



## ***Particle size distributions of pyrogenic nanosilicas and nanosilica sols, used in cement composites***

H. Madani<sup>1\*</sup>, A. Bagheri<sup>2</sup>, T. Parhizkar<sup>3</sup>, A.M. Raisghasemi<sup>4</sup>

1- Assistant professor, Department of Civil Engineering, Kerman Graduate University of Technology, Kerman, Iran

2- Assistant professor, Department of Civil Engineering, K.N.Toosi University of Technology, Tehran, Iran

3- Assistant professor, Building and Housing Research Center, Tehran, Iran

4- Lecturer, Building and Housing Research Center, Tehran, Iran

(Received 27 Aug 2011, Accepted 23 May 2014 )

### **ABSTRACT**

High attractive surface forces between particles of nanosilicas could lead to significant aggregation of these materials. This study is thus focused on the aggregation status of pyrogenic nanosilicas and nanosilica sols, as two main types of nanosilicas used in concrete. The results show that unlike nanosilica sols, which are in the form of monodispersed particles, serious aggregation of pyrogenic nanosilicas in water occurs. Increasing dispersion forces, particularly the use of ultrasonic waves, has considerable effect in breaking aggregates into smaller aggregates. Increasing the pH was found to be very effective in improving dispersion of nanosilicas and through combined use of high pH and high dispersion forces such as ultrasonic method it is possible to break all the aggregates into primary aggregates.

### **KEYWORDS**

Pyrogenic Nanosilica, Nanosilica Sol, Size Distribution, Dispersion Energy, pH.

---

\* Corresponding Author, Email: h.madani@kgut.ac.ir

## 1- INTRODUCTION

In order to explain the mechanisms by which silica materials influence the properties of concrete several assumptions have been made. Some of these assumptions are based on the behavior of monodispersed silica particles without considering their aggregation status. For instance, it has been suggested that nanosilica particles serve as sites for early precipitation of hydrate products, resulting in acceleration of cement hydration. It has also been suggested that nanosilica particles, due to their fine dimensions, could fill the pores of cement matrix; hence, these materials could improve the microstructure of cement composites and enhance the durability and mechanical characteristics of concrete. The same mechanism has also been suggested for filler effect of silica fume particles in concrete. For instance, in ACI 234 it is mentioned: "In hardened concrete, silica fume particles increase the packing of solid materials by filling the spaces between the cement grains in much the same way as cement fills the spaces between the fine-aggregate particles, and fine-aggregate fills the spaces between coarse-aggregate particles in concrete". In these studies it has not been considered that nanosilicas and silica fume may be in the form of large agglomerates.

Considering the importance of the dispersion of nanosilica powders with regards to their performance in cementitious mixes and the scarcity of information on this subject, in the current research the influence of the method and duration of applying the dispersion energy and variation of pH on the dispersion status of pyrogenic nanosilicas are investigated and compared with the silica fume and silica sols produced through polymerization of silicic acid. For this purpose, two types of nanosilicas including pyrogenic nanosilicas and nanosilica sols each with three different surface areas were investigated and compared to silica fume.

## 2- THE RESULTS

### 2-1- The aggregation status of the nanosilicas and silica fume in their initial form

The results indicate that the pyrogenic nanosilicas and silica fume are in the form large agglomerates with dimensions greater than 1µm up to a few hundred micrometers in their initial powder form. For instance, median size of aggregates of silica fume and Aerosil 200 (with SSA of 200m<sup>2</sup>/g) were determined as 7.2µm and 8.9µm, respectively. The aggregation of pyrogenic nanosilicas was more pronounced than that of silica fume. In figure 1 an agglomerate of Aerosil 200 is shown. In contrast to the pyrogenic nanosilicas and silica fume, the nanosilica sols were in the form of monodispersed particles without any sign of aggregation.

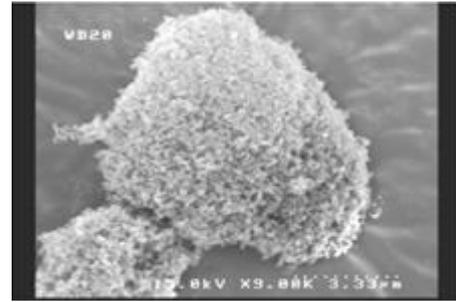


Fig1. SEM image of agglomerates of pyrogenic nanosilicas

### 2-2- Aggregation status of the pyrogenic nanosilicas and silica fume after applying low level of energy

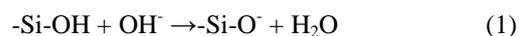
Applying low level of energy including 4 minutes 200rpm shear mixing led to pronounced agglomeration of pyrogenic nanosilicas and silica fume. For instance, the median dimensions of Aerosil 200 and silica fume increases from 8.9µm and 7.2µm in their powder form to 52 µm and 25 µm in water, respectively. This means that common procedure of mixing nanosilica powders with water in low shear mixers does not lead to appropriate dispersion of these materials. In other words, the aggregates of nanosilicas and silica fume are introduced into concrete with sizes larger than cement particles.

### 2-3- The influence of applying high levels of energy on the aggregation status of pyrogenic nanosilicas

The influence of applying high levels of energy including 3000rpm shear mixing and sonication had been investigated. The results indicate that applying high shear mixing for 60 minutes could break large agglomerates of pyrogenic nanosilicas into smaller agglomerates with dimensions mainly greater than 1µm. Applying sonication provides higher amounts of energy and broke agglomerates into aggregates with dimensions between 100nm-300nm. However, these methods could not split agglomerates into primary aggregates with dimensions smaller than 100nm.

### 2-4- the influence of applying high levels of energy and increasing pH on the aggregation status of nanosilicas

According to the following formula, increasing the pH leads to increasing the negative surface charges of particles and consequently results in higher level of repulsive electrostatic forces between particles to overcome the attractive van der waals forces.



In this study, applying high levels of energy such as sonication in conjunction with applying high pH resulted in better dispersion of nanosilicas. For instance, combined use of applying 60 min sonication and adjusting the pH to 10 decreased the median size of aggregates of Aerosil 200 from 8.9µm to 0.033 µm. However, applying high levels of energy and increasing

the repulsive electrostatic forces between particles could not break the nanosilica aggregates into individual particles. Such as sonication, by applying a few minutes of high shear mixing (3000rpm) and adjusting the pH to 10 it was possible to break some of the medium aggregates into small aggregates. By increasing the time of mixing to 60 minutes all medium aggregates converted into small aggregates. Thus the influence of using the high shear mixing in conjunction with the high pH is similar to the influence of using the sonication without adjusting pH.

### 3- CONCLUSIONS

In the powder form, the pyrogenic nanosilicas and silica fume were in the form of large agglomerates with dimensions greater than 1µm up to a few hundred micrometers. This shows that these materials are composed of adhered particles and are not in the form of monodispersed particles.

After introduction into water and applying low level of energy, the median aggregate dimensions of silica fume and the pyrogenic nanosilicas were increased significantly to dimensions mainly greater than dimensions of cement grains.

Although applying high level of energy (60 min sonication) in conjunction with adjusting pH to 10 could convert the large aggregates into primary aggregates, it could not break them into individual particles.

### 4- REFERENCES

- [1] Korpa.A, Trettin.R, K.G. Bottger, J.Thieme, C.Schmidt, "Pozzolanic reactivity of nanoscale pyrogenic oxides and their strength contribution in cement-based systems", *Advances in Cement Research*, 20, no1, 35- 46, 2008.
- [2] Jo.B.W, Kim.C.H, Lim.J.H, "Characteristics of cement mortar with nano SiO<sub>2</sub> particles", *ACI materials Journal*, Vol 104, No 4, 404- 407, 2007.
- [3] ACI Committee 234, "Guide for the use of silica fume in concrete", American Concrete Institute, 2006.
- [4] Qing.Y, Zenan.Z, Deyn.K, Rongshen.C., "Influence of nano-SiO<sub>2</sub> addition on properties of hardened cement paste as compared with silica fume", *Construction and Building Materials*, 21, 539- 545, 2007.
- [5] Li.H , Xiao.H.G, Ou.J., "Flexural fatigue performance of concrete containing nanoparticles for pavement", *International Journal of fatigue* 29, 1292- 1301, 2007.
- [6] Naji Givi.A, Abdul Rashid.S, Aziz.F.N.A, Mohd Salleh.M.A., "Experimental investigation of the size effects of SiO<sub>2</sub> nano-particles on the mechanical properties of binary blended concrete", *Composites: Part B*, 41, pp. 673- 677, 2010.
- [7] Brinkmann.U, Ettliger.M, Kerner.D, Schmoll.R., "Synthetic Amorphous Silica", Chapter 43 in *Colloidal Silica, Fundamentals and applications*, Edited by Schick.M.J, Taylor and Francis group, 2006.
- [8] Rahaman.M.N., "Ceramic Processing and sintering", 2nd ed, Marcell Dekker Inc, 2003.
- [9] Amiri.A, Øye.G, Sjöblom.J., "Influence of pH, high salinity and particle concentration on stability and rheological properties of aqueous suspensions of fumed silica", *Colloid and Interfaces A: Physicochem. Eng. Aspects*, 349, 43- 54, 2009.
- [10] Roberts.W.O., "Silica Manufacturing and applications of water-borne colloidal silica", Chapter 12 in *Colloidal Silica, Fundamentals and applications*, Edited by Schick.M.J , Taylor and Francis group, 2006.
- [11] Sauter .C, Emin. M.A, Schuchmann.H.P, Tavman.S., "Influence of hydrostatic pressure and sound amplitude on the ultrasound induced dispersion and de-agglomeration of nanoparticles", *Ultrasonics Sonochemistry* 15, pp. 517- 523, 2008.