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The aggregation status of nanosilicas and silica fume, used in cementitious mixtures

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ABSTRACT

In several studies it is suggested that enhancing the microstructure of cement composites due to the filler effect of silica particles leads to enhancing the durability characteristics of cement mixtures. However, it has not been considered that silica fume and many types of nanosilicas are in the form of large agglomerates. In this research, the aggregation status of silica fume and pyrogenic nanosilicas is investigated. The SEM images and particle size distributions indicate that in the powder form silica fume and pyrogenic nanosilicas are in the form of large aggregates with dimensions greater than 1µm to more than 100µm. Introducing the nanosilicas and silica fume into water led to higher dimensions of aggregates and applying high levels of energy could not break them into individual particles. Thus, the assumptions based on the filler effect of silica fume and nanosilica materials should consider their aggregation status in environment of cement composites.

Keywords. Nanosilica, Silica fume, filler effect, Particle, Aggregate

INTRODUCTION

The successful performance of silica fume on enhancing the durability characteristics of cement composites is well recognized (Hewlett, 2004, Taylor, 1997, Mehta, 2006). In recent years, due to structural similarities with silica fume a considerable research effort has been attracted to the investigation of the influence of nanosilicas on the properties of cement mixtures. The results of these studies indicate that like silica fume nanosilicas could improve the durability characteristics of concrete (Zhang et al, 2012, Zhang and Li, 2011, Ozyilsirim and Zedetosky, 2010)

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 (Wu and Young, 1984 and Korpa et al, 2008). 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 (Jo et al, 2007, Zhang and Li, 2011 and Zhang et al, 2012). 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”.

However, in these studies it has not been considered that silica fume and most types of the nanosilicas are initially in the form of large agglomerates. Considering the importance of aggregation status of silica materials (nanosilicas and silica fume) and scarcity of information on this subject, the present study was conducted to investigate the aggregation status of pyrogenic nanosilicas and silica fume. It is notable that the pyrogenic nanosilicas are generally produced through reaction of silicon tetrachloride, hydrogen and oxygen in high temperature furnaces with different specific surface areas ranging from about 50m^2/g to 400m^2/g (Bagheri et al, 2012).

MATERIALS AND METHODS

Materials. Two types of pyrogenic nanosilicas with different specific surface areas including Aerosil 200 and Aerosil 380 supplied by Degussa Corporation were used in this study. These products, according to the manufacture’s data, have specific surface areas of 200 and 380m^2/g and mean particle sizes of 12 and 7 nm, respectively. The silica fume used with a specific surface area of 21m^2/g was supplied by Azna Ferroalloy Company and complied with requirements of ASTMC1240. In figure 1, the images of the nanosilicas and silica fume investigated are presented. The properties of materials used are presented in table 1.

a) silica fume b) Aerosil 200 c) Aerosil 380

Figure 1. Various types of nanosilicas and silica fume, used in the current study

Table 1. Chemical composition and physical properties of silica fume and pyrogenic nanosilicas

Properties	Silica fume	Aerosil 200	Aerosil 380
Silica (SiO_2)	92.3	99.8<	99.8<
Iron oxide (Fe_2O_3)	1.0	-	-
Alumina (Al_2O_3)	1.3	-	-
Calcium oxide (CaO)	1.6	-	-
Magnesium oxide (MgO)	0.9	-	-
Sulfur trioxide (SO_3)	0.11	-	-
Sodium oxide (Na_2O)	0.25	-	-
Potassium oxide (K_2O)	0.79	-	-
Loss on ignition	1.53	<1	<2.5
Moisture content	0.2	<1.5	<2
Surface area(m^2/g)	21	200	380

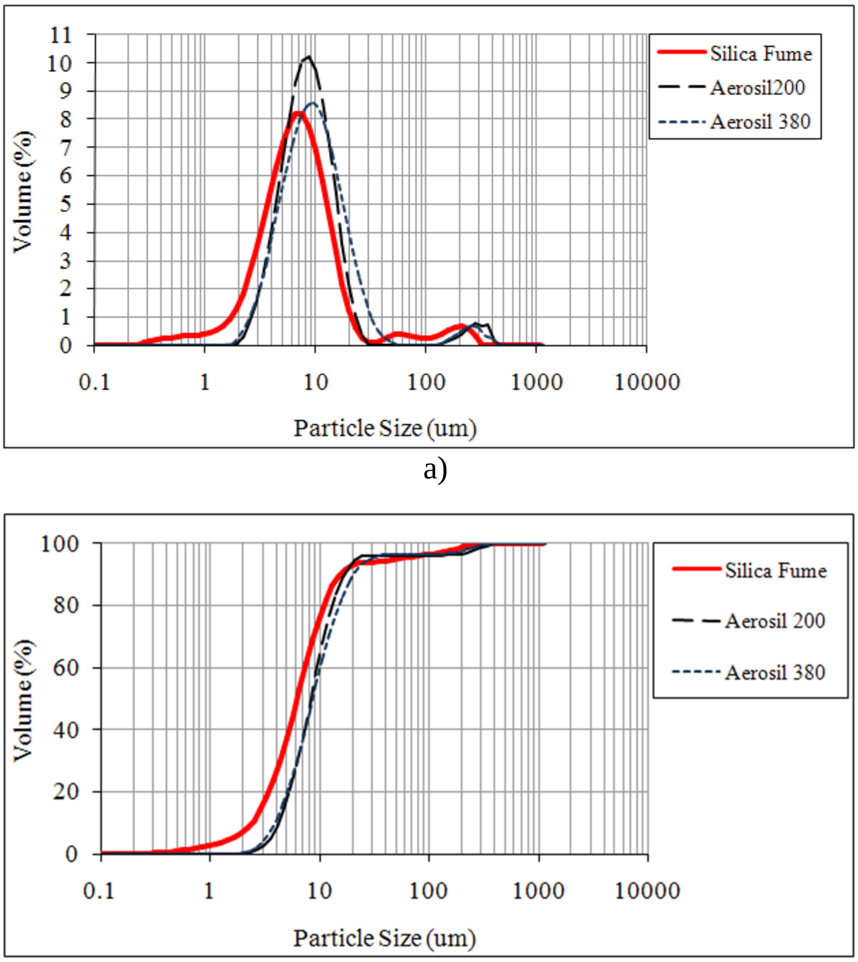
Mixtures. In order to investigate the aggregation status of silica fume, Aerosil 200 and Aerosil 380 in water two different dispersion methods were used. The first procedure used involved 4 minutes of mixing silica materials with water in a 200rpm shear mixer. The other procedure used was mixing the pyrogenic nanosilicas with water in mass concentration of 15%, adding the required amount of NaOH for adjusting the pH of suspension to 10 and dispersing the materials in water, applying 60 min sonication.

Apparatus. The particles/aggregates size distributions of silica fume and the pyrogenic nanosilicas in their powder form and mixing with water in the low shear mixer were measured by particle size analyzer Mastersizer 2000 (Malvern Instruments) designed for particles in the size range 20 nm to 2 mm. The instrument employs Mie theory to calculate particle size distributions from the scattered laser light. Furthermore, the particles/aggregates size distributions of the pyrogenic nanosilicas under 60 min sonication were determined by the Dynamic light scattering method with operating range of 0.3 nm to 10µm using Malvern Zetasizer 3000 HS instrument.

The size and shape of aggregates of nanosilica materials were also studied with a Field Emission Scanning Electron Microscope (Hitachi FE-SEM model S-4160). The apparatus used for applying the ultrasonic dispersion energy was an UPS400, Hielscer-Ultrasonic Technology.

THE RESULTS

The aggregation status of pyrogenic nanosilicas and silica fume. The size distributions determined for silica fume, Aerosil 200 and Aerosil 380 in their initial powder form are given in figure 2. As shown, the pyrogenic nanosilicas and silica fume are in the form large agglomerates with dimensions greater than 1µm up to a few hundred micrometeres. The median size of aggregates of silica fume, Aerosil 200 and Aerosil 380 were determined as 7.2µm, 8.9µm and 9.2µm, respectively. This indicates that the aggregation of pyrogenic nanosilicas is more pronounced than that of silica fume.

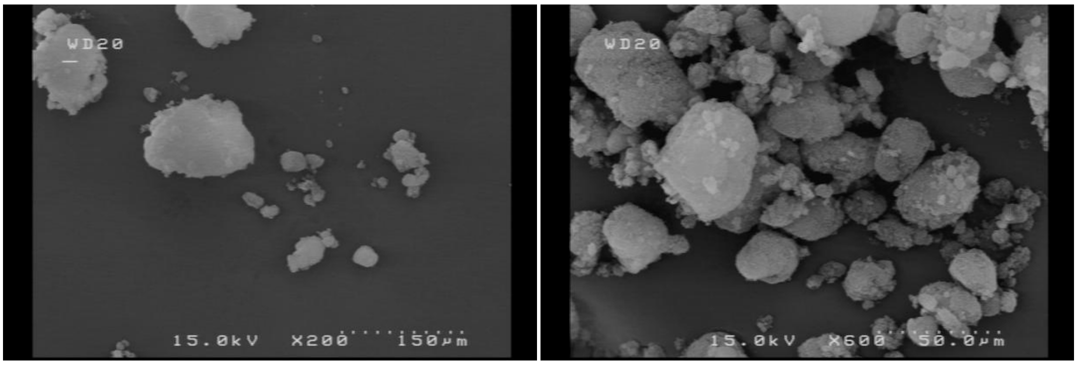


a)

b)

Figure 2. Size distribution of pyrogenic nanosilicas and silica fume in their powder form a) non-cumulative and b) cumulative

In figure 3, the SEM images of aggregates of pyrogenic nanosilicas are presented. As it is shown, despite the very fine dimensions of silica particles, the pyrogenic nanosilicas are in the form of large agglomerates and these results confirm the particle size distributions obtained from laser diffraction.



a) b)

Figure 3. FESEM images of aggregates of a) Aerosil 200 and b)Aerosil 380

The aggregation status of pyrogenic nanosilicas and silica fume in water under low shear mixing. The particles/aggregates size distributions of pyrogenic nanosilicas and silica fume in water are given in figure 4. The procedure used for dispersion of silica materials involved 4 minutes mixing of each material with water in mass concentration of 10% in a 200 rpm shear mixer. The median dimensions of Aerosil 380, Aerosil 200 and silica fume increases from 9.2µm, 8.9µm and 7.2µm in their powder form to 52 µm, 52 µm and 25 µm in water, respectively. The results indicate that the common procedure of mixing nanosilica powders with water in low shear mixers, such as conventional concrete 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.

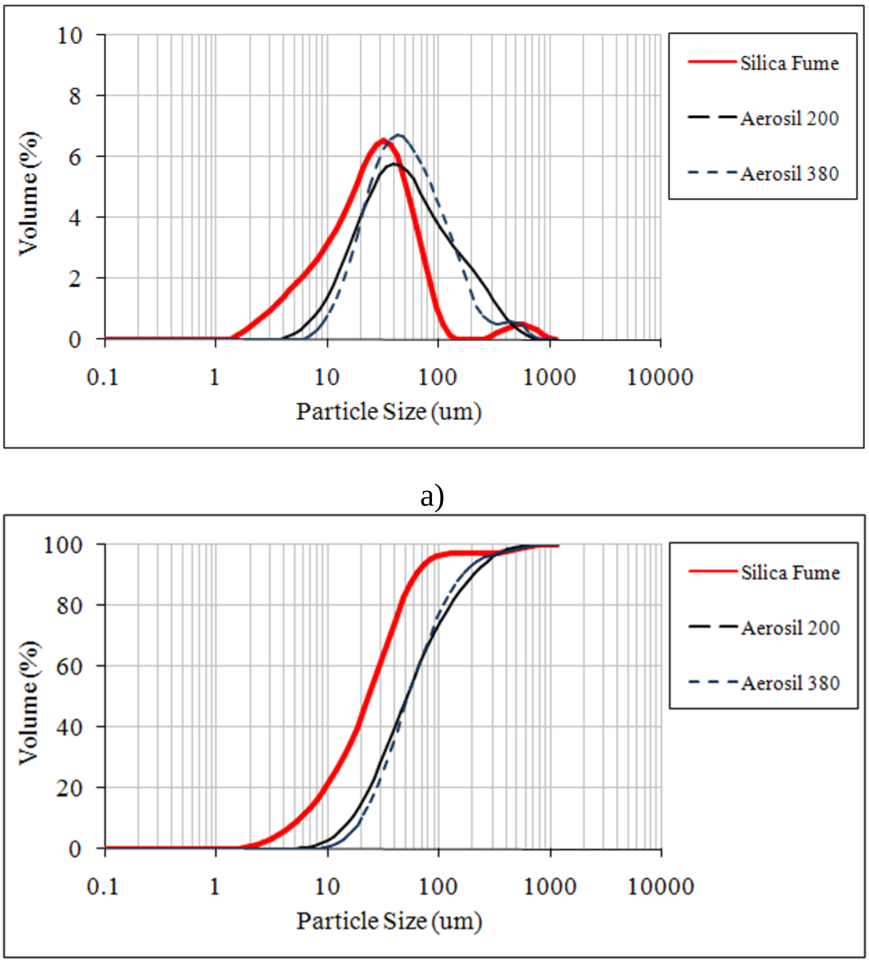
The influence of applying high levels of energy on the aggregation status of pyrogenic nanosilicas. Increasing the level of dispersion energy through applying sonication and adjusting the pH to the basic range is a common way to disperse nanosilica particles in water. However, this method is not usual for dispersion of silica fume. Thus, dispersion of silica fume aggregates using sonication in conjunction with increasing pH was not considered in this study.

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 (Chen et al, 2007, Rahman, 2003, Roberts, 2006).

$$\text{-Si-OH} + \text{OH}^- \rightarrow \text{-Si-O}^- + \text{H}_2\text{O} \qquad (1)$$

Increasing the pH can thus enhance the repulsive electrostatic forces between particles. However, at very high pHs, the risk of coagulation of nanosilicas due to creation of hydroxo bridges between particles through hydrated cations (like Na^+ ions) is increased (Madani et al, 2012). Increasing the pH to values of more than 10 also leads to significant dissolution of nanosilica (Bagheri et al, 2013). It should be noted that most of commercial nanosilica sols have a pH between 9 and 10 (Roberts, 2006). Hence, in this study pH of 10 was considered for investigation of the influence of increasing pH on the aggregation status of nanosilicas.

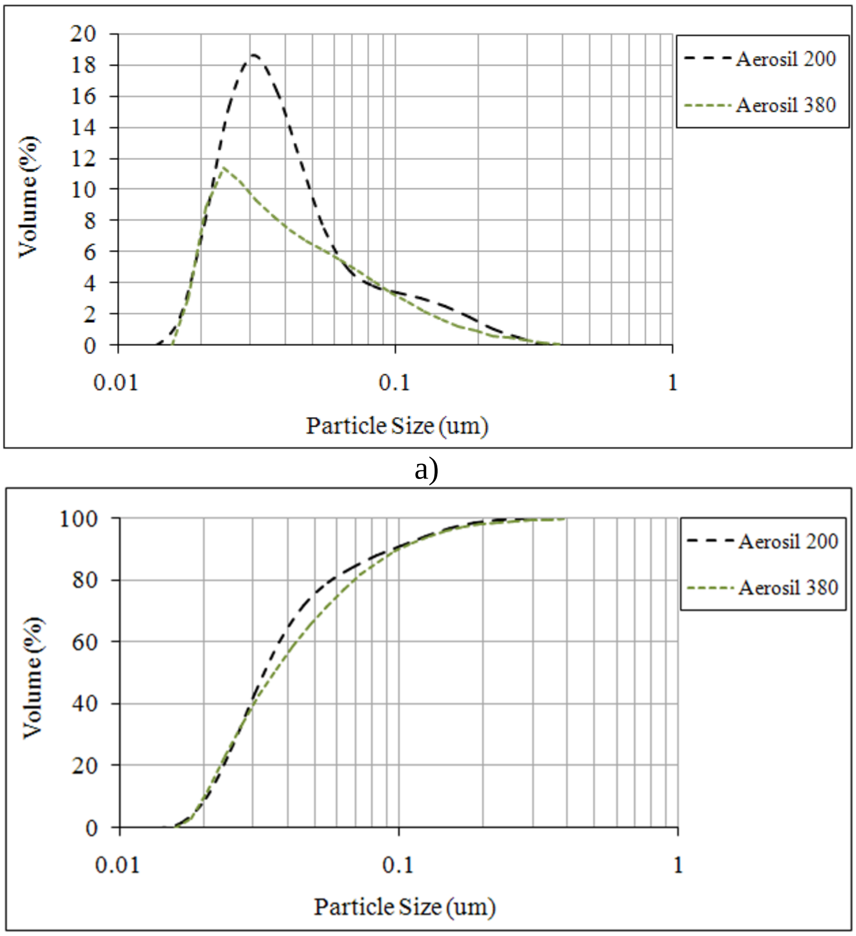
The influence of combined use of applying 60 min sonication and adjusting the pH to 10 on the aggregation status of pyrogenic nanosilicas in water was investigated. The size distributions are presented in figure 5. The median dimensions of Aerosil 200 and Aerosil 380 were 0.033 µm and 0.036 µm, indicating the dimensions of primary aggregates. However, the primary aggregates are composed of a few fused particles in each dimension. Hence, it appears that applying high levels of energy and increasing the repulsive electrostatic forces between particles could not break the nanosilica aggregates into individual particles.



a)

b)

Fig 4. Size distribution of the pyrogenic nanosilicas and silica fume under low shear mixing with water for 4 min a) non-cumulative and b) cumulative



a)

b)

Fig 5. Size distribution of the pyrogenic nanosilicas in water under 60 min sonication a) non-cumulative and b) cumulative

It should be mentioned that in a recent study, it was suggested that the ionic composition of pore fluid of cement composites influence the stability of silica particles, leading to considerable aggregation of these materials (Madani et al, 2012). The mechanisms suggested for the aggregation of nanosilica materials in cement mixtures include bridging influence of Ca^{2+} ions between particles, compression of double layer due to high concentration of ions, de-hydration of silica surfaces and creation of hydroxo bridges between particles. Therefore, although applying high levels of energy could convert the aggregate dimensions into finer ones, the ionic composition of pore fluid of cement composites influence their stability and coagulate them considerably.

As a result, the pyrogenic nanosilicas and silica fume are mixed with other ingredients of cement composites with dimensions greater than cement grains. Hence, the assumptions based on the filler effect of individual particles of nanosilica materials and silica fume or creation of nucleation sites by individual particles for precipitation of hydrate products should be modified. For instance, precipitation of hydrate products should occur at the surface of nanosilica aggregates not at the surface of individual nanosilica particles. On the other hand, considering the aggregation status of nanosilicas and silica fume, these materials could not act as individual particles in filling the pores of cement matrix.

CONCLUSIONS

In this study the aggregation status of pyrogenic nanosilicas and silica fume was investigated. The results indicate that:

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, Aerosil 200 and Aerosil 380 increased from 7.2µm, 8.9µm and 9.2 µm in their powder form to 25µm, 52µm and 52µm in water, respectively. It is notable that these dimensions are 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.

The assumptions based on the filler effect and nucleation effect of nanosilicas and silica fume should consider their aggregation status.

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