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Hydration of the silica fume-Portland cement binary system at lower temperature

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HIGHLIGHTS

- The pozzolanic activity of silica fume declines as temperature decreases.
- As temperature decreases, $Ca(OH)_2$ content of the binary system reduces.
- Lower temperature results in smaller gradient difference of the strength.
- The second exothermic peak narrows and lags at lower temperature.
- Total porosity, particularly harmful pores volume, increases as temperature decreases.

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ABSTRACT

In order to explore the hydration structure of the silica fume-Portland cement binary system at lower temperature, strengths of the cement mortars were measured at −10 °C, −5 °C, 0 °C and 5 °C, content of $Ca(OH)_2$ was quantified using thermogravimetry–differential scanning calorimetry (TG–DSC) method, and thermal analysis, scanning electron microscope (SEM) method and mercury porosimetry were employed for the microscopic mechanism analysis. The results indicated that, silica fume could contribute to the improvement of the hydration structure of the binary system. The results showed that strengths of the binary system decreased apparently, content of $Ca(OH)_2$ reduced, total heat of the hydration decreased significantly, the total porosity increased and the compactness of the structure decreased at the lower temperature. The lower temperature hindered the hydration evolution of the binary system and inhibited the pozzolanic activity of silica fume.

1. Introduction

Owning to its pozzolanic activity and micro-aggregate effect, silica fume was widely used in construction industry as a mineral admixture to cement [1–3]. There is 85% of amorphous SiO_2 or more in silica fume, which may cause secondary reactions with $Ca(OH)_2$ produced in cement hydration [4,5]. It makes significant to investigate the hydration microstructure of binary system with silica fume and Portland cement.

Performance and hydration microstructure of cement are affected by many factors, such as cement strength grade, water–cement ratio, admixtures and temperature [6–9]. Especially the change of curing temperature may bring significant variations to hydration reactions. Olli Saarinen found that [10], apparent phenomenon of 'expansion and contraction' can be observed in concrete at 5 °C to −15 °C. Therefore, property indicators, product components and microstructures are restrained by temperature variance at lower temperature.

Currently, binary or more complex binding material systems are mainly applied in construction [11–14]. Use the binding material alone usually cannot meet the need of the construction [15]. While, multiple binding material systems have more factors beyond control. As a result, binary binding material system is suitable for winter construction project considering the complexity of construction in winter [16,17]. Furthermore, silica fume can not only improve the frost resistance property, early mechanical properties and hydration degree of cement, but also can enhance its

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later age mechanical properties, impermeabilities, anti-corrosion and impact resistance property [18–20]. Therefore, it is practically significant for the application of binary system with silica fume and Portland cement in winter construction project.

Compared with curing conditions at room or high temperature, few studies were carried out on hydration microstructure of binding materials at lower temperature, especially on the development of post hydration strength and microstructure of binary binding material system [21]. Therefore, it is important to understand the characteristic of hydration of the binary system with silica fume and Portland cement at lower temperature (especially below 5 °C) from the perspectives of microstructure development and product changes.

The research performed hydration of the binary system at −10 °C, −5 °C, 0 °C and 5 °C. Sodium nitrite was added to make it possible for binding material hydrating at negative temperature [22,23]. Compressive and flexural strength of cement mortar were tested and the content of $Ca(OH)_2$ in hydration product was measured by TG–DSC and heat of hydration and the hydrated rate were measured. In addition, morphology and pore structure of the hydrates were analyzed at microscopic perspective by SEM method and mercury porosimetry.

2. Experimental

2.1. Materials

The cement (CEM II52.5R) used in this study was supplied by Dalian Onoda Ltd. Its physical and mechanical properties and main chemical composition of the cement and silica fume are shown in Tables 1 and 2, respectively. The particle size of silica fume is 1 μm or less and its average particle size is 0.1 μm. The density of the silica fume is 2.216 g cm^{-3}, the specific surface of it is 20000 m^2 kg^{-1}. The tap water, sodium nitrite and standard sand were used in this study.

2.2. Sample preparation

2.2.1. Mix design

Considering extra low temperature will stop cement from hydrating, sodium nitrite, which can lower the freezing point of aqueous solution, was chosen as admixture to prepare low-temperature liquid solution for the hydration of binding materials. In this experiment, the mixing ratio of samples was fixed, the ratio of cement to sand was 1:3 and the addition of silica fume was 0 and 8% (replacement of cement for equal mass), respectively. Mixing amount of sodium nitrite was 8.5% (Mass) while water–cement ratio was 0.42. The sample was labeled as C10−, C5−, C0, C5+, SF10−, SF5−, SF0 and SF5+ according to curing temperature and content of cement and silica fume, respectively. Details are shown in Table 3.

2.2.2. Curing

Fundamental of the experiment is keeping materials and aqueous solution staying at constant low-temperature during mixing, pouring, molding and curing until to designed age. Tests were conducted right after the specimens were taken out of the low-temperature maintaining container.

Raw materials and the prepared solution were kept in the temperature-controllable freezer before mixing. Mixing procedure was conducted for 24 h when all the raw materials were adjusted to the expected temperature. All the prepared specimens were cured at −10 °C, −5 °C, 0 °C and 5 °C in the freezer after they were rectified by Nagao thermometer with accuracy being ±0.1 °C.

2.3. Test procedure

2.3.1. Test methods

In heat of hydration test, the prepared materials were taken out from the freezer and were sealed in thermos bottles of low-temperature hydration heat test instrument immediately. The data of hydration heat was collected at different temperatures of the system.

Compressive and flexural strength tests of the specimens (40 mm × 40 mm × 160 mm) were conducted after curing for 3 days, 7 days and 14 days (GB/T17671-1999 'Test methods of cement mortar strength (ISO)').

After the tests of mechanical properties were carried out new section surface of specimens were pre-treated for SEM (S-4800) observation and mercury test(IV9500) in order to obtain information of their microstructure, and type of hydration product and distribution of pore structure of pastes in each curing age in time. Solid crushes of the pastes were ground to powder, parts of which were treated by vacuum filtration with pump. In the process of filtration, the powder was rinsed by absolute ethanol for times and was dried at 85 °C to constant weight. The powder was conducted simultaneous thermal analysis (TG–DSC) that went through the 250 mesh sieve while the rest was reserved for testing content of chemically bound water. In the process of TGA data collection (STA449-F3 simultaneous thermal analyzer), the sample was put into pre-weighed crucible while the reference substance of the experiment was prepared to be filled. Crucible fitted with the sample was put into the simultaneous thermal analyzer with nitrogen as protective gas and the heating rate was kept at 10 °C/min.

2.3.2. Data processing of $Ca(OH)_2$ content

TG–DSC analysis method, which determines the amount of mass loss basing on endothermic and exothermic of the DSC curve, reflects the proportion of the substance in total mass if the lost substance is single at specific temperature ranges [24,25]. In this experiment, results of the tests of $Ca(OH)_2$ content in the hydration product is shown in Fig. 1.

The dehydration temperature of $Ca(OH)_2$ was between 400 and 550 °C and its composition was single [26–28]. The exothermic peak was observed in Fig. 1. According to the extrapolation method determined by International Association

Table 1
Physical and mechanical properties of the Portland cement.

Type	Fineness (>0.08 mm) %	Stability	Setting time (h:min)		Compressive strength (MPa)		Flexural strength (MPa)	
			Initial	Final	3 days	28 days	3 days	28 days
CEM II 52.5R	3.4	Qualified	2:07	3:15	32.2	58.0	6.0	10.8

Table 2
Chemical composition of the Portland cement and silica fume.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Other	Loss
Portland cement	63.66	21.26	4.50	2.80	1.66	2.58	–	3.54	2.66
Silica fume	1.02	86.62	0.51	1.52	2.77	0.58	2.03	4.95	3.88

Table 3
The mix proportion of samples.

No.	Temperature (°C)	Silica fume + cement (%)	NO.	Temperature (°C)	Silica fume + cement (%)
C5+	5	0 + 100	SF5+	5	8 + 92
C0	0	0 + 100	SF0	0	8 + 92
C5−	−5	0 + 100	SF5−	−5	8 + 92
C10−	−10	0 + 100	SF10−	−10	8 + 92

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