

## **EFFECT OF MINERAL ADMIXTURES ON THE HYDRATION HEAT OF MORTAR IN SUPER HIGH STRENGTH CONCRETE**

**Liu Jianzhong (1, 2), Sun Wei (1), Miao Changwen (2), Liu Jiaping (2)**

(1) Jiangsu Key Laboratory of Civil Engineering Materials, Southeast University, Nanjing, China

(2) Jiangsu Research Institute of Building Science, Nanjing, China

### **Abstract**

The facts of high cement content, high hydration heat and high rate of heat evolution have seriously impeded the application of super high strength concrete. Mineral admixture is one of the best materials which can reduce the hydration head and the hydration exothermic rate of high performance concrete. The influences of silica fume, fly ash and ground granulated blast-furnace slag on the hydration heat and the hydration exothermic process of mortar in super high strength concrete at water to binder ratio of 0.24 were studied by the means of hydration heat experiments. The results show that the hydration exothermic process is accelerated, but the hydration exothermic peak is reduced with the addition of silica fume. On the other hand, with the addition of fly ash or ground granulated blast-furnace slag, the hydration exothermic process is delayed, the arrival time of the highest hydration exothermic rate is postponed, and the hydration heat and hydration exothermic rate are markedly reduce.

### **1. INTRODUCTION**

With the advent of superplasticizers or high-range water reducing admixtures, high and super/ultra high strength concrete with compressive strength of more than 100 MPa is now commercially available in many metropolitan areas. High and super/ultra high strength concrete, on account of their low water to binder ratio, generally perform well on exposure to some aggressive environmental conditions that are known to cause early deterioration of ordinary concrete [1- 3]. In recent years, with the development of superplasticizers based on polycarboxylate, the high flowable concrete with compressive strength of more than 200 MPa has been developed [4 - 6]. The main characteristics of polycarboxylate based superplasticizers are the following: (1) high water reduction (up to 40%); (2) high flowability; (3) polymer-design allows to control the main characteristics (setting time and workability); (4) blending of different polymers is possible; formulation of customized solutions [7].

The super high strength concrete has very high compressive strength and excellent durability. However, the facts of high cement content, high hydration heat and high rate of heat evolution have seriously impeded the application of super high strength concrete. Mineral admixture is one of the best materials which can reduce the hydration head and the hydration exothermic rate of high performance concrete. Zhang et al. [8] indicated that the addition of mineral cementitious components greatly reduced the 3-day hydration heat and exothermic rate and retarded the arrival time of highest temperature of the binder paste in HPC at water to binder rate of 0.30, particularly when two or three types of mineral admixtures were added at the same time. Langan et al. [9] investigate the influence of

silica fume and fly ash on the hydration of cement based mixtures with water to binder rate of 0.35, 0.40 and 0.50.

Few attentions were taken on the hydration heat of super high strength concrete at low water to binder ratio. Therefore, the influences of silica fume, fly ash and ground granulated blast-furnace slag on the hydration heat and the hydration exothermic process of mortar in super high strength concrete at water to binder ratio of 0.24 were studied by the means of hydration heat experiments in this paper.

## 2. EXPERIMENTATION

### 2.1 Materials

A Chinese standard(GB175-2007) type P-II52.5 Portland cement similar to the ASTM type II ordinary Portland cement, with a compressive strength of 57.8 MPa at an age of 28 days was supplied by Jingyang cement corporation in Jiansu province, China. Class F fly ash, granulate blast-furnace slag and silica fume were employed for mineral admixtures to replace partial cement. The chemical composition and physical properties of Cement, fly ash, slag and silica fume were shown in Table 1.

Polycarboxylate-based superplasticizer PCA supplied by Jiansu Bote New Materials CO. was incorporated. The water-reducing rate was much than 30% and the solid content was 20.2%. ISO standard sand was used in this research.

**Table 1: Chemical composition and physical properties of cement, silica fume, fly ash and slag**

Materials	Chemical composition /%						Specific gravity /kg·m <sup>-3</sup>	Specific surface /m <sup>2</sup> ·kg
	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	LOI		
Cement	18.6	64.5	3.28	4.88	1.61	3.22	3.06	388
Silica fume	94.2	0.23	0.44	0.72	0.12	2.38	2.20	Approximately 20000
Fly ash	54.8	2.42	4.94	32.5	0.72	1.27	1.90	420
slag	31.2	37.3	1.36	17.8	7.36	1.71	2.82	334

### 2.2 Mixture proportions

Table 2 summarizes the mixture proportions of the 9 investigated mortars, similarly to the composition of mortar in super high strength concrete. Four sets of mortar, which differed in the composition of binder were tested. In the first set, only Portland cement was used as the cementitious material. In the second set, silica fume was added as a partial replacement of the cement at levels of 10% and 20% by weight of the total cementitious materials. In the third set, fly ash was added as a partial replacement of the cement at levels of 10%, 30% and 50% by weight of the total cementitious materials. In the fourth set, slag was also added as a partial replacement of the cement at levels of 10%, 30% and 50% by weight of the total cementitious materials. All the mortars were designed to preserve the following parameters: the water to binder rate was fixed to 0.24, the sand to binder rate was 1.2, and superplasticizer content was 1.2% by weight of the total cementitious materials.

**Table 2: Mixture proportions**

No.	Composition of binder /%				Sand/binder	Water/binder	Superplasticizer /%
	Cement	Silica fume	Fly ash	slag			
C100	100	0	0	0	1.2	0.24	1.5
C90SF10	90	10	0	0	1.2	0.24	1.5
C80SF20	80	20	0	0	1.2	0.24	1.5
C90FA10	90	0	10	0	1.2	0.24	1.5
C70FA30	70	0	30	0	1.2	0.24	1.5
C50FA50	50	0	50	0	1.2	0.24	1.5
C90SL10	90	0	0	10	1.2	0.24	1.5
C70SL30	70	0	0	30	1.2	0.24	1.5
C50SL50	50	0	0	50	1.2	0.24	1.5

### 2.3 Test procedures

All the materials and the calorimetric instrument were placed in the room with the temperature of  $20 \pm 1$  °C for more than 24 hours. The mortar proportioned according to table 2 was mixed by stirrer for 3 minutes. Each test consisted of a 800-g sample that casted into a cylindrical plastic cup. The cup was immediately put into the vacuum flask, and thermocouple was inserted into the mortar. The vacuum flask was then sealed and stored in a water tank with the temperature of  $20 \pm 0.1$  °C to simulate semiadiabatic conditions. The temperature of mortar was monitored and recorded by data acquisition system at 1-min intervals for 72 h.

### 2.4 Calculation of hydration heat and exothermic rate

Firstly, heat-dissipating coefficient of heat-preserving instrument (K) is measured, and thermal capacity of the instrument including the mortar in it ( $C_p$ ), is calculated before the hydration heat test. Secondly, the hydration heat test is carried out and the temperature rise-time curve is plotted. An area value  $\sum F_{b,t}$  (where t is time) is acquired through the integral of the temperature rise-time curve. Thirdly, the total liberation heat of the mortar at t hours is calculate:  $Q_t = C_p(T_t - T_0) + K \sum F_{b,t}$ , where  $T_t$  is the temperature at t hours and  $T_0$  is the initial temperature. Finally, hydration heat is calculated:  $q = Q_t / G$ , where G is the mass of the cementitious materials (357g in this research).

The exothermic rate can be obtained through differential of the hydration heat-time curve.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of silica fume on hydration

Silica fume is one of most important components of super high strength concrete. In Figure 1, the effect of silica fume at replacement levels of 10% and 20% on the temperature rise, exothermic rate and hydration of the total cementitious materials was shown. Table 3 summarized the hydration heat characteristics of cement and silica fume mixtures.

According to Figure 1 and Table 3, it was observed that the hydration exothermic process of cementitious materials had been changed with the increase in silica fume replacement level. When 10% and 20% of cement was replaced by silica fume, the temperature rise peak

value was reduced from 59.6 °C (C100) to 57.0 °C (C90SF10) and 53.6 °C (C80SF20). For plain cement (C100), the highest exothermic rate was 76.3 J/g·h and arrived at 9.7h. The silica fume mixtures differed in that the exothermic rate peak value was lower than that of plain cement about 26~38 J/g·h, but the arrival time of the exothermic rate peak was shortened for about 0.5~1.1h. During the first 12h of hydration, the hydration heat of plain cement was lower than that of silica fume mixtures. However, after 24h the hydration heat of the silica fume mixture was lower than that of plain cement. In a word, these results indicated that the hydration exothermic process was accelerated, but the hydration exothermic peak was reduced with the addition of silica fume.

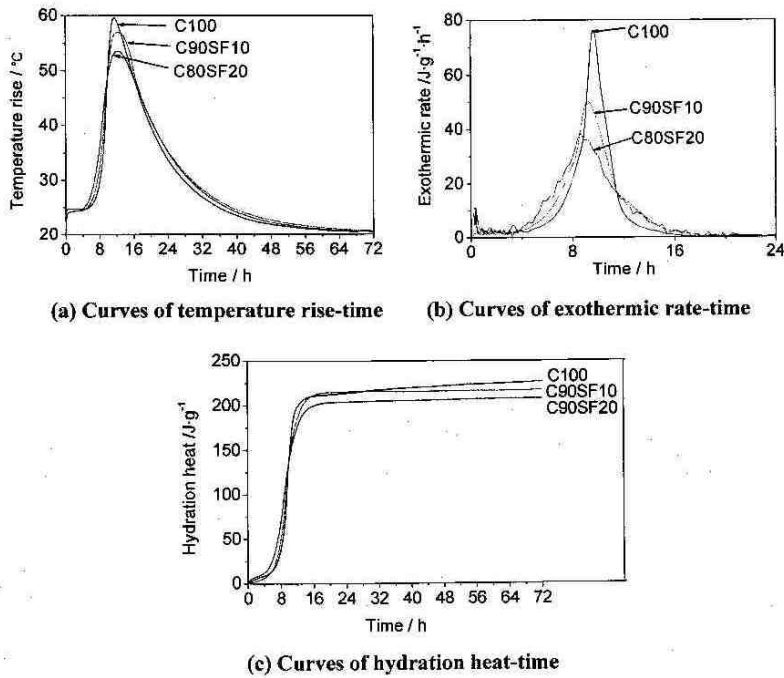


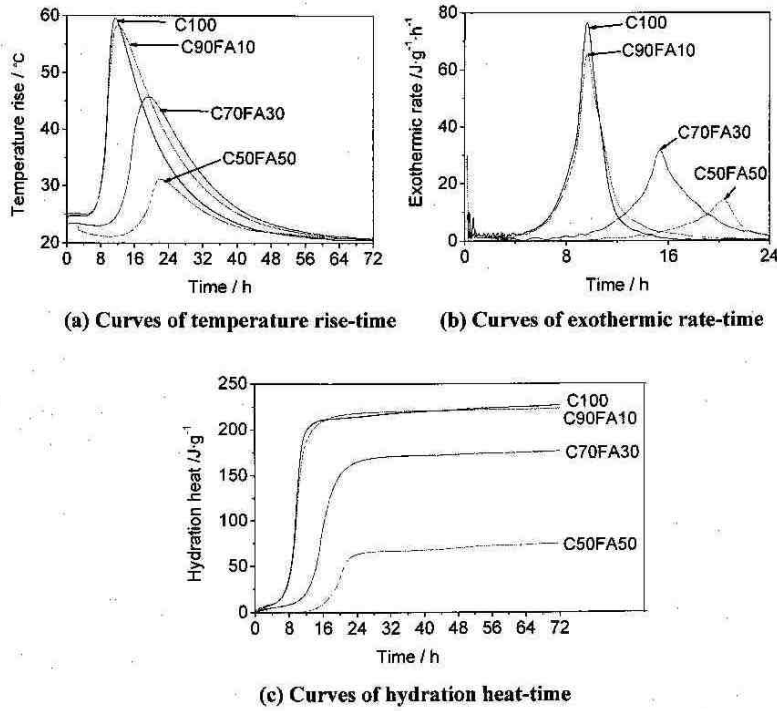
Figure 1: Effects of silica fume on the temperature rise, exothermic rate and hydration heat of mortar in super high strength concrete

**Table 3: Hydration heat characteristics of cement and silica fume mixtures**

No.	Temperature peak /°C	Time of temperature peak /h	Hydration heat /J·g <sup>-1</sup>				Exothermic rate peak /J·g <sup>-1</sup> ·h <sup>-1</sup>	Time of exothermic rate peak /h
			12h	24h	48h	72h		
C100	59.6	11.4	198.3	214.1	221.5	226.6	76.3	9.7
C90SF10	57.0	12.1	184.4	215.4	216.0	217.4	50.2	9.2
C80SF20	53.6	12.0	175.6	204.1	206.1	207.7	38.5	8.6

**3.2 Effect of fly ash on hydration**

Fly ash is another important component of super high strength concrete. In Figure 2, the effect of fly ash at replacement levels of 10%, 30% and 50% on the temperature rise, exothermic rate and hydration of the total cementitious materials was shown. Table 4 summarized the hydration heat characteristics of cement and fly ash mixtures.



**Figure 2: Effects of fly ash on the temperature rise, exothermic rate and hydration heat of mortar in super high strength concrete**

**Table 4: Hydration heat characteristics of cement and fly ash mixtures**

No.	Temperature peak /°C	Time of temperature peak /h	Hydration heat /J·g <sup>-1</sup>				Exothermic rate peak /J·g <sup>-1</sup> ·h <sup>-1</sup>	Time of exothermic rate peak /h
			12h	24h	48h	72h		
C100	59.6	11.4	198.3	214.1	221.5	226.6	76.3	9.7
C90FA10	58.3	11.9	186.0	214.1	220.9	222.7	65.4	9.7
C70FA30	45.7	18.8	21.6	218.0	172.8	176.4	31.4	15.3
C50FA50	31.1	21.6	1.4	62.8	70.1	75.0	14.1	20.3

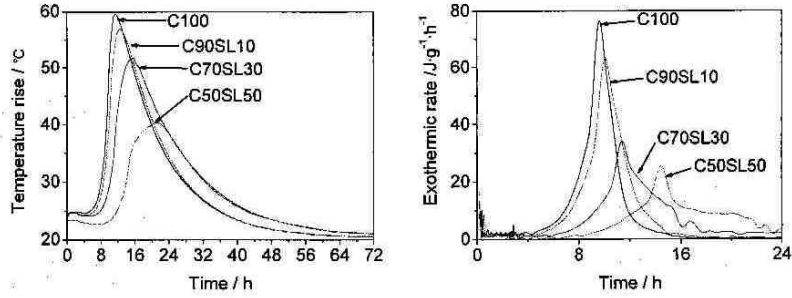
From figure 2 and Table 4, the following trends could be noted with an increase in fly ash replacement level: the hydration process was similar between the plain cement (C100) and the cementitious material with the fly ash replacement level of 10%, but the hydration heat and exothermic rate of fly ash mixture was reduce and hydration process was obviously postponed with the continued increase in fly ash replacement level. For example, the highest temperature and the highest exothermic rate of C90F10 existed little lower than that of plain cement(C100), so 10% fly ash could not influenced the hydration process of cementitious materials at low water to binder. On the other hand, as for the mixture in C70FA30 and C50FA50, 30% and 50% fly ash reduced the temperature rise peak value for 23% and 48% respectively, and retarded the arrival time of temperature peak for 7.4h and 10.2h. This means that as the increase of fly ahs replacement level, the retarding effect of fly ash increases. When 30% fly ash was added to cementitious materials, the exothermic rate peak value was reduce from 76.3 J/g·h of plain cement mixture to 31.4 J/g·h, and the arrival time of exothermic rate peak was postponed from 9.7h of of plain one to 15.3h. When 50% fly ash added, the exothermic rate peak value was reduced by 82%, and the arrival time of exothermic rate peak was delayed for 10.6h. At same time, the total hydration heat of 12h, 24h, 48h, and 72h was significantly reduced with the increase in fly ash replacement level.

### 3.3 Effect of slag on hydration

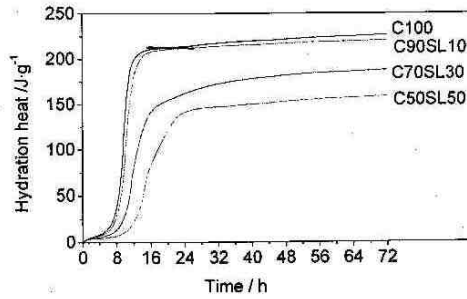
Granulate blast-furnace slag is also another one of the most important components of super high strength concrete. In Figure 3, the effect of slag at replacement levels of 10%, 30% and 50% on the temperature rise, exothermic rate and hydration of the total cementitious materials was shown. Table 5 summarized the hydration heat characteristics of cement and slag mixtures.

The curves in Figure 3 and the data in Table 5 indicated that, as with fly ash, the use of slag also significantly reduced the temperature rise peak and the exothermic rate of cement-slag system, and delayed the arrival time of the highest hydration exothermic rate. The effects of slag on hydration of mortar in super high strength concrete was similar to that of fly ash. In C90SL10, C70SL30 and C50SL50, the temperature rise peak values were 56.9 °C, 51.8 °C and 40.3 °C, and the arrival time of temperature peak was 12.4h, 15.4h and 20.9h, respectively. By adding 10%, 30% and 50% slag to the mixture, the exothermic rate peak value of cementitious materials were reduced by 17%, 55% and 67%, and the arrival time of exothermic rate peak was postponed for 0.4h, 1.7h and 4.8h, respectively. The total hydration heat of 12h, 24h, 48h, and 72h was also reduced with the increase in slag replacement level. However, when the replacement level was not less than 30%, slag makes greater contribution to reducing hydration heat and exothermic rate and retarding the arrival time of highest

temperature of the cementitious materials in super high strength concrete with low water to binder ratio than fly ash.



(a) Curves of temperature rise-time (b) Curves of exothermic rate-time



(c) Curves of hydration heat-time

Figure 3: Effects of slag on the temperature rise, exothermic rate and hydration heat of mortar in super high strength concrete

Table 5: Hydration heat characteristics of cement and slag mixtures

No.	Temperature peak (°C)	Time of temperature peak (h)	(Hydration heat /J·g <sup>-1</sup> )				Exothermic rate peak (J·g <sup>-1</sup> ·h <sup>-1</sup> )	Time of exothermic rate peak (h)
			12 h	24h	48h	72h		
C100	59.6	11.4	198.3	214.1	221.5	226.6	76.3	9.7
C90SL10	56.9	12.4	179.3	212.1	217.1	217.1	63.1	10.1
C70SL30	51.8	15.4	80.3	162.3	181.7	187.1	34.0	11.4
C50SL50	40.3	20.9	22.5	141.9	153.1	159.2	25.3	14.5

#### 4 CONCLUSION

In this study, the effects of silica fume, fly ash and slag on the hydration heat and hydration exothermic process of mortar in super high strength concrete with low water to binder of 0.24 was clear. With the addition of silica fume, the hydration exothermic process is accelerated, but the hydration exothermic peak is reduced. On the other hand, the hydration exothermic process is delayed, the arrival time of the highest hydration exothermic rate is postponed, and the hydration heat and hydration exothermic rate are markedly reduce with the addition of fly ash or ground granulated blast-furnace slag. In addition, the work will provide important insight in reducing the hydration heat of cementitious materials in super high strength concrete with low water to binder ratio.

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