Understanding the Dispersion Mechanisms of Nanosilica in Ultra High Performance Concrete

Aileen Vandenberg and Kay Wille

Abstract One of the current challenges to nanoengineering cementitious composite materials is obtaining proper dispersion of nano-sized particles in the cementitious composite matrix. Proper dispersion of particles can lead to improved particle packing density, a key parameter in improving the mechanical, chemical, and sustainable properties of the cementitious composite. Current advances in optimizing particle packing density have led to the development of higher strength, higher durable cementitious composite materials, such as ultra-high performance concrete (UHPC). Further advancement of UHPC can be achieved by the addition of properly dispersed nano-sized particles which will assist in broadening the particle size distribution for further optimization of the particle packing density. Among the vast variety of potential nano-particles, nanosilica is the most studied to date. Nanosilica has been shown to improve macroscopic properties such as mechanical strength, durability, and chemical resistivity of cementitious materials. However, as the average particle diameter size decreases the water demand increases and challenges a balanced mix design. More fundamental work needs to be done in order to understand how nanosilica disperses inside the hydrating matrix. Our research investigations will focus on the interfacial interactions between nanosilica and the hydration products, the ions of the pore solution, and the polymers of admixtures.

Keywords One nanoengineering • Cement • Composite • Nanoparticles • Hydration • Pore solution • Admixtures • Packing density • Strength • Ultra-high performance concrete • UHPC

1 Introduction

Four decades ago high range water reducing polymers revolutionized concrete material design through enhancing the dispersion of cement particles. Additionally, improved particle packing models were applied to cementitious materials to

---

A. Vandenberg (✉) • K. Wille
Civil and Environmental Engineering Department, University of Connecticut,
Mansfield, CT, USA
e-mail: aileen.vandenberg@uconn.edu; kwille@engr.uconn.edu

K. Sobolev, S.P. Shah (eds.), *Nanotechnology in Construction*,
DOI 10.1007/978-3-319-17088-6_40

optimize the particle packing density. These two improvements led to a breakthrough in concrete technology of ultra-high performance concrete (UHPC). UHPC is characterized by a very low water-to-binder (w/b) ratio (generally less than 0.2) that has a compressive strength in excess of 150 MPa, superior durability properties, and a particle size distribution typically between 100 nm and 5 mm [1]. UHPC can be further improved by increasing the particle size distribution to include nano-sized particles, defined as particles with an average diameter of less than 100 nm. Yet, introducing such small particles into UHPC brings up the question how to control self-assembly. Particles below 100 nm are completely dominated by particle-particle interactions [2]. These nano-sized particles have a large surface-to-volume ratio and high surface energy, and thus are controlled by surface forces (e.g., van der Waals) rather than volume forces (e.g., gravity). Understanding surface characteristics leads to understanding particle interactions which then leads to macroscopic properties (mechanical strength, durability, heat resistance). Macroscopic product properties are a function of particle properties (particle shape, size distribution, morphology, interfacial characteristics, chemical composition) and process properties (production method, material source, temperature, pressure, etc.). Dispersity is characterized by particle size distribution, shape and morphology, and interfacial properties [3].

The most commonly studied nano-sized particle used in cement and concrete is nanosilica [4]. It has shown to improve concrete macroscopic properties, such as compressive strength and durability [5]. In order to exploit all of the beneficial properties of nanosilica, further research needs to be done on its dispersion and stability in a cementitious hydrating environment. Therefore, more ways to control process methods and particle properties should be investigated. The following paragraphs will highlight some of these concepts.

2 Discussion

2.1 Silica Process Methods and Silica Particle Properties

When considering the different process methods for nanosilica, it is important to consider silica fume. While silica fume is considered a micro-sized particle, nano-sized particles (smaller than 100 nm) do exist in the particle size distribution. The process route of silica fume, a by-product of the silicon and ferro-silicon alloy industries, starts with reducing quartz at high temperatures (2,000 °C) in an electric arc furnace. The quartz oxidizes and condenses into small amorphous silica spheres [6]. Another high heat process method is that of fumed silica or pyrogenic silica. Pyrogenic silica is produced from the flame hydrolysis of silicon tetrachloride ($SiCl_4$) at around 1,800 °C [7]. This process produces an amorphous powder in the submicron particle range.

Additionally, there are process methods that do not require such high heat. One such process is the precipitation method first developed by Iler [8]. In this method a sodium silicate precursor is acidified at temperatures between 50 and 100 °C resulting in nanosilica precipitating out. This method has also been used with rice husk ash as a precursor [9]. Another process method is the sol-gel process, also known as colloidal nanosilica. At room temperature the pH of an organosilicon solvent (e.g., tetraethyl orthosilicate-TEOS) is adjusted to the gelling point of silica. The gel is then filtered and either dried or dispersed in solution [10]. A special method developed by Stöber falls under this process method [11]. Finally, alternative process biological methods of nanosilica do exist such as the olivine and sulfuric method [12].

The reactive sites on a silica particle surface are silanol groups (Si–O–H). Three types of silanol groups can exist on the surface- isolated (Si-OH), germinal (Si-OH2), and etherial (Si–O–Si) [2]. The frequency and density of these groups depend on the synthesis method. Pyrogenic silicas and silica fume have less silanol groups than colloidal silica and precipitated silica due to condensation that occurs during synthesis [13]. Silanol groups form hydrogen bonds with ions and other polar molecules very easily. Therefore, nanosilica can be well dispersed in water with a basic pH value of 7–9 [8, 14–17]. This is due to hydrogen bonding between the deprotonated surface silanol groups and the water molecules, leading to a formation of a water layer around the particle. However, as the pH value rises above 10 dissolution of silica leads to ion-exchange mechanisms displacing the protons of the silanol groups [8, 14, 18]. This prevents water from forming a hydrogen bond with the silanol group impeding the particle dispersion. In high pH silica bonding can occur, if one silica particle contains a dissociated silanol and another silica particle contains an associated group. They link together through an acid-base interaction. Beyond pH of 12 it is postulated that silanol groups will fully disassociate, leading to destabilization and aggregation of silica particles [15, 18]. Thus, in a cementitious pore environment well-dispersed nanosilica hydrosols will most likely experience a degree of re-agglomeration. This degree is still unkown and may depend on the initial hydrosol stabilizer, the specific surface area, surface reactivity, primary particles size, and porosity of the nanosilica particle. Further investigations will need be undertaken to examine this degree of re-agglomeration and how detrimental the re-agglomeration is.

2.2 Silica Particle in Hydrating Cementitious Matrix

The process method chosen will greatly influence the particle dispersity. Dispersity is a function of particle shape, size, size distribution, morphology, surface-to-volume ratio, porosity, and chemical characteristics [3]. In order to understand the dispersity of silica in a cementitious matrix these property parameters need to be taken into consideration. In a recent study Quercia et al. [10] compared how different process methods change the morphological and textural characteristics of different amorphous nanosilicas. Particle parameters such as specific surface area (SSA), particle size, pore size distribution, porosity, and shape were compared to see how slump-flow properties of normal concrete mortar were affected. Their study demonstrated that SSA, porosity, and average primary particle size are the parameters with the largest influence on slump. In a related study, Quercia et al. [19] studied the water demand of these different nanosilicas. They noticed that the pH of the pore fluid differed depending on the process route of the silica used. Additionally, they found that colloidal silica had less relative pozzolanic index compared to other production methods. They postulated that surface area determines the agglomeration state which in turn determines the relative pozzolanic reactivity. While these studies show that textural and morphological parameters have a large influence on the water demand and on the agglomeration state of the silica particles in normal concrete environments, considerations of the chemical reactivity of the silica surface, the superplasticizer-silica particle interactions, and lower water-to-cement (w/c) ratios were not investigated.

Recently, Oertel et al. [7, 13, 20] attempt to address some of these issues. In their investigations they compared conventional silica fume, pyrogenic silica, and Stöber synthesized nanosilica particles comparing the specific surface area, silanol group densities, and solubility in alkaline suspensions. Oertel proposed two reaction paths for silica: (i) pozzolanic reaction or (ii) nucleation seeding effect. Interestingly though, the authors found that the Stöber particles did not appear to follow either path. Instead they found that silicate ions, formed from the dissolution of silica, interacted with alkali ions (Na^+ and K^+) that were immediately released upon hydration of cement clinker. These alkali cations react with silicate ions and form alkali silicate oligomers. Additionally, Ca^{2+} ions that are released from the dissolution of cement clinker interact with silicate ions to form calcium silicate oligomers and in some cases calcium alkali silicate oligomers. This oligomerization may lead to a calcium rich silicate gel layer that surrounds the silica particles. This gel layer may prevent the silica particles from acting as nucleation seeding sites for calcium-silicate-hydrate (C-S-H) or taking part in a pozzolanic reaction with calcium hydroxide (CH). Furthermore, the UHPC mix with Stöber particles did not show increased early day strength or accelerated heat curves like the pyrogenic silica and silica fume UHPC mixes. However, the Stöber particle mixes did show that the 28 day compressive strength was comparable and even a little higher than the other forms of silica. While, the authors' findings show that surface reactivity of silica is an important parameter to consider in understanding dispersion mechanisms, their investigations focused on particle sizes larger than 100 nm. Additionally, consideration of the superplasticizer-silica interactions were not addressed.

Nanosilica not only has potential to interact with the cement hydration products, but also to interact with high range water reducing polymers in the matrix. It has been shown that current commercially available superplasticizer polymers exhibit incompatibilities with nanosilica [21]. Glotzbach et al. [22] used AFM to study silica-silica particle interactions in a closed fluid cell. The fluid cell was injected with a fluid environment similar to the pore environment of a cement paste. Four different plasticizer polymers were injected at separate times into the fluid cell to observe the interaction forces between silica particles in the presence of plasticizer. In this study a commercially available PCE with a high molecular weight, and three custom-made polymers were used. Shear and force measurements showed that the commercial polymer was most incompatible with silica particles. Its large backbone and long side chains might lead to particle bridging. The smaller polymers with shorter side chains and different functionalities were more compatible. The study by Glotzbach demonstrated that better dispersing polymers are needed for nanosilica. One possible route is functionalization of nanosilica surface with organic molecules similar to current dispersing polymers used for cement and silica fume. Shin et al. [23] functionalized nanosilica particles with poly(ethylene glycol) methacrylate (PEGMA) by treating Stöber silica particles with triethoxyvinylsilane (VTES) before grafting PEGMA via UV-photopolymerization on them. While, the research intentions were not for cement this could be a possible route to take in finding more compatible dispersing polymers for nanosilica.

3 Conclusion

This paper has attempted to address important parameters to consider for understanding dispersion mechanisms of nanosilica. Dispersity mechanisms are influenced by synthesis methods, particle surface properties, and particle size properties. Incompatibilities of superplasticizers with nanosilica show that better admixtures need to be developed. One possible route to this is surface functionalization. Additionally, some degree of agglomeration will take place. Understanding this degree of agglomeration and how detrimental its effects are to the hydrating cementitious matrix needs further investigation.

References

1. Wille, K., Naaman, A. E., & Parra-Montesinos, G. J. (2011). Ultra high performance concrete with compressive strength exceeding 150 MPa (22 ksi): A simpler way. *ACI Structural and Materials Journal, 108*, 46–54.
2. Parida, S. K., Dash, S., Patel, S., & Mishra, B. K. (2006). Adsorption of organic molecules on silica surface. *Advances in Colloid and Interface Science, 121*, 77–110.
3. Peukert, W., Schwarzer, H., Götzinger, M., Günther, L., & Stenger, F. (2003). Control of particle interfaces — the critical issue in nanoparticle technology. *Advanced Powder Technology, 14*, 411–426.
4. Singh, L. P., Karade, S. R., Bhattacharyya, S. K., Yousuf, M. M., & Ahalawat, S. (2013). Beneficial role of nanosilica in cement based materials – A review. *Construction and Building Materials, 47*, 1069–1077.
5. Sobolev, K., Flores, I., Hermosillo, Torres-Martinez L, Valdez, P. L., Zarazua, E., & Cuellar, E. L. (2009). *Engineering of SiO2 nanoparticles for optimal performance in nano cement-based materials*. In Z. Bittnar, P. J. M. Bartos, J. Nemecek, V. Smilauer, & J. Zeman (Eds.), *Nanotechnology in Construction Proceedings of the NICOM3* (pp. 139–148). Prague/Berlin/Heidelberg: Czech Republic/Springer, doi:10.1007/978-3-642-00980-8.
6. Snellings, R., Mertens, G., & Elsen, J. (2012). Supplementary cementitious materials. *Reviews in Mineralogy and Geochemistry, 74*, 211–278.

7. Oertel, T., Hutter, F., Helbig, U., & Sextl, G. (2014). Amorphous silica in ultra-high performance concrete: First hour of hydration. *Cement and Concrete Research, 58*, 131–142.
8. Iler, R. K. (1979). Chemistry of silica – Solubility, polymerization, colloid and surface Properties and biochemistry, 896, Wiley, New York.
9. Thuadaj, N., & Nuntiya, A. (2008). Preparation of nanosilica powder from ride husk ash by Precipitation Method. *Chiang Mai Journal of Science, 35*, 206–211.
10. Quercia, G., Lazaro, A., Geus, J. W., & Brouwers, H. J. H. (2013). Characterization of morphology and texture of several amorphous nano-silica particles used in concrete. *Cement and Concrete Composites, 44*, 77–92.
11. Stöber, W., Fink, A., & Bohn, E. (1968). Controlled growth of monodisperse silica spheres in the micron size range. *Journal of Colloid and Interface Science, 26*, 62–69.
12. Lazaro, A., & Brouwers, H. J. H. (2010). *Nano-silica production by a sustainable process; Application in building materials*. 8th fib PhD symposium in Kgs Lyngby, Denmark.
13. Oertel, T., Hutter, F., Tänzer, R., Helbig, U., & Sextl, G. (2013). Primary particle size and agglomerate size effects of amorphous silica in ultra-high performance concrete. *Cement and Concrete Composites, 37*, 61–67.
14. Amiri, A., Øye, G., & Sjöblom, J. (2009). Influence of pH, high salinity and particle concentration on stability and rheological properties of aqueous suspensions of fumed silica. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 349*, 43–54.
15. Chen, S., Øye, G., & Sjöblom, J. (2007). Effect of pH and salt on rheological properties of aerosil suspensions. *Journal of Dispersion Science and Technology, 28*, 845–853.
16. Ding, P., & Pacek, A. W. (2008). De-agglomeration of silica nanoparticles in the presence of surfactants. *Journal of Dispersion Science and Technology, 29*, 593–599.
17. Pacek, A. W., Ding, P., & Utomo, A. T. (2007). Effect of energy density, pH and temperature on de-aggregation in nano-particles/water suspensions in high shear mixer. *Powder Technology, 173*, 203–210.
18. Depasse, J. (1999). Simple experiments to emphasize the main characteristics of the coagulation of silica hydrosols by alkaline cations: Application to the analysis of the model of Colic et al. *Journal of Colloid and Interface Science, 220*, 174–176.
19. Quercia, G., Huesken, G., & Brouwers, H. J. H. (2012). Water demand of amorphous nano silica and its impact on the workability of cement paste. *Cement and Concrete Research, 42*, 344–357.
20. Oertel, T., Helbig, U., Hutter, F., Kletti, H., & Sextl, G. (2014). Influence of amorphous silica on the hydration in ultra-high performance concrete. *Cement and Concrete Research, 58*, 121–130.
21. Fernández, J. M., Duran, A., Navarro-Blasco, I., Lanas, J., Sirera, R., & Alvarez, J. I. (2013). Influence of nanosilica and a polycarboxylate ether superplasticizer on the performance of lime mortars. *Cement and Concrete Research, 43*, 12–24.
22. Glotzbach, C., Stephan, D., & Schmidt, M. (2013). Measuring interparticle forces: Evaluation of superplasticizers for microsilica via colloidal probe technique. *Cement and Concrete Composites, 36*, 42–47.
23. Shin, Y., Lee, D., Lee, K., Ahn, K. H., & Kim, B. (2008). Surface properties of silica nanoparticles modified with polymers for polymer nanocomposite applications. *Journal of Industrial and Engineering Chemistry, 14*, 515–519.