Effect of Particle Size Change on the Hydration Behaviour of Calcium Aluminate Cements

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In this work, the effect of particle size change on the hydration behaviour of a commercial calcium aluminate cement (CAC) after grinding for different times was studied. The hydration heat curves of the cements with and without milling were tested through the semi-adiabatic method, and the setting time was measured by Vicat apparatus. The vacuum freeze drying method was utilized to terminate the cement hydration at the designated time, and X-ray diffraction was conducted to analyse the phase composition of the hydrated products.

1 Introduction

Calcium aluminate cement (CAC) is a hydraulic binder widely used in refractory castables [1, 2] as CAC can endow castables with sufficient demoulding strength within 24 h [2]. It is known that the working and demoulding times of castables are closely related to the hydration process of calcium aluminate cement [3, 4] and the hydration behaviour of CAC is influenced by phase compositions, curing temperatures, additives, and particle sizes of CAC.

As mentioned above, the particle size of cement influences the hydration behaviour of cement [5], and consequently affects the setting and hardening processes of castables [6]. It was reported that monocalcium aluminate (CA) powder had an extended dormant period and a higher hydration degree after hydration for 10 h when the particle size of CA was decreased [7]. It was also observed that calcium aluminate cements with decreased particle sizes have shorter initial and final setting times [8]. It is seen from the above reports that the influence of particle size on the hydration rate of CAC shows varied results.

In this work, a commercial calcium aluminate cement was ground to obtain cement samples with different particle sizes. The hydration behavior of the cement pastes and mortars were determined by exothermic reaction and setting times. Moreover, the cement pastes with hydration halted by vacuum freeze drying method after curing for the designated times were analysed by XRD.

2 Experimental procedure

A commercial calcium aluminate cement was used in this work. The chemical composition and mineralogical composition of the cement are listed in Tab. 1 and Tab. 2 respectively.

A laboratory mill, 500 mm in length and 500 mm in diameter, was used to grind the cement. A combination of 100 kg cylindrical steel rods and spherical steel balls was used as the grinding media. For each batch, 5 kg of the commercial cement was fed into the mill so that the cement-to-grinding media ratio was 1 : 20. And the rotational speed of the mill was set at 48 rpm. The cement was dry ground for one hour and two hours respectively.

The particle size distributions of the cements without grinding (Z–0 h) and with grinding for 1 h (Z–1 h) and 2 h (Z–2 h) were measured using a laser granulometry. The specific surface areas of the cement before and after grinding were determined by the Blaine method.

The hydration heat curves of cement pastes and mortars were detected by a semi-adiabatic method at 20 °C. The cement paste was prepared with a water/cement ratio of 0,3. The temperature caused by the exothermic heat as a function of time was recorded by a T-type thermocouple

Tab. 1 Chemical composition of cement

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O
Content [mass-%]	0,06	73,97	0,3	24,91	0,35	0,12	0,04	0,25

Tab. 2 Mineralogical composition of cement

Component	CA	CA_2	$C_{12}A_7$	C_4AS	C_2AS	α-Al_2O_3	β-Al_2O_3
Content [mass-%]	57,76	16,15	0,16	0,18	0,8	23,83	1,13

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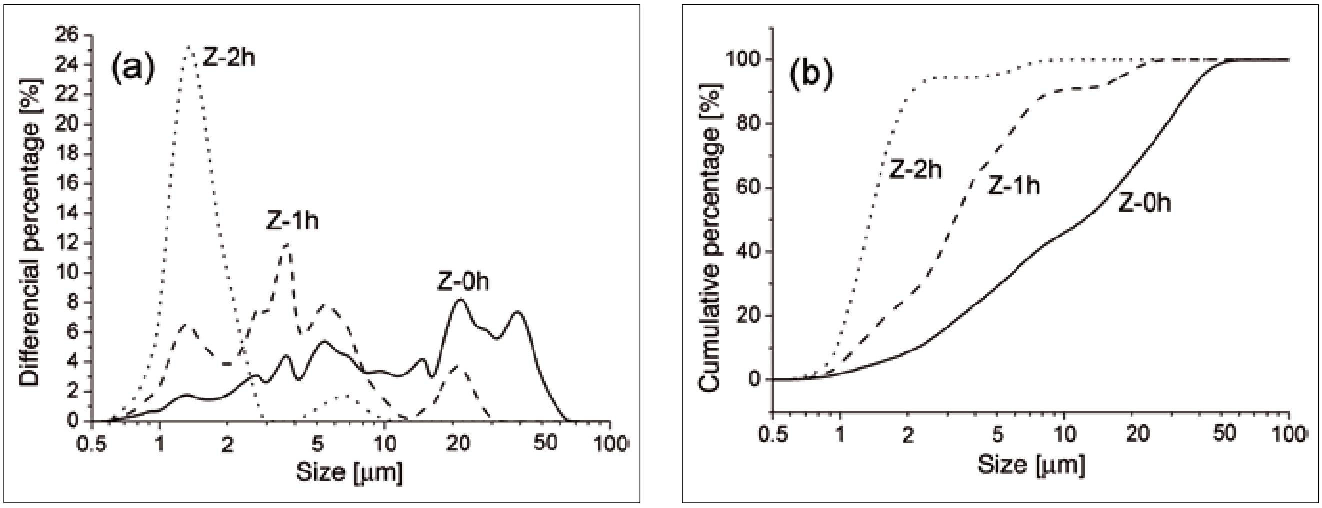

Fig. 1 Differential distribution (a) and cumulative distribution (b) of the cements after grinding for 0 h, 1 h and 2 h

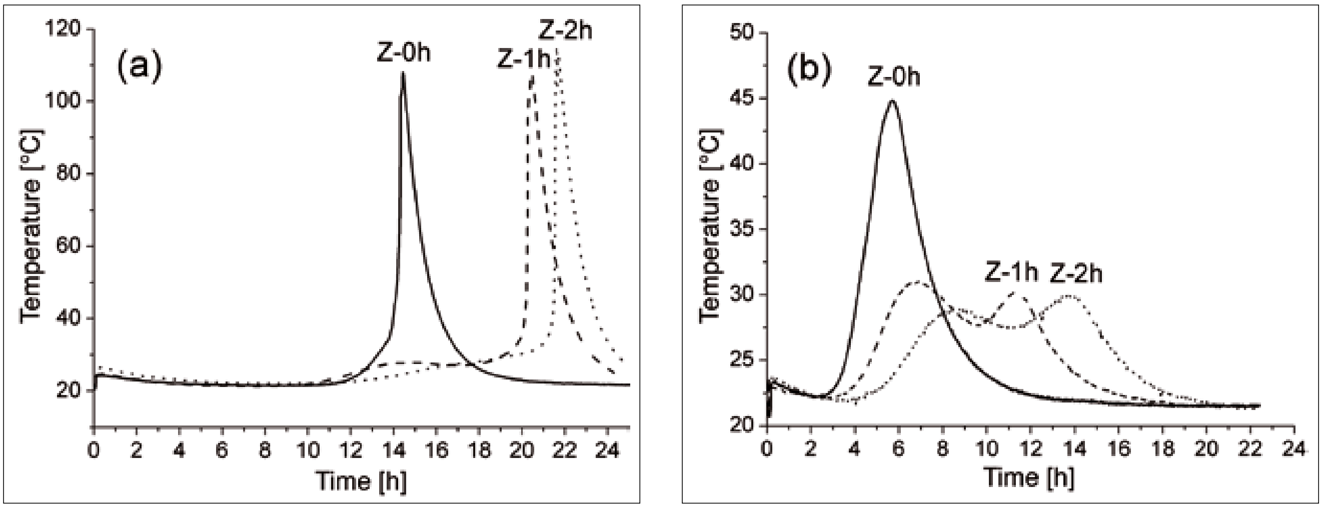

Fig. 2 Hydration heat curves at 20 °C of cement paste (a) and mortar (b)

immersed into the paste, and this thermocouple was connected to a data capture system which can store the data of temperature and time. Similarly, the mortar was prepared with a cement/sand ratio of 0,33 and a water/cement ratio of 0,5 and the exothermic heat evolution of the mortar at 20 °C was measured in the same way as described above. Meanwhile, the setting times of cement mortars were determined by Vicat apparatus based on European standard at 20 °C.

The as-prepared cement pastes after curing for a certain time at 20 °C were frozen for 1~2 h at –40 °C to halt the hydration of the cement pastes. The frozen pastes were immediately dried in a vacuum box at 20 °C. Then XRD was used to determine the phase composition of the cement pastes.

3 Results and discussion

Fig. 1a–b show the particle size distributions of the cements after grinding for 0 h, 1 h and 2 h. It is seen from Fig. 1a that the cement without grinding (Z–0 h) has the largest particle size of about 65 µm and the peaks of coarse particle size range (20–50 µm) are high. For the cement after grinding for 1 h (Z–1 h), the largest particle size is reduced to about 30 µm, and the particle fraction of smaller than 8 µm, especially the particle fraction of 3–4 µm, is increased at the expense of the coarse particles in the range of 30–50 µm.

And for the cement after grinding for 2 h (Z–2 h), the largest particle size is dropped to about 10 µm, and the peak of fine particle size range (1–2 µm) is very high, while the particle fraction of 5–10 µm is decreased.

It is seen from Fig. 1b that the particle fraction of larger than 30 µm is 20 % for the cement without grinding (Z–0 h). In comparison, there is not the particle fraction of larger than 30 µm for the cements after grinding for 1 h (Z–1 h) and 2 h (Z–2 h). The particle fraction of larger than 10 µm accounts for 55 % for the cement without grinding (Z–0 h), 10 % for the cement after grinding for 1 h (Z–1 h), while the particle fraction of larger than 10 µm is 0 for the cement after grinding for 2 h (Z–2 h). Meanwhile, the particle fraction of smaller than 3 µm is 16 % for the cement without grinding (Z–0 h), 45 % for the cement after grinding for 1 h (Z–1 h) and 94 % for the cement after grinding for 2 h (Z–2 h).

In addition, the median particle sizes (D_{50}) of the cement samples are 12,39 µm for sample Z–0 h, 3,22 µm for sample

Z–1 h and 1,36 µm for sample Z–2 h, and specific surface areas (SSA) of the cement samples are 446 m^2/kg for sample Z–0 h, 544 m^2/kg for sample Z–1 h and 552 m^2/kg for sample Z–2 h. Therefore, the above results indicate that the particle size of the cement is considerably reduced with the grinding time.

The hydration heat curves of cement pastes after grinding for 0 h, 1 h and 2 h are shown in Fig. 2a. It is seen from the figure that the peak temperature of the sample without grinding (Z–0 h) appears after hydration for 14,4 h. In comparison, the peak temperatures of the samples after grinding for 1 h (Z–1 h) and 2 h (Z–2 h) appear after hydration for about 20,5 h and about 21,5 h respectively. It is also seen from the figure that the sample without grinding (Z–0 h) has a dormant period of about 11 h, while the samples after grinding for 1 h (Z–1 h) and 2 h (Z–2 h) have a dormant period of 19 h. The above results show that the peak time is retarded and the dormant period is extended with the increasing grinding time, demonstrating that the hydration rate of the cement paste decreases with the reduced particle size of the cement.

Fig. 2b shows the hydration heat curves of cement mortars containing the cements after grinding for 0 h, 1 h and 2 h. It is seen from the figure that the peak temperature of the sample without grinding (Z–0 h) arises after 5,7 h of hydration time. In contrast, the peak temperatures of the samples after grinding for 1 h (Z–1 h) and 2 h (Z–2 h) appear after 11 h and 13,8 h of hydration time respectively. Similar to the hydration heat curves of cement pastes (Fig. 2a), the peak time for mortar is delayed with the increasing grinding time, illustrating that the hydration rate of the cement mortar is reduced with the decreasing particle size of the cement.

The setting times of cement mortars containing the cements after grinding for 0 h, 1 h and 2 h are shown in Fig. 3. Both the initial and final setting times of the sample Z–0 h are shorter than those of the sample Z–1 h, and the initial and final setting times of the sample Z–1 h are shorter than those of the sample Z–2 h. The setting times are prolonged with the increasing grinding time, which is in agreement with the hydration heat curves (Fig. 2b). The setting times of cement mortars also confirm that the hydration rate of the cement mortar decreases with the diminishing particle size.

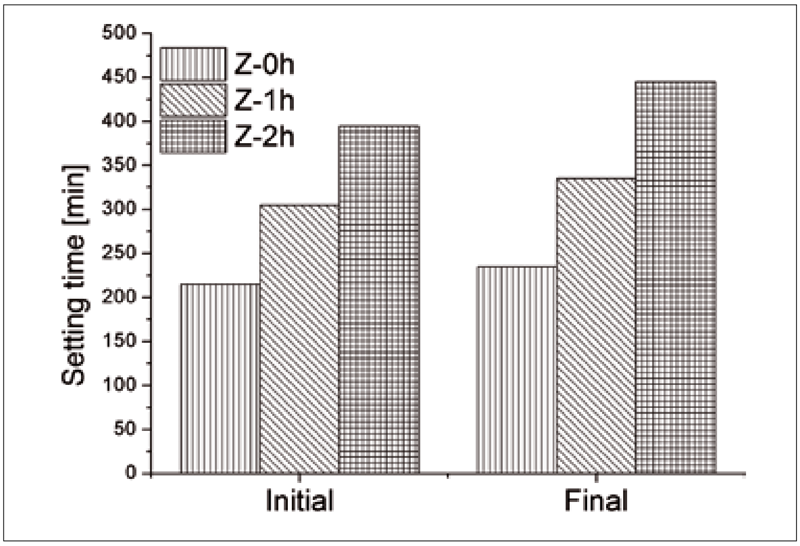

Fig. 3 Setting times of the cement mortars at 20 °C

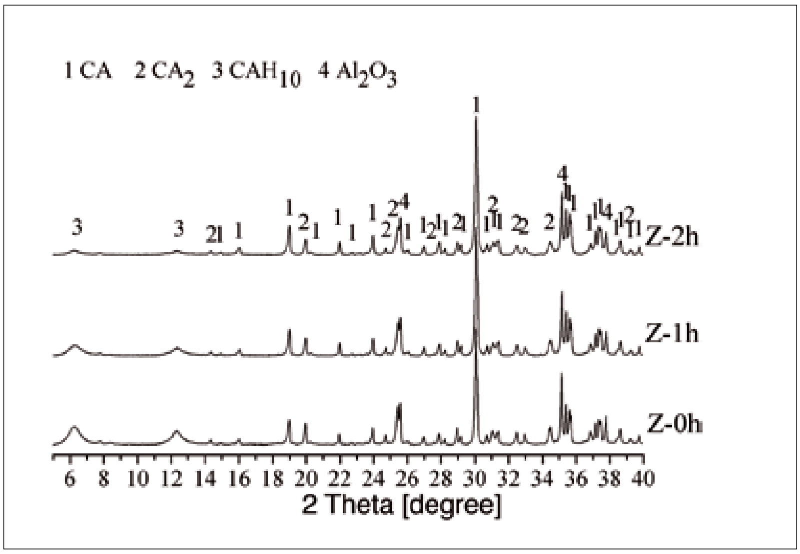

Fig. 4 XRD patterns of the cement pastes prepared for 18 h at 20 °C

Fig. 4 shows the XRD patterns of the cement pastes containing the cements after grinding for 0 h, 1 h and 2 h and after curing at 20 °C for 18 h. CAH_{10} is the only hydration phase identified in all the samples and the CAH_{10} peaks of the Z–0 h paste are the highest and those of the Z–1 h and Z–2 h are lower with the prolonging grinding time of the cement, indicating again that the hydration rate of the cement paste decreases with the reducing particle size of the cement.

4 Conclusions

The particle size of the cement is considerably reduced with the grinding time of 1 h and 2 h. The peak times and dormant periods of the cement pastes and mortars during curing are extended, the setting times of the cement mortars are prolonged and the amount of hydrated products of the cement pastes after curing for the same time is reduced with the decreasing cement particle size, indicating that the hydration rate of cement is decreased with the decreasing cement particle size.

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