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Effect of HEMC on the early hydration of Portland cement highlighted by isothermal calorimetry

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Abstract The effects of hydroxyethyl methyl cellulose (HEMC) on the early hydration and main hydrates evolutions of Portland cement were quantitatively investigated by the isothermal calorimetry, setting times, X-ray diffraction analysis, and environmental scanning electron microscope analysis. The results show that HEMC definitely affects the early hydration process of cement paste and retards the beginning of the hydration induction period and acceleration period, but increases the length of these two periods. HEMC decreases the hydration heat evolution rate during the initial reaction period and the acceleration period, but increases the hydration heat evolution rate during the deceleration period. HEMC decreases the hydration heat amount and hydration degree of cement paste at the early hydration time, especially in the first thirty-six hours. There are good positive correlations between the setting time, the length of induction period and the dosages of HEMC. HEMC also delays the formation of the hydrates and affects the morphologies of hydrates. Accordingly, HEMC remarkably retards the cement hydration at the early hydration time, and with its dosage increasing, the retardation effect of HEMC enhances.

Keywords Portland cement · Hydroxyethyl methyl cellulose (HEMC) · Early hydration · Isothermal calorimetry

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Introduction

Nowadays, dry mix mortars, especially polymer-modified mortars, have assumed greater importance in construction applications due to their advantages over conventional mortars. Since introduced into cement mortar in the 1960s [1, 2], today cellulose ethers have been applied in almost all dry mix mortars such as wall renders and plasters, repair mortars, tile adhesives, floor screeds, self-leveling mortars, and water proofing mortars [3]. The most frequently used cellulose ethers are methyl cellulose (MC), hydroxyethyl cellulose (HEC), hydroxyethyl methyl cellulose (HEMC), and hydroxypropyl methyl cellulose (HPMC) [4, 5]. Among these cellulose ethers, HEMC is predominantly applied in dry mix mortars such as renders, water proofing mortars, and tile adhesives.

HEMC greatly improves the workability and water retention of cement mortars [6–10], and these properties allow for the use of thin layers of the mortars, instead of thick layers of unmodified mortar, and preventing uncontrolled water loss into porous substrates such as brick and aerated concrete by suction. These advantages further help to decrease the material and labor requirements, and associated costs. However, HEMC can reduce compressive strength of the hardened cement mortar, especially at the early hydration time [7, 9], and remarkably extend the setting time of cement mortars [11].

The properties of cement mortar are related to the cement hydration, hydrates, and chemical interactions [12]. Understanding the influence of HEMC on cement hydration is critical to explain the changes in the properties of fresh and hardened mortars, and will help to design products through taking full advantages of HEMC [13]. Muller [14] used XRD analysis to study the development of cement hydrates of Portland cement and found a

Table 1 Physical properties of Portland cement type P.II 52.5R

Bulk density/g cm^{-3}	Specific surface/m^2 kg^{-1}	Setting time/min		Compressive strength/MPa		Flexural strength/MPa	
		Initial	Final	3d	28d	3d	28d
3.11	348	140	270	39.2	60.3	6.8	8.2

retardation effect of HEMC on the formation of second ettringite. Knapen [15] used TG to measure the $Ca(OH)_2$ content in the cement paste during the early age and found that HEMC increases the time at which the $Ca(OH)_2$ content increases significantly. Ciobanu et al. [16] studied different HEMC types on the cement hydration through using TG-DSC and found that HEMC greatly decreases the $Ca(OH)_2$ content, and at the same hydration time, with the different viscosities and different degrees of modification, HEMCs cause variations in narrow limits of the proportion of $Ca(OH)_2$ and the degree of cement hydration. Pourchez et al. studied the influence of HEMC and HPMC on water retention capacity and revealed the significant influence of the molecular mass on the delay of cement hydration induced by cellulose ethers from 10 min up to several hours [17]. Jenni et al. investigated the microstructure changes in cement mortar with HEMC [18]. They proposed that due to the decrease of the water surface tension, the air entrapped during mixing process was stabilized by HEMC, and polymer films were observed between two juxtaposed air voids and along the pore wall of a single air void. These literatures demonstrate the hydration and mechanisms of cement pastes with cellulose ethers from different aspects. However, few literatures have expatiated upon the influence of HEMC and its dosage variations on the hydration degree, the hydrates, and their morphologies variation in the cement paste at the early hydration time.

The aim of this paper is to evaluate the influence of HEMC on the early hydration of Portland cement. Isothermal calorimetry has been widely used to quantify the hydration and to study the hydration kinetics and mechanism of Portland cement in situ [19–21], since it provides continuous measurements and shows versatility in studying the hydration kinetics of cementitious systems. Therefore, it was used to test the influence of HEMC on the hydration process evolution of Portland cement during the hydration time of 72 h. The study was followed by the setting time measurement, and the hydrates and morphologies evolution measurements through using X-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM), allowed to quantitatively expound the effects of HEMC and its dosage variations on the cement hydration at the early hydration time, an important task from dry mix mortars design and application point of view.

Experimental

Portland cement type P.II 52.5R (according to China standard GB 175), deionized water, and HEMC were used. The physical properties, chemical compositions, and clinker compounds were shown in Tables 1 and 2, respectively. The characteristics of HEMC are listed in Table 3. The viscosity of 2 % HEMC solution was determined through a Brookfield viscometer, with an RV type spindle turning at 20 rpm and at the temperature of 20 °C. Other characteristics were taken from the technical data sheet of the manufacturer.

In the cement pastes, the dosage of HEMC was 0, 0.5, 1, 2, and 3 % (mass ratio to cement), the water/cement mass ratio (*W*/*C*) was kept constant as 0.50. And the cement paste with no HEMC was set as the reference. Cement pastes were prepared according to China standard GB/T 1346. For XRD and ESEM tests, they were cured under the conditions of 20 ± 2 °C and 65 ± 5 %RH. For the setting time measurement, they were cured under the conditions of 20 ± 2 °C and 95 ± 5 % RH. An isothermal calorimetry (TAM AIR C80, Thermometric, Sweden) was used to measure the hydration heat evolution of cement pastes. The experimental temperature was kept at 20 ± 0.1 °C. All materials were kept at 20 ± 1 °C for 24 h before mixing, and then the water was injected into the reaction vessels and the samples were stirred in the calorimetry for several minutes. This procedure allowed monitoring the heat evolution from the very beginning when water was added to the cement pastes. Data logging continued for 72 h with one datum per minute.

Setting time was determined using an automatic Vicat apparatus under the conditions of 20 ± 2 °C and 95 ± 5 % RH, according to China standard GB/T 1346.

The XRD analysis was carried out with a graphite-monochromatized Cu *Ka* radiation generated at 40 kV and 200 mA in a Rigaku D/max 2550 X-ray diffractometer. The step scanning was conducted with the step length 0.02° and the dwell time 4 s for each step. Before the test, the samples, taken at a depth of > 1 mm from the surfaces of the cured pastes, were broken into pieces and stored in absolute alcohol for hydration interruption, and dried in vacuum oven under 40 °C until their masses became constant. And then they were ground to powder under 45 μm using a Planetary Micro Mill. The integrate areas of

Table 2 Chemical compositions & clinker compounds of Portland cement type P.II 52.5R/mass %

SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	Free CaO	C_3S	C_2S	C_3A	C_4AF
21.5	64.4	6.15	2.80	1.89	0.65	0.28	0.36	0.26	53.4	21.4	11.6	8.5

Table 3 Physical characteristics of HEMC

Viscosity[a]/ mPa s	Degree of substitution[b]	Molecular substitution[b]	Methoxy content[b]/ % OCH_3	Hydroxyethoxyl group[b]/% OC_2H_4OH	Modification[b]	Ash content[b] (as sulfate)/%
75,000	1.7	0.15	27.5	4.5	Unmodified	0.85

[a] Brookfield RV, 2 %, 20 °C, 20 rpm

[b] Information is provided by the manufacturer

ettringite (AFt) and portlandite ($Ca(OH)_2$) were calculated automatically by the software of MDI Jade 5.0 with the function of ''Profile fitting''.

The morphologies of cement pastes were observed through using the environmental scanning electron microscope (ESEM) FEI Quanta 200 FEG. For the analysis, freshly broken surfaces were prepared without hydration interruption before observation, and then were observed in the ESEM using a beam voltage of 20 kV and a working distance of around 10 mm. During the observation, samples were exposed to the environmental conditions of 5 °C and 2.7 Torr.

Results and discussion

Effects of HEMC on the hydration heat evolution rate

The hydration heat evolution curve of pure cement paste with no HEMC (the reference) is shown in Fig. 1. The hydration heat evolution curves of cement pastes with different HEMC dosages are shown in Fig. 2. Similar to that of C_3S [22], the hydration heat evolution of the reference also can be divided into five periods: I. The initial reaction period from 0 to 20 min, II. The induction period from 20 to 70 min, III. The acceleration period from 70 min to 9 h, IV. The deceleration period from 9 to 36 h, and V. The stable hydration period after 36 h (Fig. 1).

HEMC decreases the peak value of the initial reaction period, but HEMC and its dosage variations have little effect on the length of this period (Fig. 2a). While previous researches describe that HEMC has no effect on the initial reaction period [11, 14, 23]. The initial reaction period is characterized by the dissolution of C_3S, C_3A, calcium sulfate, and free CaO into water, with the evolution of a significant quantity of exothermal heat, and first portions of AFt, $Ca(OH)_2$, and CSH gels are produced at this period [24]. The reasons why HEMC can decrease this period peak value may be that as water soluble polymer, HEMC quickly dissolves in water to increase the viscosity of fresh cement paste, accordingly inhibits the dissolution of particles mentioned above.

HEMC significantly increases the length of the induction period, and with its dosage increasing, the effect of HEMC enhances (Fig. 2b). The induction period of cement paste with 0.5 % HEMC lasts 130 min from 20 min to 2.5 h, being 80 min longer than that of the reference. When the dosages of HEMC are 1, 2, and 3 %, the lengths of the induction periods

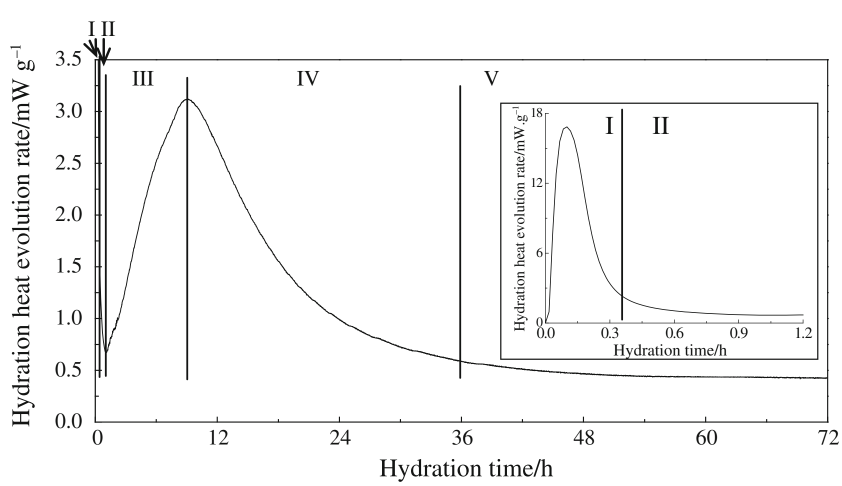

Fig. 1 The hydration heat evolution rate of the reference paste without HEMC

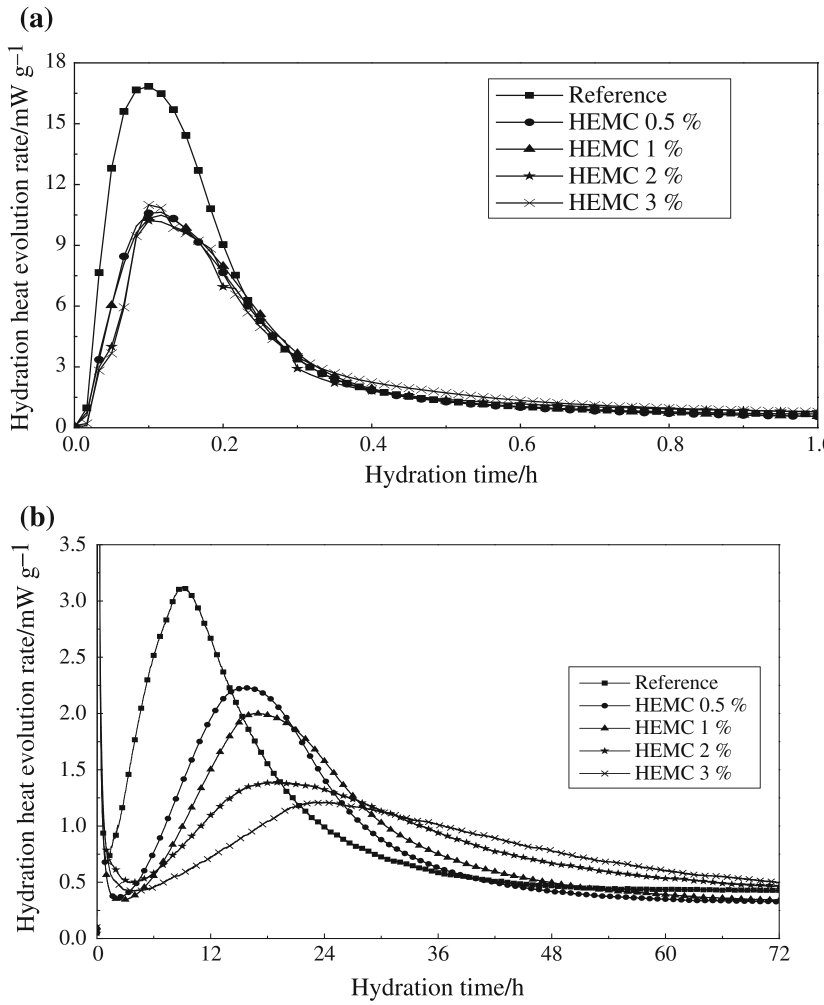

Fig. 2 The hydration heat evolution rate of cement pastes with HEMC: **a** for the first hour, **b** for 72 h

are 160, 280, and 340 min, respectively. The effect of HEMC on the induction period is almost the same to those of two HEMCs in literatures [11, 14]. The main difference of these three HEMCs is that the viscosity of HEMC in this research is 75000 mPa s, while the viscosities of HEMCs in literatures [11, 14] are 15000–40000 mPa s. Therefore, it may be concluded that to some extent, the viscosity variation of HEMC hardly affects the induction period. But compared to that of MC and HEC [15], the retardation of HEMC on the induction period is a little more significant. HEMC significantly increases the length of the acceleration period and postpones the beginning of the acceleration period, and with its dosage increasing, the effect of HEMC enhances. The acceleration period of the reference is from 70 min to 9 h. In the cement paste with 0.5 % HEMC, the acceleration period lasts 13.5 h from 2.5 to 16 h, longer than those in the literatures [11, 14]. When the dosages of HEMC are 1, 2, and 3 %, the acceleration periods further last to 17, 19, and 23 h, respectively.

HEMC greatly reduces the hydration heat evolution rate during the acceleration period and the second peak hydration heat evolution rate value of the cement pastes. And with the dosage of HEMC increasing, the heat evolution rate gradually decreases. Compared to that of the reference (3.12 mW g^{-1}), the second peak heat evolution rate value of the cement paste with 0.5 % HEMC decreases about 30 percent to 2.23 mW g^{-1}, while the peak values in the literatures [11, 14] decrease about 30 and 15 %, respectively. When the dosages of HEMC are 1, 2, and 3 %, the second peak heat evolution rate values are 2.00, 1.39, and 1.21 mW g^{-1}, respectively. So the retardation of HEMC on the acceleration period in this research is greater than those in the literatures [11, 14].

HEMC also postpones the beginning of the deceleration period and the stable hydration period, and increases the length of the deceleration period. Moreover, with its dosages increasing, the effect of HEMC enhances. For example, the deceleration period of the reference lasts 27 h from 9 to 36 h. When the dosage of HEMC is 3 %, the deceleration period lasts 47 h from 23 h to about 70 h. Additionally, HEMC increases the hydration heat evolution rate in the later deceleration period and the stable hydration period, and especially when its dosage is over 2 %, the hydration heat evolution rates of cement pastes with HEMC are greatly higher than that of the reference during the hydration time of 30 to 72 h. But the literature [25] demonstrates that the dosage variation of HPMC has little effect on the deceleration period and the stabilization period.

Some literatures reported the retardation of cellulose ethers on the content of hydration products such as ettringite and $Ca(OH)_2$ during these two periods [14, 25–27]. However, few literatures analyze the effects of HEMC, especially its dosage variation, on the lengths and hydration heat evolution rate of these two periods. From the analysis, it can be concluded that HEMC and its dosage variation have great effects on the lengths and hydration heat evolution rate of different hydration periods of Portland cement, and with the time prolonging, the retardation of HEMC on the cement hydration gradually weakens.

Effects of HEMC on the hydration heat amount

The hydration heat amount variations of cement pastes are shown in Fig. 3. It can be seen that as the hydration time extends, the hydration heat amount increases. In about 60 h of hydration, the higher the dosage of HEMC is available in the cement paste, the lower the hydration heat is. After this time, the hydration heats of cement pastes with HEMC are still lower than that of the reference. Moreover, for cement pastes with 0.5, 1, and 2 % HEMC, their hydration heats are almost the same, and for cement paste with 3 % HEMC, the heat is still the lowest. For example, at 12 h, the hydration heat of the reference is 104.5 J g^{-1}, and when the dosages of HEMC are 0.5 and 3 %, the hydration heat decreases to 48.8 and 34.6 J g^{-1}, respectively, being 46.7 and 33.1 % of that of the reference. At 36 h, the hydration heat of the reference is 208.0 J g^{-1}, and when the dosages of HEMC are 0.5 and 3 %, the hydration heat amounts decrease to 174.9 and 127.0 J g^{-1}, respectively, being 84.1 and 61.1 % of that of the reference. At 72 h, the hydration heat of the reference increases to 268.2 J g^{-1}, and when the dosages of HEMC are 0.5, 1, 2, and 3 %, the hydration heat amounts are 227.6, 226.2, 229.8, and 218.7 J g^{-1}, respectively, being all above 80 % to that of the reference. The effect of HEMC on the hydration heat before 24 h in the research is in agreement with the previous study [11]. But hardly any literature reported the effect of HEMC, especially its dosage variation, on the hydration heat after 24 h. It can be concluded that HEMC significantly decreases the hydration heat of cement paste, especially at the early hydration time, and with its dosage increasing, the effect of HEMC enhances.

Effects of HEMC on the hydration degree

Since the hydration heat is positively related to the hydration degree of cement paste, the hydration degree can be calculated from the hydration heat. The theoretic hydration heat of completely hydrated Portland cement is 479.1 J g^{-1}, determined from the formula proposed by Bogue [28, 29].

$$Q_{max} = 500m(C_3S) + 260m(C_2S) + 866m(C_3A) + 420m(C_4AF) + 624m(SO_3) + 1168m(\text{f-CaO}) + 850m(MgO), \quad (1)$$

where Q_{max} is the theoretic hydration heat of the completely hydrated Portland cement and $m(x)$ is mass ratio of compound in terms of the total cement content.

The hydration degrees of cement pastes are given according to Eq. (2) [30–32].

$$\alpha(t) = \frac{Q(t)}{Q_{max}}, \quad (2)$$

where $\alpha(t)$ is the hydration degree of cement paste at time t, $Q(t)$ is the hydration heat of cement paste at time t, J g^{-1},

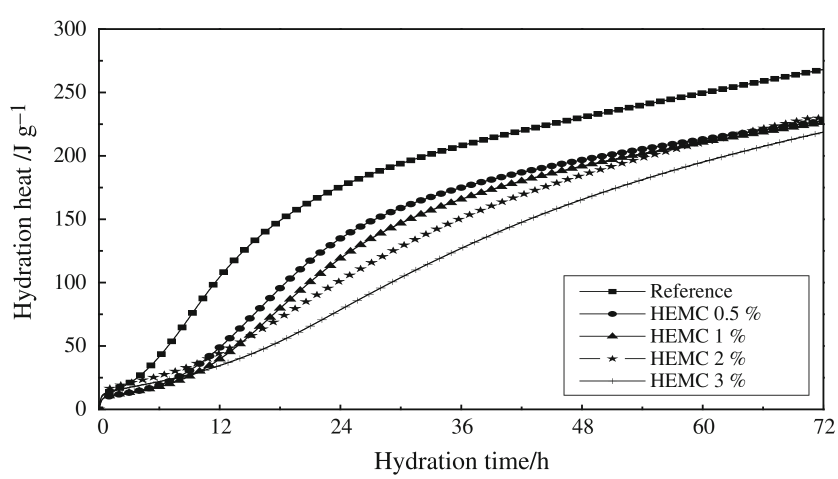

Fig. 3 The hydration heat amount of cement pastes with HEMC

and Q_{max} is theoretic hydration heat of completely hydrated Portland cement, J g^{-1}.

The hydration degrees of cement pastes are shown in Fig. 4. It can be seen that with the hydration time prolonging, the hydration degrees of cement pastes gradually increase. In about 60 h of hydration, the higher the dosage of HEMC is available in the cement pastes, the lower the hydration degree is. After this time, the hydration degrees of cement pastes with HEMC are still lower than that of the reference. Moreover, for cement pastes with 0.5, 1, and 2 % HEMC, their hydration degrees are almost the same, while for cement paste with 3 % HEMC, the hydration degree is the lowest. For example, at 12 h, the hydration degree of the reference is already 21.8 %, while the hydration degrees of the cement pastes with 0.5 % HEMC and 3 % HEMC are only 10.2 and 7.2 %, respectively. For the cement paste with 0.5 % HEMC, its hydration degree just reaches 21.8 % at 20 h. For the cement paste with 3 % HEMC, its hydration degree just reaches 21.8 % at 30 h. At 36 h, the hydration degree of the reference reaches 43.4 %, the hydration degrees of the cement pastes with 0.5, 1, 2, and 3 % are 36.5, 34.6, 31.5, and 26.5 % respectively. At 72 h, the hydration degree of the reference reaches 56.0 %, while the hydration degrees of the cement pastes with 0.5 to 3 % are all about 46.5 ± 1 %, being over 80 percent of that of the reference. Therefore, it can be concluded that HEMC significantly decreases the hydration degree of cement pastes, especially at the very early hydration time, and with its dosage increasing, the effect of HEMC enhances. The effect of HEMC on the hydration degree after 1 d is similar to that of HPMCs with different viscosities through the comparison of hydration heat [25] and the $Ca(OH)_2$ content proportions [26, 27].

Effect of HEMC on the setting time

The initial and final setting time of cement pastes are presented in Table 4. The initial and final setting times of the reference are 240 and 355 min, respectively. When the dosages of HEMC are 0.5, 1, 2, and 3 %, the initial setting time of cement pastes are 475, 585, 830, and 1140 min, respectively, and the final setting time are 635, 820, 1095, and 1345 min, respectively. It can be concluded that HEMC remarkably extends the initial and final setting time of cement pastes, which is in agreement with the retardation of HEMCs in the literatures [9, 33]. And with HEMC dosage increasing, the setting time further extends. However, the literature [33] shows that the higher the viscosity of HEMC is, the shorter the setting time is.

From Fig. 2 and Table 4, it can be seen that the longer the lengths of the induction period and the acceleration period are, the longer the initial and final setting time are, and there are linear positive correlations among them. So the results confirm that the initial and final setting time of cement paste have close correlations with the length of the induction period and the length of the acceleration period, respectively [34]. HEMC does not affect the length of the initial reaction period. Therefore, the increase of the setting time indirectly that HEMC extends the lengths of the induction period and the acceleration period.

Generally, CSH is produced slowly in the induction period. With the termination of this period and the initiation of the main reaction, more CSH gels and $Ca(OH)_2$ are formed, leading to the normal setting [35]. However, HEMC reduces the rates of CSH gels and $Ca(OH)_2$ formation, and subsequently delays the formation of CSH gels and $Ca(OH)_2$ [11, 15, 17, 23]. As a result, the initial setting time is much longer than the length of the induction period, and their differences have a good linear positive correlation with the dosages of HEMC. For example, the difference between the initial setting time and the length of the induction period of the reference is 190 min, while the differences between the initial setting time and the length of the induction period of the cement pastes with 0.5 and 3 % HEMC are 345 and 800 min, respectively. But the difference between the final setting time and the length of

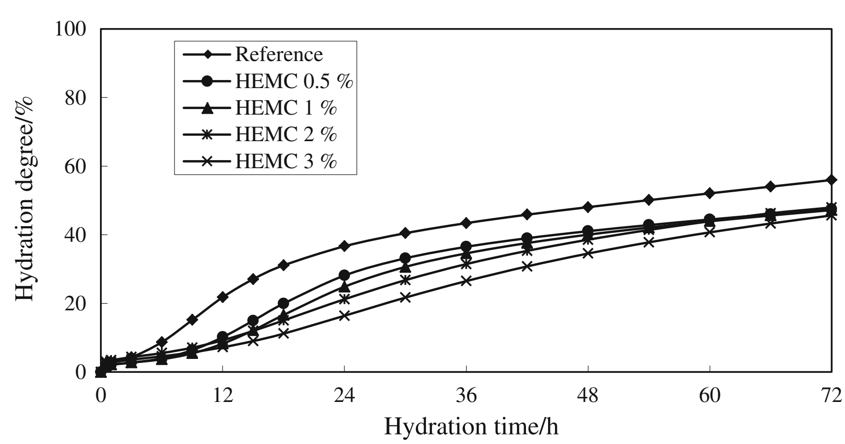

Fig. 4 The hydration degree of cement pastes with HEMC

Table 4 Setting time of cement pastes

Cement paste	Setting time/min	
	Initial	Final
Reference	240	355
With 0.5 % HEMC	475	635
With 1 % HEMC	585	820
With 2 % HEMC	830	1,095
With 3 % HEMC	1,140	1,345

the acceleration period is relatively smaller, especially when the dosage of HEMC is over 2 %.

Effect of HEMC on hydration products and morphologies

The XRD spectra of the cement pastes hydrated for different time periods are shown in Fig. 5. The integrate areas of AFt and $Ca(OH)_2$ in XRD patterns are shown in Figs. 6 and 7, respectively. The morphologies of the cement pastes hydrated for different time periods are shown in Figs. 8–13. At 30 min and 1 h, a very small peak of AFt at 2θ of 9.1° appears in the reference (Fig. 5a), some AFt crystals have formed (Fig. 6), while there are no hydration products (AFt and $Ca(OH)_2$) formed in the cement paste with 1 % HEMC (Figs. 5b, 6, 7). And very small columnar crystals precipitated on cement particles can be found in the reference at 30 min (Fig. 8a), while this phenomenon cannot be observed in the cement paste with 1 % HEMC (Fig. 8b). There are very fine AFt crystals and some foil-like CSH gels formed in the reference at 1 h (Fig. 9a), only some more plate-like products can be observed in the cement paste with 1 % HEMC (Fig. 9b).

At 6 h, the peak for AFt remarkably increases and the peak for $Ca(OH)_2$ at 2θ of 18.0° appears, much more AFt crystals and some $Ca(OH)_2$ crystals have formed in the reference (Figs. 5a, 6, 7), and more fine fibrous CSH gels and small AFt crystals cover the surfaces of cement particles (Fig. 10a). In the cement paste with 1 % HEMC, a very small peak for AFt at 2θ of 9.1° appears in the cement

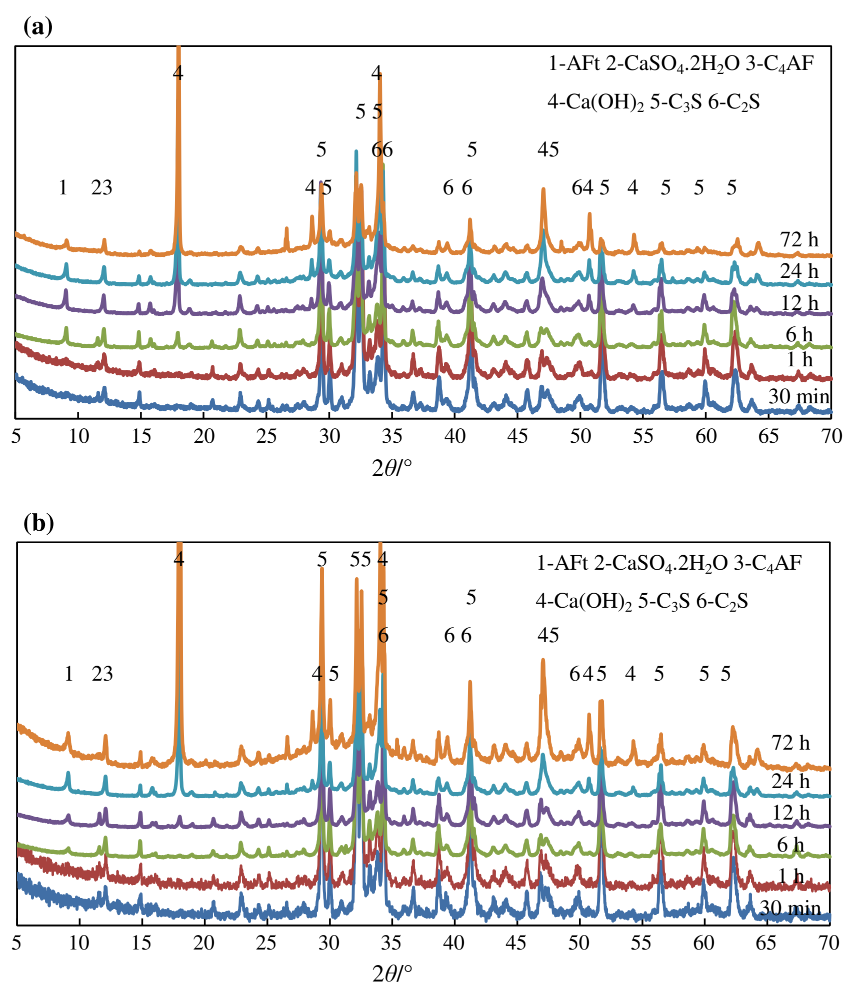

Fig. 5 XRD patterns of cement pastes hydrated for different time periods: **a** reference, **b** cement paste with 1 % HEMC

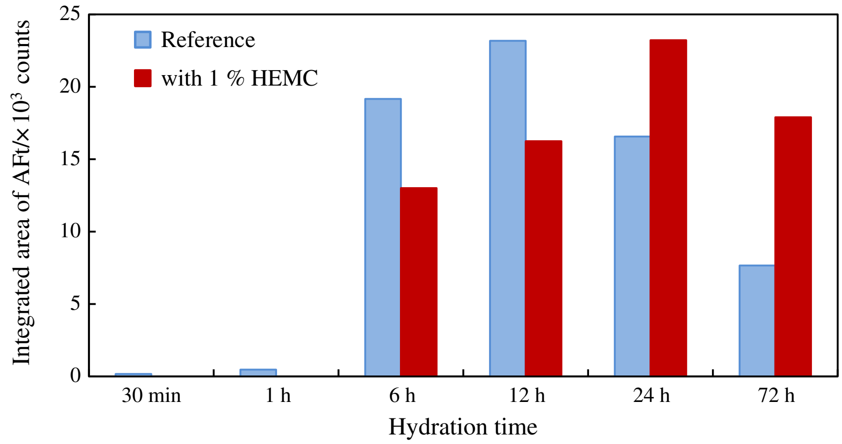

Fig. 6 Integrate area of AFt in XRD patterns of cement pastes hydrated for different time periods

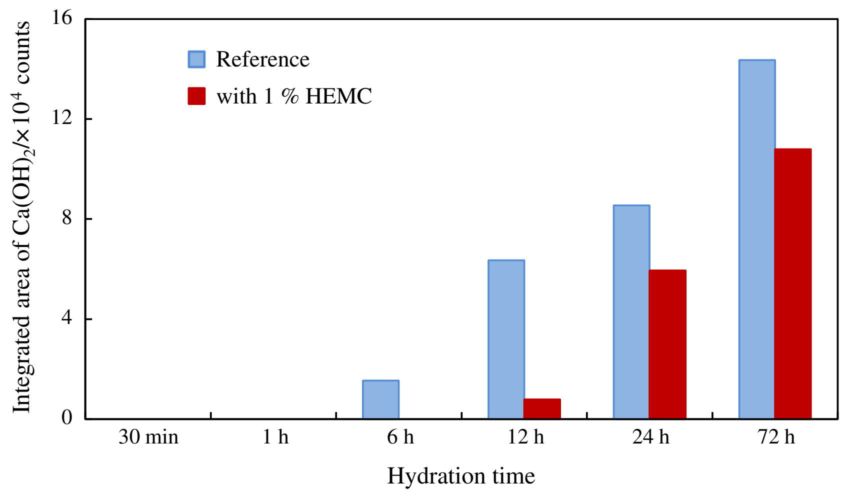

Fig. 7 Integrate area of $Ca(OH)_2$ in XRD patterns of cement pastes hydrated for different time periods

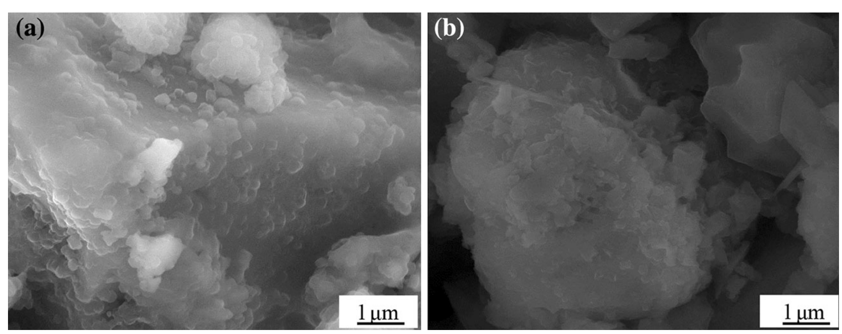

Fig. 8 Morphologies of cement pastes hydrated for 30 min: **a** the reference, **b** cement paste with 1 % HEMC

paste with 1 % HEMC, some AFt crystals have formed (Figs. 5b, 6), while there are no $Ca(OH)_2$ crystals or CSH gels, but some small columnar crystals precipitate on the cement particles (Fig. 10b), this phenomenon is similar to that of the reference at 30 min. So it can be concluded that at the very early hydration time, HEMC has affected the formation of hydrates. The reasons may be due to that HEMC can quickly dissolve in water to increase the viscosity of the liquid phase of cement pastes [8, 10], resulting in the reduction of the migration rate of ions such as Ca^{2+}, SO_4^{2-}, and OH^-, and its adsorption on cement particles [13] leads to the retardation of cement particles contacting

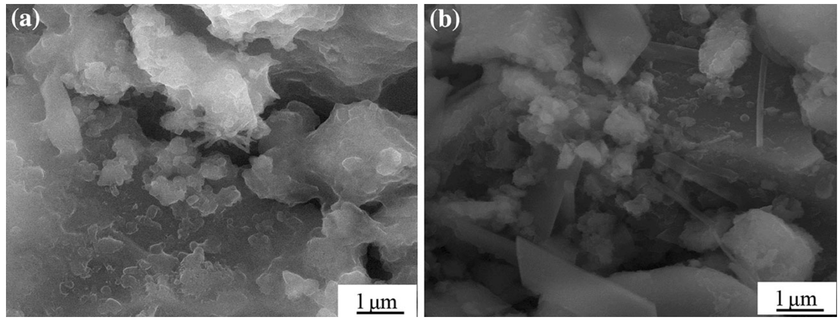

Fig. 9 Morphologies of cement pastes hydrated for 1 h: **a** the reference, **b** cement paste with 1 % HEMC

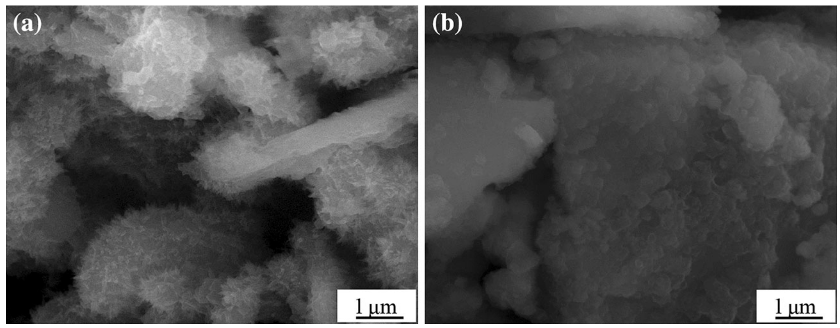

Fig. 10 Morphologies of cement pastes hydrated for 6 h: **a** the reference, **b** cement paste with 1 % HEMC

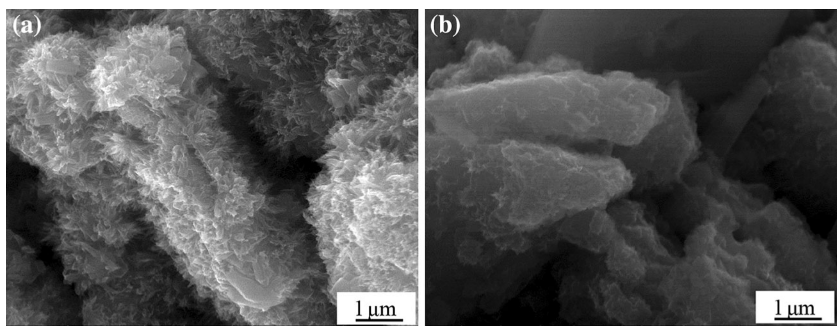

Fig. 11 Morphologies of cement pastes hydrated for 12 h: **a** the reference, **b** cement paste with 1 % HEMC

with water and hydrates nucleating, growing, and precipitating.

At 12 h, the peaks for AFt and $Ca(OH)_2$ further increase and the peak for gypsum disappears, more AFt and $Ca(OH)_2$ have formed in the reference (Figs. 5a, 6, 7), and it can be observed that fibrous CSH gels grow up and more AFt and $Ca(OH)_2$ coexist in the reference (Fig. 11a). In the cement paste with 1 % HEMC, the peak for AFt slightly increases and the peak for $Ca(OH)_2$ appears (Fig. 5b), a little more AFt and some $Ca(OH)_2$ have formed (Figs. 6, 7), some foil-like CSH gels can be observed in it (Fig. 11b), which is similar to that of the reference at 1 h.

At 24 h, the peak for AFt decreases and the peak for $Ca(OH)_2$ further increases (Fig. 5a), the content of AFt decreases, indicating its conversion to monosulfate (AFm) that occurs, while more $Ca(OH)_2$ have formed in the reference (Figs. 6, 7), and the sizes of CSH gels and needle-like AFt crystals remarkably increase (Fig. 12a). While much more AFt and $Ca(OH)_2$ have formed in the cement paste with 1 % HEMC (Figs. 5b, 6, 7), and the sizes of CSH gels also increase but still much smaller than those in the reference (Fig. 12b).

At 72 h, the peak for AFt further decreases and the peak for $Ca(OH)_2$ increases (Fig. 5a), the content of AFt further decreases and much more $Ca(OH)_2$ have formed in the reference (Figs. 6, 7). Additionally, CSH gels grow much longer to collude with each other and more foil-like AFm can be observed in the reference (Fig. 13a). While the peak for AFt keeps higher and the peak for $Ca(OH)_2$ further increases (Fig. 5b), the contents of AFt and $Ca(OH)_2$

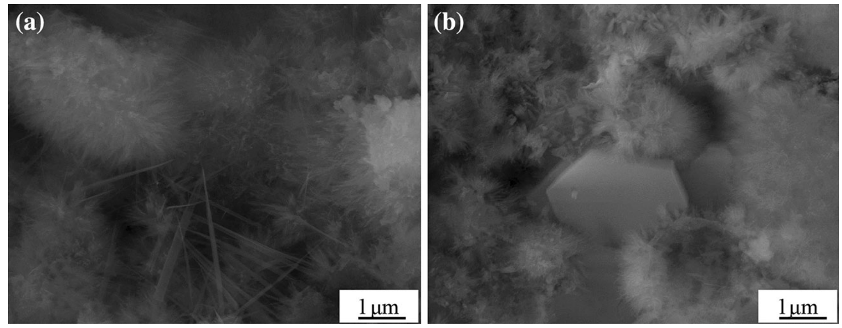

Fig. 12 Morphologies of cement pastes hydrated for 24 h: **a** the reference, **b** cement paste with 1 % HEMC

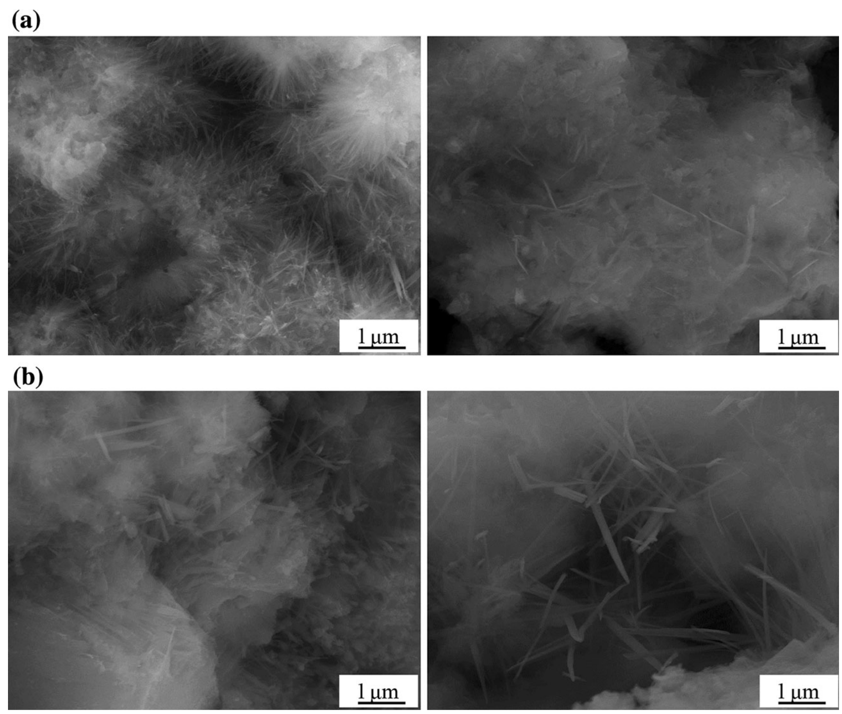

Fig. 13 Morphologies of cement pastes hydrated for 72 h: **a** the reference, **b** cement paste with 1 % HEMC

maintain higher in the cement paste with 1 % HEMC (Figs. 6, 7), while CSH gels are still much finer than those in the reference and more AFt crystals can be observed (Fig. 13b).

Therefore, it can be concluded that HEMC remarkably retards the cement hydration, has great effects on different hydration heat evolution periods, delays the formation of the hydrates, and to some extent affects the morphologies of hydrates, especially at the early hydration time.

Conclusions

HEMC and its dosage variations have significant effects on the beginning, the length and the hydration heat evolution rate of different hydration evolution periods of cement paste. HEMC does not affect the length of the initial reaction period but decreases its hydration heat evolution rate value. HEMC significantly delays the beginning of the induction period and acceleration period, increases their lengths and greatly reduces the hydration heat evolution rate during these two periods. HEMC also postpones the beginning of the deceleration period and the stable hydration period, but increases the hydration heat evolution rate in the later deceleration period and the stable hydration period. And with its dosage increasing, the effect of HEMC enhances.

HEMC greatly decreases the hydration heat and hydration degree of cement paste and retards the hydration of cement paste, especially at the very early hydration time. Moreover, with its dosage increasing, the retardation effect of HEMC gradually enhances. But with the hydration time prolonging, the retardation of HEMC gradually weakens.

Due to its retardation, HEMC delays the setting time of cement paste and the formation of the hydrates, and accordingly to some extent affects the morphologies of hydrates. The setting time and the hydrates variations have good correlations with the hydration process evolution of cement paste. Therefore, HEMC remarkably retards the cement hydration at the early hydration time, and with its dosage increasing, the retardation effect of HEMC enhances.

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