Effect of colloidal nano-silica on the hydration of Ultra-High Performance Concrete (UHPC)

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Abstract:
This paper presents the effect of colloidal nano-silica on the hydration of Ultra-High Performance Concrete (UHPC). Results reveal that because a high amount of superplasticizer is utilized to produce UHPC in this study, the induction and acceleration period of the cement hydration are significantly retarded. However, due to the nucleation effect of nano-silica, a number of C-S-H seeds can be generated on the nano-silica surface, which causes that the formation of C-S-H-phase is no longer restricted to occur at the surface of cement grain and therefore the hydration of cement can be promoted.

1. Introduction

During the recent years, with the development of new plasticizing concrete admixtures and fine pozzolanic materials, it has become possible to produce high performance concrete (HPC) or even ultra-high performance concrete (UHPC). For the production of UHPC, the pozzolanic materials (silica fume, ground granulated blast-furnace slag, fly ash) are widely utilized. Nevertheless, the new developments of nano-technology guarantee that various forms of nano-sized amorphous silica can be produced, which have higher specific surface areas and activities compared to conventional silica fume. Hence, a considerable investigation effort has been paid on synthetizing nano-silica and clarifying its effect on the properties of concrete [1].

Based on the available literature, with the addition of nano-silica in cement and concrete, even at small dosages, nano-silica can significantly improve the mechanical properties of cementitious materials. This should be attributed to the influence of nano-silica on the hydration of cement. In interpreting this, some fundamental and theoretical mechanisms have been investigated. For instance, Land [2] found that the hydration heat of Ordinary Portland Cement blended with nano-silica in the main period increases significantly with increasing the silica surface area. Thomas et al. [3] showed that the hydration of tri-calcium silicate (C₃S) can be accelerated by addition of nano-scaled silica or C-S-H-particles. Björnström [4] monitored the
hydration process of C₃S pastes and the accelerating effects of a 5 nm colloidal silica additive on the rate of C₃S phase dissolution, calcium-silicate-hydrate C₅S-H gel formation and removal of non-hydrogen bound OH groups. Nevertheless, it can be noticed that the investigation of the effect of nano-silica on cement hydration of UHPC is insufficient. Furthermore, it is not suitable to predict the pozzolanic activity of nano-silica under low water/binder ratio, based on the experimental results that are obtained under high water/binder ratio.

The objective of this study is to investigate the effect of nano-silica on the cement hydration of UHPC. Isothermal calorimetry is employed to evaluate the cement hydration of the UHPC.

2. Materials and experimental methodology

2.1 Materials

The cement used in this study is CEM I 52.5 R, provided by ENCI (the Netherlands). A polycarboxylic ether based superplasticizer is used to adjust the workability of UHPC. The limestone and quartz powder are used as fine fillers. Two types of sand are used, one is normal sand with the fractions of 0-2 mm and the other one is microsand (sandstone waste) with the fraction 0-1 mm (Graniet-Import Benelux, the Netherlands). One type of colloidal nano-silica is used in this study. The recipe of the concrete mix design is shown in Table 1.

<table>
<thead>
<tr>
<th>Mix Type</th>
<th>Cement (kg/m³)</th>
<th>Limestone Powder (kg/m³)</th>
<th>Quartz Powder (kg/m³)</th>
<th>Microsand (kg/m³)</th>
<th>Sand 0-2 (kg/m³)</th>
<th>Nano-silica (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>SP (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>439.5</td>
<td>263.7</td>
<td>175.9</td>
<td>218.7</td>
<td>1054.7</td>
<td>0</td>
<td>175.8</td>
<td>43.9</td>
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<tr>
<td>UHPC-1%</td>
<td>435.1</td>
<td>263.7</td>
<td>175.9</td>
<td>218.7</td>
<td>1054.7</td>
<td>4.4</td>
<td>175.8</td>
<td>43.9</td>
</tr>
<tr>
<td>UHPC-2%</td>
<td>430.7</td>
<td>263.7</td>
<td>175.9</td>
<td>218.7</td>
<td>1054.7</td>
<td>8.8</td>
<td>175.8</td>
<td>43.9</td>
</tr>
<tr>
<td>UHPC-3%</td>
<td>426.3</td>
<td>263.7</td>
<td>175.9</td>
<td>218.7</td>
<td>1054.7</td>
<td>13.2</td>
<td>175.8</td>
<td>43.9</td>
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<td>UHPC-4%</td>
<td>421.9</td>
<td>263.7</td>
<td>175.9</td>
<td>218.7</td>
<td>1054.7</td>
<td>17.6</td>
<td>175.8</td>
<td>43.9</td>
</tr>
<tr>
<td>UHPC-5%</td>
<td>417.5</td>
<td>263.7</td>
<td>175.9</td>
<td>218.7</td>
<td>1054.7</td>
<td>22.0</td>
<td>175.8</td>
<td>43.9</td>
</tr>
</tbody>
</table>

2.2 Calorimetry analysis

For the heat flow calorimetry test, cement, limestone and quartz powder are mixed with silica slurry and superplasticizer, which is diluted with deionised water to bring the total water/binder mass ratio to 0.2. Silica/binder mass ratios from 1% to 5% are investigated. The paste is mixed for two minutes and then injected into a sealed glass ampoule, which is then placed into the isothermal calorimeter (TAM Air, Thermometric). The instrument is set to a temperature of 20 °C.
After 7 days, the measurement is stopped and the obtained data is analyzed. All results are ensured by double measurements (two-fold samples).

3. Results and discussion

Based on the calorimetry test results, the effect of the nano-silica amount on the cement hydration of UHPC is investigated. From Figure 10, it is apparent that with the increase of the nano-silica amount, the height of the early rate peak is increased, and the time required to reach the maximum rate is simultaneously reduced. This should be attributed to the nucleation effect of nano-silica. After the hydration begins, hydrate products diffuse and envelop nanoparticles as kernels, which can promote the cement hydration and makes the cement matrix more homogeneous and compact. Additionally, the time of reaching the main rate peak varied significantly with the change of the reactivity of the silicas. Therefore, in this study, with the increase of nano-silica amount, more reactive kernels will be generated during the hydration, and the time to reach the main rate peak will be correspondingly decreased.

From the literature, the hydration process of cement is classified into four principle stages [2]. The first stage is the initial phase of just a few minutes which is due to the superficial reaction of C₃S, rapid dissolution of free lime and aluminate phases and the immediate formation of ettringite. A low rate of hydration heat is characteristic for the following induction period, where the C-S-H and portlandite-nucleation begins. Then, one hour after mixing the cement with water, the acceleration period begins. After three hours the reaction gets more and more controlled by the diffusion and heat evolution rate starts to decrease. However, in this study, the induction and acceleration period of cement hydration are obviously longer than the normal ones. For instance, in the reference sample, the induction and acceleration period are about 30 hours and 25 hours, respectively. This should be attributed to the retardation influence of the superplasticizer. According to the investigation of Jansen [40], a complexation of Ca²⁺ ions from pore solution by the superplasticizer should be the substance that can absorb the polymer on the nuclei or the anhydrous grain surfaces, which in turn might lead to the prevention of the growth of the nuclei or the dissolution of the anhydrous grains. Hence, due to that a large amount of superplasticizer is utilized to produce UHPC in this study, the cement hydration is significantly retarded.
Fig. 1: Calorimetry test results of UHPC with different amount of nano-silica

4. Conclusions

From the results addressed in this paper, it can be concluded that because of the nucleation effect of the nano-silica, a number of C-S-H seeds can be generated on the silica surface, which causes that the formation of C-S-H-phase is no longer limited to occur at the cement grain surface and therefore the hydration of cement is promoted. However, because a large amount of superplasticizer is utilized to produce UHPC, the cement hydration is significantly retarded. This should be attributed to the complexation of the released Ca$^{2+}$ ions from the pore solution and the polymer from the superplasticizer, which in turn leads to the prevention of the growth of the nuclei or the dissolution of the anhydrous grains.

Bibliographical references


