

Water layer thickness of silica fines and their effect on the workability of cement pastes

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Abstract

Concrete is used in infrastructure and in buildings. It is composed of granular materials of different sizes and the grading of the composed solid mix covers a wide range. The overall grading of the mix, containing particles from 300 nm to 32 mm, determines the mix properties of the concrete. The properties in fresh state (flow properties and workability) are for instance governed by the particle size distribution (PSD) and the resulting particle packing (PP). One way to further improve the packing is to increase the solid size range, e.g. by including particles with sizes below 300 nm. Possible materials, which are currently available, are limestone and silica fines like silica fume (mS) and nano-silica (nS). This paper addresses the characterization of six different silica fines with respect to their application in cement paste. Given that the fines provide by far the highest percentage of specific surface area in a mix, their packing behavior and water demand is of vital interest for the design of concrete. In the present work, different mixes are compared and analyzed using the mini spread-flow test method. In this way, a deformation coefficient derived by the spread-flow test is confirmed to correlate with the product of computed specific surface area (SSA) based on measured PSD and intrinsic density of the individual silica fines. Similarly, correlations with equal accuracy are found with a computed SSA using the BET method. With the flow experiments of different mixes it is possible to derive an individual deformation coefficient of the silica particles. It is demonstrated that the computed and the BET surface area values have a constant ratio (0.76 to 0.70). Finally, the value of a constant water layer thickness around the powder particles (24.8 nm) is computed for all silica fines at the onset of flowing. This implies the possibility to predict the flow behavior of paste only based on the knowledge of their SSA, either determined by computation or by BET measurements.

Originality

The results obtained for the water demand (β_p), deformation coefficient (E_p) and water film (δ) of silica fines, specifically of amorphous silica nano particles have never been reported in the literature using the mini spread flow test method. This is an opportunity to publish new findings in the field of concrete technology related with nano particles addition and their effect on the rheology and workability of cement based materials. Also these parameters will allow for a tailor made design of new types of silica produced by olivine dissolution in acid, and the prediction of their water demand in cement paste, mortars and concrete mixes. The understanding of the effects of silica fines in cements paste allows for an optimized design of concrete mixes and contributes to the future application of these types of materials as cement replacement.

Chief contributions

Concrete is the most widely produced man-made material after drinking-water. Current micro silica is only applied in special cases, due to its high price, and nano silica is not used in practice yet. Nano silica can be produced in such quantities and for low prices that the mass application in concrete is within reach. It may replace cement in the mix, which is the most costly and environmentally unfriendly component in concrete. The use of nano silica makes the produced concrete financially more attractive and reduces the CO₂ footprint of the produced concrete products. The nano silica will also increase the product properties of the concrete: the workability and the properties in hardened state, enabling the development of high performance concretes for extreme constructions. That means that a concrete with better performance, lower costs and an improved ecological footprint can be designed. The application of these concretes is possible both in infrastructure and in buildings.

Keywords: Nano silica, Cement, Concrete, Water demand, Workability

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Introduction

The fresh concrete properties, like flow behavior and workability are governed by the particle size distribution, but also the properties of the concrete in hardened state, such as strength and durability, are affected by the mix grading and resulting particle packing (Reinhardt, 1998). One way to further improve the packing is to increase the solid size range. Possible materials, which are currently available, are limestone and silica fines like silica fume (mS) and nano silica (nS). The main characteristic of silica fines, such as particle size distribution, specific density, specific surface area and reactivity (surface silanol groups), depend on the production method (Sovolev et al., 2006). For the design of a concrete mix, it is important to consider the fine particles, as they have an influence on the water demand and, consequently, the fresh and hardened concrete properties. In granular state, a layer of adsorbed water molecules surrounds the fine particles and additional water is required to fill the remaining void fraction (Ψ) of the granular system. Since the fine powders contribute to the total specific surface area most, they have the strongest influence on the total water demand of a concrete mix. As a result, the powders should have a preferably low water demand. The mini spread flow test described by Okamura and Ozawa (1995) is an efficient and classical technique that is used nowadays by several researchers as an accurate measurement for the water demand of powders and mortars. This paper presents an extended analysis of the effects of amorphous silica fines on the water demand and workability of cement paste. Analysis of the granular structure of the paste and the relation to the calculated void fraction are presented as a previous understanding of the effect of nano particles addition to concrete mixes.

2. Materials and experimental methods

2.1 Materials

An ordinary Portland cement (CEM I 52.5N), as classified in EN 197-1, was used. Six different commercial silica fines (amorphous SiO_2 particles) were selected to perform the tests on the water demand and the subsequent analysis. The samples were classified and named as follows: two colloidal nano silica suspensions (samples CnS-1 and CnS-2), one nano silica fume (PnS-3) in powder form, one standard micro silica fume in slurry form (PmS-4) and two synthetic pyrolytic silica fumes with different specific surface area (PmS-5 and PmS-6). Their general characteristics are shown in Table 1.

Table 1: General characteristics of silica fines and reference cement used.

Name	Type	PSD by SEM/STEM (nm)	PSD by LLS and DLS (nm)	Specific density (g/cc)	BET (m^2/g)	SSA_{Sph} (cm^2/cm^3) $\times 10^{-4}$
CnS-1	Colloidal	5 - 50	0.9 - 2.3	1.10	234	3642
CnS-2	Colloidal	19 - 156	79 - 186	1.39	50	46
PnS-3	Powder	14 - 187	73 - 291	2.10	56	48
PmS-4	Slurry	14 - 332	78 - 1.3 (μm)	1.39	23	34
PmS-5	Powder	23 - 391	194 - 446	2.05	50	22
PmS-6	Powder	29 - 658	348 - 12 (μm)	2.19	12	8
CEM I 52.5N	-	-	10 (μm)	3.06	-	2

2.2 Experimental methods

2.2.1 Characterization of the silica fines and cement

The most relevant material characteristics of the selected silica fines were determined to allow for a proper incorporation of its in concrete. In this respect, the particle size distribution of the selected materials was determined using a Malvern Mastersizer 2000 based on laser light diffraction (LLD) and a Malvern Nanosizer based on dynamic light scattering (DLS). The computed specific surface area (SSA_{Sph}) was calculated according to Hunger (2010) assuming a sphere shape. Density

measurements according to EN 1097-7 were performed using a calibrated glass pycnometer. Additionally, specific surface areas were determined based on BET measurements ($SSA_{BET_{total}}$ and $SSA_{BET_{ext}}$) using a Micromeritics device model Tristar. Furthermore, size and morphology of the silica fines were analyzed with a SEM/STEM FEI Tecnai electron microscope model 20FEG. The obtained results are summarized in Table 1.

2.2.2 Water demand and workability

The mini spread flow test was deployed, as it is a suitable test method for materials with a collapsed slump. The procedure is described in detail in Hunger (2010). In total, 97 mixes were tested according to EN 196-1 and prepared using different silica concentration and water content. The spread flow tests were carried out first by filling the sample into the Hägermann cone and followed by lifting it to allow a free flow of the sample over a dry and clean glass plate. The relative slump is calculated from:

$$\Gamma_p = \left[\left(\frac{d_1 + d_2}{2} \right) / d_0 \right]^2 - 1 \quad (1)$$

Where d_1 and d_2 are calculated from the average value of the two perpendicular diameters measured from the spread sample. The relative slump flow value versus the volumetric water to powder ratio (V_w/V_p) was plotted. At least five mixes with different V_w/V_p were measured in order to obtain a statistically reliable trend line for the regression analysis. The linear trend line was fitted to the plotted values, reading as (Hunger, 2010):

$$V_w / V_p = \beta_p + E_p \Gamma_s \quad (2)$$

Where $\beta_{p,mix}$ value indicates the minimum amount of water to assure a fluid cement paste. The deformation coefficient ($E_{p,mix}$) indicates the sensitivity of the mix on changes in the water content for a specified workability. Knowing the calculated value for $E_{p,CEMI}$, $E_{p,nS}$ of the nano silica particles was derived indirectly invoking a linear relation and the work of Domone and Hsi-Wen (1997) as follows:

$$E_{p,mix} = f_1 \cdot E_{p,CEMI} + f_2 \cdot E_{p,nS} \quad (3)$$

Where f_1 and f_2 are volume fractions or concentration of cement and silica respectively, in the mix. The void fraction (ψ) was calculated based on the water retention ratio ($\beta_{p,mix}$) according to the equation given by Brouwers and Radix (2005):

$$\Psi(\Gamma = 0) = \frac{V_w}{V_{total}} = \frac{V_w}{V_w + V_s} = \frac{\beta_p}{\beta_p + 1} \quad (4)$$

In which V_w , V_s and V_{total} are the volume of water, solids and total volume of the mix, respectively, and β_p is the intersection of the spread flow line with the ordinate.

3. Results and discussion

3.1 Water demand and workability

In Fig.1, the computed Γ_p are plotted versus the respective V_w/V_p . Furthermore, a list of the different coefficients ($E_{p,mix}$ and $\beta_{p,mix}$) derived is presented. In general, the results shown in Fig. 1 are in line with the theories presented by Brouwers and Radix (2005) where $E_{p,mix}$ depends on the total SSA of the granular materials of the composed mix (cement and silica). It is evident that with decreasing particle size of the silica and consequently increasing SSA the values of $E_{p,mix}$ increase for all tested samples. Moreover, it is obvious that the relative concentrations are increasing too. On the contrary, the water demand changes in function of the packing and void fraction of the final cement paste. In case of improved packing, more water is available to lubricate the particles (Hunger, 2010); (Brouwers and Radix, 2005), and therefore producing a larger slump flow diameter. Considering a linear relation the E_p coefficients of six selected nano and micro silica samples were calculated. Higher deformation coefficients (E_p) for silica fines with nano particles were obtained (0.715 to 9.031), which are bigger

than that of cement (0.0562). This indicates that water has a bigger influence on the workability of the hydrating system containing nano silica. An explanation for this is given by the *SSA* of the applied silica (between 281769 and 3,641,736 cm^2/cm^3), which is smaller than that of the cement (26,458 cm^2/cm^3). In addition, nS influences the setting time of cement paste (acceleration effect). In the same way, a higher water retention ratio (β_p) was found for different silica concentrations. In several cases, a lower value of β_p was found than determined for the applied cement and which is related to the improved PP. This reduction in the water demand was also reported elsewhere (McCabe and Smith, 1956), (Brouwers and Radix, 2005), (Hüsken and Brouwers, 2008) (Hunger, 2010) and (Senff et al., 2010).

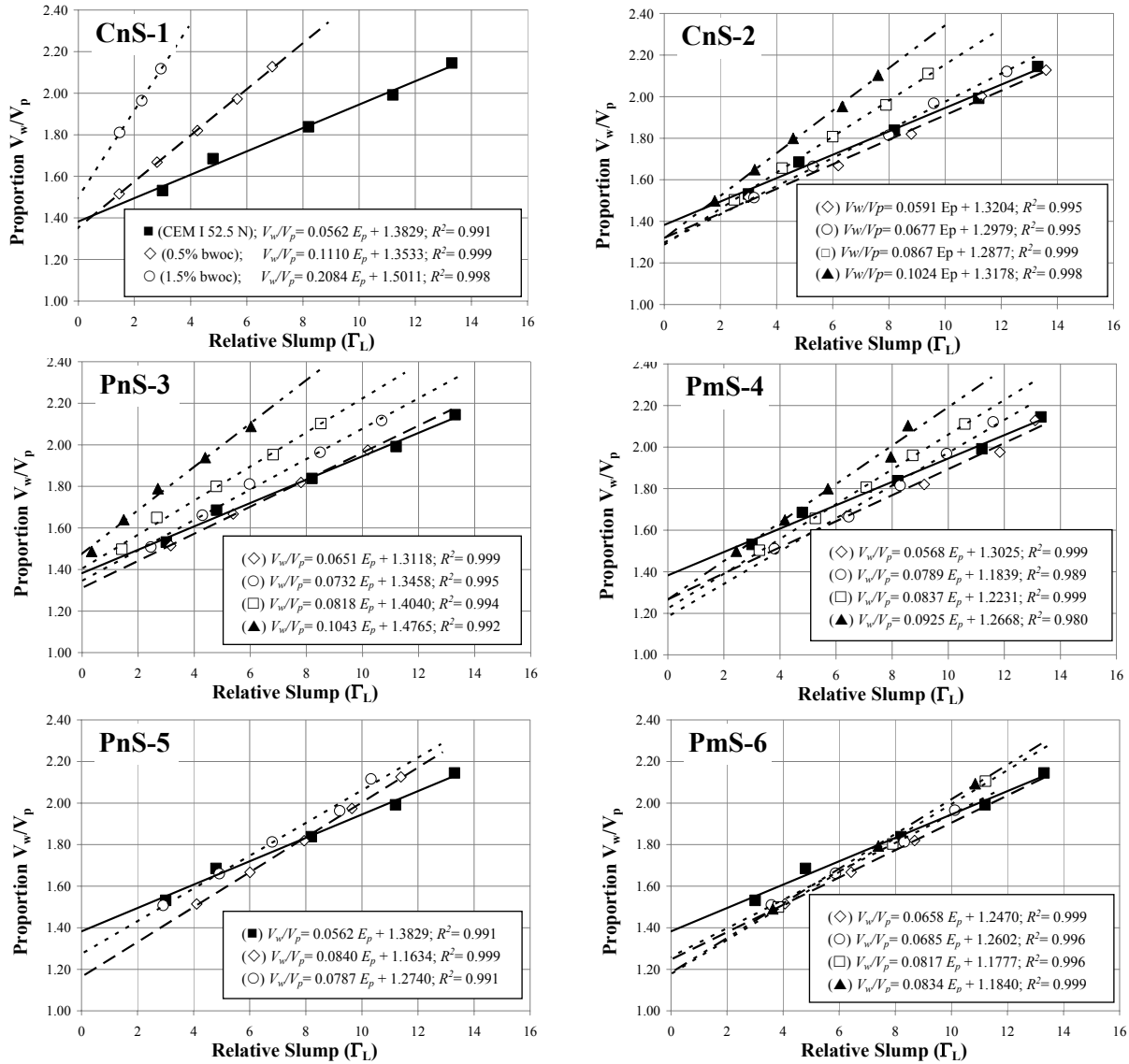


Figure 1: Variation of the water/powder proportion as function of the relative slump flow of cement paste with different addition of nS/mS (\diamond 0.5%, \circ 1.5%, \square 3.0% and \blacktriangle 4.5%) by based weight of cement (\blacksquare).

In order to analyze the results and to unify the effect of the parameters determined by the spread flow test ($E_{p,mix}$ and $\beta_{p,mix}$), the void fraction (Ψ) of each mix was calculated from its $\beta_{p,mix}$ values using Eq.(4). These Ψ were compared with the theoretical water demand (V_w/V_p) needed for each cement paste with silica to obtain a relative slump (Γ_p) of 5.3, which is equivalent to a flow diameter of 250 mm. This value is considered as optimum to obtain a good workability in pure cement paste (Hunger,

2010). The results obtained for the six selected silica fines and the reference CEM I are illustrated in Fig. 2. Analyzing this, it can be concluded that it is possible to reduce the Ψ of cement paste with 0.5% bwoc of CnS-1, but 15% more water is required to obtain a 250 mm slump diameter. This fact is caused by the extreme difference between the *SSA* of the CnS-1 compared with CEM I. For the other colloidal nano silica (CnS-2), the reduction of the Ψ is followed by a reduction in the water demand. The result is in concordance with the different theories related with improved PP of continuously graded mixes composed of two different powder materials. Nevertheless, the minimum Ψ derived from the analysis is not related to the point of minimum water demand in the curve (Fig. 2a) shown for this sample. It means that another mechanism probably exists that is acting in the mix and which modifies the PP. Similar phenomena have already been reported by Palm and Wolter (2009) as main problem of the application of particles with high *SSA* or with nano sized particles. At nano scale level, interparticle forces, like Van der Waals forces, electrostatic repulsion and attraction, play a principal role in the PP. Also Yu et al., (1997) reports that mixes of nano particles result in lower packing fractions than similar compositions of larger particles. In contrast to this, it can be noticed from Fig. 2a that it is possible to reduce the water demand by 3% of the cement paste adding CnS-2 at concentrations below 2% bwoc. Similar trends were found for the computed Ψ and water demand of the samples PnS-3 and PmS-5, which reduce the water demand in small additions.

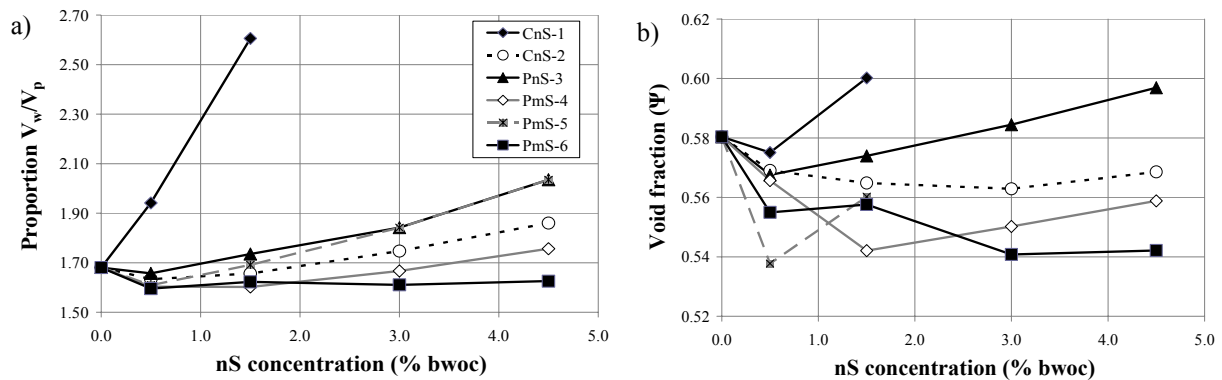


Figure 2: a) Theoretical water/powder proportion for a slump flow of 250 mm, b) calculated void fraction for cement pastes with different addition of nS/mS.

Contrary to the previously described samples, sample PmS-4 shows a minimum water demand when minimum Ψ is obtained (Fig.2). The reduction in the water demand is around 4.5% for addition of 1.5% bwoc. Moreover, it is possible to obtain a cement paste with the same water demand for a sample concentration of about 3.4% bwoc. It is in line with other work found in the literature and related with the water reduction effect of micro silica in cement paste when this type of material is added at concentration less than 5% bwoc (Senff et al., 2010). However, it is remarkable that the effect on the water demand due to the incorporation of particles that result in an increase in the *SSA* is extensive. In contrast PmS-6 shows a water demand reduction and reduced Ψ in the entire interval of concentrations studied. This synthetic pyrolytic silica shows a wide PSD that apparently improves the PP of the paste when it is combined with CEM I. In this case, the spherical shape of the particles results in a rolling effect similar to fly ash that reduces the inner friction of the paste and the related viscosity. The PmS-6 sample consists of coarse spherical silica particles that are less reactive (reduced accelerating effect of the nano silica) than the smaller ones. As a result, the average water demand was reduced by 5% for all the mixes studied. In general, the water demand to obtain a slump diameter of 250 mm increases for all silica fines with the reduction of the particle size and increasing concentrations in the cement paste. One exception of this observation is the sample CnS-1 due to its high *SSA* compared with the other analyzed silica samples.

3.2 Specific surface area (SSA) and water layer thickness (δ)

As discussed before, a thin layer of adsorbed water molecules around the particles is necessary to assure the flow characteristics of the hydrating system. Brouwers and Radix (2005) reported that the thickness of this water layer (δ) is related to the E_p and the SSA of the material used, which was later confirmed by Hunger (2010), and reads as follows:

$$E_{p,nS} = \xi \cdot \delta \cdot SSA_{Sph} \quad (6)$$

Whereby ξ is the shape factor and SSA_{Sph} is the specific surface area computed using the PSD and assuming a spherical shape. In the present study, using the different SSA computed and the E_p calculated, a water film of 24.8 nm was derived for the silica fines (Fig. 3a). This value is in line with the results reported by Brouwers and Radix (2005) of 44.6 nm (δ_{Blaine}) based on the Blaine's specific surface area. Furthermore, this value is also confirmed by Hunger (2010) who reported a δ_{SSA} of 24.9 nm for different powders and binders. As the computed SSA depends on the efficient dispersion and breaking of the primary agglomerated of nano particles, a similar approach as performed before was carried out using the BET SSA. In this case, all E_p were plotted against the BET specific surface area (total and external), multiplied by each particle density. In this case, a shape factor is not necessary for correction, because the total BET SSA considers the entire accessible particle surface, including pores. As the surface of the pores is included in computing the water film, a BET external SSA becomes more important. The result of such an analysis is shown in Fig.3a, where the δ values decrease from 24.8 nm to 19.0 nm, considering only SSA_{BEText} , and 17.4 nm, considering the surface area of the pores, respectively ($SSA_{BETtotal}$). Furthermore, the computed SSA calculated by LLS or DLS was plotted against the normalized respective BET SSA (Fig.3b). It is shown that the empirical relation between SSA and BET is linear with a factor in the range of 0.70 to 0.77 for BET total and BET external surface area.

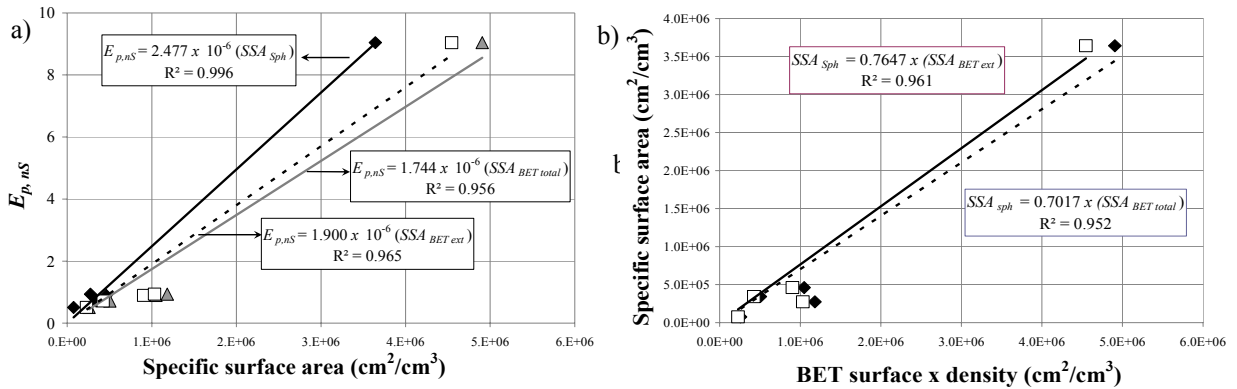


Figure 3: a) Computed and BET volume based specific surface areas against respective deformation coefficient for different silica derived from spread flow tests, b) Linear relation between computed and volume based BET specific surface areas.

Conclusion

The present work addresses the mini spread flow test for the determination of water demands, water film and their impact on the workability of cement paste with silica fines. Different correlations have been derived which express these values in terms of the particles properties and concentrations. Some of them are confirmed by literature, others are new. Several conclusions can be drawn and expressed as follows:

- Higher deformation coefficients (E_p) for silica fines with high content of nano particles were found, which are bigger than that of cement. This indicates that water has a bigger influence on the workability of the hydrating system containing nano silica with high surface area.

- A linear relationship between the deformation coefficient and the specific surface area of nS/mS particles was confirmed. A similar thickness of the water layer of nS particles (24.8 nm), as reported by Hunger (2010) for microsized powders, was confirmed and determined, assuming perfect spheres. Also, taking into account the BET total and external specific surface area a smaller water film was established for amorphous silica samples used in concrete. These values are helpful to calculate the water demand of any silica sample with known specific surface area.
- In the experimental condition in the present research, the addition of 0.5 to 4.0 % bwoc of nano silica in cement paste can reduce the water retention ratio without the use of superplasticizer.

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