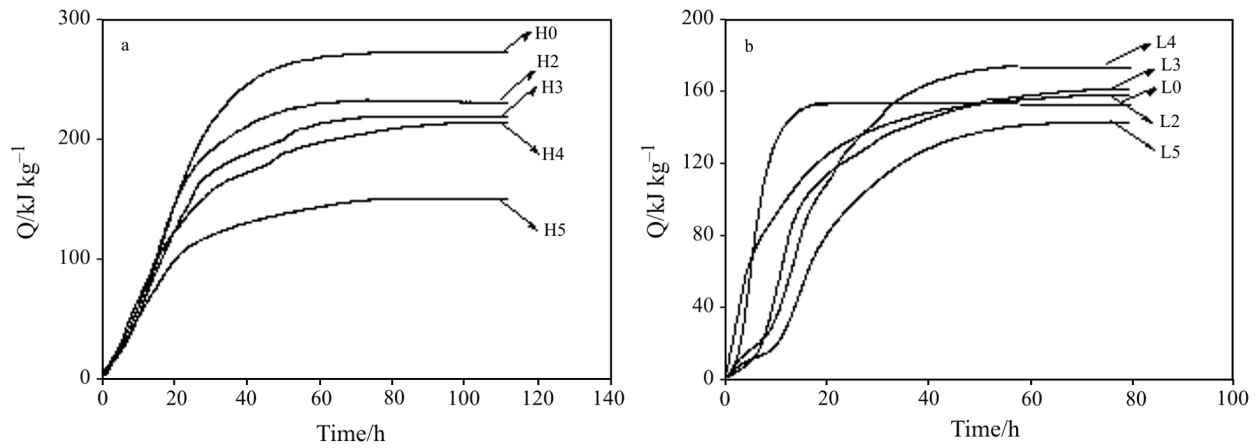**Fig. 2** Influence of dosage of fly ash on maximal degree of hydration and Q_{maxcf}

Fig. 3 Influence of dosage of fly ash on hydration heat evolution of binder; a – w/b=0.53; H0 – 0% FA, H2 – 20% FA, H3 – 30% FA, H4 – 40% FA, H5 – 50% FA; b – w/b=0.25; L0 – 0% FA, L2 – 20% FA, L3 – 30% FA, L4 – 40% FA, L5 – 50% FA
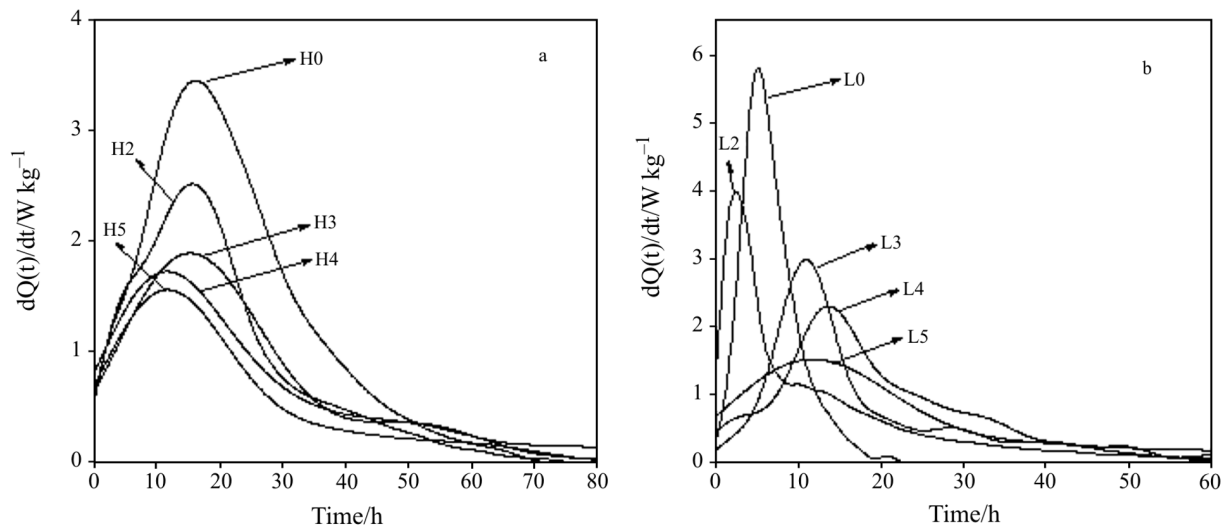

Fig. 4 Heat evolution rate of binder in concrete with different dosage of fly ash; a – w/b=0.53; H0 – 0% FA, H2 – 20% FA, H3 – 30% FA, H4 – 40% FA, H5 – 50% FA; b – w/b=0.25; L0 – 0% FA, L2 – 20% FA, L3 – 30% FA, L4 – 40% FA, L5 – 50% FA

Figure 3a shows that heat evolution of binders with w/b=0.53 decreases when the dosage of fly ash increases from 0 to 50%. While Fig. 3b indicates that heat evolution of binders with w/b=0.25 increases when dosage of fly ash increases from 0 to 40%, and decreases when dosage of fly ash is 50%.

The heat evolution of binder is determined together by Q_{max} and hydration degree at early age. Q_{max} decreases with increasing dosage of fly ash. The hydration degree of binder increases when dosage of fly ash increases at low w/b if it is not over the threshold of 40%. The variance of dosage of fly ash does not obviously influence the hydration degree of binder at high w/b. Therefore, heat evolution of binder decreases with the increase of dosage of fly ash at high w/b because the absolute heat evolution of binder decreases. Fly ash has higher contribution for the hydration of binder as well as the properties of concrete at low w/b than at high w/b. High volume fly ash concrete can exert its efficiency only at low w/b.

The influence of dosage of fly ash on heat evolution rate of binder at adiabatic conditions is shown in Fig. 4. The hydration ability of fly ash is lower than that of Portland cement, so the peak value of rate of heat evolution will decrease with increasing dosage of fly ash regardless of w/b. The time reaching the peak of heat evolution rate shortens with the increasing dosage of fly ash at high w/b because the quantity of Portland cement decreases. The quantity of binder is high in the sample series L. There is still enough amount of Portland cement taking part in the hydration reaction even if the dosage of fly ash is as high as 40% of binder. On the contrary, addition of fly ash with low activity improves the hydration environment of Portland cement at low w/b owing to the increase of actual water–cement ratio that enhances the hydration of Portland cement. Therefore, appropriate dosage of fly ash in binder benefits the hydration of Portland cement at low w/b.

Conclusions

Initial casing temperature and dosage of fly ash affect significantly the heat evolution and heat evolution rate of binder in concrete. When initial casting temperature of concrete rises, the hydration reaction time of binder is shortened, liberated heat amount of binder at early age decreases and the heat evolution rate of binder increases. The dosage of fly ash in concrete has different effects on the heat evolution of binder with different w/b. At high w/b ratio the heat evolution of binder decreases when dosage of fly ash increases. At low w/b ratio the heat evolution of binders increases when dosage of fly ash increases from 0 to 40% of total quantity of binder. The heat evolution of binder decreases after the dosage of fly ash over 40%. An appropriate dosage of fly ash in binder benefits the performance of concrete at low w/b.

References

1 R. Springenschmid, Thermal Cracking in Concrete at Early Age, E&FN SPON, 1995.
2 ACI Committee 116 R-85, Cement and concrete terminology, ACI Manual of Concrete Practice, American Concrete Institute Pubs., USA 1989.
3 W. Ma, D. Sample, R. Martin and P. W. Brown, Cem. Concr. Aggr., 16 (1994) 93.
4 J. G. Cabrea and C. D. Atiş, Proceedings of Gramado Conference, Brasil, SP-186, American Concrete Institute Pubs., USA 1999, p. 21.
5 P. B. Bamforth, Proc. Inst. Civil Eng., 69 (1980) 777.
6 Z. Giergiczny, J. Therm. Anal. Cal., 76 (2005) 1.
7 M. D. A. Thomas, P. K. Mukherjee, J. A. Sato and M. F. Everitt, Proceedings of Milwaukee Conference, SP-153, American Concrete Institute Pubs., USA 1995, p. 81.
8 B. Fournier, W. S. Langley and V. M. Malhotra, Proceedings of Milwaukee Conference, SP-153, American Concrete Institute Pubs., USA 1995, p. 561.
9 P. Y. Yan, F. Zheng and Z. Q. Xu, J. Therm. Anal. Cal., 74 (2003) 201.
10 A. L. A. Farry, J. M. Bijen and Y. M. Haan, Cem. Concr. Res., 19 (1989) 235.
11 H. F. W. Taylor, Cement Chemistry, 2nd Edition, Thomas Telford Services Ltd., 1997.
12 A. K. Schindler and K. J. Folliard, ACI Mater. J., 102 (2005) 24.