EFFECTS OF THE FINENESS OF DENSIFIED SILICA FUME ON THE HYDRATION OF PORTLAND CEMENT

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Abstract

As one of the mineral admixtures, silica fume (SF) with high pozzolanic reactivity is generally used to improve the properties of concrete. Most commercial silica fume used in concrete project is dry densified silica fume (DSF). It consists of a good deal of agglomerates of sizes ranging from 10 μm to several millimeters. The size of the undispersed silica fume is usually larger than that of the cement particle. At present, the effect of DSF on the hydration of cement is lack of studied.

In this study, the commercial dry DSF is sifted into three sections (>150 μm, 80 ~ 150 μm, 35 ~ 80 μm) by different sieves. The amount of densified silica fume in mixture is 5% by weight of total binder. The used water/binder ratio (w/b) is 0.5. The effect of the fineness of DSF on the setting time of cement paste is firstly discussed. The hydration process of cement incorporated with different fineness of SF is investigated by a semi-adiabatic calorimetric for 3 days at 20 °C and x-ray diffraction (XRD). The obtained results indicate that the setting time of cement paste increases with the decrease of the fineness of DSF. At the w/b ratio of 0.5, the addition of SF has little effect on the hydration period of cement paste. But the hydration rate of cement is decreased with the increase of the size of DSF particles.

Keywords: Densified silica fume, hydration, fineness

1. INTRODUCTION

Silica fume (SF) is a very fine amorphous silica powder produced in electric arc furnaces as a by-product of the manufacture of alloys with silicon or elemental silicon. Normally, SF is considered as a spherical particle. Actually, SF particle is not isolated each other. It is in the form of linked clusters of adjacent spheres[1, 2]. The size of original SF is between 10 nm and 500 nm. The specific surface area of SF is around 20000 m^2/kg, which is 13 to 20 times higher than that of other pozzolanic materials, determined by Nitrogen adsorption. Due to these characteristics, SF has high pozzolanic reactivity. It can rapidly react with calcium hydroxide produced by the hydration of cement.

The use of SF can improve the properties of concrete, such as strength, porosity and extend the service life of concrete structures. It is generally used in producing high-performance

concrete (HPC). In practice, SF is marketed as densified silica fume (DSF), since it is difficult to transport SF due to its extreme fineness and low density. Dry DSF is the aggregation of many linked clusters of adjacent spheres. The size of these aggregation ranges from tens to hundreds microns. That could results in the change of some physical properties of SF, such as particle size, particle size distribution and bulk density.

The silica fume agglomerations are still observed in the cement pastes and concretes mixed with densified silica fume after 1 year of curing[1, 3, 4]. It is found that the core of agglomeration does not take part in hydration. These undispersed agglomerations sometimes can act as extremely reactive alkali-silica reaction (ASR) aggregates[5-8]. Besides, the effects between raw SF and DSF in the paste, mortar and concrete under low water to binder ratio are different[3, 9, 10]. Raw silica fume always can make more contribution to the compressive strength of paste, mortar and concrete than DSF in the case of same replacing level. In concrete, the fineness of SF has little influence on the content of CH at early ages, whereas the CH contents decreases with the increase of the fineness of SF at 90 days. The particle size distribution of silica fume also has influence on the strength of Portland cement paste[11].

In the view of above, the presence of silica fume agglomeration in concrete seems unavoidable under mixing by ordinary commercial concrete mixers. This work tends to evaluate the capacity of hydration of cement paste mixed with different particle size DSF. In this paper, the commercial dry DSF is sifted into three sections (>150 μm, 80 ~ 150 μm, 35 ~ 80 μm) by different sieves. The amount of densified silica fume in mixture is 5% by weight of total binder. The used water/binder ratio (w/b) is 0.5. The effect of the fineness of DSF on the setting time of cement paste is firstly discussed. The hydration process of cement paste incorporated with different fineness of SF is investigated by semi-adiabatic calorimetric for 3 days at 20 ºC and x-ray diffraction (XRD).

2. EXPERIMENTAL PROGRAMME

2.1 Materials

P.I 42.5 Portland cement with a specific surface area of 340 m^2/kg was used in this study. Densified silica fume was a kind of commercial product from Szechwan, China. The DSF was screened into three particle size ranges, which are >150 μm (DSF I), 80~150 μm (DSF II) and 35~80 μm (DSF III). The chemical compositions of raw materials are shown in Table 1 and Table 2 analysed by X-ray Fluorescence (XRF).

Table 1: Chemical compositions of cement, wt/%.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_{eq}	f-CaO	LOI
Cement	22.37	4.36	3.38	61.08	2.43	2.45	0.506	0.86	1.33

Table 2: Chemical compositions of silica fume, wt/%.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	K_2O	Na_2O	LOI
Silica fume	91.53	0.203	0.059	0.218	0.87	0.487	0.436	0.134	5.56

The particle characteristics of DSF are shown in Fig. 1. It can be found that the range of DSF particles size is from a few to hundreds micron range. Each particle is made up of many tens of

nanometers spheres. Its crystalline structure was tested by X-ray diffraction (XRD). From the XRD pattern (Fig. 2), the characteristic diffraction broad peak centered at 23° (2θ) confirms its amorphous nature. The median size d50 of DSF I, DSF II and DSF III was 172 μm, 81.7 μm and 42.8 μm respectively, determined.by laser particle size analyzer (Malvern Masterizer 2000).
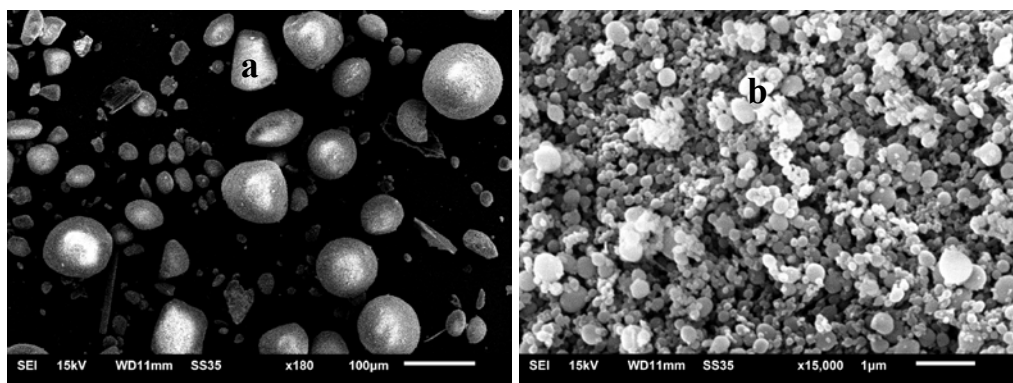
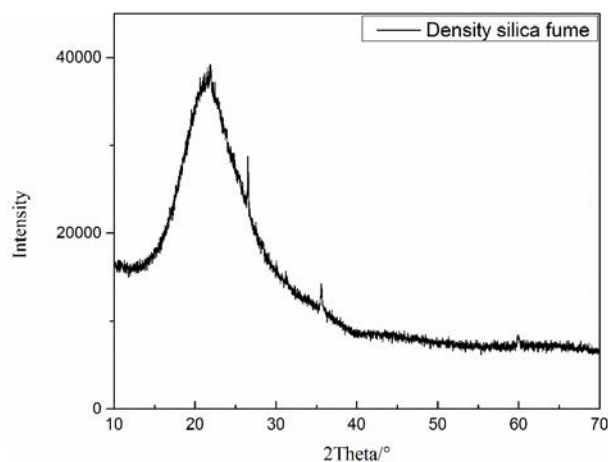**Figure 1: SEM figures of DSF: (a) agglomeration; (b) original SF particle.**

Figure 2: XRD pattern of density silica fume.

2.2 Specimens preparation

The replacement of DSF was 5% by weight of total binder. The water to binder ratio of all mixtures was set as 0.5. All specimens were prepared by overhead stirrers under 800 revolutions per minute, cast in plastic bottles, sealed and cured under 20 ± 1 ℃. At specified time, the sample was soaked in ethanol for 24 h to stop hydration.

2.3 Test methods

The setting time of standard consistency of cement paste was determined according to GB/T1346-2011[12]. The start of hardening of the cement paste after the addition of water to cement is called setting and it is divided into two parts called initial (IST) and final (FST) setting times.

Hydration process of the pastes was measured using an eight-channel isothermal calorimeter (TAM Air; Thermometric AB, Sweden). During the measurement, 4 g of cement and silica fume powder were mixed with 2 g of deionized water for 2 min in a sample vial. Then, the sample vials were loaded into isothermal calorimeter. Heat-flow curves were recorded for 72 h at a constant temperature of 20°C.

For XRD measurement, the specimens were crushed and ground by pestle in a agate mortar, In order to avoid the phase transformation or decomposition, ethanol was poured in the mortar when grinding the hydrated cement pastes. The ground powder was dried at 40 °C for 12 h in oven. XRD analysis was performed by using Rigaku SmartLab 3000A diffractiometer with CuKa radiation. All XRD scans were determined in the 2θ angle between 5 ° and 65 ° at the speed of 5° per minute.

3. RESULT AND DISCUSSION

3.1 The setting times of mixture

Water requirements for standard consistencies of cement paste mixed with DSF are given in Fig. 3(a). It is found that the addition of DSF increases the water requirement regardless of the fineness of DSF. The water requirement increases obviously with the decrease of particle size of DSF.

Variations of initial and final setting times are shown in Fig. 3(b). In the presence of 5 % DSF, two setting times are both increased. And the initial and final setting times increase with decreasing the particle size of DSF. It can be concluded that the addition of DSF retards the setting time of cement. This retarding effect is obvious when the size of DSF is in the range of 35 ~ 80 μm.
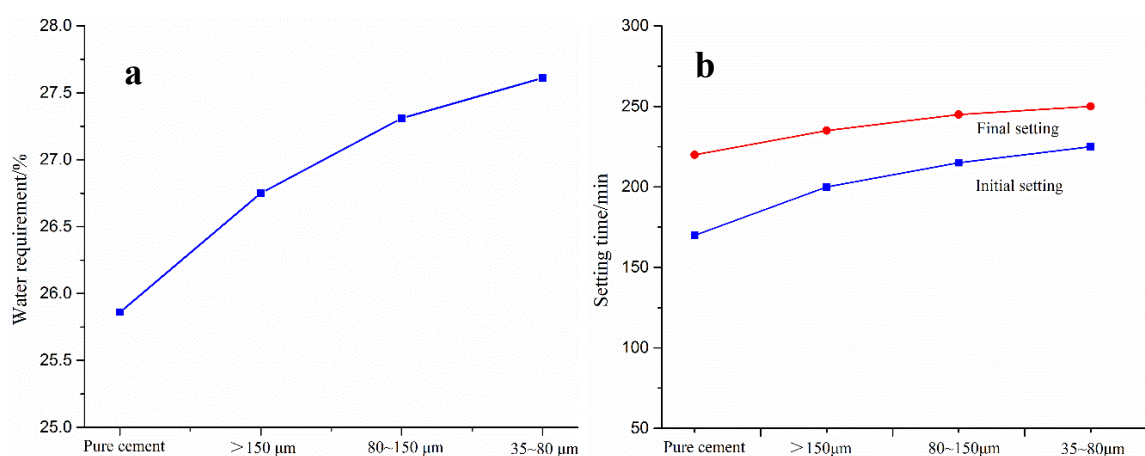

Figure 3: Variation of (a) water requirement and (b) setting time

3.2 Heat evolution

The Isothermal calorimetry data of cement paste are shown in Fig. 4. Four groups (Blank, >150 μm, 80~150 μm, 35~80 μm) are considered.

The hydration process of cement paste can be divided into five stages: the initial reaction period, the induction period, the acceleration period, the deceleration period, and the stable reaction period. As shown in figure 4(a), the addition of DSF does not change the induction process obviously. Due to its large particle, DSF can not provide extra nucleation site to cement

hydration. At early hydration state, DSF does not significantly change the hydration of cement. These experimental results are different from the results of some references because the DSF used are dispersed well by ultrasonic treatment [13,14]. Furthermore, it is clear that the rate of cement hydration tends to decrease when the particle size of DSF increases.

The cumulative heat curves corresponding to the heat flow curves are shown in Figure 4(b). The total hydration heat of blank simple is higher than the samples mixed with DSF. In 72 h, it seems that finer DSF generates more hydration heat.
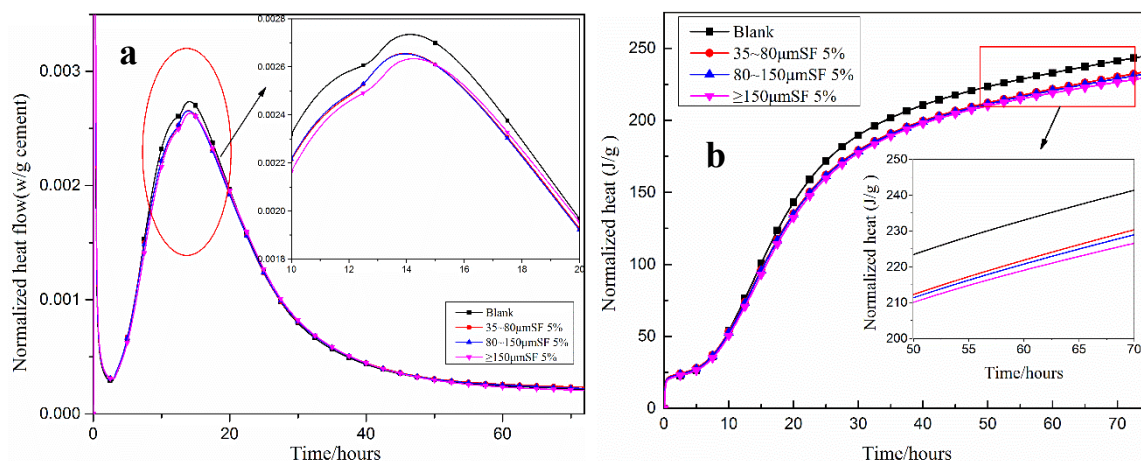

Figure 4: Isothermal calorimetry data of cement paste. (a: heat flow curves; b: cumulative heat curves.)

3.3 X-ray diffraction analyses

X-ray diffraction analysis was conducted to qualitatively investigate the effects of particle size of DSF on the mineralogical composition of cement paste. The experimental results are illustrated in Fig. 5.

Some main phases, such as ettringite, calcium hydroxide (CH), tricalcium silicate (C_3S) and dicalcium silicate (C_2S) are found in all mixtures. That indicates the addition of different sizes of DSF can not change the hydration products during the hydration of cement. However, differences in the intensity of individual peak are observed. For the hydration product, viz. CH, the intensity of characteristic peak ($2\theta = 18°$) [15-18] increases with the decrease of the particle size of DSF at 15 h. It is clear that the presence of DSF promotes the formation of CH. At this period, it seems that the pozzolanic activity of DSF is not dominant.
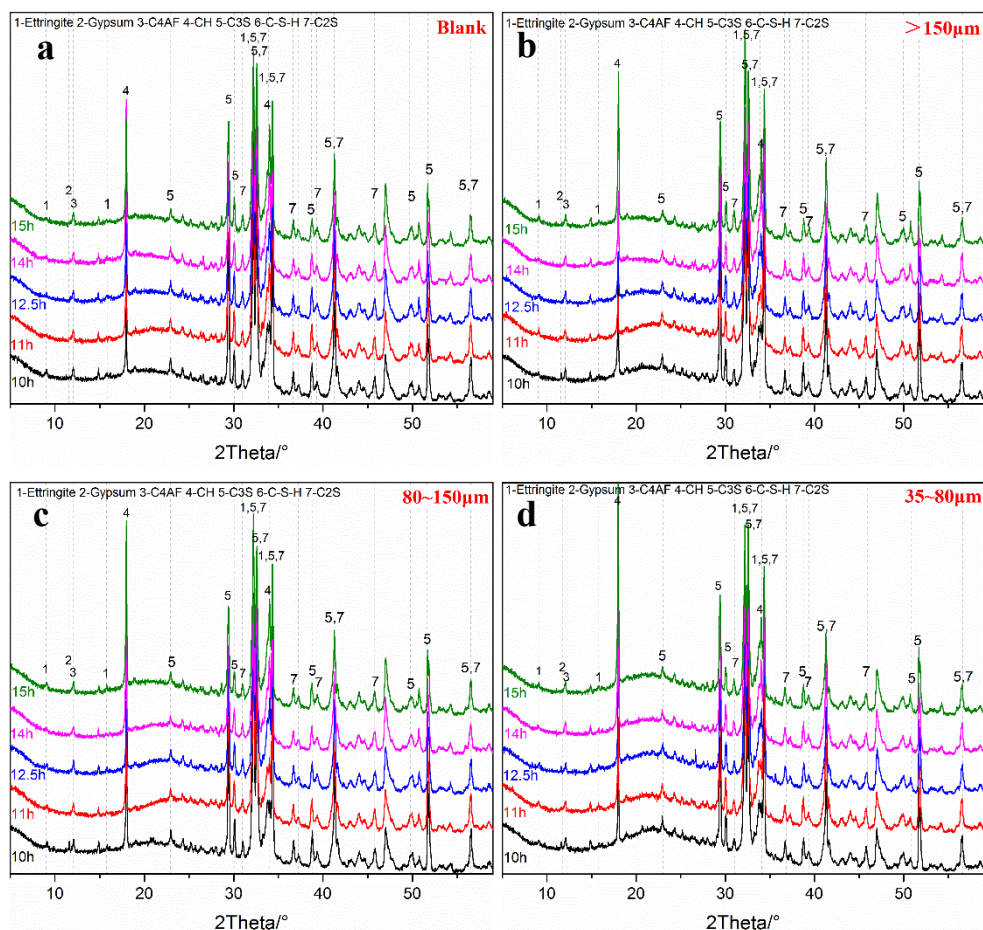
Figure 5: XRD patterns of hydrated cement pastes at different curing ages: (a) Blank cement; (b) ＞150 µm; (c) 80~150 µm; (d) 35~80 µm.

4. CONCLUSIONS

− The addition of DSF increases the setting time of cement. The particle size of DSF smaller, the retarding effect is more significant.

− The fineness of DSF affects the formation of CH during the hydration of cement. More hydration product, CH is generated in the samples mixed with the DSF III (35~80 µm). Meanwhile, in 15 hours, it seems that the pozzolanic activity of DSF is not dominant.

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