Nano Fumed Silica Particles on Cement Properties

Zhi Li¹*, Yanmin Wang¹ and Yanling Wu¹

¹ School of transportation and civil engineering, Shandong Jiaotong University, Jinan, Shandong, 250357, China

*Corresponding author’s e-mail: 1024453023@qq.com

Abstract. The hydration of cement paste is generally responsible for the development of essentially every engineering property of cement paste. The compressive strength and early hydration performance of cement mortar can be improved by adding nano silica into ordinary strength mortar, which is related to the pozzolanic properties of nano silica. Hence, this paper investigated the effects of different amounts (2%, 4% and 6%) of fumed silica on hydration and hardening of cement. The result indicates that water consumption of standard consistency of cement increases with the addition of nano fumed silica particles. In addition, with the dosage increase of fumed silica, the setting time gradually becomes shorter. It is worth noting that the setting time of slurry becomes shorter obviously when the addition amount of nano fumed silica is 2%. The result of cement sand test indicates that the addition of fumed silica reduces the strength of cement, which is related to the hydration reaction. It is suggested that nano fumed silica should be used in combination with high efficient plasticizer, which decreases the agglomeration and directly impacts kinetics of hydration and leads to improvement in workability as well as concrete strength through the increase in the formation of silicate calcium hydrate.

1. Introduction

Nanomaterials exhibit outstanding special properties in electrical, magnetic and optical fields due to their surface effects, quantum size effects, macroscopic quantum tunneling effects and dielectric limiting effects, and are widely used in various fields[1]. Concrete is one of the most widely used materials in the construction industry[1]. Ordinary concrete has large rigidity and low flexibility. At the same time, due to some natural defects, concrete often appears cracking in the process of use, and even causes structural damage. At present, one of the common methods to improve the performance of concrete is the recombination of materials[2-4]. The incorporation of nano-materials into concrete can improve the physical and mechanical properties of concrete to a certain extent. In terms of microstructure, nano-materials can fill the micropores and improve the interfacial transition zone of concrete due to their small size. In addition, the addition of nano-materials may affect the hydration reaction of cement to a certain extent, but also affect the crosslinking of cement hydration products[5-6]. At present, there is still a lack of systematic research on the mechanism of performance change of nano-materials introduced into cement and cement concrete[7-13]. In recent years, scholars at home and abroad have added different nano-materials (such as nano SiO₂, CaCO₃, TiO₂) into concrete and studied its mechanics and durability[14-16]. For example, Ye et al. used different proportions nano-silica (0%, 1%, 2%, 3% and 5%) instead of cement, and the experiment found that the compressive strength of the material was optimal when 5% cement was replaced[17]. Maheswaran et al. reported that the physical and chemical properties of cement paste are improved when the addition of nano-silica to cement paste. The experiment exhibits that the compressive strength of cement mortar is...
improved, and the early hydration of cement mortar can be made[18]. Cheuny et al. reported that the strength and durability of concrete are improved by using nano-silica with strong dispersity and adding additives such as water reducer or plasticizer to reduce the agglomeration of nano-materials during the reaction[19]. The gas phase silica materials have been widely used in rubber, plastics, adhesives, coatings and other fields because of their large surface area, amorphous morphology and surface polyhydroxyl functional groups. But the application of this material in cement and cement concrete is less. It has also been proved that nano-silica has pozzolanic properties. The addition of nano-silica in cement hydration process will accelerate the formation of early hydrated calcium silicate gel particles, grain arrangement and reduce the content of calcium hydroxide, thus reducing the chemical leaching of calcium hydroxide and sulfate erosion, thus changing the macroscopic and microscopic properties of cement and cement concrete[20].

Therefore, In this thesis, the gas phase SiO2 was studied by using gas phase silica nanoparticles as admixture. Taking composite portland cement (P•C42.5) as the research object, the effects of nano-SiO2 on water consumption of cement standard consistency, setting time and cement-sand strength were studied.

2. Raw materials and testing section

2.1. Raw materials

The cement is made of composite portland cement, P•C42.5. In addition, the setting time, compressive strength and density of cement were tested according to the test method for《water consumption, setting time and stability of cement standard consistency》(GB/T 1346-2011), 《the test method for strength of cement glue sand (ISO method)》(GB/T 17671-1999) and 《the test method for density of cement》(GBT 208-2014). The test results are shown in Table 1. The measured indexes meet the requirements of the current standard《General Portland Cement》(GB 175-2007). Nano SiO2 gas phase silica (XZ-G01) was used and its main technical indicators are shown in Table 2.

| Projects                      | Indicators          |
|-------------------------------|---------------------|
| SiO2 content (dry)            | ≥90%                |
| (4.5 μm)                      | ≤0.5%               |
| Heating reductions            | 4.0-8.0%            |
| Burn reduction (dry)          | ≤7.0%               |
| Density                       | True density        | 2.0 g/ml            |
|                               | False density (bulk density) | 0.2 g/ml         |
|                               | Particle size       | 10~20 nm            |

Table 1. Physical and mechanical properties of cement.

| Technical nature | Initial setting time (min) | Final setting time (min) | Compressive strength (MPa) | Flexural strength (MPa) | Density (g/cm³) |
|------------------|---------------------------|--------------------------|----------------------------|------------------------|-----------------|
| Test results     | 258                       | 288                      | 3 d 28 d                   | 3 d 28 d               | 15.6 43 3.6 6.8 | 3.09            |
| Technical requirements | ≥45               | ≤600                      | 15                          | 42.5                   | 3.5 6.5        | 3.00-3.15       |
2.2. Test section
Nano SiO\textsubscript{2} the same amount of cement with different ratios was replaced by the internal doping method. The relevant performance test of cement slurry is based on the test method of 《water consumption, setting time and stability of cement standard consistency》 (GB/T 1346-2011). The strength of cement is carried out by the test method of 《cement mortar strength (ISO)(GB∕T 17671-1999), and the ratio of water to glue is 0.5.

3. Results and analysis

3.1. Effect on slurry fluidity for nano fumed silica particles
Different SiO\textsubscript{2} alternative rates of cement paste standard consistency water consumption (P\%) are shown in Table 3. As can be seen from Table 3, the standard consistency water consumption of the slurry SiO\textsubscript{2} with the nanometer the increase of the amount of admixture increases. And the gradient is larger. When the nano SiO\textsubscript{2} content is 0%, the water consumption for the standard consistency of the pure cement slurry is 29.2%. When the nano SiO\textsubscript{2} content is 2%, the water consumption for the standard consistency is 33.0%, which is 13% higher than that for the pure cement slurry. When the nano SiO\textsubscript{2} content is 4%, the water consumption is 55% higher than that of the pure cement slurry. When the nano SiO\textsubscript{2} content is 6%, the water consumption is increased by 108% compared with the net cement slurry. This indicates that nano-SiO\textsubscript{2} requires more water than cement, and has better plasticizing effect if it can be used in cement or concrete. If it can be used in cement or concrete, it may affect the fluidity of concrete, so water reducing agent is needed. In particular, when the amount of the nano SiO\textsubscript{2} used is greater than or equal to 2%, it needs to be combined with superplasticizer in order to meet the prescribed construction technical requirements and ensure the quality of early and late engineering[21].

Table 3. Water consumption for standard consistency of cement slurry with the different ratio for nano fumed silica particles.

| Cement quality (g) | SiO\textsubscript{2} of nano-gas phase Quality (g) | SiO\textsubscript{2} of nano-gas phase percentage of admixture (%) | Water consumption | P\%   |
|--------------------|---------------------------------|-------------------------------------------------|------------------|-------|
| 500                | 0                               | 0                                              | 146              | 29.2  |
| 490                | 10                              | 2                                              | 165              | 33.0  |
| 480                | 20                              | 4                                              | 226              | 45.2  |
| 470                | 30                              | 6                                              | 303              | 60.6  |

The effect of gas phase SiO\textsubscript{2} on the setting time of cement paste is shown in Table 4. The experimental results show that the initial setting and final setting time of the slurry are shortened with the increase of the content. When the nano-SiO\textsubscript{2} content was 2%, the setting time of the slurry was significantly shorter than that of the plain cement slurry. The initial setting time changed from 258 min to 200 min, and the final setting time from 288 min to 254 min. When the SiO\textsubscript{2} content is between 2% and 6%, the setting time gradually gets shorter with the increase of the content, but the shortening range is not obvious. The addition of SiO\textsubscript{2} makes the setting time shorter, which indicates that the hydration reaction rate of nano-SiO\textsubscript{2} is obviously faster than that of ordinary portland cement. And it's mainly due to nano SiO\textsubscript{2} caused by the unique small size effect and surface effect, the smaller the size, the higher the surface energy, the proportion of atoms located on the surface is quite large, and the contact area with water is large. As the particle size decreases, the number of surface atoms increases rapidly due to the sharp increase of surface area, these surface atoms have very high activity, and the extremely unstable performance is that the reaction rate is faster. Hence, when using nano gas phase SiO\textsubscript{2} to prepare cement concrete, attention should be paid to its effect on setting time, which can be adjusted by adding additives. Adding nano-silica to cement can accelerate the formation of early hydrated calcium silicate gel particles and reduce the amount of calcium hydroxide. It is reported that...
under microscopic observation, nano-silica can refine calcium hydroxide grains and change the grain arrangement of hydrated calcium silicate gel. Nano-silica can change grain orientation, promote nucleation and growth of crystal nucleus, in which ettringite acts as communication-bridge, nano-silica fills pores, refines hydration products, compact structures[22].

Table 4. The initial and final setting time influence of the different doping ratio for nano fumed silica particles on slurry.

| SiO$_2$ of nano-gas phase of dosage (%) | Initial setting time (min) | Final setting time (min) |
|----------------------------------------|---------------------------|-------------------------|
| 0                                      | 258                       | 288                     |
| 2                                      | 200                       | 254                     |
| 4                                      | 197                       | 245                     |
| 6                                      | 191                       | 231                     |

3.2. Influence on cement stability for SiO$_2$ of nano-gas phase

The different content of the slurry was tested for stability, and the experimental results are shown in Table 5. The results show that SiO$_2$ of nano-gas phase has no adverse effect on cement stability.

Table 5. The stability influence of the different doping ratio for nano fumed silica particles on cement.

| Nano SiO$_2$ of dosage (%) | Stability                      |
|----------------------------|--------------------------------|
| 0                          | No warping, cracking, etc., good |
| 2                          | No warping, cracking, etc., good |
| 4                          | No warping, cracking, etc., good |
| 6                          | No warping, cracking, etc., good |

3.3. Effect on strength of cement sand for SiO$_2$ of gas phase

According to the ratio of cement: standard sand: water is 1:3:0.5, the rubber sand specimen is formed, curing to a certain age for cement sand compression and folding test, in which nano-gas phase silica equivalent replacement cement. The effect of nano-gas-phase silica on the strength of cement mortar is shown in Table 6.

Table 6. The strength influence of the different doping ratio for nano fumed silica particles on cement sand.

| SiO$_2$ of dosage (%) | 3 d | 28 d | 3 d | 28 d | 3 d | 28 d |
|-----------------------|-----|------|-----|------|-----|------|
| Flexural strength (Mpa) | 3.6 | 6.8  | 3.3 | 6.2  | 3.0 | 5.9  |
| Compressive strength (Mpa) | 15.6 | 43.0 | 12.8 | 39.6 | 10.5 | 34.9 |

It can be seen from Table 6 that the incorporation of nano silica reduces the compressive and flexural strength of cement sand. The main reason for the decrease of the strength is that the water consumption of the standard consistency of nano-silica is changed greatly, which has a great influence on the hydration process. In the curing process, we find that some nano-silica is analyzed from the voids of cement sand, which leads to the further increase of the void ratio of cement sand, so the compressive and flexural strength of cement sand is reduced. Therefore, it is suggested that nano-silica
should be used in conjunction with superplasticizer, or we can try to adjust the ratio of water glue to sand.

4. Conclusions
In this paper, the influence of gas phase silica on cement properties is studied. The results show that:
(1) nano-gas phase silica has thickening effect on cement, which will increase the water consumption of cement standard consistency. When the amount of incorporation is less than 6%, the amount of incorporation is positively correlated with the water consumption of standard consistency. (2) The incorporation of appropriate amount of gas-phase silica can accelerate the hydration reaction of cement and shorten the setting time of cement paste. (3) Without adding superplasticizer, cement mortar test shows that silica incorporation reduces the strength of cement sand.

Acknowledgments
The research is supported by Natural Science Foundation of Shandong Province (Grant No. ZR2017LEM006), Fundamental Research Funds for the Shandong Jiaotong University (Grant No. Z201918), and the Shandong Jiaotong University “Climbing” Research Innovation Team Program.

References
[1] Jiang, R. (2013) Dimensional Effects of Phase Transitions of Several Nanomaterials. Xiangtan University.
[2] Li, J., Liao, Q. (2018) Thermal properties and phase transition properties of Cu/SiO$_2$ nanocomposites. Journal of University of Chinese Academy of Sciences, 35: 248-253.
[3] Zhang, T., Gao, P., Gao, P., et al. (2013) Effectiveness of novel and traditional methods to incorporate industrial wastes in cementitious materials - An overview. Resources, Conservation and Recycling, 74: 134-143.
[4] Wang, L.G., Zhang, S.P., Li, D.X. (2016) Research and application progress of nanomaterials modified cement-based materials. Silicate Notification, 35: 2128-2134.
[5] Meng, T., Qian, K.L., Qian, X.Q., Zhan, S.L. (2008) Effect of nano-modified composite mineral admixture on cement properties and microstructure. Rare Metal Materials and Engineering, 37: 1-3.
[6] Li, X.J. (2015) A study on interfacial properties of cement matrix composites modified by nanomaterials. Harbin University of Technology.
[7] Luo, J.L., Duan, Z.D. (2008) Damping and mechanical properties of nano-cube/cement-based composites. Journal of Beijing University of Chemical Technology (Natural Science Edition), 35: 63-66.
[8] Zhu, K.Z., Li, I.W., Zhu, H. Y., et al. (2011) Advances in nano-modified cement. New Century Cement Bulletin.
[9] Vera, W. (2013) Effect of nano CaCO$_3$ on cement-based materials and study on mechanism of action. Harbin University of Technology.
[10] Du, T. (2014) Study on the properties of graphene oxide cement matrix composites. Harbin University of Technology.
[11] Yang, L., Gao, Y.N., Wang, F.Z., et al. (2016) TiO$_2$@Ag modified fly ash microaggregate enhanced photocatalytic performance of cement substrate. Journal of Catalysis, 38: 357-364.
[12] Feng, Y.S., Liu, S.Q., Liu, H.T., et al. (2018) Mechanical properties of carbon nanotubes modified cement stone. Drilling fluid and completion fluid, 35: 93-97.
[13] Pan, R.Z., Zhang, S.P., Zheng, D.P., et al. (2018) Advances in multidimensional nano-reinforced cement matrix composites. Material guide, 31: 97-103.
[14] Xu, Z.F., Zhang, M.X., Xu, C.Y. (2007) Analysis on mechanism of nanoscale SiO$_2$ modified cement-based materials. Mining and Metallurgical Engineering, 27: 99-102.
[15] Qian, K.L. (2011) The effect, mechanism and application of nano CaCO₃ on cement-based materials. Zhejiang University.

[16] Meng, T., Qian, K.L., Qian, X.Q., et al. (2008) Effect of nano-calcium carbonate particles on hydration properties and interfacial properties of cement. Rare Metal Materials and Engineering, 37: 667-669.

[17] Qing, Y., Zenan, Z., Deyu, K., et al. (2007) Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume. Construction and Building Materials, 21: 539-545.

[18] Maheswaran, S., Bhuvaneshwari, B., Palani, G., et al. (2013) An overview on the influence of nano-silica in concrete and a research initiative. Research Journal of Recent Sciences, 2: 17-24.

[19] Cheuny, J., Jeknavoria, A., Roberts, L., et al. (2011) Impact of admixtures of the hydration kinetics of Portland cement. Cement and Concrete Research, 41: 1289-1309.

[20] Liu, M., Tan, H., He, X. (2019) Effects of nano-SiO₂ on early strength and microstructure of steam-cured high volume fly ash cement system. Construction and Building Materials, 194: 350-359.

[21] Zhou, L.M., Wang, C., Li, D.L., et al. (2014) Effect of nano SiO₂ on properties of polymer modified cement-based materials. Journal of Shenzhen University: Tech Edition, 31: 227-232.

[22] Cong, L.Q. (2004) A study of nano SiO₂ on the synthesis and its effect on properties of cement-based materials with silica fume. Guangxi University.