THE INFLUENCE OF MICROSILICA ON THE HYDRATION OF CALCIUM ALUMINATE CEMENT

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ABSTRACT

Different sources of microsilica in China have varied compositions and properties, which could influence the setting behavior of calcium aluminate cements (CAC)-containing castables. The influence of microsilica from the four sources on the hydration of CAC was investigated in this work. The exothermic temperature development of cement pastes was monitored by semi-adiabatic method. The hydration process of cement pastes was halted by a freeze vacuum drying method to examine the evolution of phase composition and microstructure of hydrates with XRD and SEM, respectively. The experimental results show that the addition of microsilica can obviously promote the hydration process of CAC.

INTRODUCTION

Calcium aluminate cement (CAC) is widely used as a hydraulic binder in refractory castables[1,2], and the speed of cement hydration influences the working time and demolding time of castables[3,4]. There are many researches[5-9] about the effect of microsilica on the properties and performance of CAC bonded castables, but there are no comparison study on the effect of different sources of microsilica on the hydration rate of CAC because different sources of microsilica in China have varied compositions and properties. Therefore, four sources of microsilica from different by-products with varied chemical compositions and pH values are chosen. This work is to study the influence of different sources and amounts of microsilica with varied pH value and impurity content on the hydration rate of CAC.

EXPERIMENTAL PROCEDURE

A commercial CAC was used in this work. The major chemical composition and mineralogical composition of the cement are listed in Tab. 1.

Tab. 1 Chemical composition (wt.%) and mineral composition of CAC .

Chemical composition	wt%	Phase composition	wt%
Al_2O_3	69.63	CA	59.06
CaO	29.68	CA_2	35.95
SiO_2	0.22	$C_{12}A_7$	0.3
K_2O+Na_2O	0.26	α-Al_2O_3	1.79

Four sources of microsilica, supplied from different manufacturers, were used in the experiment, denoted as A, B, C, D, respectively. Tab. 2 shows the chemical compositions and pH values of the microsilica. Microsilica A is the by-product of desilicated zirconia, B is that of ferroalloy, and C and D are those of silicon metal.

The mixtures of different ratios of CAC and microsilica according to Tab. 3 were prepared. A water/solid phase ratio of 0.33 was used for all of the experiments. The hydration behavior of these four mixtures was characterized by measuring the heat evolution by the semi-adiabatic method with pure CAC as the reference.

Tab. 2 Chemical compositions and pH values of microsilica

Chemical composition	A (wt%)	B (wt%)	C (wt%)	D (wt%)
SiO_2	98.93	98.14	97.24	97.73
Al_2O_3	0.00	0.03	0.00	0.23
Fe_2O_3	0.28	0.18	0.02	0.12
CaO	0.05	0.18	0.27	0.97
MgO	0.00	0.82	0.19	0.00
K_2O+Na_2O	0.19	0.35	1.90	0.72
$P_2O_5+SO_3$	0.50	0.27	0.33	0.20
Loss	1.17	4.38	5.08	3.40
pH value	2.77	7.86	6.91	8.68

The as-prepared pastes of cement and microsilica mixtures after curing for a predetermined time at 20°C were frozen at -40°C to halt the hydration of the cement pastes. The frozen pastes were immediately dried in a vacuum box at 20°C. The phase compositions and morphology of the dried cement pastes were characterized by XRD (Panalytical Xpert, Holland) and SEM (Zeiss-FESEM Merlin Compact, Germany), respectively.

Tab.3 The formulation of themixtures

Material	Composition（wt%）	
CAC	50	66.67
Microsilica	50	33.33
Water	33	33

RESULTS AND DISCUSSION

As can be seen from Table 2, the four sources of microsilica have different pH values, which are possibly related to different levels of impurities. The microsilica (A) with lower contents of alkaline oxides (K_2O+Na_2O) and higher contents of the acid oxides ($P_2O_5+SO_3$) have a lower pH value of 2.77[9]. In comparison, the other three sources of microsilica (B-D) have higher contents of alkaline oxides (K_2O+Na_2O) and lower contents of the acid oxides ($P_2O_5+SO_3$), and consequently have higher pH values of about 7 or above.

It is seen from Fig. 1 that, the particle size distribution (PSD) of sample A is wide (50nm-300nm in diameter), and only a few particles are over 500nm. The PSD of sample B is concentrated at around 100nm, and most of the particles are aggregated together. The PSD of C is centralizer (50nm-400nm) than sample A, and most of the particles are standard spherical. The PSD range of spherical sample D is narrow (50nm-250 nm). These results showed that the morphology and PSD of microsilica from varied sources are different.

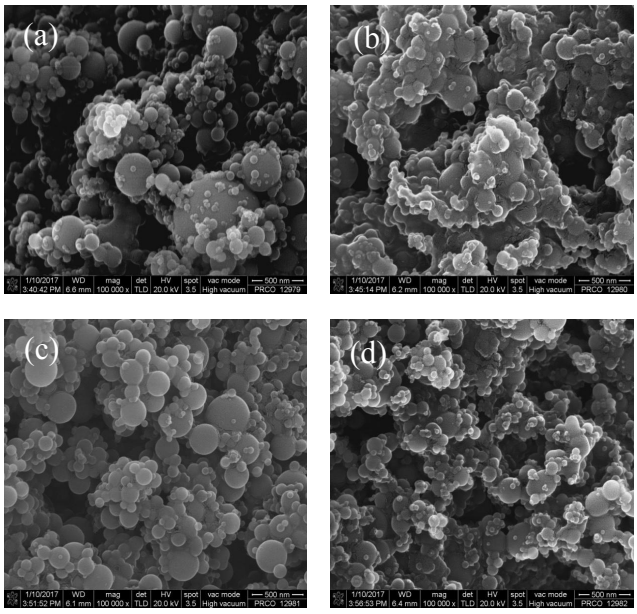

Fig. 1: Morphology of microsilica A, B, C and D.

Figure 2 shows the hydration heat curves of the pastes of CAC and mixtures. It can be seen from Fig. 2a that the peak temperature of the paste of CAC appears after hydration for about 12.72h. In comparison, the peak temperatures of the mixtures of CAC with 33.33% microsilica A, B, C and D appear after hydration for about 4.34h, 3.19h, 3.68h and 2.40h, respectively. These results show that the hydration rate of the cement paste increases with the addition of microsilica. As seen in Table 2, the pH value of these four microsilicas is 2.77, 7.86, 6.91 and 8.68, respectively. The above results show that the hydration rate of the cement paste increases with the addition of microsilica, and the microsilica with the higher pH valuehas a more pronounced promoting effect on the hydration rate of the cement.

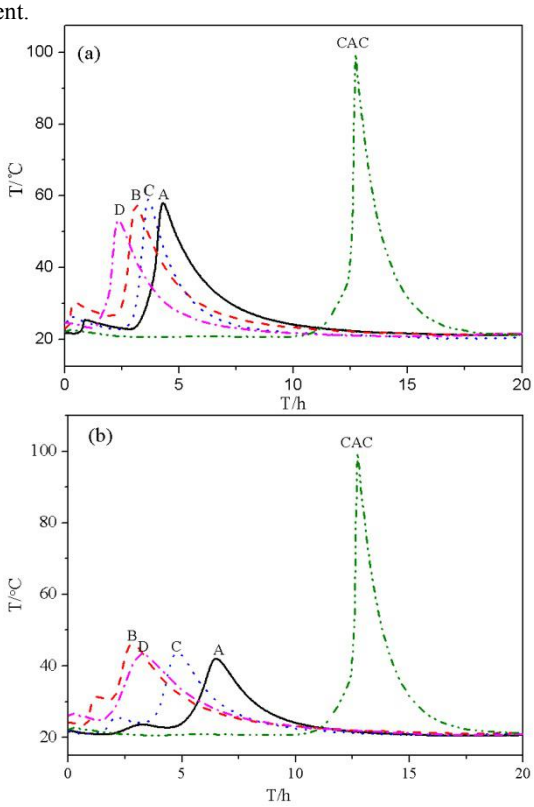

Fig. 2: CAC hydration curve with different types and different amounts of microsilica (a:33.33%; b: 50%).

As shown in Fig. 2b that the peak temperatures of the mixtures of CAC with 50% microsilica A, B, C and D appear after hydration for about6.49h, 2.78h, 4.79h and 3.34h, respectively. These observations also indicate the hydration rate of the cement is accelerated by the addition of and the microsilica with a higher pH value has a more pronounced promoting effect on the hydration rate of the cement.

Figure 3 shows the XRD patterns of CAC with 50% microsilica i n different curing time at 20°C. From Fig.3a, it can be seen that the crystalline phases are CAH_{10} in all the pastes of mixtures with microsilica. Moreover, the peaks of C_2AH_8 appeared in mixtures with microsilica B, C and D, but the peak height of C_2AH_8 in samples B and D was higher than that in sample C. These results indicate that all samples except pure CAC have begun to hydrate, while hydration rate of mixture with microsilica B (7.86) and D (8.68) is faster than microsilica C (6.91), and hydration rate of mixture with microsilica A (2.77) is the slowest. The above results demonstrated again that the hydration rate of the cement paste increases with the addition of 50% microsilica, and microsilica with a higher pH value has a more pronounced promoting effect on the hydration rate of the cement.

As shown in Fig.3b,the crystalline phases are C_2AH_8 and CAH_{10} in all the samples containing microsilica after curing 20°C for 10h. However, the peaks of C_2AH_8 do not exist in the CAC paste. These results also indicate that the hydration rate of the cement paste increases with addition of the four microsilicas.

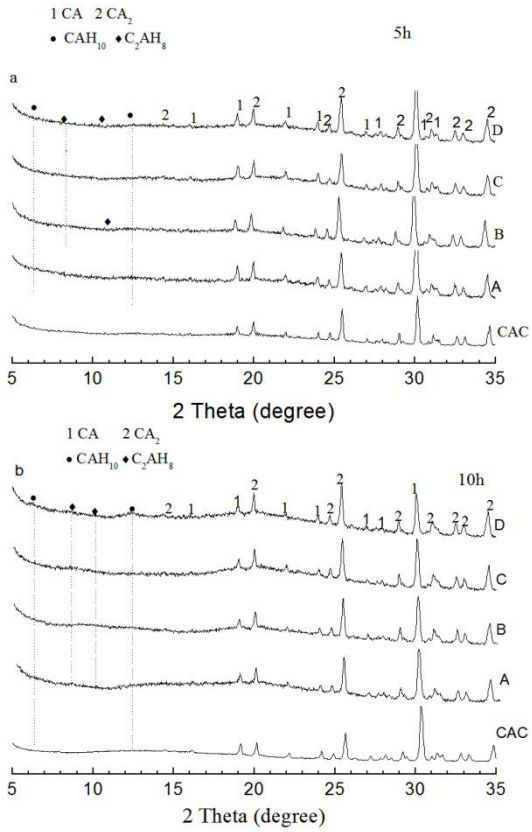

Fig. 3: XRD patterns of cement with different quality of 50% microsilica at different curing time (a: 5h and b: 10h).

The microstructure of CAC with and without 50% microsilica after hydration for 5h at 20 °C is shown in Figure 4. It is seen in Figs. 4a-4d that the fibrous hydration products were formed on the CAC and microsilica particles. These fibrous hydration products should be CAH_{10} according to the phase composition from Fig. 3. As seen in Figs. 4b-4d, the plate-like hydration products C_2AH_8 are found on the CAC particles in the cement pastes. Moreover, the crystal size of C_2AH_8 in Figs. 4b and 4d is larger than that in Fig. 4c. These results further proved that the

microsilica promoted the hydration rate of the cement, and the microsilica with the higher pH value has a more pronounced promoting effect on the hydration rate of the cement.

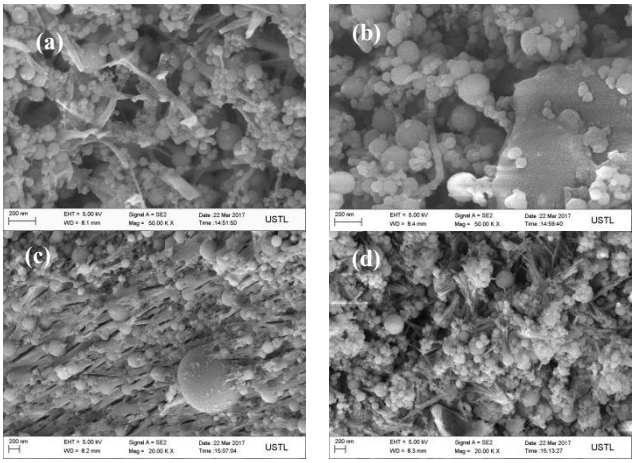

Fig.4: SEM of pastes of CAC with 50 % different microsilica (a: A; b: B; c: C; d: D) after curing 5h at 20 °C.

CONCLUSION

The hydration rate of CAC is accelerated by incorporation of microsilica, and the microsilica with a higher pH value leads to a more pronounced accelerating effect on the hydration rate of the CAC.

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