

Synthesis of nano-silica at low temperatures and its application in concrete

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SYNTHESIS OF NANO-SILICA AT LOW TEMPERATURES AND ITS APPLICATION IN CONCRETE

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Abstract

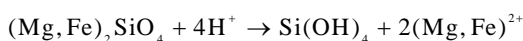
Nowadays, the two most important commercial processes in the production of nano-silica are the thermal route (also known as flame hydrolysis) and the wet route (e.g., the neutralization of sodium silicate solutions). A high temperature process is involved in both production methods. The production of nano-silica by the dissolution of olivine is an interesting alternative to the existing commercial methods because of the good quality of the resulting silica and low energy requirements and CO₂ emissions. The produced nano-silica has a specific surface area between 100 and 400 m²/g; a primary particle size between 10 and 25 nm, which are agglomerated in clusters; and an impurity content below 5 wt.%. In addition, olivine nano-silica can be classified as a pozzolanic material with an activity index of 101 %. The optimum replacement level of olivine nano-silica in conventional vibrated concrete is around 5% by volume resulting in: 1) a compressive strength increase of 20 %; 2) a CO₂ emission reduction of 3 %. Therefore, the use of the olivine nano-silica in CVC does not only improve the compressive strength but also reduces the CO₂ emissions.

Key Words: Olivine, nano-silica, CO₂ reduction, environmentally friendly, concrete.

1. INTRODUCTION

Nano-silica is one of the most used nano-materials, and its use is rising 5.6 per cent per year to reach a projected 2.8 million metric tons in 2016. Likewise, the market for specialty silicas is estimated to grow 7.5 % per year reaching a total value of \$6.4 billion in 2016. The current production methods involve steps with high temperatures. To reach these temperatures, vast amounts of fuel are consumed making these processes: a) unsustainable because of the scarcity of fuels; b) environmentally unfriendly because of the high amount of CO₂ emitted; and c) expensive because of the fuel price. The production of nano-silica by the dissolution of olivine is an interesting alternative to the existing commercial methods because of the good quality of the resulting silica and low energy requirements and CO₂ emissions.

The dissolution of olivine in acid at low temperatures (between 50 and 95 °C) produces amorphous silica:



The dissolution yields a slurry consisting of a mixture of magnesium/iron salts, amorphous silica, unreacted olivine and inert minerals. 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 around 20 wt.% solid content of nano-silica is obtained. A flow chart of this process is presented in Figure 1.

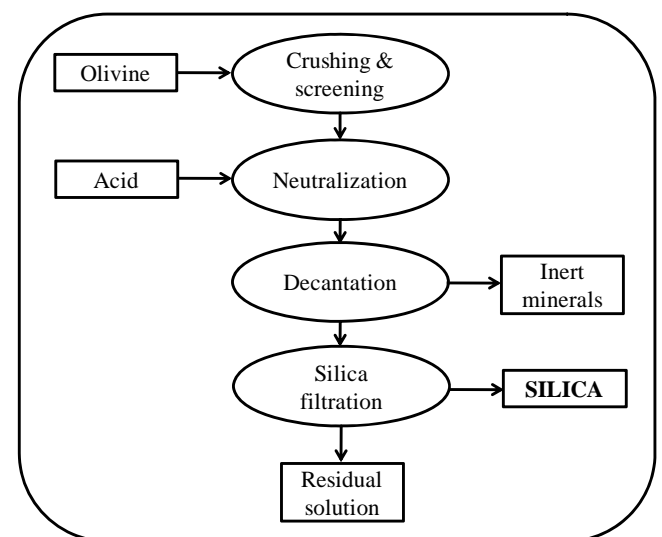


Fig. 1: Flow chart of the production of nano-silica by the dissolution of olivine

In addition to the low temperature of this procedure (below 95 °C), it is remarkable that the process is exothermic with a reaction heat of 223 kJ per mole of olivine [1], which

generates more than enough energy to keep the system at the desired temperature (between 50 and 90 °C) provided the reactor is sufficiently insulated (an estimation of the energy requirements of this process can be found in [2]).

2. EXPERIMENTAL METHOD

Nano-silica production experiments were carried out at constant temperatures between 50 and 90 °C with fraction of olivine particles between 100 and 600 µm in a stirred, thermostated reactor of one liter. The reagents used were 500 ml of 3 M sulfuric acid and the stoichiometric amount of olivine. The neutralization reaction continued until the $[H^+]$ was above 0.1 mol/L when it was stopped. Then the suspension was separated from the solid residue by sedimentation. Subsequently, the remaining slurry was washed and filtered to obtain the clean amorphous nano-silica (more details can be found in [3]). A review of the common silicas employed in concrete can be found in [4].

The nano-silica produced was characterized by nitrogen physisorption, transmission electron microscopy (TEM), X-ray fluorescence (XRF), and combustion infrared analysis (determination of sulfur content). A Micromeritics TriStar 3000 equipment using N_2 with a soaking time of 240 min at 190 °C. The specific surface area, SSA_{BET} , was calculated using the BET [5,6].

The effect of this type of nano-silica in conventional vibrated concrete (CVC), which is the most commonly used concrete, was investigated by casting three mixtures with different replacement levels of CEM I 52.5N with olivine nano-silica (5, 7 and 10 % by volume). The olivine nano-silica was applied in concrete after dispersing the silica cake in water using a high shear mixer for around 10 minutes. The mix designs were based on a commercial recipe (see Table 1); eighteen cubes were cast using a vibrating table and were tested for their compressive strength after 1, 7 and 28 days. Additionally, the workability of the fresh concrete was investigated by analyzing the slump following 206-1 standard [7]. The SP used was Ha-BE 100 (polycarboxylate ether type).

Table 1: Mix designs of CVC with and without replacement of cement with olivine nano-silica (NS)

Materials (kg/m ³)	Ref.	5 (%)	7 (%)	10 (%)
Olivine NS	0	6.9	10.3	13.7
CEM I 52.5 N	210	199.6	194.3	189.1
Fly-Ash	88.2	88.2	88.2	88.2
Sand 0-4	780.6	780.6	780.6	780.6
Gravel 4-16	1086.3	1086.3	1086.3	1086.3
Water	158.8	159.1	158.1	158.1
SP (% bwob)	0.5	1.12	1.33	1.75
w/f	0.54	0.54	0.54	0.54
Slump class	S2	S2	S1	S1
d_{slump} (mm)	60	60	40	40

Where w/f refers to the ratio between water and fines, and bwob to the acronym “based on the weight of binder”.

3. RESULTS

3.1 Preparation of olivine nano-silica

The olivine nano-silica presented here was washed and filtered up to 6 times to reduce the amount of impurities. Table 2 shows the SSA_{BET} , the sulfur and SO_3 content and the purity of silica (more details about the chemical composition can be found in [8]). According to the norm “NEN – EN 13263-1+A1”, the SO_3 limit for the application of silica in concrete is 2 %. Thus, after 4 filtration steps, olivine nano-silica fulfils the sulfur content regulation. Figure 2 shows a TEM picture of olivine nano-silica [3], where it can be seen that this type of material is agglomerated in clusters.

Table 2: Specific surface area, SO_3 content and purity of silica for samples of olivine nano-silica with different numbers of washing and filtration steps [8].

Sample	SSA_{BET} (m ² /g)	S (%)	SO_3 (%)	P_{Si} (%)
NS-3F	233	1.75	4.37	93.96
NS-4F	324	0.33	0.82	98.59
NS-5F	346	0.05	0.12	99.45
NS-6F	348	0.03	0.07	99.27

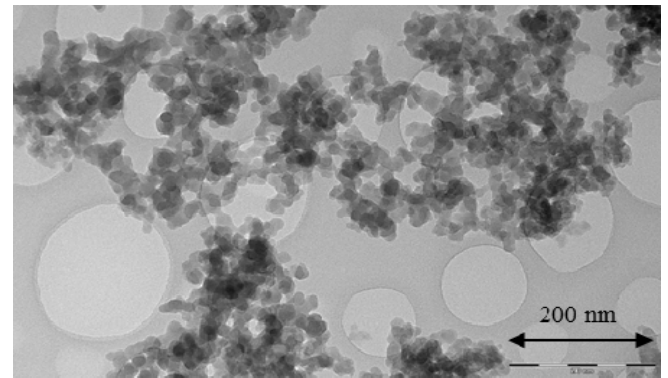


Fig. 2: TEM picture of olivine nano-silica [3].

3.1 Application in concrete

Table 1 also presents the results of the slump test. The only mix with similar slump values to the reference mix was the one with 5 % replacement by volume. The SP requirement for this mix was more than double compared to the reference mix. In the cases of 7 and 10% replacement, even though the SP contents were higher than for concrete with 5 % replacement, it was not possible to obtain the desired slump class (S2). Therefore, when the specific surface area of the mix was increased by addition of nano-silica, more SP was required to maintain the same slump class. This is a clear disadvantage of the use of nano-silica, and it needs to be addressed in the future in order to find the type of SP that works more efficiently with olivine nano-silica. Another possible solution for this problem could be to tailor the properties of olivine nano-silica to get lower specific surface areas and more spherical particles.

The compressive strengths of concrete after 1, 7 and 28 days are depicted in Figure 3. This figure shows that the strength after one day was not significantly affected by the increase of the SP content in these mixes. Only the mix with 10 % replacement showed a lower strength than the reference. The 7-day compressive strength, on the other hand, displayed an increase for all the substitution levels. The 28-day compressive strength showed similar trends as the 1-day compressive strength; only the mix with 10 % replacement showed a lower strength than the reference. The best result after 28 days was obtained for the mix with 5% replacement, where the compressive strength increase by 20 % compared to the reference mix. This suggests that the optimum substitution of olivine nano-silica should be around this value.

Figure 4 presents the estimated CO₂ footprint per cubic meter of reference CVC and CVC with 5 % replacement. These estimations were performed using the CO₂ footprint of each compound from a database of the Dutch precast concrete organization. The CO₂ footprint of olivine was estimated from a life cycle analysis performed by VTT (ProMine internal report, FP7). The reduction of CO₂ emissions for CVC with 5% replacement was 3% with respect to the reference concrete. This could be improved by tailoring the properties of olivine nano-silica so less SP would be necessary to maintain the same rheological properties or slump class. Since the compressive strength of CVC with 5% replacement was 20% higher than the reference concrete, there would be the possibility of reducing the total amount of cement used while maintaining the same compressive strength as the reference material, therefore, minimizing CO₂ emissions.

CONCLUSIONS

Amorphous nano-silica can be produced by the dissolution of olivine, having a specific surface area between 100 and 400 m²/g, a primary particle size between 10 and 25 nm (agglomerated in clusters) and a SiO₂ content above 95 %.

The olivine nano-silica process is: a) more sustainable because it requires less fuel (so fewer CO₂ emissions), and it is possible to use waste materials as a silica source. Preliminary results demonstrated that the possible optimum replacement of olivine nano-silica in conventional vibrated concrete was around 5 % with an improvement in the compressive strength of 20 %. The superplasticizer content has to be increased when cement is replaced with olivine nano-silica to maintain similar rheological properties. The CO₂ emissions were reduced by 3 % for the CVC with 5 % replacement compared to the reference concrete. The CO₂ emissions could be further reduced if the SP content could be diminished by tailoring the properties of olivine nano-silica. Therefore, the use of the olivine nano-silica in CVC does not only improve its compressive strength but also reduces CO₂ emissions. This green nano-silica can also be used in any other applications where the high specific surface area is required.

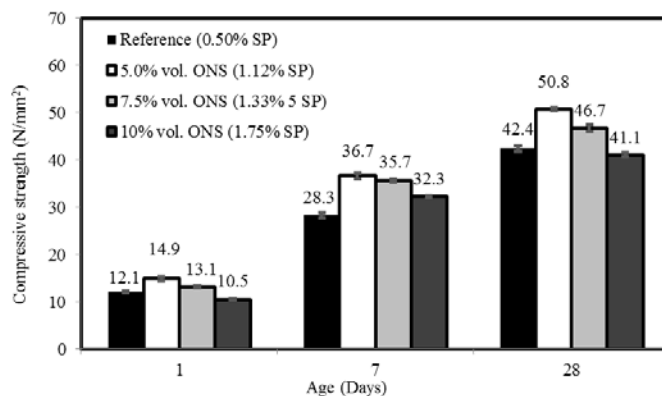


Fig. 3: Compressive strength development of CVC at different replacement levels of cement with olivine nano-silica (ONS)

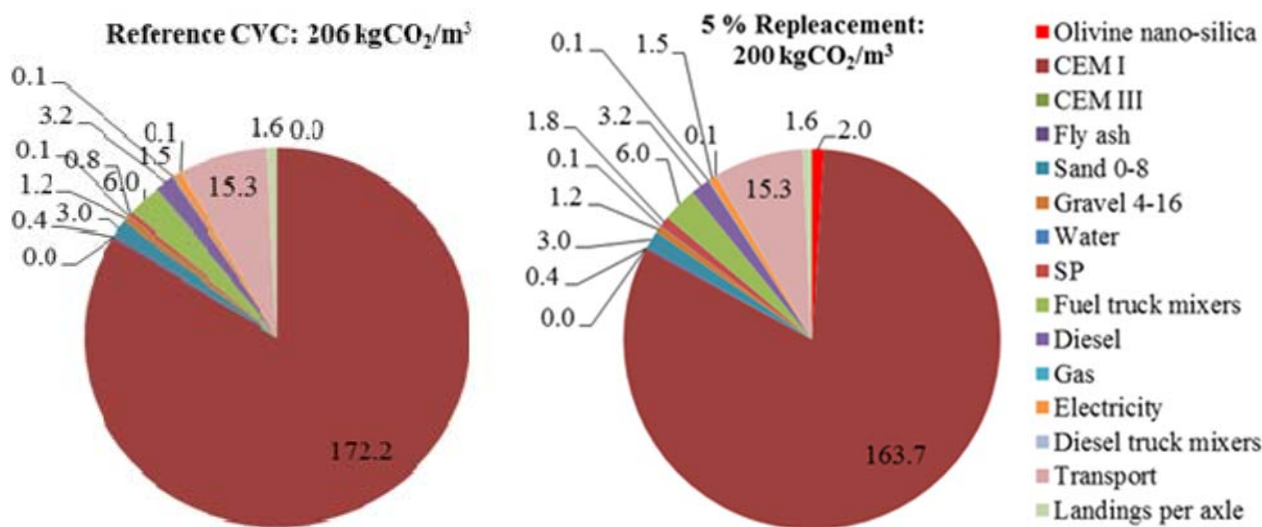


Fig. 4: CO₂ footprint of CVC and of CVC with 5% replacement of cement with olivine nano-silica

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BIOGRAPHIES



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