

Influence of fineness on hydration kinetics of supersulfated cement



Shuhua Liu^{a,b,*}, Lu Wang^a, Yuxin Gao^c, Baoying Yu^c, Wan Tang^a

^a State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University, Wuhan 430072, China

^b Department of Civil, Environmental and Geomatic Engineering, University College London, Gower Street, London WC1E 6BT, UK

^c China Construction Ready Mixed Concrete Co., Ltd., Wuhan 430000, China

ARTICLE INFO

Article history:

Received 30 July 2014

Received in revised form 8 November 2014

Accepted 17 February 2015

Available online 19 February 2015

Keywords:

Supersulfated cement

Fineness

Hydration heat

Kinetic parameters

ABSTRACT

Hydration heat evolution rate and quantity of supersulfated cements (SSCs) with three different specific surface areas (335 m²/kg, 445 m²/kg and 518 m²/kg) were measured at 25 °C by isothermal calorimetry. The hydration heat evolution quantity of SSCs improves with the increase of cement fineness, but is much lower than that of ordinary Portland cement. The hydration of supersulfated cement is accelerated by the elevated fineness, and the hydration process of supersulfated cement after induction period was divided into three periods, nucleation and crystal growth (NG), phase boundary reaction (I), and diffusion (D), which are well simulated through Krstulovic–Dabic model. The connecting points of NG process and I process, I process and D process both decrease with the increase of fineness which shows that the second exothermic peak is in advance. I process also decreases with the increase of fineness, which indicates that I process is accelerated by fineness. The hydration of supersulfated cement is sensitive to fineness, especially for the specific surface area reaching up to 518 m²/kg.

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1. Introduction

Portland cement is the most popular and also one of the most important cementing materials in the modern concrete [1], and during the year of 2012, there are more than 2.2 billion tons cement produced in China [2]. Because of the high hydration heat emission of cement as well as the low thermal conductivity of concrete, the hydration of cement always produces a large number of heat and leads to a raise of internal temperature in massive concrete, which may make concrete cracking during the cooling period [3]. In order to reduce the hydration heat emission from the cementitious materials, mineral admixtures are widely used in modern concrete [3–6], which can reduce the hydration heat emission and the rate of cementing materials [7,8].

So, in this paper, one kind of more environment-friendly cement with three different specific surface areas will be studied. Supersulfated cement (SSC) is a kind of cement with less clinker or even without clinker, which contains almost 80% ground granulated blast furnace slag, 15% gypsum as sulfate activator and less than 5% clinker or lime as alkali activator [9–11]. SSC is made directly by the mixtures of these three raw materials, often

added with 1% mass ratio of coagulant, and in ball mill to be ground to suitable fineness. High content slag in SSC can make full use of the potential activity of slag and also benefit for environment. Studies show that granulated blast furnace slag is suitable for producing SSC and have a reasonable strength development process because of its high content of calcium and alumina (at least 14–15%) [11,12].

Some researchers have pointed out that the hydration heat of SSC is much lower than that of ordinary Portland cement [9–12]. Grinding can affect the specific surface area, i.e. fineness, which can influence the hydration process of the binders [13]. So not only addition of mineral admixture can affect the hydration degree, hydration heat evolution rate and total hydration heat of cement, but also the fineness of raw materials has great influence on the hydration properties. In order to understand the hydration process of SSC with different finenesses, study of detailed heat evolution behavior is needed. The hydration heat curves of SSCs with three different finenesses were measured to analyze the interaction among them on hydration heat emission and rate.

2. Experimental

2.1. Materials

The SSCs are ground with three specific surface areas. SSC1, SSC2 and SSC3 are short for the SSC with specific surface area of 335 m²/kg, 445 m²/kg and 518 m²/kg respectively. The chemical

* Corresponding author at: State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University, Wuhan 430072, China. Tel.: +86 27 68772233; fax: +86 27 68772310.

E-mail address: shliu@whu.edu.cn (S. Liu).

Nomenclature

List of acronyms and parameters identification

SSC	Supersulfated cement
SSCs	Supersulfated cements
NG	Nucleation and crystal growth
I	Phase boundary reaction
D	Diffusion
SSC1	Supersulfated cement with specific surface area of 335 m ² /kg
SSC2	Supersulfated cement with specific surface area of 445 m ² /kg
SSC3	Supersulfated cement with specific surface area of 518 m ² /kg
W/C	Water to cement ratio
P	The heat evolution quantity
α	The hydration degree
C–S–H	Calcium silicate hydrate
CH	Calcium hydroxide
K	The reaction rate constant of hydration reaction
n	Reaction order
R	The diameter of reacted particle
t ₀	The end time of the induction period

compositions of SSC are shown in Table 1. From Table 1, SSC contains high content of SO₃ up to 13.42% due to high content of gypsum.

2.2. Test methods

The hydration heat evolution rate and total hydration heat emission of SSC1, SSC2 and SSC3 were measured with an isothermal calorimeter (TAM Air) at 25 °C within 96 h. TAM Air has eight parallel twin-chamber measuring channels maintained at a constant temperature: one chamber containing the sample, the other containing the reference. The temperature fluctuation is less than ±0.02 °C, the precision can reach ±20 μW. The water to cement ratio (W/C) was 0.4 and 10 g samples for each SSC were used. First take 4.00 g pure water into a bottle, and then pour 10.00 g sample powder into. At the same time, stirring quickly and putting it into the chamber to measure hydration heat. The hydration heat evolution rate and total hydration heat of SSC can be continuously monitored as a function of time.

3. Results and discussions

3.1. Characteristics of hydration heat evolution

Fig. 1 shows the hydration heat emission rate curves of the three SSCs and Fig. 2 shows the hydration heat emission quantity at the constant temperature 25 °C within 96 h. The acceleration period and the end time of induction period of SSCs are shown in Fig. 3. The rate of the second heat emission peak and the total heat emission at different hydration ages determined from heat evolution curves of SSCs are shown in Table 2.

Table 1

Chemical composition of SSC (mass fraction%).

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅
SSC	25.63	10.87	1.18	41.45	4.93	13.42	0.23	0.60	0.40

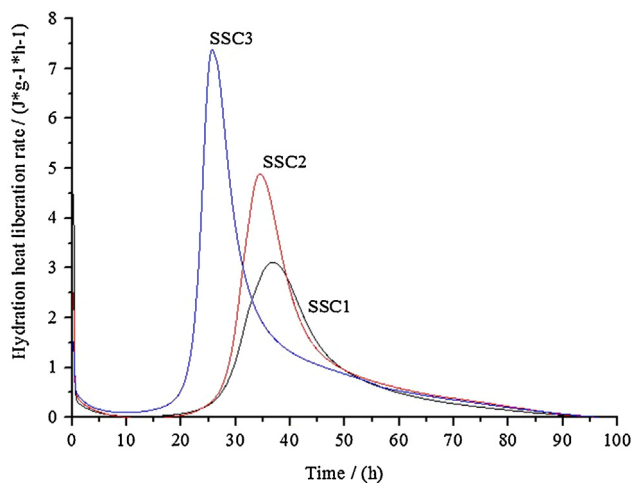


Fig. 1. Hydration heat evolution rate curves of the three SSCs.

As the hydration heat evolution rate curves of the three SSCs shown in Fig. 1, in the first several minutes after mixing SSC powder with water, a sharp and transient exothermic peak occurs, which is formed by a quick formation of ettringite due to the rapid dissolution of aluminates and sulfate from slag and gypsum, as well as from the small amount of cement clinker. Then the heat emission rate decreases rapidly, and the hydration heat increases very slowly. After that, the hydration goes to the induction period, and the hydration heat rate is closed to zero. As shown in Fig. 1, there is little difference of the hydration induction period between SSC1 and SSC2, which lasts for about 24 h, ending at about 24.37 h and 24.80 h (Fig. 3), which are much longer than that of ordinary Portland cement. However, the induction period of SSC3 lasts for about 18 h, and ending at about 18.74 h, which is ahead about 6 h for SSC1 and SSC2. The induction period of hydration for SSC is prolonged due to low clinker content in the cements. Since the content of slag reaches up to 80% and it has high potential activity, a large amount of Ca²⁺ produced during the hydration of cement clinker and is absorbed on the surface of slag, which reduces Ca²⁺ concentration in the solution, delays Ca(OH)₂ (CH) nucleation and generates unstable C–S–H gel with low Ca/Si ratio (it will slowly change into a stable C–S–H gel). Thus the ending time of the induction period is prolonged [14].

Subsequently, the acceleration period comes with rapid hydration of C₃S, fast formation of C–S–H gel and ettringite.

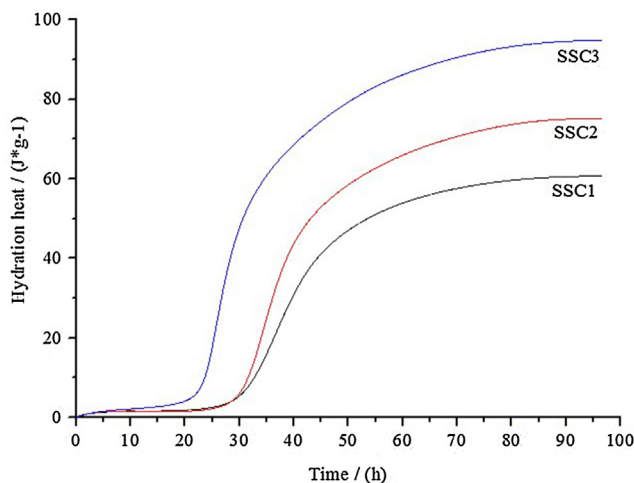


Fig. 2. Hydration heat quantity curves of the three SSCs.

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