INFLUENCE OF ALUMINA POWDERS ON THE HYDRATION BEHAVIOR OF COMMERCIAL CALCIA LUMINATE CEMENT AT ROOM TEMPERATURE

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ABSTRACT

In this paper, the influence of different alumina powders on the hydration behavior of different calcium aluminate cements was studied at room temperature. The hydration behavior of these calcium aluminate/alumina mixtures was evaluated by measuring the exothermic temperature development of pastes and by determining the setting time of mortars using the Vicat needle. Moreover, X-ray diffraction was used to identify the phases of the hydrates after halting hydration by vacuum freeze drying at the designated curing times. The results reveal that additions of different alumina powders have different effect on the hydration behavior of different commercial calcium aluminate cements.

INTRODUCTION

Calcium aluminate cement (CAC) is widely used as a hydraul- ic binder in refractory castables,\(^{[1,2]}\) and the speed of cement hydration influences the working time and demolding time of castables.\(^{[3,4]}\) As castables usually contain alumina powders for higher performance in application,\(^{[5]}\) recently several investigations have been done concerning the effect of alumina powders on the hydration rate of pure CA and CA/CA, mixtures\(^{[6-8]}\). It has been found that the alumina powders with higher specific surface areas lead to more pronounced shortening of the induction period and the Na\(_2\)O content plays an additional role. But little information exists regarding the influence of alumina powders on commercial calcium aluminate cement. Therefore, in this work, the effect of different alumina powders on the hydration behavior of different commercial calcium aluminate cements was investigated.

EXPERIMENTAL PROCEDURE

Two kinds of commercial CACs (CA 70 and Secar 71) containing 70 wt.% Al\(_2\)O\(_3\) were used. The chemical composition and mineralogical composition of the cements are listed in Table 1 and Table 2 respectively. Two alumina powders (A1, A2) with different specific surface areas and nearly the same Na\(_2\)O content were selected and the characterization of the alumina powders are shown in Table 3. The four mixtures (CA 70/A1, CA 70/A2, Secar 71/A1 and Secar 71/A2) with a CAC/alumina ratio of 60/40 were prepared and the hydration and setting behavior of these mixtures were investigated, with calcium aluminate cement as the reference.

RESULTS AND DISCUSSION

The neat pastes of CA 70 and the CA 70-containing mixtures were prepared with a water/solid ratio of 0.37, and the neat pastes of Secar 71 and the Secar 71-containing mixtures were prepared with a water/solid ratio of 0.30. The cement mortars were prepared with a cement/sand ratio of 0.33 and a water/cement ratio of 0.5 and the mixture mortars were prepared with a mixture/ sand ratio of 0.33 and a water/mixtures ratio of 0.5. The hydration behavior of the CACs and these four mixtures were characterized by measuring the heat evolution in dependence with time by the semi-adiabatic method, and the setting times of mortars were determined using the Vicat needle. The vacuum freeze drying method was utilized to terminate the cement hydration at the designated curing times, and X-ray diffraction (XRD; D4, Bruker, Germany) was conducted to identify the phase composition of the hydrated products.

![Figure 1: Hydration heat curves of the CA 70 paste in presence of alumina.](image)

Table 1: Chemical composition of cement (wt.%).

<table>
<thead>
<tr>
<th></th>
<th>Al(_2)O(_3)</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>Fe(_2)O(_3)</th>
<th>MgO</th>
<th>TiO(_2)</th>
<th>Na(_2)O+K(_2)O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secar 71</td>
<td>69.63</td>
<td>29.68</td>
<td>0.22</td>
<td>0.15</td>
<td>0.22</td>
<td>0.03</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>CA 70</td>
<td>69.37</td>
<td>28.81</td>
<td>0.47</td>
<td>0.39</td>
<td>0.43</td>
<td>0.17</td>
<td>0.29</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 2: Mineralogical composition of cement (wt.%).

<table>
<thead>
<tr>
<th></th>
<th>CA</th>
<th>CA(_2)</th>
<th>C(_2)A</th>
<th>C(_2)AS</th>
<th>C(_2)AS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secar 71</td>
<td>59.06</td>
<td>35.95</td>
<td>0.3</td>
<td>0.46</td>
<td>0.69</td>
</tr>
<tr>
<td>CA 70</td>
<td>51.03</td>
<td>41.61</td>
<td>0.1</td>
<td>1.13</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Table 3: Characterization of the alumina powders.

<table>
<thead>
<tr>
<th>alumina powder</th>
<th>S.S.A (m(^2)/g)</th>
<th>Na(_2)O content (%)</th>
<th>Grain size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>D(_{10}) (µm)</td>
</tr>
<tr>
<td>A1</td>
<td>7.48</td>
<td>0.1</td>
<td>0.47</td>
</tr>
<tr>
<td>A2</td>
<td>1.78</td>
<td>0.1</td>
<td>1.62</td>
</tr>
</tbody>
</table>

The hydration heat curves of the pastes of CA 70 and the CA 70-containing mixtures were investigated, with calcium aluminate cement as the reference.
ever, the addition of A1 with a higher specific surface area retards the hydration rate of the cement paste far more significantly than the addition of A2. So the higher specific surface area of the alumina in the mixes leads to a more pronounced lengthening of the induction period.

It is also seen from Fig. 1 that the peak temperature of the paste of CA 70 appears after hydration for about 2.3h. In comparison, the peak temperatures of the samples of the CA 70/A1 and CA 70/A2 mixtures appear after hydration for about 3.8h and about 3.0h respectively. So the hydration rate of the cement CA 70 is hindered by the addition of alumina powder, and the alumina powder with the higher specific surface area has a more pronounced retarding effect on the hydration rate of the cement.

As proposed in the literature\cite{6-8}, the alumina powder with higher specific surface areas leads to more pronounced shortening of the induction period and accelerates the hydration rate of pure CA and CA/CA\textsubscript{2} mixtures. However, it is found in this work that the addition of alumina powder hinders the hydration of the CA 70 paste.

As shown in Fig. 2, the CA 70 mortar has an initial setting time of about 130min and a final setting time of about 145min. In comparison, the CA 70/A1 mortar has an initial setting time of about 155min, a final setting time of about 185min and CA 70/A2 mortar has an initial setting time of about 160min, and a final setting time of about 180min. So both the initial and final setting times are extended with the addition of the alumina powders, confirming that the hydration behavior of calcium aluminate cement CA 70 is hindered by the adding of the alumina.

As shown in Fig. 3, the crystalline phases are CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} in all the samples containing CA 70 after curing 20\degree C for 6h. However, the peaks of CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} in the CA 70/A1 and CA 70/A2 samples are lower than those in the CA 70 paste, demonstrating again that the hydration rate of the cement paste decreases with the addition of Al\textsubscript{2}O\textsubscript{3} powders.

As shown in Fig. 4, the exothermic heat evolution of the pastes of Secar 71 and the mixtures as a function of time is given in Fig. 4. In comparison with the Secar 71 paste, the length of the induction period of the samples is noticeably shortened by the addition of alumina powders. As proposed in the literature\cite{6}, the acceleration is caused by a preferential nucleation of the hydration products on the surface of alumina particles. Therefore, the alumina powders with a higher specific surface area should lead to a more shortening of the induction period. However, it is interesting to note that no significant differences exist between the hydration rates of Secar 71/A1 and Secar 71/A2 pastes, although there is big difference between the two alumina powders in specific surface area.

It is also seen from Fig. 4 that the peak temperature of the sample of Secar 71 paste appears after hydration for about 13.2h. In contrast, the peak temperatures of the samples of the Secar 71/A1 and Secar 71/A2 mixtures occur after hydration for about 8.2h and about 8.5h respectively. So alumina powders accelerate the hydration rate of the Secar 71.

It is seen in Fig. 5 that the Secar 71 mortar has an initial setting time of about 160min and a final setting time of about 180min. In comparison, Secar 71/A1 mortar has an initial setting time of about 135min, a final setting time of about 150min and Secar 71/A2 mortar has an initial setting time of about 145min and a final setting time of about 160min. Both the initial and final setting times of the Secar 71 mortar are shorter than the mixtures Secar 71/A1 and Secar 71/A2, demonstrating that the hydration rate of the cement mortar increases with addition of the two alumina powders.
As seen in Fig. 6, CAH$_{10}$, C$_2$AH$_8$ and C$_3$AH$_6$ are detected in all the samples containing Secar 71 after curing 20°C for 24h. Nevertheless, the peaks of CAH$_{10}$, C$_2$AH$_8$ and C$_3$AH$_6$ of the Secar 71/A1 and Secar 71/A2 are higher than those of the Secar 71 paste samples, further confirming that the hydration rate of the cement paste increases with the addition of the Al$_2$O$_3$ powders.

CONCLUSIONS

The hydration rate of the cement CA 70 is hindered by the addition of alumina powders, and the alumina powder with the higher specific surface area leads to a more pronounced retarding effect on the hydration rate of the cement. On the other hand, the hydration rate of the cement Secar71 is remarkably accelerated through the incorporation of alumina powders, and the specific surface area shows little effect on hydration rate of the cement pastes and the setting time of the cement mortars.

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REFERENCES


