Effect of Silica Fume and Nano SiO₂ on Properties of High Water Materials

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Abstract. In order to improve workability and strength of new high water materials, the influence of silica fume and nanometer on the physical and mechanical properties of high water materials was studied. By changing the content of silica fume or gas-phase nano-SiO₂ in the new high-water materials, the workability of the materials was observed, and the strength of the materials at different ages was measured. The results showed that the increase of nano-SiO₂ content significantly shortened the coagulation time of the high-water materials and improved the cohesion of the high-water materials. When the water-cement ratio was 1:1, the optimal content of silica fume was 3%, and the strength of the specimen in seven days was 43.7% higher than that of the original high-water material. At the water-cement ratio of 1.5:1, the optimal content of nano-SiO₂ was 2%, and the strength of the specimen in seven days was 21.2% higher than that of the original high-water material. Through SEM scanning the microstructure of the material, it was found that the hydration reaction of the high-water material with nano-sio₂ was more sufficient and the structure was denser.

1. Introduction.
High water materials are characterized by low cost, convenient use, also it can be used to pump and shorten the setting time. It has obvious advantages in the application of filling and grouting technology[1]. Due to the large amount of water ash, high water materials often have poor consistency of slurry, and are prone to bleeding and segregation[2]. However, the study on the reaction mechanism of high water materials is not enough, and the study on improving the properties of high water materials with pozzolanic materials is even less.

Many researchers have made fruitful achievements in improving the performance of cement-based materials with silica fume[3]. Nano-SiO₂ and silica fume have the same composition, but nano-materials are ultrafine materials with particle size in the nanometer scale (1~100nm). At present, nano-SiO₂ has become a popular material for scholars at home and abroad to improve the properties of concrete[4]~[7]. Many studies have also shown that nano materials can improve the early hydration strength of cement-based materials, but the conclusions about nano content and its influence on the strength of cement-based materials vary greatly. Ding xiangqun believed that the content of 1% nano could improve the one day and three days compressive strength of cement by 48% and 28%[8]. Hou Xuebiao's research shows that when the nano content is 1.5%, the concrete strength can be increased by about 17.1%[9]. However, researchers generally believe that there is an optimal amount of nano in cement-based materials. At present, the research on the effect and mechanism of silica fume and nano-SiO₂ in high water materials is very limited.
In this paper, the hydration rate of compressive strength of novel high water materials with silica fume and nano-silica was obtained by experiments. The optimal dosage of silica fume or nano-SiO$_2$ in high-water materials was determined. With the help of SEM scanning the microstructure of the materials, the mechanism of the hydration reaction of the materials with silica fume or nano-SiO$_2$ was analyzed in the paper.

2. Experiment.

2.1. Experimental materials.

The new grouting high water material used in this experiment has been determined the best mix proportion after many tests, which composed of A slurry and B slurry. A slurry consists of calcium sulfoaluminate cement, additive A and water. B slurry is composed of plaster, lime, additive B and water as well. Additive A and B are national high-tech products developed by Yangzhou new material co. LTD. Additive A ensures the pumpability of A slurry and prevents the slurry from settling and bleeding. It contains retarder and suspension agent. Additive B contains suspension agent to ensure the pumpability of B slurry. It also contains accelerants can accelerate the coagulation of materials, when mixed the A slurry and B slurry, so as to improve the early strength of materials.

Commercially available nanomaterials were used in the experiment. The nanometer powder was hydrophilic nanometer silica powder. In order to obtain better experimental results, the dispersive solution was prepared in the laboratory. The particle size of the vapor phase nanometer powder was 15nm. The specific surface area of nanometer powder was 250±30m$^2$/g. The nanometer content in the nanometer dispersion solution is 20%, and its pH value is 4-7.

The experiment used silica fume of model V2000-95 produced by Weishen new material company, in which the content of SiO$_2$ exceeds 95%, it has few impurities. The specific surface area of silica fume after the BET test was 21.709 m$^2$/g. Water demand ratio of silica fume was 116%. Most particle size of silica fume distributions were under 1μm, and its D50 was about 200 nm.

2.2. Experimental test.

The mixing process of the new high-water materials is as follows: firstly, A is mixed with additive A and then mixed with water; meanwhile, B is mixed with additive B and then mixed with water; Finally, A slurry is mixed with B slurry. The vapor phase nano-SiO$_2$ dispersion and silica fume are added in equal mass to replace calcium sulfoaluminate cement in the A slurry. Firstly, the nanometer material and water were mixed evenly in advance, and then divide into three times and mix with evenly, finally mixed with material B slurry. Water-cement ratios of 1:1 and 1:1.5 were used in the experiment. Water content in nanomaterials is also considered when calculating water-cement ratio.

The method for determining the setting time of mixed high water materials is described below: first pour the slurry into the cup, then tilt the slurry 45 every 30 seconds, finally note the setting time when the slurry completely loses fluidity.

The strength test adopts ISO method, and the test sample size is 40mm×40mm×160mm. The flexural strength of the sample is obtained by uniformly applying the load vertically to the side of the prism in the central loading method until it breaks. The two prisms obtained from the bending test were subjected to compression test and averaged. The compressive and flexural strength of each age is the average value of three specimens.

Finally, the microstructure of the materials was analyzed by SEM.

2.3. Experimental result.

2.3.1. Setting time and fluidity

Original high water material was marked as WG. The group of high water materials with silica fume is GSF. Silica fume replaces 2%, 3%, 4% cement with the same quality were recorded as GSF-2 ~ GSF-4 respectively. The group of high water materials with nano-SiO$_2$ is GNS. Nano-SiO$_2$ replaces 0.5%,
1%, 2%, 3% cement with the same quality were recorded as GNS-0 ~ GNS-3 respectively. The setting time of each group was recorded during the test, as shown in table 1.

| Water cement ratio | WG GSF-2 GSF-3 GSF-4 GNS-0 GNS-1 GNS-2 GNS-3 |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1:1                | 8           | 10          | 10          | 10          | 6           | 5           | 3           | -           |
| 1:5                | 14          | 15          | 18          | 18          | 12          | 12          | 10          | 10          |

In the figure "-" indicates the rapid setting of the material.

① Setting Time
According to the experimental results, the setting time of the new high water material mixed with silica fume was slightly delayed. However, with the increase of nano-SiO₂ content, the setting time of the new high-water material slurry will be shortened significantly. When the water-cement ratio was 1:1, in the test group with the nano-SiO₂ content of 3%, the rapid coagulation phenomenon occurred when mixing the A and B slurry.

② Workability
When the water-cement ratio is 1:1, the slurry fluidity decreases with the increase of silica fume powder content. However, with the increase of nano-SiO₂ content, the slurry fluidity decreased significantly. GNS-3 group even lost liquidity, and it was difficult to fill the entire mold without sufficient vibration. When the water-cement ratio was 1.5:1, the fluidity of the new high-water material mixed with silica fume did not change significantly. However, the fluidity of the new high water materials mixed with nano-SiO₂ still decreased significantly. When the water-cement ratio was 1:1, no water seepage phenomenon was observed in the specimens. When the water-cement ratio was 1.5:1, the WG group and GSF group showed slight bleeding. However, the cohesion of GNS group materials with nano-SiO₂ increased significantly, and no bleeding was observed even if only 0.5% was added.

When the water-cement ratio is 1:1, the free water in the slurry material is less, and the silica fume absorbs and aggregates more free water, so the fluidity decreases with the increase of silica fume content. When the ratio of water ash to 1.5:1, water ash is higher, and free water is also relatively more. Small admixture of silica fume has little effect on improving the fluidity of high water materials. Even because the particle size of silica fume is smaller than that of cement and the specific surface area is larger, the gap between cement particles in the material will be filled, and the free water in the material slurry will increase relatively, so the fluidity will increase slightly instead. The particle size of nano-SiO₂ is nanoscale, the specific surface area of the material is more than ten times that of silica fume, therefore the particle surface will absorb a large amount of water, could greatly reducing the rheological properties of the new high-water materials. It is because of the small particle size and large specific surface area, the reaction speed is fast, so the setting time of high-water materials is greatly reduced.

2.3.2. Compressive strength.
At present, it is generally believed that adding silica fume or nano-SiO₂ to cement-based materials can improve the early strength of materials. Through the analysis of the compressive strength of the test block, it was found that when the water-cement ratio was 1:1, the strength of the test piece with 3% silica fume increased fastest. The compressive strength was 3.5MPa at six hours. At the age of two hours, four hours and six hours, the compressive strength of GDF-3 specimens increased by 39.40%, 68.42% and 30.77 % compared with that of WG group. The compressive strength of GDF-3 specimens reached 9.7 MPa at seven days. At the age of one day, three days and seven days, the compressive strength of GDF-3 specimens increased by 42.31%, 42.14% and 43.75% compared with that of WG group. Nano-SiO₂ has smaller particle size and larger specific surface area than silica fume particles. However, when the water-cement ratio was 1:1, the compressive strength of the GNS group specimens mixed with nano-SiO₂ increased less than that of the GSF group specimens mixed with
silica fume. When the water-cement ratio was 1:1, the optimal content of nano-SiO$_2$ was 1.0%. The strength growth rate of the new high water materials with nano-SiO$_2$ varied greatly at different ages. The early strength of the GNS-1 specimens at two hours, four hours and six hours was 45.45%, 45.37% and 1.54% higher than that of the original specimens with high water content. The compressive strength increased by 29.81%, 1% and 28.75% at the age of one day, three days and seven days. Since silica fume and nanoparticles are very fine and have volcanic ash effect, both GSF and GNS have a large increase in strength compared with WG group in the early stage. Between one and seven days, the strength of GSF specimens still increased significantly, but the strength growth rate of GNS specimens began to decrease. Generally speaking, when the water-cement ratio was 1:1, the effect of adding silica fume to high-water materials was better than that of adding nano materials, as shown in figure 1. Moreover, when the content of the two materials was too high, the strength of the high water material decreased.

When the water-cement ratio was 1.5:1, the average compressive strength at the six hours age of WG group was only 0.95 MPa. As the water-cement ratio was increased, the strength of high-water materials fluctuated greatly, and the compressive strength of some specimens was only 0.4 MPa at the age of six hours. Figure 2 shows that the optimal content of silica fume is 4%. When the water-cement ratio was 1.5:1, and the strength of GSF-4 reached 1.25 MPa for six hours. Its compressive strength at the age of six hours, one day, three days and seven days was 31.58%, 36.67%, 12.5% and 13.6% higher than that of the WG group. The optimal content of nano-SiO$_2$ is 2%. The strength of the GNS-2 specimens reached 1.4MPa at the age of six hours. Its compressive strength at the age of six hours, one day, three days and seven days was 47.4%, 20.0%, 5.0% and 21.2% higher than that of the WG group. The compressive strength of concrete reached 4MPa in seven days. When the water-cement ratio was 1.5:1, the compressive strength of high-water materials with nano-SiO$_2$ was 6.67% higher than that doped with silica fume. Compared with the variation rule of compressive strength of WG group, the compressive strength of GSF group mixed with silica fume increased rapidly within three days, and then the grow rate of strength slowed down. The compressive strength of the GNS specimens was significantly higher than that of the WG specimens within one day. The compressive strength increased slowly between one and three days, but there was a secondary increase in the strength between three and seven days.
2.3.3. Flexural Strength.
The flexural strength of high water materials mixed with nano-SiO$_2$ and silica fume showed a similar change law to that of compressive strength. When the water-cement ratio was 1:1, the optimal content of silica fume in the new high-water materials was 3%, and the flexural strength at the age of seven days was 38.46% higher than that in the WG group. The optimal content of nano was 1%, and the flexural strength at seven days was 26.92% higher than that of WG group. When the ratio of water-cement was 1.5:1, the flexural strength of GSF group at seven days was 27.27% higher than that of WG group, and the flexural strength of GNS group at seven days was 36.36% higher than that of WG group. But the content of silica fume increased in the high-water materials, the flexural strength did not change much. The flexural strength of each group was very close when nano-SiO$_2$ dosage was 1%~3%.

3. Micromorphology analysis.

3.1. Effect of silica fume on microstructure of specimen.
According to the above test conclusion, the setting time of new grouting high-water material is too short at water-cement ratio of 1:1, and the slurry is too viscous after mixing. In the grouting and filling construction, the quick setting and too small fluidity of high water materials are unfavorable to the construction, and will block the grouting pipe. Therefore, the specimens with 4% silica fume, the specimens with 2% nano-SiO$_2$ and the original high-water material WG specimens with water-cement ratio of 1.5:1 were studied. First, the three kinds of specimens were cured to the age of seven days, and then the electronic scanning was conducted. From figure 5, it can be found that the surface of the new high-water material without doping has some pits and obvious cracks. A large amount of columnar ettringite is produced, but it is more dispersed, and there is calcium silicate hydrate, some aluminum hydroxide gel AH$_3$ as well. FIG. 6 shows that a large number of hydration products appear on the surface of the high-water material after the addition of silica fume, which is much better than the original high-water material in terms of coverage. There were no obvious cracks in the sample, and the pores and voids in the sample were significantly reduced. In the interstitium, needle-flake hydrates Aft interweave. Therefore, the material structure is more compact.

According to the SEM figure of silica fume as shown in figure 7, it can be seen that silica fume particles are spherical and small in size, so the hydration products are more likely to be deposited on the surface of the silica fume particles, which accelerate the crystallization and precipitation of the hydration products, thus accelerating the early hydration of cement. This water absorption of silica fume reduces the free water in the material, which speeds up the reaction speed and improves the early strength of the material. When the content is too high, as mentioned above, the material workability will decline, cement hydration is not complete as well, the compressive strength will also decline.

Figure 5. SEM scanning electron microscopy of WG sample(3000 times)
Figure 6. SEM scanning electron microscopy of GSF-4 sample(3000 times)
3.2. Effect of silica fume on microstructure of nano-SiO₂.
After curing for seven days, the high-water material doped with nano-SiO₂ presented a blocky structure, which was obviously denser. In the hydration process, a large number of hydrated calcium silicate C-S-H gels were produced with smaller nanoparticles as the core. The amount of gels was significantly higher than that of the new high-water materials with silica fume or the original high-water material. In FIG. 9, the pores and voids of GNS-2 specimen are further reduced compared with FIG. 6, and the voids are filled with a large number of hydration products, which are in the shape of needle and stick and smaller block products, forming the shape of nest. The hydration product is aluminum gel phase, and the structure has less ettringite Aft.

As can be seen from the electron scanning figure 8 of the nanometer dispersion solution, although the gas-phase nanomaterials have been dispersed, some nanoparticles are still agglomerated. Therefore, when the nano content in the high water materials is too high, the agglomeration phenomenon is serious, which affects the hydration reaction. The particle size of gas phase was 15nm and that of silica fume was 200nm. The nanometer specific surface area used was 100 times that of silica fume. Therefore, when water cement ratio is 1:1, nano-SiO₂ adsorption of a large amount of water causes the phenomenon of water loss and over-drying, and the hydration effect of the material is not as good as that of silica fume. However, the water-cement ratio is 1.5:1, and there is a large amount of free water in the material. The small size of nano-SiO₂ particles provides nucleation effect for hydration products, and the hydration rate is very fast. As a result, the hydration products are more lumpy and have lower porosity and tighter structure than the high-water materials mixed with silica fume. Calcium hydroxide CH is the hydration product of high-water materials, it reacts with alumina hydroxide gel AH₃ to form
ettringite, therefore the hydration product of new high-water materials is rare CH commonly seen in ordinary cement materials. Moreover, silica fume and nano-SiO₂ have good pozzolanic activity\textsuperscript{[10]}. They react quickly with CH, especially when the nanoparticles are smaller and react faster with CH. Therefore, from one day to three days, the Ca²⁺ reaction in the samples with nanomaterials is basically complete and the strength increase decreases. The hydration product Ca(OH)₂ can produce a secondary hydration reaction with the active SiO₂, during which the material strength increases.

4. Conclusion.
In this paper, the preparation method of adding nano-SiO₂ and silica fume in high water materials was described, and the working performance and mechanical properties of nano-SiO₂ and silica fume in high water materials were studied. By comparing and analyzing the results of three groups of experiments in which the original high-water materials, the high-water material mixed with nano-SiO₂ and the high-water material mixed with nano-SiO₂, the influence law and action mechanism of nano-SiO₂ and silica fume on the high-water materials were investigated.

- Adding silica fume or nano-SiO₂ to new high-water materials will improve the workability of mixing materials and shorten the setting time. When the water ash is large, the improvement effect of silica fume on the workability of new grouting materials with high water content is not obvious. However, with the increase of nano-SiO₂ content, the setting time of the new high-water material slurry was still significantly shortened and the slurry became significantly viscous.

- The addition of silica fume or nano-SiO₂ improves the early compressive and flexural strength of the new high-water materials, especially the early intensity within six hours. When the water-cement ratio was 1:1, the optimal content of silica fume was 3%, its compressive strength reached 3.5MPa at six hours and 9.7 MPa at seven days. And the strength was 43.75% higher than the original high-water material at seven days. The optimal content of nano-SiO₂ was 1%, and its strength was 28.75% higher than the original high-water material at seven days. When the water-cement ratio was 1.5:1, the optimal content of silica fume was 4%, and its strength was 13.6% higher than the original high-water material at seven days. The optimal content of nano-SiO₂ was 2%, its compressive strength reached 4.0MPa at seven days. The strength was 21.2% higher than the original high-water material at seven days.

- The hydration reaction of the high-water material mixed with nano-SiO₂ was more sufficient, and a large number of hydration products were filled in the gap, presenting a needle-stick shape and a smaller block shape, forming a nest shape.

- When the water-cement ratio is 1:1, a large amount of water is needed for the full reaction of nano-SiO₂ particles with a small particle size, so the particles are easy to aggregate and affect the hydration effect. When the water-cement ratio is 1.5:1, the advantage of small nanoparticles in the hydration process can be brought into full play, and the reactive SiO₂ will produce a secondary hydration reaction with the hydration product Ca(OH)₂.

In short, the high-water materials contain a large amount of free water, and the addition of silica fume and nano-SiO₂ with the characteristics of volcanic ash to the material can further play the advantages of the high-water materials. The significance of this study is to obtain more stable and stronger high-water materials with better performance, which is more conducive to the application of new high-water materials in downhole filling and grouting technology.

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