



## Technical note

# A starch-based admixture for reduction of hydration heat in cement composites



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## HIGHLIGHTS

- A starch-based admixture (SA) used to modify the cement hydration heat process was reported.
- Temperature variation of mortar and effects of starch-based admixture on setting time and strength were assessed experimentally.
- The evolution of the hydration process and micro-structure of cement paste with SA was monitored to reveal the mechanism.

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## ABSTRACT

In this paper, the effect of a new starch-based chemical admixture (SA) on cement hydration is investigated and its preliminary action mechanism is discussed. The results from isothermal calorimeter and semi-adiabatic calorimetry test show that SA could decrease the maximum heat flow from the 2.6 mW/g to 1.5 mW/g and the peak temperature from 35.9 °C to 24.9 °C when the SA dosage increased from 0% to 0.6% (weight ratio of SA/cement). The effect of SA with different dosage on cement hydration has also been investigated by electrical resistance test and X-ray diffraction analysis. Though the cement hydration rate is decreased at early stage, it has no influence on the final total heat release and no influence on concrete compress strength at 28 d. Such results show that it might have great sense to control thermal crack in mass concrete in practical application which is normal problem in mass concrete.

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## 1. Introduction

Though more than 10 million m<sup>3</sup> mass concrete are consumed every year in China, the thermal crack is still normal problem in dams, long-span bridges, harbor constructions and skyscrapers projects [1]. Concrete is low thermal conductive material meaning that the temperature of concrete would keep rising until the rate of hydration heat release equal to rate of heat dissipation when the cement hydration is beginning. After the peak temperature inside of concrete, thermal shrinkage due to the temperature decrease would happen and shrinkage stress would be generated. When the thermal stress is large than tensile stress, crack is formed [2,3]. The formed cracks would lead to lower performance of concrete such as strength and durability especially in severe environment.

Reducing the total heat release and improving the heat dissipation condition are the two primary ways to control thermal crack in engineering projects. From the perspective of material, supplementary cementitious materials with low hydration heat release are selected such as GGBS and fly ash (about 30% volume in dam project), or using low-heat cement instead of Portland cement [4]. Pipe cooling system has been taken to improve the heat dissipation condition [5,6]. Cool mixing water and pre-cooling aggregates also have been used to decrease the concrete temperature to control thermal crack. Yet the convenience of constant mixing promotion in pipe cooling system are offset by cumbersome installation work as well as additional construction time and cost.

Chemical admixtures are used to improve the concrete properties, such as workability, setting process, mechanical performance, shrinkage and durability [7]. Except for the accelerating admixture, most of admixtures are observed as a retardation effect, such as retarder and superplasticizer. For superplasticizer, a complexation of Ca<sup>2+</sup> ions from pore solution by the superplasticizer is as thinkable as the adsorption of the polymer on the nuclei or the

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anhydrous grain surfaces which in turn might lead to the prevention of the growth of the nuclei or the dissolution of the anhydrous grains [8]. Jansen et al. concluded that the superplasticizers in question retard both the aluminate reaction and the silicate reaction [9]. Besides the polysaccharides or saccharides such as starch and maltodextrin, glucose and sucrose exhibit differences in their alkaline reaction properties and performances in cement hydration behaviors. Solid-state  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  nuclear magnetic fields (19T) have been taken to distinguish and quantify the different molecular species, their chemical transformations and their site-specific adsorption properties on different aluminate and silicate moieties [10]. It is concluded that nonselective adsorption of glucose and degradation products containing carboxylic acids occurs on both hydrated silicates and aluminates. But in contrast, sucrose adsorbs intactly at hydrated silicate sites and selectively at anhydrous, but not hydrated, aluminate moieties [11].

It has been proved that there is no direct relation between the thermal crack control and the setting time, which means that there is no obvious effect on thermal crack control when only setting time (retardation) is delayed. Real temperature change shows that the temperature rises to highest temperature which is caused by placing temperature and the hydration of cement [1]. To improve the thermal crack resistance ability in massive concrete structures, phase change material (PCM) is proved to be an effective way. It is shown that when Barium-based PCM is used in the concrete mixture, the peak heat temperature is decreased more than  $10\text{ }^\circ\text{C}$  with manageable negative effects on mechanical properties and durability [12]. However, in other research it is proposed that PCM might decrease the mechanical properties greatly [14,15]. Besides PCM, H. Justnes [13] has developed the chemical admixture of “hardening retarders” by combining small amount of strong setting retarders with a setting accelerator, and such materials can reduce the maximum temperature from  $57\text{ }^\circ\text{C}$  to  $52\text{ }^\circ\text{C}$ . If there are approaches that can reduce the thermal cracking risk of concrete, they shall limit peak temperature without affecting mechanical property and resist the rate of large change in section temperature caused by cement hydration.

In this paper, a new starch-based chemical admixture (SA) was used and its effect on cement hydration to prevent the risk of thermal cracking at different dosage was investigated. With the results from X-ray diffraction analysis and electrical resistance test, SA action mechanism on cement hydration is discussed.

## 2. Materials and methods

### 2.1. Material

This study used Ordinary Portland cement from Qufu China United Cement Co., LTD, ASTM C150 1 cement without any additive. The phase composites of cement is determined by X-ray diffraction analyses (XRD) using a Bruker D8 Advance diffractometer in a  $\theta$ - $\theta$  configuration using  $\text{Cu-K}\alpha$  radiation. The content of calcium silicates is 67.8% and the compositions of the cement are listed in Table 1. The starch-based chemical admixture is produced

**Table 1**  
Chemical and phase compositions of investigated ordinary Portland cement.

Chemical composition (wt%)				Phase composition (wt%)	
Oxides	XRF	Oxides	XRF		
CaO	61.123	TiO <sub>2</sub>	0.271	C <sub>3</sub> S	58.6
SiO <sub>2</sub>	19.701	Na <sub>2</sub> O	0.154	C <sub>2</sub> S	11.2
Al <sub>2</sub> O <sub>3</sub>	4.653	K <sub>2</sub> O	0.695	C <sub>3</sub> A	4.6
SO <sub>3</sub>	3.007			C <sub>4</sub> AF	11.5
Fe <sub>2</sub> O <sub>3</sub>	3.482			CaSO <sub>4</sub> ·2H <sub>2</sub> O	3.3
MgO	2.059			CaSO <sub>4</sub> ·0.5H <sub>2</sub> O	0.1
				MgO	1.0

by the Jiangsu Sobute New Materials Co., Ltd, characteristics of which include functional group are tested by Fourier transform infrared spectrometry (FTIR) whose results is shown in Section 3. Fourier transform infrared (FTIR) spectra of samples (palletized with KBr powder) were recorded using Bruker Equinox 55 with a resolution of  $0.4\text{ cm}^{-1}$ .

### 2.2. Sample preparation and test methods of different performance

The heat release process of cement was measured by isothermal calorimeter (TA CO., TAM Air) with a sensitivity of  $0.4\text{ }\mu\text{J}$  and a baseline stability of  $\pm 0.08\text{ }\mu\text{W/h}$ . All experiments were conducted at  $20 \pm 1\text{ }^\circ\text{C}$  and the water/cement mass ratio (W/C) of the paste was set at 0.38 because of the good flowability of cement paste and the good dispersion of chemical admixture. The paste was mixed for 2 min at 3200 rpm before putting in calorimeter.

To determine the influences of chemical admixture on temperature evolutions, cone (75 mm diameter higher surface and 150 mm diameter lower surface) specimens were used. The ratios of water to sand and water to binder are fixed at 3 and 0.38, respectively. Fresh mortar was poured into sealed cone molds made of polyvinyl chloride (PVC), and their temperature evolution was recorded over time. Thermocouples were positioned in the sample using dowels in both the radial and longitudinal directions, such that temperature evolutions/gradients can be measured at precise locations through the volume. Assessments were carried out wherein the instrumented mold was placed in a water environmental chamber (within  $20 \pm 0.2\text{ }^\circ\text{C}$ ) and subjected to thermal cycling.

The setting time was determined according to ASTM C191 2001c. The Vicat apparatus is utilized to test the initial and final setting time. Compressive strength of composites (blank cement pastes, pates including 0.2%, 0.4% and 0.6% wt. chemical admixture) were measured as describe in ASTM C109 at 3, 7, 14, 28 days on specimens that were cured in a sealed state at  $25 \pm 1\text{ }^\circ\text{C}$ .

The phase composites of cement is determined by X-ray diffraction analyses (XRD) using a Bruker D8 Advance diffractometer in a  $\theta$ - $\theta$  configuration using  $\text{Cu-K}\alpha$  radiation. The scanning range was  $5\text{--}70^\circ$  ( $2\theta$ ) with a scanning rate of  $0.02^\circ/\text{s}$  and the relative quantitative analysis is conducted using the TOPAS supported by Bruker. The samples were casted in ring-shaped molds of dimensions  $770\text{ mm} \times 55\text{ mm} \times 42\text{ mm}$  and data was collected at 1 min intervals over one week. The electrical resistivity was measured by non-contact electricity resistivity measurement device (Cement and Concrete Resistivity –III) to investigate development of microstructure of cement paste by measuring the variation of resistivity timely. The samples were casted in ring-shaped molds of dimensions  $770\text{ mm} \times 55\text{ mm} \times 42\text{ mm}$  and data was collected at 5 s intervals over one week.

## 3. Results and discussion

### 3.1. Characteristics of starch-based chemical admixture

Fig. 1 shows the FTIR spectra of chemical admixture. A broad peak at  $3300\text{ cm}^{-1}$  is found in the spectrum of admixture, which corresponds to the stretching of hydroxyl ( $-\text{OH}$ ). The weak absorption band at  $2933\text{ cm}^{-1}$  in Fig. 1 can be attributed to C–H stretching vibration of chemical admixture. The adsorption between  $1454\text{ cm}^{-1}$  and  $1372\text{ cm}^{-1}$  can be attributed to ring skeleton vibration peak of starch while between  $1016\text{ cm}^{-1}$  and  $1062\text{ cm}^{-1}$  is the adsorption caused by the stretching vibration of the C–O. The weak peak adsorption in  $857\text{ cm}^{-1}$  can be attributed to the stretching vibration of C–O–C. These findings indicated that the chemical admixture contains a large number of starch-based  $-\text{OH}$  hydrophilic.

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