

# The Effect of Nano-SiO<sub>2</sub> Dispersed Methods on Mechanical Properties of Cement Mortar

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## ABSTRACT

Nano-SiO<sub>2</sub> is added to the cement by using different dispersion methods, through the macroscopic mechanical properties to characterize its dispersion in the cement, it can be used to explore the best experimental process. The results show that the compressive strength of cement samples with different dispersion methods is different. When the physical dispersion method is used, the intensity is not improved, but the ultrasonic dispersion method is the smallest, and the dispersion of nano-SiO<sub>2</sub> is -9.11%. When the surfactant is used as dispersant, the dispersion of nano-SiO<sub>2</sub> by Naphthalene water reducer is the best, and the compressive strength is increased by 6.68%. By using polymeric dispersing agent, polyethylene glycol has a certain effect on the dispersion of nano-SiO<sub>2</sub>, but it has some damage to the cement (set-retarder, etc.). Based on the above experiments, we have obtained the best dispersion method, which uses ultrasonic dispersion, and also needs to add naphthalene water reducer.

**Keywords:** nano-SiO<sub>2</sub>, ultrasonic dispersion, water reducing agent, polyethylene glycol

## 1. INTRODUCTION

Nanomaterial has unique physical and chemical properties, the nanoparticles evenly dispersed in the concrete matrix, which can greatly improve the mechanical properties of the matrix. Studies show that nano-SiO<sub>2</sub> can reduce the porosity of cement paste and transition zone, not only can be used as a filler to plug the pores but also with Ca(OH)<sub>2</sub> to produce hydrated calcium silicate gel, can refine the grain size of Ca(OH)<sub>2</sub>, and reduce the orientation of Ca(OH)<sub>2</sub>. However, because of the large surface area of nano-SiO<sub>2</sub> particles, the surface atoms have many dangling bonds, and the surface energy is high, which belongs to the unstable system, which is very easy to have the particle agglomeration phenomenon, which seriously affects the full play of the advantages of nano-SiO<sub>2</sub>. Therefore, effectively solve the dispersion of nanoparticles is the key and basis to realize its application of nano-SiO<sub>2</sub> particles in cement. In recent years, there are a lot of researches on the dispersion of nanomaterials in cement. The results obtained by different methods are different, so we use different dispersion methods to disperse the nano-SiO<sub>2</sub> into cement. We take the mortar strength as an index to distinguish the pros and cons, the optimal process parameters in the cement system are determined.

## 2. RAW MATERIALS AND EXPERIMENTAL METHOD

### 2.1 Raw materials

In this study, Ordinary Portland cement (OPC) was obtained from SUNNSY Group Cement Plant. The chemical compositions and physical properties of the OPC are presented in Table 1. Hydrophilic-300 nanosilica dioxide come from Aladdin, the content of silica is 99.8%, the particle size range is 7–40 nm, and the specific surface area is 300 m<sup>2</sup>/g.

**Table 1.** Chemical composition and compressive strength of cement.

|  | Chemical composition (%) |                  |                                |      |                                | Strength (MPa)  |        |         |
|--|--------------------------|------------------|--------------------------------|------|--------------------------------|-----------------|--------|---------|
|  | CaO                      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO  | Fe <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> | 3 days | 28 days |
|  | 60.1                     | 21.37            | 5.67                           | 3.94 | 3.09                           | 2.65            | 32.43  | 50.43   |

### 2.2 Dispersion method

#### 2.2.1 Physical dispersion method

Physical dispersion methods include mechanical dispersion and ultrasonic dispersion. Mechanical dispersion method is a method for the full dispersion of nanoparticles in the medium with the help of mechanical energy such as shear force or impact force. It mainly includes grinding, general ball milling,

mechanical stirring, etc. The ultrasonic wave has the characteristics of short wave length, approximate straight line propagation, and easy to focus. Ultrasonic dispersion is a method that the particle suspension was placed directly with the appropriate ultrasonic power and frequency in ultrasonic field processing, which is a kind of high strength dispersion method.

In this experiment, the mechanical dispersion is mainly (1) direct mixing, (2) mechanical pre mixing, and (3) ultrasonic dispersion. (1) Direct mixing is to refer to the nanomaterials and cement at a given speed to stir 5 min by using cement mortar mixer, (2) mechanical pre mixing is a mixture of 5 min to be mixed with a mixer (a certain amount of small steel ball is added in the mixing machine, increasing the impact force to produce more mechanical energy, so that the nanoparticles are dispersed more evenly), (3) ultrasonic dispersion (Zhang, Islam, & Peethamparan, 2012) refers to ultrasonic dispersion 5 min using ultrasonic cleaner (the ultrasonic frequency is 40 kHz).

Mechanical dispersion is to disperse the 3% nano-silica (NS) and 97% cement after mixing; however, the ultrasonic dispersion is to mix nano-silica with 80% of the water in advance, and then the mixture is dispersed for 5 min (because too long the ultrasonic time will lead to an increase in temperature, so the time need to be controlled in a certain range) by ultrasonic cleaner. The remaining water mixed with the ultrasonic dispersion of the silica solution was added to the cement. In addition to pre mixed raw materials in the experiment, the remaining steps are to follow the standard process for the production of mortar. Nano-SiO<sub>2</sub> substituted for cement by 3% wt, water-binder ratio was 0.5, the cement–sand ratio was 1:3, and the flow rate was achieved by adding 0.8% of superplasticizer (SP). Mix proportions of physical dispersion method are given in Table 2.

**Table 2.** Mix proportions of physical dispersion method.

|                   | G1 | G2  | G3            | G4                    | G5                    |
|-------------------|----|-----|---------------|-----------------------|-----------------------|
| Dispersion method | –  | –   | Direct mixing | Mechanical pre-mixing | Ultrasonic dispersion |
| NS (%)            | 0  | 0   | 3             | 3                     | 3                     |
| SP (%)            | 0  | 0.8 | 0.8           | 0.8                   | 0.8                   |

### 2.2.2 Chemical dispersion method

The dispersion of nanoparticles in water medium is a process of dispersing and flocculation, although the physical method can solve the dispersion of nanoparticles in water and other liquid media, but once the mechanical force is stopped, due to the role of particles between the van Edward force, and the nanoparticles will gather together. And the chemical method can be used to adsorb on the surface of the

particles and change the properties of the surface of the particles, so as to change the interaction between the particles and the liquid medium or between the particles and the particles, so that the particles have a strong repulsive force, and the role of inhibition of slurry flocculation will be more durable.

There are several kinds of chemical dispersing agents: surfactants, polymers, low molecular weight inorganic electrolytes, or inorganic polymers, surfactants have steric effect, hydrophilic groups are adsorbed on the surface of the powder, hydrophobic chain are extended to the solvent, which has good effect on improving the rheological properties of the slurry; polymer dispersant has a large molecular weight, which is adsorbed on the surface of solid particles, and the polymer chains are fully extended in the medium to form a few nanometers to tens of nanometers thick layer, resulting in the space steric effect can effectively organize the inter particle aggregation. (1) The surface active agent (water reducer in cement is a kind of anionic surfactant) and (2) the polymer dispersant were used in the experiment. In this experiment, the physical and chemical dispersions are combined together, the physical method can be used to solve the agglomeration, and the stability of the slurry is realized by adding dispersant, which can achieve better dispersion effect.

#### 2.2.2.1 Surfactant

Surfactant are chosen to use common water reducer in cement, the water reducing agent used in the experiment is liquid state of polycarboxylic series of water reducer PSW-1 (water reducing rate is 28%), powder of naphthalene series water reducer FDN-2 (water reducing rate is 22%), powder of polycarboxylic series of water reducer PS-3. Because of the different water reducing efficiency of water reducing agent, in order to maintain a certain degree of mobility, it is necessary to adjust the content of nano-SiO<sub>2</sub>. Nano-SiO<sub>2</sub> substituted for cement by 2% wt, the dosage of water reducing agent is 0.6%, water-binder ratio was 0.5, and the cement–sand ratio was 1:3. Mix proportions of chemical dispersion method (water reducer) are given in Table 3.

**Table 3.** Mix proportions of chemical dispersion method (water reducer).

|                              | H1 | H2    | H3    | H4   |
|------------------------------|----|-------|-------|------|
| NS (%)                       | 0  | 2     | 2     | 2    |
| Type of water reducing agent | –  | PSW-1 | FDN-2 | PS-3 |
| SP (%)                       | 0  | 0.6   | 0.6   | 0.6  |

#### 2.2.2.2 Polymers

Based on the dissociation of the polymer, the polymer can be divided into ionic and non-ionic. Non-ionic polymer is used to stabilize the slurry through the space position, the molecular weight of 400 and 2000

of the polyethylene glycol (PEG-400, PEG-2000) used in this experiment is a kind of non-ionic polymer dispersant. Water, nano-SiO<sub>2</sub>, and polyethylene glycol with ultrasonic dispersion for 5 min, as mixing water was added into cement. Nano-SiO<sub>2</sub> substituted for cement by 3% wt, water-binder ratio was 0.5, and the cement–sand ratio was 1:3. Mix proportions of chemical dispersion method (water reducer) are given in Table 4.

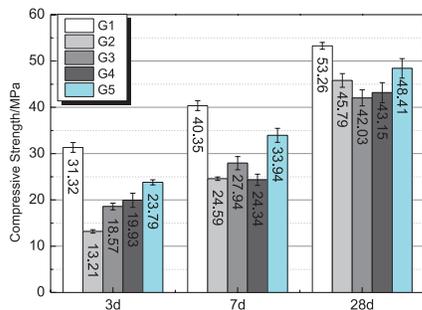
**Table 4.** Mix proportions of chemical dispersion method (polymers).

|              | K1 | K2  | K3  | K4  | K5  |
|--------------|----|-----|-----|-----|-----|
| NS (%)       | 0  | 0   | 0   | 3   | 3   |
| PEG-400 (%)  | 0  | 0.5 | 0   | 0.5 | 0   |
| PEG-2000 (%) | 0  | 0   | 0.5 | 0   | 0.5 |
| SP (%)       | 0  | 0   | 0   | 2.2 | 2.2 |

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Physical dispersion method

We can see from Figure 1, although the proportion of the experiments is the same, the difference between the compressive strengths is great. And the compressive strength of G1 doped with nano-SiO<sub>2</sub> was lower than that of the control group (in the literature, the compressive strength of mortar increased obviously after adding a certain amount of nano-SiO<sub>2</sub>), whereas the strength of G2 with the same water reducing agent is high. So, this result may be caused by water reducing agent. In these methods, the effect of ultrasonic dispersion is the best. Compared with the G2 group, the compressive strength was significantly improved, and the compressive strength of 28 days increased by 5.72%. After mechanical stirring and mechanical grinding, the macromorphology is different, but the compressive strength is basically the same. In other words, for the low intensity of mechanical dispersion, the dispersion effect of nanomaterials in cement is not good.



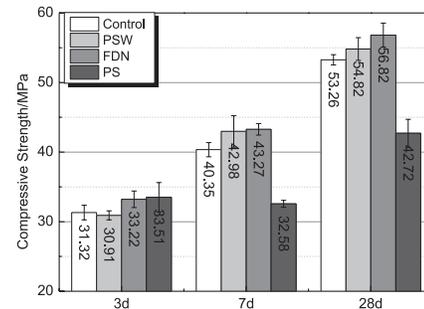
**Figure 1.** Effect of different physical dispersion methods.

#### 3.2 Chemical dispersion method

##### 3.2.1 Surfactant

It can be seen from Figure 2, as far as liquid state of polycarboxylic series of water reducer PSW-1,

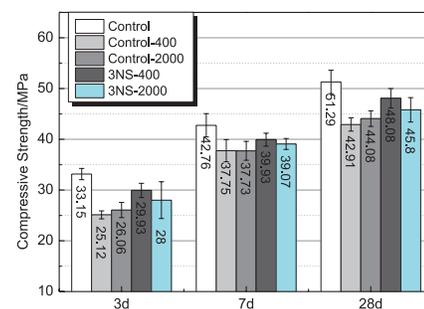
its 3 days compressive strength is decreased, but after curing 7 and 28 days, the compressive strength is gradually increasing. It may be due to the agglomeration problem, which leads to the increase of the particle size, the positive effect of the nanomaterial is reduced. While the poly carboxylic acid powder leads gas, there will be a lot of bubbles in the forming process, which will cause a decrease in compressive strength after certain curing age. For naphthalene series water reducer, the strength of 3, 7, and 28 days is increased, and there is a rising trend, this has a certain auxiliary effect on the dispersion.



**Figure 2.** Effect of water reducer on the compressive strength of mortar mixed with nanomaterials.

##### 3.2.2 Polymers

From the Figure 3, it can be seen that the strength of cement mortar is reduced after adding polyethylene glycol, which shows that the strength of polyethylene glycol has a certain influence on the strength. From the 28-day curing age, it can be seen that the polyethylene glycol not only has a negative effect on the early stage but also has the same effect on the latter. The reduction ratio is close, and the effect of PEG-400 and PEG-2000 is similar. Therefore, 4 and 5 of the control group are 2 and 3, the compressive strength of 3, 7, and 28 days are increased by 19.14, 6.91, 12.03, and 7.43, 3.55, 3.89%, respectively. To sum up, the dispersion effect of PEG-400 is better than that of PEG-2000. Although it can be beneficial to the dispersion of nano-SiO<sub>2</sub> by the addition of polyethylene glycol, polyethylene glycol has a certain damage to cement, so polyethylene glycol is not selected as dispersant.



**Figure 3.** Effect of dispersing agent on the compressive strength of cement mortar with nanomaterial.

#### 4. CONCLUSION

- (1) In the physical dispersion method, the effect of ultrasonic dispersion is the best, and the compressive strength is lower, and it is -9.11%;
- (2) In the chemical dispersion method, the effect of adding naphthalene water reducer is the best, and the 28-day compressive strength is increased by 6.68%;
- (3) In summary, we conclude an optimal process flow, and the concrete experimental steps are as follows: all nano-silica and 75% water are mixed first using ultrasonic mixer with 50 W power input for 5 min. The naphthalene water reducer is mixed in a mortar mixer with sand and cement for 2 min at low speed. After that, the sonicated mixture and the remaining water are added and mixed for 1 min at low speed and 2 min at high speed. The 28-day compressive strength of the casting specimens is improved by 10.67%.

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#### REFERENCES

- Instruments Malvan. (2004). *Zetasizer nano series user manual*. England: Malvan, (1.1), pp. 14–116.
- Iwasaki, M. (1997). New route to prepare unitrafien  $Z_nO$  particles and its reaction mechanism. *Materials Science Letter*, 16(18), 1503–1505.
- Jin, F., Chu, P. K., Tong, H., & Zhao, J. (2006). Improvement of surface porosity and properties of alumina films by incorporation of Fe micrograins in micro-arc oxidation. *Applied Surface Science*, 253(2), 1–6.
- Kawashima, S., Hou, P., Corr, D. J., & Shah, S. P. (2013). Modification of cement-based materials with nanoparticles. *Cement Concrete Composites*, 36, 8–15.
- Sonebi, M., Garcia-Taengua, E., & Hossain, K. M. A. (2015). Effect of nanosilica addition on the fresh properties and shrinkage of mortars with fly ash and superplasticizer. *Construction and Building Materials*, 84, 269–276.
- Stefanidou, M., & Papayianni, I. (2012). Influence of nano-SiO<sub>2</sub> on the Portland cement pastes. *Composites Part B: Engineering*, 43(6), 2706–2710.
- Zhang, M.-H., Islam, J., & Peethamparan, S. (2012). Use of nano-silica to increase early strength and reduce setting time of concretes with high volumes of slag. *Cement Concrete Composites*, 34(5), 650–662.