Influence of Nano-SiO$_2$ on the Consistency, Setting Time, Early-Age Strength, and Shrinkage of Composite Cement Pastes

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The study outlined the raw materials and mix proportions to prepare composite cement pastes with the addition of silica-based micro- and nanoparticles. The effects of amorphous nano-SiO$_2$ on the early-age properties, including the consistency, setting time, early-age strength, and chemical and autogenous shrinkages, were investigated. Under the condition of the same dosage of superplasticizer used, the consistency of cement paste with nano-SiO$_2$ is higher than that with silica fume. Significant reductions of the initial and final setting times are observed especially for nano-SiO$_2$ addition groups, and the time difference between the initial and final setting times goes up with the increasing proportions of nano-SiO$_2$. The addition of nano-SiO$_2$ is more helpful to the improvement of early-age strengths of the paste with or without fly ash admixed than silica fume additive for the same mass proportion. Both the chemical and autogenous shrinkages of cement paste develop with the increasing amount of micro- or nanolevel silica particles; however, nano-SiO$_2$ plays a more active role than silica fume in inspiring early-age shrinkage. The physical and chemical mechanisms of nano-SiO$_2$ in cement paste are also discussed.

1. Introduction

Silica fume, as the most widely used supplemental cementitious materials (SCMs) in cement-based materials, has been successfully studied and applied for more than 80 years. Silica fume (SF for short), consisting essentially of silica in non-crystalline form with a high specific surface, exhibits great pozzolanic activity and thus has been commonly adopted to manufacture HPC. In recent years, nanotechnology has attracted considerable scientific interest due to the new potential uses of particles in nanometer ($10^{-9}$ m) scale, such as the application of nano-SiO$_2$ (NS) to manufacture Ultra-HPC [1, 2] or high-volume fly ash concrete [3] or the addition of nano-TiO$_2$ photocatalysis into cementitious materials to minimize air pollution in urbanized areas [4] and to produce self-cleaning concrete [5].

It was reported that dramatically improved properties could be obtained with NS added to cement-based materials if compared to the conventional grain-size materials of the same chemical composition [6–8]. Based on mini spread-flow test, Quercia et al. [9] found that water demand of cement paste decreased when amorphous NS was added. However, Lin et al.’s research [10] indicated that the amount of water needed at standard consistency increased as more NS was added; and obvious increasing values of the torque, yield stress, and plastic viscosity in mortar samples prepared with the use of 0–3% NS and 0.5 water/binder weight ratio were measured [11]. Therefore, the influence of NS particles on the water demand and consistency of cement paste still needed more testing and verification.

Zhang and Islam [12] reported that, in comparison to the reference concrete with 50% fly ash, the incorporation of 2% NS by mass of cementitious materials, respectively, reduced the initial and final setting times by 90 and 100 min and raised 3 d and 7 d compressive strengths by 30% and 25%. It was also demonstrated that the NS was more valuable in enhancing strength than SF [13, 14], and the results of SEM examinations [15, 16] showed that NS reacted with calcium hydroxide (CH) and increased the amount of calcium silicate hydrate (C-S-H) produced, leading to a compact microstructure. Not only did NS particles behave as a filler to improve microstructure, but also they behaved as an activator to promote pozzolanic
reaction, resulting in the consequently improving mechanical properties of hardened mixtures [17–19]. Though there were some confirmed conclusions about the effects of NS on both setting time and early-age strength of cement paste, a comparative analysis of the addition of silica-based micro- and nanoparticles at the same additive levels seemed valuable. Besides, it should be noted that though the volume stability (especially at early ages) of cement-based materials with the nanoscale additives is of much significance for the application in civil engineering structures, very limited research has been conducted.

The presented study outlined the raw materials and mix proportions to prepare composite cement pastes with the addition of silica-based micro- and nanoparticles. And by comparative analysis, the effects of NS on the early-age properties, including the consistency, setting time, early-age strength, and chemical and autogenous shrinkages as the main focuses, were investigated in detail.

### 2. Experiment Program

2.1. Materials and Properties. Cementitious materials used were ordinary Portland cement (OPC), fly ash (FA), silica fume (SF), and amorphous nanosio-

<table>
<thead>
<tr>
<th>Items</th>
<th>OPC</th>
<th>FA</th>
<th>SF</th>
<th>NS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>23.4</td>
<td>59.5</td>
<td>98.0</td>
<td>99.9</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>5.1</td>
<td>28.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO (%)</td>
<td>60.3</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO (%)</td>
<td>1.5</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>4.4</td>
<td>5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>2.5</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LOI (%)</td>
<td>2.6</td>
<td>2.1</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Specific gravity (g/cm²)</td>
<td>3.17</td>
<td>2.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg. particle size</td>
<td>16 μm</td>
<td>12 μm</td>
<td>0.1 μm</td>
<td>30 ± 10 nm</td>
</tr>
</tbody>
</table>

Table 1: Chemical compositions and properties of cementitious materials.

Mixing using ultrasonic mixer with 90 W power input; at last, all other cementitious materials were blended to make homogenous mixtures. The mixing consisted of a sequence of mixing that involved a total of 2 min at a paddle speed of both 62 rpm (revolution) and 140 rpm (rotation), a 15 s stop, and another total of 2 min at a speed of both 125 rpm (revolution) and 285 rpm (rotation).

The following experiments were carried out:

1. Test of consistency and setting time of cement pastes: the consistency and setting time of fresh pastes were tested according to GB 1346-2011 [20]. The consistency was ascertained by putting the paste in a mold consisting of a steel ring (40 mm in height) on a sheet of glass and by determining the penetration depth of a plunger applied to the top surface of the paste specimen. The initial and final setting time were determined using the needle of the Vicat apparatus.

2. Test of strength: compressive strength tests were carried out on 40 mm cube specimens and bending strength tests used 40 × 40 × 160 mm beam specimens, which were demolded 20 h after casting, cured in 23 ± 0.5°C water, and then dried 4 h prior to testing for every mix at 1, 3, and 7 days. Each specimen was tested for at the given ages by a hydraulic press with 100 kN capacity and 0.5 MPa/s loading speed.

3. Test of chemical and autogenous shrinkages: chemical shrinkage of cement pastes was measured basically according to ASTM C1608-2012 [21]. However, the glass bottles for chemical shrinkage measurement might crack due to the inconsistent deformation of the samples and the bottles, leading to the interruption of testing. So the modified ASTM C1608 method was recommended. As illustrated in Figure 2, an open ultrathin elastic cap was adopted to be filled with the paste mixtures to avoid its direct contact with the internal wall of the glass bottle. The chemical shrinkage values of the paste at the ages of 90 min, 3 h, 6 h, 12 h, 24 h, 48 h, 3 d, 7 d, and 14 d were recorded. Autogenous shrinkage of cement pastes was surveyed in strict accordance with ASTM C1698-2014 [22].

<table>
<thead>
<tr>
<th>Serial number</th>
<th>OPC</th>
<th>FA</th>
<th>SF</th>
<th>NS</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0#</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>A1</td>
<td>98.0</td>
<td>2.0</td>
<td></td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>A2</td>
<td>96.0</td>
<td>4.0</td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>A3</td>
<td>94.0</td>
<td>6.0</td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>B1</td>
<td>98.0</td>
<td>2.0</td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>B2</td>
<td>96.0</td>
<td>4.0</td>
<td></td>
<td></td>
<td>0.9</td>
</tr>
<tr>
<td>B3</td>
<td>94.0</td>
<td>6.0</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>C1</td>
<td>70</td>
<td>30</td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>C2</td>
<td>66.0</td>
<td>30</td>
<td>4.0</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>C3</td>
<td>66.0</td>
<td>30</td>
<td></td>
<td>4.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 2: Mix proportions of composite cement pastes (unit: wt%).

2.2. Mix Proportions and Tests. Referring to Table 2, cement pastes with different silica addition for test were prepared. Based on pretests, the ratio of water to the total cementitious materials in mass for all mixes was determined as a typical value of 0.36 for moderate paste consistency in general, in order that the properties of composite cement pastes could be investigated on the condition of the same water-to-cementitious materials ratio. First, the designed dosage of SP was diluted in a proper amount of water; then, SF or NS powder was added to the produced liquid for 5 min ultrasonic mixing.

The presented study outlined the raw materials and mix proportions to prepare composite cement pastes with the addition of silica-based micro- and nanoparticles. And by comparative analysis, the effects of NS on the early-age properties, including the consistency, setting time, early-age strength, and chemical and autogenous shrinkages as the main focuses, were investigated in detail.

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Figure 1: SEM photographs of SF (a) and NS (b).

![SEM photographs of SF and NS](image)

Figure 2: Sketch map of improved experimental apparatus for ASTM C1608 #1, A2, B2, and C1 samples at the age of 3 d.

![Sketch map of experimental apparatus](image)

3. Results and Discussions

3.1. Consistency and Setting Time. In the present study, the dosage of SP added was accurately adjusted to produce each mix until the standard consistency of cement paste was obtained. Test results were illustrated in Figure 3. Compared to the control group 1#, with the increasing of the mass percentages of SF or NS, the needed SP obviously rises, but the increments for NS addition groups are more dramatic than those for SF added. For instance, on the basis of 4.0% amorphous silica addition, the SP dosage for A2 is 0.4%, while that for B2 is 0.9%. In particular, when the NS amount reaches 6.0%, B3 mixture needs an amazing 1.2% of SP to achieve the standard consistency. When 30% FA in mass percentage is blended into cement paste, a similar conclusion can be made.

The increase of paste consistency is due to the improvement of water adsorption by fresh mixture, since very high specific surface areas in the paste are created by NS. The effectiveness of SP in adjusting the flow behavior (after mechanical mixing) in pastes with distinct concentrations of NS is very important for the control of the following impact of nanoparticles. Moreover, the rheological behavior of nanoparticle dispersed in a suspension depends not only on the particle diameter but also on an adequate relation between solid fractions and the optimum molecular weight of dispersant [11]. At high dosages of SP, the long chains of polycarboxylic superplasticizer are forced by mutual repulsion out into the solution where they interact with other particles, and consequently, the plastic viscosity values increase [23].

The setting times of all mixes were provided in Table 3. Significant reductions of the initial and final setting times
Table 3: Setting time and early-age compressive strength of cement pastes.

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Initial</th>
<th>Final</th>
<th>Time difference</th>
<th>1d</th>
<th>3d</th>
<th>7d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0#</td>
<td>8 hr 15 min</td>
<td>9 hr 20 min</td>
<td>1 hr 5 min</td>
<td>12.3</td>
<td>27.1</td>
<td>34.0</td>
</tr>
<tr>
<td>A1</td>
<td>8 hr 10 min</td>
<td>9 hr 10 min</td>
<td>1 hr</td>
<td>13.0</td>
<td>28.4</td>
<td>36.7</td>
</tr>
<tr>
<td>A2</td>
<td>6 hr 50 min</td>
<td>8 hr 5 min</td>
<td>1 hr 15 min</td>
<td>14.5</td>
<td>31.3</td>
<td>40.1</td>
</tr>
<tr>
<td>A3</td>
<td>6 hr 35 min</td>
<td>7 hr 55 min</td>
<td>1 hr 20 min</td>
<td>15.2</td>
<td>35.4</td>
<td>45.0</td>
</tr>
<tr>
<td>B1</td>
<td>5 hr 50 min</td>
<td>7 hr 20 min</td>
<td>1 hr 30 min</td>
<td>15.3</td>
<td>36.0</td>
<td>45.4</td>
</tr>
<tr>
<td>B2</td>
<td>5 hr 25 min</td>
<td>7 hr 15 min</td>
<td>1 hr 50 min</td>
<td>16.7</td>
<td>38.2</td>
<td>47.2</td>
</tr>
<tr>
<td>B3</td>
<td>4 hr 50 min</td>
<td>6 hr 45 min</td>
<td>1 hr 55 min</td>
<td>16.0</td>
<td>39.4</td>
<td>47.5</td>
</tr>
<tr>
<td>C1</td>
<td>9 hr 10 min</td>
<td>10 hr 20 min</td>
<td>1 hr 10 min</td>
<td>6.7</td>
<td>14.5</td>
<td>28.4</td>
</tr>
<tr>
<td>C2</td>
<td>7 hr 40 min</td>
<td>9 hr</td>
<td>1 hr 20 min</td>
<td>10.8</td>
<td>28.7</td>
<td>38.6</td>
</tr>
<tr>
<td>C3</td>
<td>6 hr 15 min</td>
<td>7 hr 45 min</td>
<td>1 hr 30 min</td>
<td>14.0</td>
<td>32.5</td>
<td>41.7</td>
</tr>
</tbody>
</table>

were observed for both SF and NS addition groups by contrast with group 1#. The incorporation of 2.0%, 4.0%, and 6.0% SF reduces the initial and final setting times of cement pastes by 5, 8, and 10 min and 10, 75, and 85 min, respectively; and the corresponding reduction values for NS additives are 145, 170, and 208 min and 120, 125, and 155 min. The effects of NS are remarkably surprising, even though FA is also admixed to produce composite cement paste. Besides, the time difference between the initial and final setting times goes up with the increasing proportions of SF or NS in cement paste, while there are by far wider time gaps for NS groups than SF ones at the same mass content.

Test data indicate that the time shortened is mainly a result of the shortening of the initial setting, which is caused by the reduction in the hibernation period of hydration. With NS added to the paste, the increase in surface energy of the mixes speeds up the rate of the hydration reaction. Therefore, the C-S-H gel and Ca(OH)$_2$ are generated at a faster speed, and an early initial setting time is achieved. The reduction in setting time becomes noticeable when the increased amount of NS is admixed [10].

3.2. Early-Age Strength. Figure 4 shows the compressive strength development of all specimens at the ages of 1d, 3d, and 7d. As can be seen, the early-age compressive strength developed in pastes containing SF or NS particles in every case is apparently higher than that of the reference group 1#. The strengths of A1, A2, and A3 specimens with the addition of 2.0%, 4.0%, and 6.0% SF improve obviously, but the strengthening effects are far inferior to those of NS. In general, it is noticed that the compressive strengths of the specimens, especially before the age of 7d, sharply drop as a large amount of FA is added, which is mainly due to the immature pozzolanic reaction in the paste and the preventive growth of C-S-H gel caused by the blended SCMs. As demonstrated in Figure 4, the addition of NS is more helpful to the improvement of early-age compressive strength of the paste with FA admixed than SF additives on the condition of the same mass proportion. The compressive strength of C2 with 4.0% SF rises by 61.2%, 98.0%, and 35.9% at 1d, 3d, and 7d, respectively, compared to that of the reference group C1, while the corresponding increments of C2 with the same amount of NS are 109.0%, 124.1%, and 46.8%.

Table 4 provided the compressive and bending strengths, as well as the ratios of bending to compressive strength of cement stone at the prescribed age of 7d. As for SF and NS additives concerned, their effects on the bending strength are quite similar to those on the compressive strength, while from the data of ratios of bending to compressive strength at the same age, 3 fundamental principles can be deduced: (1) both SF and NS particles are helpful to increase the early-age strength, but it seems that bending strength increments are more significant by comparison; (2) with the increasing amount of SF or NS, the development of bending strength is clearly superior to that of compressive strength; and (3) on the condition of the same 4.0% of SF and NS admixed (i.e., C1, C2, and C3), the addition of FA appears very estimable to further improve the bending strength along with SF or NS.

Both NS and SF are highly reactive silica, but the average primary particle size of the former is about 10 times smaller...
Table 4: Strength and ratio of bending to compressive strength of hardened cement paste at 7 d.

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Compressive strength (MPa)</th>
<th>Bending strength (MPa)</th>
<th>Ratio of bending to compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0#</td>
<td>34.0</td>
<td>3.6</td>
<td>0.106</td>
</tr>
<tr>
<td>A1</td>
<td>36.7</td>
<td>3.9</td>
<td>0.106</td>
</tr>
<tr>
<td>A2</td>
<td>40.1</td>
<td>4.4</td>
<td>0.110</td>
</tr>
<tr>
<td>A3</td>
<td>45.0</td>
<td>5.1</td>
<td>0.113</td>
</tr>
<tr>
<td>B1</td>
<td>45.4</td>
<td>5.3</td>
<td>0.117</td>
</tr>
<tr>
<td>B2</td>
<td>47.2</td>
<td>5.6</td>
<td>0.119</td>
</tr>
<tr>
<td>B3</td>
<td>47.5</td>
<td>5.7</td>
<td>0.120</td>
</tr>
<tr>
<td>C1</td>
<td>28.4</td>
<td>3.3</td>
<td>0.116</td>
</tr>
<tr>
<td>C2</td>
<td>38.6</td>
<td>4.8</td>
<td>0.124</td>
</tr>
<tr>
<td>C3</td>
<td>41.7</td>
<td>5.1</td>
<td>0.122</td>
</tr>
</tbody>
</table>

than that of the latter, referred to in Figure 1. The mechanisms by which SF modifies cement paste, mortar, and concrete were summarized in ACI Committee 234 report [24]. As the particle sizes of the NS are much smaller than those of the SF, the physical and chemical effects of the former are likely more substantial than the latter, which are discussed in the later section.

3.3. Chemical and Autogenous Shrinkages. With SF or NS additives in paste, the early-age shrinkage of cement paste undoubtedly gets more complicated. Figures 5 and 6 provide test results of the chemical shrinkage of all mixes listed in Table 2. The following conclusions can be drawn:

1. Vigorous hydration of cementitious materials in turn results in significant growth of the chemical shrinkage in all pastes with time passing. Until the age of 14 d, as an example, 1#, A2, B2, C1, C2, and C3 are measured at 0.0411, 0.0478, 0.0678, 0.0287, 0.0433, and 0.0611 mL/g of chemical shrinkage individually, based on the absolute volume method according to modified ASTM C1608.

2. Compared to pure cement paste (1#), both SF and NS promote the chemical shrinkage of all cement pastes during the time period under study, except that A1 with only 2.0% SF addition indicates almost similar development of the chemical shrinkage, because of its very low admixing amount. In general, the chemical shrinkage of cement paste goes up with the increasing amount of micro- or nanolevel silica particles; however, it is evident that NS plays a more active role than SF in inspiring early-age shrinkage. Based on the control group 1#, the chemical shrinkage of A3 with 6.0% SF admixed, for instance, increases by 83.9%, 48.0%, and 45.7% at the age of 6 h, 48 d, and 7 d separately, while the values recorded for B3 with the same amount of NS reflect the corresponding increments of 148.4%, 83.2%, and 73.7%.

3. The line, the closest one to cross axis in Figure 5, illustrates the growth of chemical shrinkage of C1, whose cement is replaced by 30% of FA in mass percentage. As can be seen, the amorphous spherical FA particles, uniformly dispensing into the cement matrix, are very helpful to reduce its chemical shrinkage at early ages. Nevertheless, the influences of SF and NS on the chemical shrinkage of composite cement paste with admixture of FA are quite similar to those on pure cement paste.

Self-desiccation driving the development of autogenous shrinkage has been used extensively across literature [25, 26]. In reality, a volume change commences immediately after the cementitious materials and water come in contact during mixing. Therefore, less pozzolanic activity of FA is beneficial to control the autogenous shrinkage of cement paste, but both SF and NS, due to their very high potential and ability of hydration, have the opposite effects, which are clearly demonstrated in Figure 7.

Three different incorporation percentages, 2.0%, 4.0%, and 6.0%, are all taken into consideration, and the addition of SF in cement paste leads to 15.8%, 33.0%, and 31.7% of the average increasing percentages of autogenous shrinkage, separately at 3 d, 7 d, and 14 d in contrast with the control group 1#. In addition, the corresponding average values
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OPC
2.0% SF
4.0% SF
6.0% SF
2.0% NS
4.0% NS
6.0% NS
30% FA
4.0% S

2.0% SF
4.0% SF
6.0% SF
2.0% NS
4.0% NS
6.0% NS
30% FA
4.0% S

3. Conclusions

(1) The needed SP to produce cement pastes with SF or NS added rises, and its dosages for NS addition groups are more than those for SF added. Under the condition of the same dosage of SP used, the consistency of cement paste with NS is higher than that with SF.

(2) There are significant reductions of the setting times for SF or NS addition groups by contrast to pure cement. But the effects of NS are remarkably surprising, even though FA is also admixed. The time difference between the initial and final setting times goes up with the increasing proportions of NS in cement paste.

(3) The early-age compressive strength develops in pastes containing SF or NS particles, and the improvement of bending strength seems more evident. But the strengthening effects of SF are inferior to those of NS, and the addition of FA appears estimable to further improve the bending strength along with SF or NS.

(4) Both chemical and autogenous shrinkages of cement paste develop with the increasing amount of SF or NS; however, NS plays a more active role than SF in inspiring early-age shrinkage. The extra admixture of FA in cement paste shows the similar principals.

change to 68.8%, 70.5%, and 54.1% at the same ages, as NS is admixed. Though FA additive limits the autogenous shrinkage of cement paste before 14 d, seen from C1 group, the compound adding of NS (C3) still endows 57.9% and 35.9% of the autogenous shrinkage increments at 7 d and 14 d, if compared to the pure paste (1#).

Early-age shrinkage of cementitious matrices is the result of several complex physicochemical phenomena. Those phenomena are related to the hydration reactions between cementitious materials and water and to the progressive hardening of the mineral skeleton. It is generally considered that when cement hydrates, chemical shrinkage occurs, because the hydration products occupy less space than the original reactants, and that at mature ages, in autogenous conditions, the autodesiccation of the material, that is, the progressive desaturation of its porosity, generates compressive forces high enough to cause volume changes called autogenous shrinkage. These forces are particularly intense in cement-based matrices with low water-to-cementitious materials ratio.

As an example, Figure 8 reveals that different additives result in the diverse hydration products and microstructures at 3 d, leading to different early-age shrinkages. The addition of SF consumes the bulky crystal Ca(OH)$_2$ produced by cement (seen from Figure 8(a)) and promotes the hydration of composite paste, generating a large amount of C-S-H and short needle AFt (shown in Figure 8(b)). More complex hydration products and denser microstructure bring the higher chemical and autogenous shrinkages. Moreover, Figure 8(c) is the SEM photograph intensified by 5000 times of the sample B2 with the admixture of 4.0% NS. By comparison with Figure 8(b), the hydration products are smaller, are more uniformly distributed, and have more homogenous and compact microstructure. Besides, the incorporation of a certain amount of FA also consumes Ca(OH)$_2$, but limits the hydration and shrinkage of paste because as indicated in Figure 8(d), quite a number of unhydrated FA particles fill and support the microstructure to keep its volume stable to a certain extent.

In summary, the effects of NS on the early-age properties of cement paste can be explained as follows: from the chemical point of view, the extremely fine particles of amorphous NS not only have high surface energy (atoms in the surface have a high activity, which leads the atoms to react on outer ones easily) but also greatly develop the very early-age hydration by providing high amount of nucleation sites for precipitation of cement hydration products. From physical perspective, in addition to the nucleation effect, NS may act as reactive filler to reduce bleeding and increase packing density of solid materials by occupying space between cement and FA particles. Besides, the small amount of aggregating NS is not a weak zone, so the strength of cement paste increases with the increasing content of NS even when the small amount of NS is not well dispersed. Consequently, the pozzolanic activity of NS at early ages is higher than that of SF. The microstructure of the mixture containing NS reveals a dense, compact formation of hydration products and a reduced number of Ca(OH)$_2$ crystals [15, 16].

4. Conclusions

Figure 6: Chemical shrinkage of composite cement pastes at 14 d.

Figure 7: Autogenous shrinkage of composite cement pastes at early ages.

In summary, the effects of NS on the early-age properties of cement paste can be explained as follows: from the chemical point of view, the extremely fine particles of amorphous NS not only have high surface energy (atoms in the surface have a high activity, which leads the atoms to react on outer ones easily) but also greatly develop the very early-age hydration by providing high amount of nucleation sites for precipitation of cement hydration products. From physical perspective, in addition to the nucleation effect, NS may act as reactive filler to reduce bleeding and increase packing density of solid materials by occupying space between cement and FA particles. Besides, the small amount of aggregating NS is not a weak zone, so the strength of cement paste increases with the increasing content of NS even when the small amount of NS is not well dispersed. Consequently, the pozzolanic activity of NS at early ages is higher than that of SF. The microstructure of the mixture containing NS reveals a dense, compact formation of hydration products and a reduced number of Ca(OH)$_2$ crystals [15, 16].

4. Conclusions

(1) The needed SP to produce cement pastes with SF or NS added rises, and its dosages for NS addition groups are more than those for SF added. Under the condition of the same dosage of SP used, the consistency of cement paste with NS is higher than that with SF.

(2) There are significant reductions of the setting times for SF or NS addition groups by contrast to pure cement. But the effects of NS are remarkably surprising, even though FA is also admixed. The time difference between the initial and final setting times goes up with the increasing proportions of NS in cement paste.

(3) The early-age compressive strength develops in pastes containing SF or NS particles, and the improvement of bending strength seems more evident. But the strengthening effects of SF are inferior to those of NS, and the addition of FA appears estimable to further improve the bending strength along with SF or NS.

(4) Both chemical and autogenous shrinkages of cement paste develop with the increasing amount of SF or NS; however, NS plays a more active role than SF in inspiring early-age shrinkage. The extra admixture of FA in cement paste shows the similar principals.
(a) 1#: pure cement  
(b) A2: addition of 4.0% SF  
(c) B2: addition of 4.0% NS  
(d) C1: addition of 30% FA

Figure 8: SEM photographs of 1#, A2, B2, and C1 samples at the age of 3 d.

(5) The above phenomena resulting from the NS additive can be explained as follows: since the particle sizes of NS are much smaller than those of SF, the physical and chemical effects of the former are likely more substantial than the latter. Extremely fine particles of the NS, with high surface energy and high activity, accelerate cement and FA hydration by providing high amount of nucleation sites for precipitation of cement hydration products. Besides, NS may act as superfine filler to manufacture more homogeneous and denser microstructure of cement stone.

Competing Interests

The authors declare that they have no competing interests.

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