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# Production and application of a new type of nano-silica in concrete

## Abstract

In this paper the application of a new nano-silica in concrete is studied. This nano-silica is produced by the dissolution of olivine. The production of nano-silica by the olivine route is a cheaper method than the commercial methods (neutralization of sodium silicate solutions and the flame hydrolysis) because of the low cost of raw materials and the low energy requirements. The produced nano-silica has a specific surface area between 100-400 $m^2$/g, primary particles between 10 to 25 nm (agglomerated in clusters), and an $SiO_2$ content above 95 %. In addition, the pozzolanic properties and the dispersion state of the nano-silica were studied. From these results it is concluded that olivine nano-silica can be applied successfully in concrete because of its high pozzolanic activity.

## Introduction

At present a wide range of silica products is manufactured industrially for various applications. Amorphous silicas are mainly used for reinforcement of elastomer products, thickening of liquid systems such as paints, thermosetting resins, and printing inks, and as fillers in silicone rubber [1]. World demand for specialty silicas, which includes precipitated silica, fumed silica, silica gel and silica sol, was 1.9 million metric tons in 2009 and will rise to 2.7 million metric tons in 2014 with a total value of $5.8 billion [2], making it one of the most used nano-materials. Nowadays, the two most important commercial processes in the production of nano-silica are the neutralization of sodium silicate solutions with acid and the flame hydrolysis. Both processes are expensive because of the price of the raw materials and the energy requirements. Nano-silica could be applied even more widely if a new industrial, low cost, production process could be developed.

## Production of nano-silica by the dissolution of olivine

Initial research [3-6] has demonstrated that nano-silica can be produced by dissolving olivine in acids. The acid is neutralized by olivine mineral, following

$$(Mg,Fe)_2SiO_4 + 4H^+ \rightarrow Si(OH)_4 + 2(Mg,Fe)^{2+}.$$
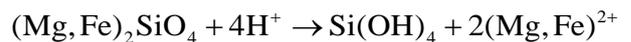
The neutralization yields a mixture of a magnesium/iron salt solution, silica, unreacted olivine and inert minerals (see Figure 1). Once the reaction is complete, the unreacted olivine and inert minerals are removed from the final suspension by sedimentation. Subsequently, the silica can be cleaned from the resulting mixture by washing and filtering. After the filtration, a cake with a 20 % solid content of nano-silica is obtained. This cake can be stored in this form, dried or redirpersed for application in concrete.
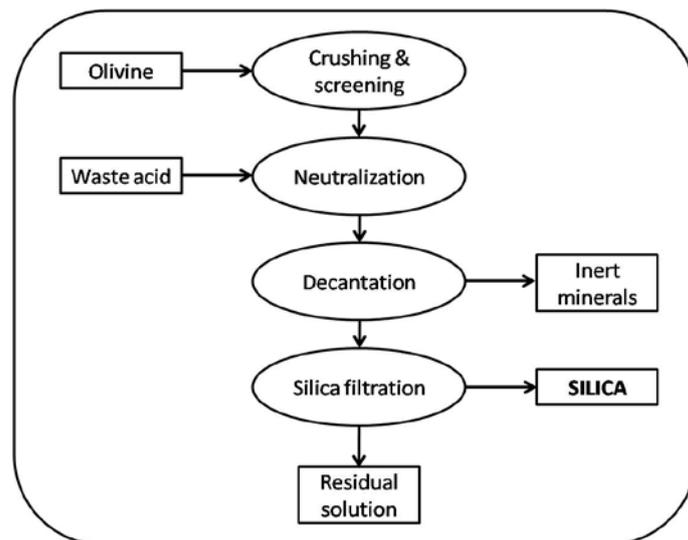
**Figure 1**
**Schematic process flow diagram of the olivine process**

The specific surface area of olivine nano-silica depends on the kinetics of the reaction of olivine and the amount of magnesium sulfate in the porous solution. Likewise, the kinetics of the dissolution of olivine depends on the temperature, surface area of olivine and hydrogen ion activity. Thus, increasing the temperature, the surface area of olivine, the hydrogen ion activity and/or the number of washing steps results in an increase in the nano-silica surface area. In this way, different types of nano-silica can be produced by changing the process conditions.

**Properties of nano-silica produced by the olivine route**

The synthesis of nano-silica by the dissolution of olivine is a feasible method to prepare amorphous porous nano-silica [3,7,8]. This nano-silica has a specific surface area between 100 and 400 m$^2$/g (see Table 1) and primary particles consist of between 10 and 25 nm. These particles are agglomerated in clusters (see Figure 2), forming a porous material with an average pore diameter between 17 and 28 nm. The impurity content depends on the washing steps, being able to obtain a material above 98 % of purity, with an SO$_3$ content below 1 %, fulfilling the norm [9]. Because of the good properties of the olivine nano-silica and the low energy requirements, the olivine dissolution process is a convenient alternative to the commercial methods of nano-silica production.

**Table 1**
**Summary of the properties of different amorphous nano-silica [3,7,10]**

| Parameters | Pyrogenic | Precipitated | Lieftink | This work |
|---|---|---|---|---|
| Purity, SiO$_2$ (%) | >99.8 | >95 | - | >95 |
| SSA$_{BET}$ (m$^2$/g) | 50-400 | 30-500 | 100-400 | 100-400 |
| d (nm) | 5-50 | 5-100 | 8-25 | 10-25 |
| d$_p$ (nm) | None | >30 | >10 | >10 |
| Reference | Ecetoc | Ecetoc | Lieftink | - |
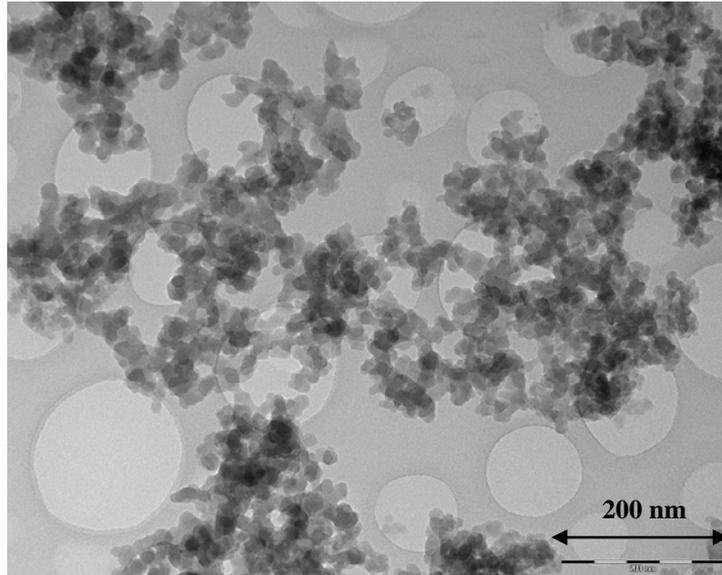
**Figure 2**
**Transmission electron microscope photograph (89 kx) of the olivine nano-silica**

## Application of nano-silica in mortar and concrete

The use of silica fume (a type of microsilica) in concrete continues to increase despite its relatively high cost because its fine particles and its pozzolanic behavior are particularly valued in making high performance concretes. By far the largest use of silica fume is for the purpose of producing concrete with enhanced properties, mainly high early strength or low penetrability concretes [11].

Nano-silica has a great impact on the mechanical properties of concrete and mortars. The addition of this material increases density, reduces porosity and bleeding, and improves the bond between cement matrix and aggregates [12-20]. Thus, a concrete with high compressive and flexural strengths can be produced when using nano-silica. However, the use of nano-silica is even more restricted than the micro-silica due to the high price of the commercial products.

## Preparation of a colloidal dispersion

The slurry previous to the filtration is a mix between nano-silica and sulfate salts, having a D50 particle size of 110 μm (see Figure 3) and $\zeta$-potential of about -2. After filtration, a cake is produced with some minor impurities, such as iron, magnesium, calcium and sulfates. This silica cake was dispersed in a $NH_4OH$ solution of pH 9-10 with a high energy mixer, featuring a $\zeta$-potential of about -38 (see Table 2) and D50 particle size of 23 μm. The great difference between the particle sizes calculated from nitrogen physisorption (see Table 1) and laser light scattering is because the nitrogen physisorption measures the specific surface area by the adsorption of gas on the surface, and from this value, the size of the primary particles can be calculated; while laser light scattering measures the particle sizes of the agglomerates, being these one much bigger than the size of the primary particles. In spite of the low $\zeta$-potential (a $\zeta$-potential of –

40 is usually high enough to avoid any gelling or settling of the particles), the $NH_4OH$ dispersion was unstable, settling in just a couple of minutes. This instability is due to the presence of ions in the medium, decreasing the size of the diameter of the double layer, and therefore, letting the particles agglomerate and settle.

To test the use of different additives, colloidal dispersions were prepared in different solutions with 1 % in mass of $SiO_2$ (see Table 3). These additives stabilize the suspension either by charge repulsion or by steric stabilization. The best result was obtained when additive $Na_5O_{10}P_3$ was used at pH 9-10. Three dispersions using $Na_5O_{10}P_3$ additive and with a $SiO_2$ concentration of 1, 5 and 10 % were prepared. The 1 and 5 % dispersions were stable for 3 days while the 10 % dispersion was stable for 3 weeks. In this case, the dispersion stability was longer because of the increase in viscosity, decreasing the precipitation rate. However, a stability of three weeks is not long enough to prepare a commercial colloidal nano-silica. The PSD of the supernatant of the 10 % dispersion is shown in Figure 3.
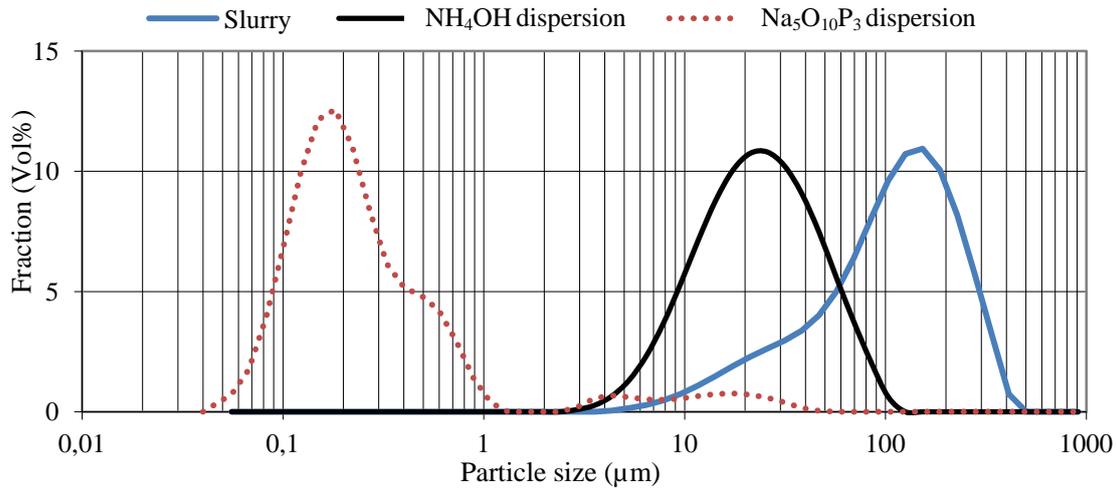


**Figure 3**
**Particle size distribution of the nano-silica slurry and dispersions**

**Table 2**
**ζ-potential of a nano-silica dispersion of 1 wt% in a $NH_4OH$ solution at pH 9-11**

| Name | pH | ζ–potential |
|------|-------|-------------|
| 1 | 9.05 | -36.0 |
| 1 | 9.05 | -37.5 |
| 1 | 9.52 | -34.2 |
| 1 | 9.52 | -34.6 |
| 1 | 10.08 | -32.0 |
| 1 | 10.08 | -33.2 |
| 1 | 10.50 | -34.8 |
| 1 | 10.50 | -36.4 |
| 1 | 11.00 | -38.0 |
| 1 | 11.00 | -39.6 |

**Table 3**
**Colloidal dispersions using different additives**

| Solution | Mass SiO$_2$ (%) | Composition | Optimum concentration (M) | pH | ζ–potential |
|---|---|---|---|---|---|
| 1 | 1 | KCl | - | 4.5-6.5 | -8 |
| 2 | 1 | Citric Acid (C$_6$H$_8$O$_7$) | - | 2-3 | -2 |
| 3 | 1 | NH$_4$OH / Na$_5$O$_{10}$P$_3$ | 0.02 | 8-10 | -42 |
| 4 | 1 | C$_5$H$_5$O$_7$K$_3$·H$_2$O | 0.03 | 6-8.5 | -35 |
| 5 | 1 | NH$_4$OH / P1 | - | 9.5-10 | -15 |
| 6 | 1 | NH$_4$OH / P2 | - | 9-10 | -13 |

P1 is an ethoxilated surfactant C12-C15 and P2 is polycarboxylate polymer.

## Pozzolanic activity of olivine nano-silica

To determine the pozzolanic index of the olivine nano-silica, different cement mortars were prepared and tested following the guidelines [21]. A 7% bwoc (based on the weight of binder, cement plus nano-silica) replacement was selected based on the procedure described by Justnes [22]. The SP (superplasticizer) content (see Table 4) of the mixes was adjusted to obtain a spread flow of 175 ± 15 mm. The flexural and compressive strengths of the mixes were determined at 1, 7 and 28 days, respectively. Finally, the pozzolanic activity index was computed based on the results of the standard cement mortar. In addition, the pozzolanic index was compared with the results obtained for a commercial micro-silica used in well cementing applications.

The strength development of the different mortars tested is shown in Figure 4. The flexural and the compressive strengths at one day for nano-silica mortar are lower than the values of the standard and the micro-silica mortar. This can be due to the highest dose of SP in nano-silica mortar. The flexural strength at 28 days of the nano-silica mortar was the lowest. The compressive strength at 28 days with nano-silica mortar showed higher values than the standard mortar, but lower than the micro-silica mortar.

**Table 4**
**Mix designs of mortars used for determining the pozzolanic index**

| Materials (g) | CEM I 52.5N | Nano-silica | Micro-silica |
|---|---|---|---|
| CEM I 52.5N | 450.0 | 418.5 | 418.5 |
| Olivine nano-silica | 0 | 31.5 | 0 |
| Micro-silica powder | 0 | 0 | 31.5 |
| Water | 225 | 225 | 225 |
| Standard sand | 1350 | 1350 | 1350 |
| SP (Glenium® 51) | 0 | 2.25 | 0.50 |
| SP (% bwob) | 0 | 0.50 | 0.11 |
| w/c | 0.50 | 0.54 | 0.54 |
| Spread flow (mm) | 180 ± 3 | 167 ± 8 | 184 ± 7 |
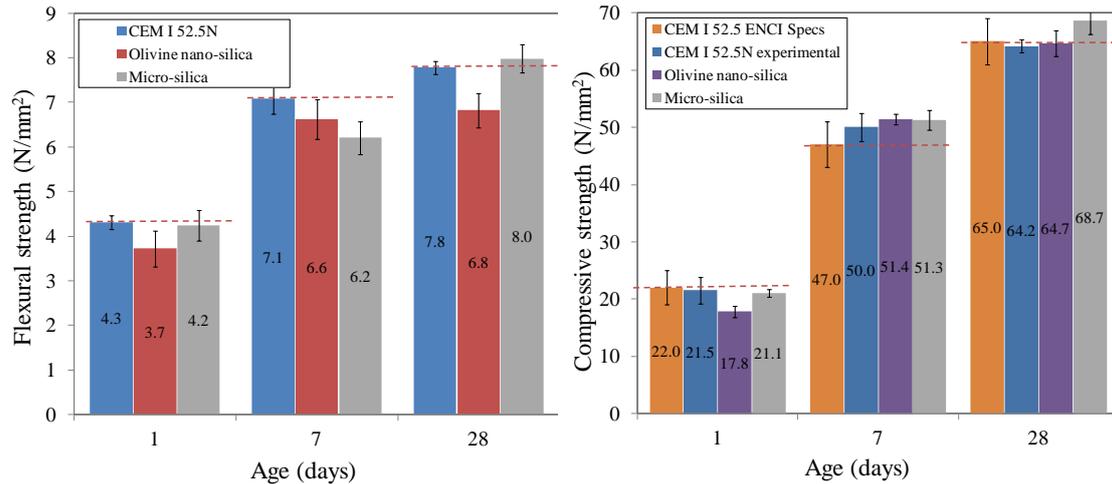
**Figure 4**
**Development of the mechanical properties of the tested mortars**

The 7-day and 28-day compressive strengths were used to estimate the relative pozzolanic activity index of the olivine nano-silica and the micro-silica sample. The pozzolanic index was calculated based on the compressive strength of the reference mortar (see Figure 5).

The computed activity index shows that the olivine nano-silica has a high pozzolanic reactivity (101%). Therefore, olivine nano-silica can be classified as a pozzolanic material [9]. Nevertheless, the 28-day activity index was lower than the activity index of micro-silica (107%). This is probably caused by the higher specific surface area and the agglomerated state of the nano-silica. In addition, at 7% replacement of cement, the maximum wet packing is not obtained, which results in lower strength. Despite the positive results that were obtained, further research is needed to understand the strength development of the olivine nano-silica.
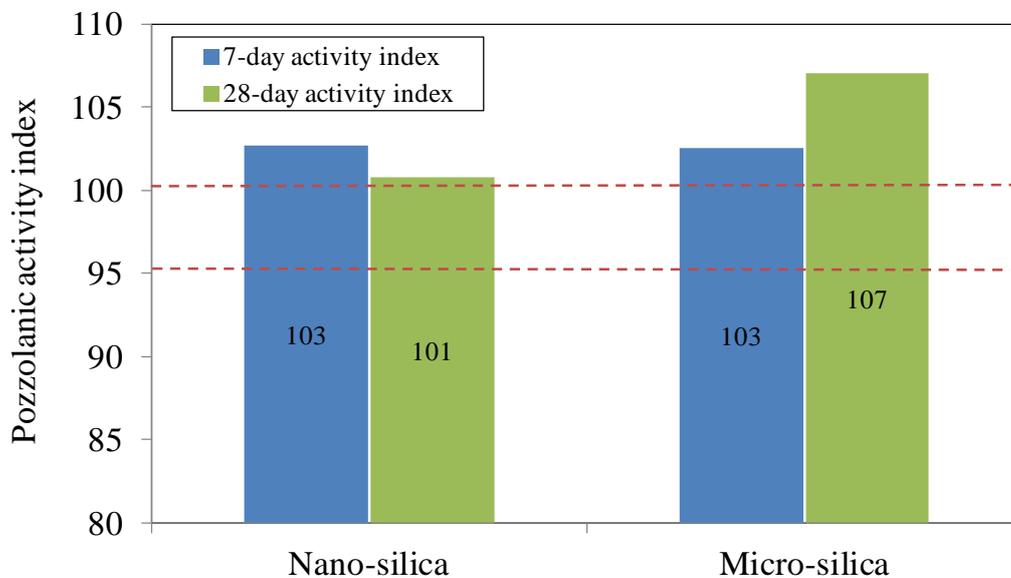


**Figure 5**
**Pozzolanic activity index of the different slurries tested**

## Conclusions and further research

The synthesis of nano-silica by the dissolution of olivine is a feasible method to prepare amorphous porous nano-silica. This nano-silica can be used as pozzolanic material in concrete, having a pozzolanic index of 101 %. However, the pozzolanic activity of olivine nano-silica is lower than that of standard micro-silica at the same replacement level. This phenomenon is likely to be because i) olivine nano-silica adsorbs a lot of water in its pores and ii) it is structured in 3D agglomerated chains reducing the packing factor of the aggregate mix. In addition, it was not possible to prepare a stable colloidal dispersion with this olivine nano-silica.

Further research will focus on the Ostwald ripening of nano-silica, which means dissolving the nano-silica and polymerizing it again under controlled conditions. Thus, the nano-silica produced should have a lower specific surface area, higher particle size, lower porosity and spherical shape. In addition, a colloidal dispersion should be more stable due to the bigger size of the particles. Finally, this treated nano-silica will be tested in concrete and mortar.

## Acknowledgment

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