

Synthesis of a Green Nano-Silica Material Using Beneficiated Waste Dunites and Its Application in Concrete

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ABSTRACT

Nano-silica, one of the substances boosting the field of nanomaterials, can be produced by dissolving olivine in acid. The dissolution of olivine is a convenient alternative route to the existing methods of nano-silica production (neutralization of sodium silicate and flame hydrolysis) because the olivine dissolution is a low temperature process making this method cheaper and greener. Furthermore, this process can use waste olivine materials for the production of nano-silica. 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 is 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 reduce the CO₂ emissions.

Keywords: Olivine; Nano-Silica; CO₂ Reduction; Environmentally Friendly; Concrete

1. Introduction

1.1. Current Production of Nano-Silica

At present, a wide range of silica products (see **Figure 1**) are manufactured industrially for a diverse array of applications. Silicas are mainly used for reinforcing, thickening and flattening purposes. World demand for specialty silicas, which include precipitated silica, fumed silica, silica gel and silica sol, will rise 6.3 percent per year to 2.7 million metric tons in 2014 [1].

There are two main routes for the productions of synthetic amorphous silica: the thermal route and the wet route [2]. In the thermal route, also called flame hydrolysis, highly dispersed silicas are formed from the gas phase at high temperatures. Silicon tetrachloride, which is the usual raw material, is continuously vaporized, mixed with dry air, then, with hydrogen and finally fed to a burner where it is hydrolyzed in an oxygen-hydrogen flame. The flame temperature depends on the properties of the burner and the desired characteristics of nano-silica. Moore patented a cooled plug burner to produce py-

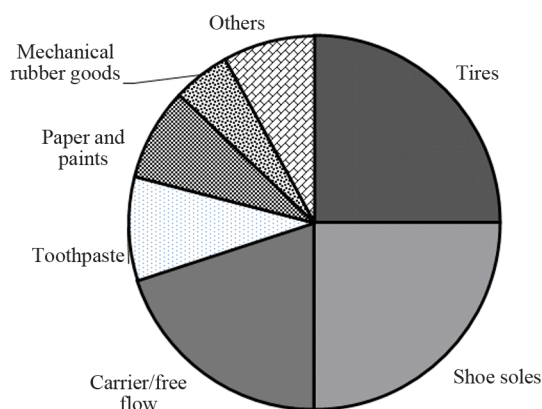


Figure 1. Worldwide consumption and use of precipitated silica in 1999 [5].

rogenic silica in a temperature range between 1000°C and 1200°C [3]. In the wet route or sol-gel process, a water-glass solution is mixed with acid (e.g. sulfuric acid) releasing the silica. Waterglass is produced by melting quartz sand with soda from temperatures of 1000°C to

1300°C [4]; subsequently, the resulting solid waterglass is hydrothermally dissolved in water. Apart from silica produced by these processes, we also have to take into account the silica fume because it is the main silica used in cement materials. Silica fume is a byproduct of the reduction of quartz for the production of silicon and ferrosilicon. It is a very fine powder consisting of non-crystalline silica spheres with an average diameter of ca. 0.1 µm, and it is produced at temperatures of about 2000°C [6,7].

In the above production methods, a high-temperature process is involved. To reach these temperatures, huge amounts of fuel are consumed making these processes: a) unsustainable because of the scarcity of fuels; b) environmental unfriendly because of the huge amount of CO₂ emitted; and c) expensive because of the fuel price.

This paper is structured in two parts: first, the production of olivine nano-silica using beneficiated waste dunite; and second, the application of olivine nano-silica in concrete. Here, we demonstrate that the dissolution of olivine is an optimal method to produce an amorphous nano-silica. This method is greener and cheaper than the conventional production methods because the reaction temperature is between 50°C and 95°C. The reaction is exothermic [8], and because of waste dunites, after beneficiation, it can be used as a silica source. The use of nano-silica in conventional vibrated concrete can reduce the CO₂ emissions by 3% and increase the compressive strength by 20%.

1.2. Application of Nano-Silica in Concrete

Concrete is the most widely used construction material and consists of water, aggregates and cement. World production of cement increased up to 3.6 billion tons in 2011 [9]. Nano-silica in concrete is not yet commonly applied, but silica fume, which is considered a micro-silica, has already been used in concrete for several years to make high-performance concrete. The use of micro-silica in concrete continues to increase despite its relatively high cost because of its pozzolanic behavior and its content of fine particles. These two features of the micro-silica confer some benefits to the concrete. The pozzolanic behavior refers to the reaction between silica and portlandite, Ca(OH)₂, to produce CSH (calcium silicate hydrate) gel, which is the main phase contributing to the concrete's strength.

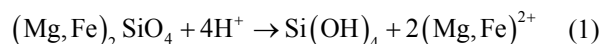
Also, because of its small particle size, micro-silica fills the voids between the cement particles; this improves the packing factor and reduces the porosity. Besides the above mentioned features, nano-silica has the following effects on cement pastes and concrete mixes: acceleration of the setting, cement matrix densification and improvement of the interparticle transition zone (ITZ) of aggregates (filling effect).

Because of the pozzolanic reaction, micro-silica can replace cement (1 part silica instead of 3 to 4 parts cement) for medium-strength concrete, while the strength is unaffected by the replacement [10]. Considering that the main difference between nano-silica and micro-silica is their particle sizes—assuming pozzolanic behaviors in each are similar—nano-silica will react faster with the cement due to its smaller particles. Therefore, the replacement of cement by nano-silica should considerably reduce the CO₂ emissions of the concrete. That is important because the cement industry is one of the industrial sectors that releases large amounts of CO₂ into the environment accounting for 8% of global CO₂ emissions [11]. In addition to this interesting application, the largest use of micro-silica is for producing concrete with enhanced properties, such as high early strength or low permeability.

1.3. Olivine Silica Production

Before beginning this section, it is necessary to clarify the difference between olivine and dunite for readers unacquainted with geology terms. Olivine refers to the mineral (Mg,Fe)₂SiO₄ and dunite refers to a rock where 90% of the volume is made up of olivine. The remaining 10% present in dunite ores can consist of pyroxenes, amphiboles, micas, carbonates, serpentines, etc. In many weathering and dissolution studies, pure olivines were used [12–14], but in this study, and our previous work [15], dunite had been used because we focused on the commercial production of olivine nano-silica.

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



The dissolution yields a slurry consisting of a mixture of magnesium/iron sulfates, amorphous silica, unreacted olivine and inert minerals. The silica can be separated from the resulting suspension by washing and filtration. A flow chart of this process is presented in **Figure 2**. The colloidal chemistry of silica strongly depends on the amount of salt and the pH of the solution. At the pH levels of the olivine silica process (−0.5 to 1), a colloidal solution of silica is usually unstable, and the silica particles polymerize [4].

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 [8]. The energy generation during the olivine nano-silica process for an adiabatic reactor is shown in **Table 1**. When 1.5 moles of olivine react with sulfuric acid, the temperature of the mixture will increase to 84°C. Therefore, the reaction generates more than enough energy to keep the system at the desired temperature (between 50°C and 90°C) provided the reactor is sufficiently large and well insulated.

2. Materials and Methods

The chemical composition of different dunites analyzed by X-ray fluorescence (XRF) is shown in **Table 2**. The first three dunites were from Norway, and the others were from Greece. The Greek dunites were a waste material generated from the magnesite mining activities in Gerakini. The loss of ignition (LOI) of GR-PROMGM-1 and GR-PROMGM-3 is too high, which is presumably related to the presence of serpentine and carbonate minerals, but not to olivine. These waste rocks were beneficiated by dense media separation, resulting in samples GR-PROMGM-4, -8 and -10, with a LOI below 2.5%. The olivine content of these samples was determined by X-Ray diffraction (XRD), XRF and thermogravimetric (TG) techniques. The olivine content was about 89 % for the Norwegian dunites whereas in the Greek dunites it

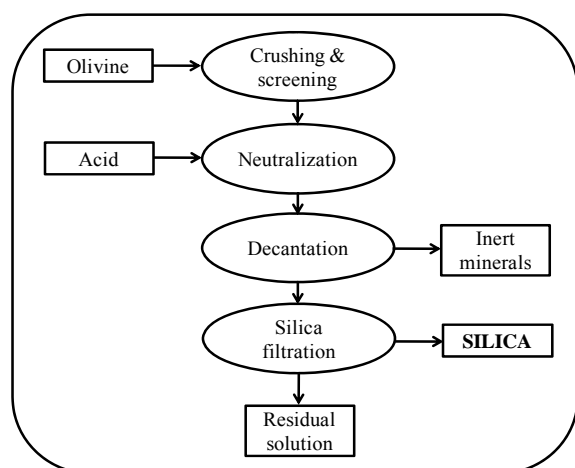


Figure 2. Flow chart of the olivine process.

Table 1. Energy generation during the olivine nano-silica process.

H_r (kJ/mol)	n_{ol} (mol)	$V_{H_2SO_4}$ (l)	$[H_2SO_4]$ mol/l	X	Q (kJ)	T (°C)
223	1.5	1	3	100	333.5	84

was lower (see **Table 2**). The samples after beneficiation, PROMGM-4, -8 and -10, doubled the olivine content of the original non beneficiated waste material.

Nano-silica production experiments were carried out at 50°C, 70°C and 90°C with olivine particles of 125 - 150, 250 - 300 and 500 - 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, previously dried. The neutralization reaction continued until the $[H^+]$ was below 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 [15]).

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 above 100°C was used for the gas physisorption analysis [16] in order to remove the physisorbed water. The physisorbed water is completely removed from the silica at 200°C, but all the silanol groups still remain [17]. The presence of remaining water decreases the adsorption of nitrogen on the surface of the solid material. The difference in the SSA_{BET} between an olivine nano-silica with a soaking temperature of 120°C and 190°C was around 20% for an olivine nano-silica of 345 m^2/g with a soaking temperature of 190°C. In this study two soaking temperatures for olivine nano-silica are used in order to compare the results of Greek dunite with Norwegian dunite, which were analyzed at 120°C in our previous study [15]. The specific surface area, SSA_{BET} , was calculated using the BET [16,18]. The specific external surface area, SSA_E , and the specific micropore surface area, SSA_{MP} , were calculated using the t-plot method [19,20] from the slope of the t-plot curve [21]. The particle size of the nano-silica was calculated from the geometrical relationship between surface area and mass given by

Table 2. Chemical composition of the different dunites.

Dunite	MgO	Fe ₂ O ₃	SiO ₂	Cr ₂ O ₃	Al ₂ O ₃	NiO	MnO	CaO	Na ₂ O	LOI	Other Oxides	Olivine
NO-CRS-1	47.41	7.84	41.42	0.31	0.75	0.33	0.12	0.34	0.06	1.29	0.13	88.4
GL50	49.32	7.32	41.44	0.31	0.46	0.32	0.09	0.15	0.02	0.59	0.00	88.9
GR-PROMGM-1	41.62	8.63	41.46	0.5	0.52	0.3	0.15	0.69	0.09	5.92	0.12	44.0
GR-PROMGM-3	34.47	7.95	43.51	0.45	1.78	0.25	0.14	1.33	0.33	9.6	0.19	29.0
GR-PROMGM-4	43.93	9.01	43.60	0.44	0.56	0.32	0.13	0.70	0.00	1.33	0.00	75.0
GR-PROMGM-8	43.79	8.90	42.67	0.41	0.59	0.31	0.13	0.65	0.00	2.55	0.00	75.0
GR-PROMGM-10	45.12	8.79	41.92	0.42	0.54	0.31	0.12	0.83	0.00	1.95	0.00	75.0

$$d\text{ (nm)} = \frac{6000}{SSA_{BET} \cdot \rho} \tag{2}$$

where d is the particle size of nano-silica considered to be spherical (nm), ρ the density of the material, 2.2 (g/cm³) for nano-silica, and SSA the surface area (m²/g). This particle size is an average value considering that the particles are spherical.

3. Results

3.1. Olivine Nano-Silica from Norwegian Dunite

The experiments performed with Norwegian dunite are presented in **Table 3** together with the amount of reagents, the molecular ratio of hydrogen ion versus olivine, the average particle size of olivine (d_{OL}) and the reaction temperature. The values of the specific surface area, pore size and particle size of olivine nano-silica (equation (1)) are collected in **Table 4**. **Figure 3** shows a TEM picture of sample NS-7 [15]. The chemical composition of the nano-silica produced in these experiments is shown in **Table 5**. The total sulfate, the sulfate limit for the appli-

cation of silica in concrete “norm NEN – EN 13263-1 + A1” and the number of filtration steps of the olivine nano-silica are shown in **Figure 4**. The maximum sulfate content (SO₄) from the norm is 2.4% or 0.8% expressed as sulfur content.

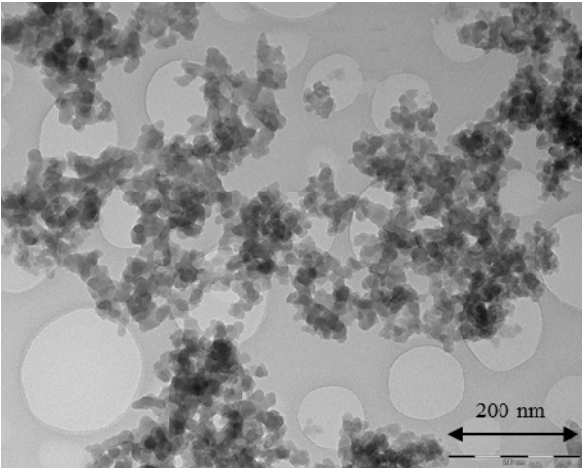


Figure 3. TEM picture (89 kx) of the olivine nano-silica NS-7 [15].

Table 3. Initial conditions of the nano-silica production experiments.

Title	m _{H₂SO₄} (g)	m _{ol} (g)	Ratio H ⁺ /Ol	d _{ol} (μm)	T _{reactor} (°C)
NS-1	589.1	109.8	4.5	138	48.7
NS-2	593.5	125.0	4.0	200	52.0
NS-3	555.8	121.7	3.8	400	55.0
NS-4	532.7	112.6	4.0	313	70.2
NS-5	593.9	122.9	4.0	400	70.7
NS-6	594.2	113.1	4.4	550	69.9
NS-7	593.7	119.4	4.2	275	87.7
NS-8	592.3	121.5	4.1	400	86.2

Table 5. Chemical analysis of olivine nano-silica produced using Norwegian olivine.

Title	S (%)	Mg (%)	Al (%)	Ca (%)	Fe (%)	Ni (%)	P _{Si} (%)
NS-1	3.89	1.88	0.02	0.05	0.36	0.02	86.01
NS-2	1.18	0.18	0.01	0.03	0.04	0.00	96.20
NS-3	1.26	0.29	0.02	0.08	0.06	0.00	95.76
NS-4	1.17	0.16	0.01	0.03	0.03	0.00	96.26
NS-5	1.19	0.26	0.02	0.04	0.05	0.00	96.06
NS-6	0.92	0.39	0.04	0.05	0.05	0.00	96.68
NS-7	1.36	0.28	0.02	0.04	0.06	0.00	95.52
NS-8	2.16	0.96	0.03	0.03	0.15	0.01	92.34

Table 4. Properties of olivine nano-silica produced using Norwegian olivine.

Title	SSA _{BET} (m ² /g)	SSA _{MP} (m ² /g)	SSA _E (m ² /g)	d _{p,A} (nm)	d _{p,D} (nm)	d _{BET} (nm)
NS-1	131	27	104	21	21	26
NS-2	150	27	123	18	17	22
NS-3	165	43	122	18	18	22
NS-4	218	52	166	18	17	16
NS-5	198	58	139	19	19	20
NS-6	179	47	132	28	24	21
NS-7	266	72	194	25	22	14
NS-8	185	36	149	18	17	18

^aSoaking temperature was 120 °C.

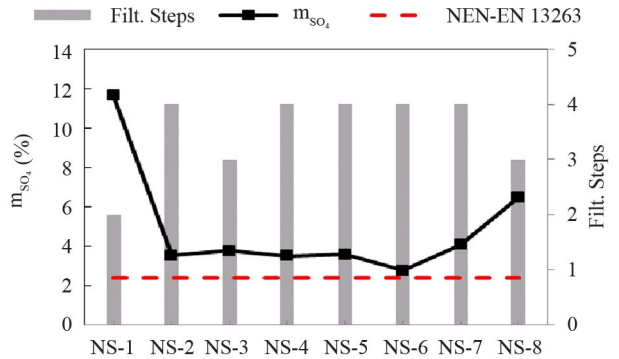


Figure 4. Sulfate content in olivine nano-silicas, sulfate limited by the norm and filtration steps.

The silica produced in these batches contained higher amounts of sulfate than permissible in the application of silica in concrete. The sulfur content can be decreased by adding extra washing steps [22,23]. In the additional cleaning steps, the rinsing liquid should be distilled water instead of H_2SO_4 0.1 M in order to achieve a more effective removal of the sulfur. Purities above 99 % were obtained with 6 filtration steps [22].

3.2. Olivine Nano-Silica Using Greek Dunite

In addition to the experiments carried out with Norwegian dunite, which were performed to validate the production of nano-silica by the olivine route, experiments with waste Greek dunite were conducted as well. PROMGM-1, -3, -4, -8 and -10 were tested at 90°C using the procedure previously described.

Although the dunite PROMGM-1 and PROMGM-3 reacted with sulfuric acid, the following problems were encountered in the treatment of the reaction mixture: a) the amount of silica produced was too low to make this process economically feasible; b) carbonates present in the Greek dunite consumed part of the hydrogen ions without producing silica; c) the violent reaction of the carbonates made control of the reactor temperature at the beginning of the experiment difficult; and d) the separation of the silica from the slurry was too difficult. The filtration issues, which is one of the major problem of this process, was due to the presence of talc and precipitate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the slurry, which were likely to be formed because of the high content of CaO in the Greek dunites. Therefore, we conclude that PROMGM-1 and PROMGM-3 are not suitable for the production of nano-silica by the dissolution of olivine; and that a dunite material with an olivine content equal or higher than 75 wt.% should be used for the production of nano-silica.

The beneficiated waste Greek dunite, on the other hand, gave excellent results producing a nano-silica of high purity and high specific surface area (see **Tables 6 and 7**). The purity of nano-silica (P_{Si}) was calculated by subtracting impurity values from an absolute purity (100%), considering sulfur was in the sulfate form. With beneficiated waste dunites, no problems arose when the slurry was decanted and the silica was filtered. Nano-silica from PROMGM-8 and -10 (NS-GM-8 and -10) exhibited a higher specific surface area than NS-GM-4 and nano-silica produced from Norwegian dunite. This was mainly because the silicas contain fewer impurities. It could also be due to the high reaction temperature and short aging time, thus preventing agglomeration of silica [15], as well as the higher soaking temperature (190°C) compared to the previous analysis.

The only silica that fulfilled the norm about the sulfur content in concrete was NS-GM-10, while the two other

Table 6. Properties of olivine nano-silica produced using beneficiated waste dunite (NS-GM-4, -8 and -10).

Title	SSA_{BET} (m^2/g)	SSA_{MP} (m^2/g)	SSA_{E} (m^2/g)	$d_{\text{p,A}}$ (nm)	$d_{\text{p,D}}$ (nm)	d_{BET} (nm)
NS-GM-4 ^a	275.9	37.6	238.3	15	14	10
NS-GM-8 ^b	390.0	52.0	338.0	18	17	7
NS-GM-10 ^b	480.0	58.0	422.0	19	19	6

^aSoaking temperature was 120°C, ^bSoaking temperature was 190°C.

Table 7. Chemical analysis of olivine nano-silica produced using beneficiated waste dunite.

Title	S (%)	Mg (%)	Fe (%)	Ca (%)	Al (%)	Ni (%)	P_{Si} (%)
NS-GM-4	2.32	1.21	0.30	0.11	0.03	0.01	91.39
NS-GM-8	1.61	0.60	0.15	0.06	0.02	0.01	94.33
NS-GM-10	0.68	0.41	0.11	0.08	0.02	0.01	97.34

silicas would require additional cleaning steps for the application in concrete. From these results, it can be concluded that nano-silica of high purity and high specific surface area can be obtained from beneficiated waste dunite as long as the necessary cleaning procedure is carried out.

3.3. Characterization of Different Nano-Silica Additives for Concrete

Six different amorphous commercial silica samples containing either micro- or nano-particles were selected to determine their physicochemical properties (more info about the characterization of silicas for concrete can be found in [24]). The samples are classified and named as follows: two colloidal nano-silicas prepared by the water glass route (samples CNS-1 and CNS-2, respectively); one nano-silica fume in powder form (PNS-3); one micro-silica in slurry form (PMS-4); and two synthetic pyrogenic silicas in powder form (PMS-5 and PMS-6). In addition, one sample prepared by the dissolution of olivine in acid (ONS) was studied for comparison. **Tables 8 and 9** display the general characteristics (taken from the product data sheets) and their chemical composition (determined by XRF), respectively.

Olivine nano-silica presents a lower density than expected due to the amount of water in the sample. This water can be present as physically adsorbed water, water involved in surface silanol and internal silanol. This nano-silica has an acidic character because it was synthesized at low pH (below the isoelectric point of the silica). In addition, this material has a high specific surface area and a low particle size. The primary particles, 10 to 25 nm, are agglomerated forming 3-D network clusters (see **Figure 3**) [15]. The agglomerates are mesoporous, and

Table 8. Characteristics of commercial and olivine nano-silicas.

Name	CNS-1	CNS-2	PNS-3	PMS-4	PNS-5	PNS-6	ONS
Type	Colloid	Colloid	Powder	Slurry	Powder	Powder	Powder
Production route	Water glass	Water glass	Pyrolysis	Fume	Pyrolysis	Pyrolysis	Olivine dissolution
Specific density (g/cm ³)	-	-	2.2	1.4	2.2 - 2.3	2.2 - 2.3	1.9 - 2.1
Bulk density (g/cm ³)	1.05 ^(*)	1.40 ^(*)	0.09 - 0.11 ^(*)	1.40 ^(*)	0.09 - 0.11 ^(*)	0.15 - 0.70 ^(*)	0.1
pH	9 - 11	9 - 11	5 ⁽⁺⁾	5 - 7	5 ⁽⁺⁾	5 - 7 ⁽⁺⁾	3 - 6 ⁽⁺⁾
Solid content (%)	15 ^(*)	48-52 ^(*)	-	48-50 ^(*)	-	-	-
Viscosity (mPa.s)	< 50 ^(*)	< 50 ^(*)	-	-	-	-	-
LOI (%)	-	-	0.5 ^(*)	4 ^(*)	0.5 ^(*)	0.5 ^(*)	5
BET (m ² /g)	200 - 500	50	50	15 - 35	50	10	100 - 400
d (μm)	-	-	<0.4	-	-	-	<0.1

(-): Not displayed by product data sheet or not applicable; (+): 4% m/m in water; (*): values taken from product data sheet.

Table 9. Chemical analysis of commercial and olivine nano-silicas.

Name	CNS-1	CNS-2	PNS-3	PMS-4	PMS-5	PMS-6	ONS
SiO ₂	97.29	99.33	99.55	96.12	99.62	99.55	98.97
Al ₂ O ₃	0.15	0.07	< 0.01	0.86	0.18	0.3	0.05
Fe ₂ O ₃	0.03	0.03	0.34	0.34	0.05	0.03	0.28
MnO	-	-	-	0.04	-	-	-
MgO	<0.01	<0.01	<0.01	0.53	<0.01	<0.01	0.31
CaO	0.02	0.01	<0.01	0.39	0.01	0.01	0.04
Na ₂ O	2.15	0.35	<0.01	0.21	<0.01	0.01	<0.01
K ₂ O	0.27	0.09	<0.01	1.05	0.04	0.01	0.04
TiO ₂	0.02	0.02	0.01	<0.01	0.01	<0.01	0.01
P ₂ O ₅	0.01	0.01	0.01	0.07	0.02	0.01	0.02
Cr ₂ O ₃	0.01	0.01	0.01	<0.01	0.01	0.02	0.03
SO ₃	0.03	0.05	0.03	0.36	0.03	0.03	0.24
C-Total	0.08	0.08	0.08	0.66	0.08	0.07	0.03

the porosity of the agglomerates is due to the voids between the primary particles. The morphological properties of nano-silica are of crucial importance for the application in concrete because they affect the adsorption of water and the packing factor.

3.4. Pozzolanic Activity of Olivine Nano-Silica

To determine the pozzolanic index of the olivine nano-silica, different cement mortars were prepared and tested following guideline CEN EN 196-1 [25]. A replacement of 7%, based on the weight of binder (bwob), that is cement plus nano-silica, was selected using the procedure

described by Justnes [26]. In addition, two cement mortars, with and without the replacement of cement with micro-silica (PmS-4), were prepared. The superplasticizer (SP) content (see **Table 10**) of the mixes was adjusted to obtain a spread flow of 175 ± 15 mm ensuring the desired rheological properties of the mixture. The SP used was a polycarboxylic ether (PCE) type with a solid content of 35% and density of 1.095 g/ml. Olivine nano-silica needed more than 4 times of SP than micro-silica to exhibit a similar spread flow, and still, the result of this test was 20 mm smaller. There are three reasons why the rheological properties of olivine nano-silica are more

viscous than those of micro-silica. 1) Olivine nano-silica reduced the amount of free water in the mix making it

Table 10. Mix designs of mortars used to determine the pozzolanic index.

Materials (g)	CEM I 52.5N	ONS	PMS-4
CEM I 52.5N	450	418.5	418.5
Olivine nano-silica	0	31.5	0
Micro-silica	0	0	31.5
Water	225	225	225
Standard sand	1350	1350	1350
SP	0	2.25	0.5
SP (% bwob)	0	0.5	0.11
w/c ratio	0.5	0.54	0.54
Spread flow (mm)	180 ± 3	167 ± 8	184 ± 7

Where ONS and PMS-4 refer to olivine nano-silica and micro-silica.

unavailable for the cement. This occurred because olivine nano-silica captured a high amount of water inside its structure as a result of its high specific surface area and mesoporosity. Therefore, less water was available to provide the correct rheological properties of the mix. 2) Also, nano-silica accelerated the hydration process of cement [27,28]. 3) The last factor influencing the rheological properties of the mixture was the shape of nano-silica particles. The 3-D clusters of olivine nano-silica made the slurry more viscous than the spheres of micro-silica.

The flexural and compressive strengths of the mixes were determined after 1, 7 and 28 days. Finally, the pozzolanic activity index was calculated based on the results of the standard cement mortar. The strength development of the different mortars is shown in **Figures 5** and **6**. The flexural and the compressive strengths after one day were lower for the nano-silica mortar than those of the standard and micro-silica mortars. This may be due to the higher dose of SP in the nano-silica mortar. The flexural

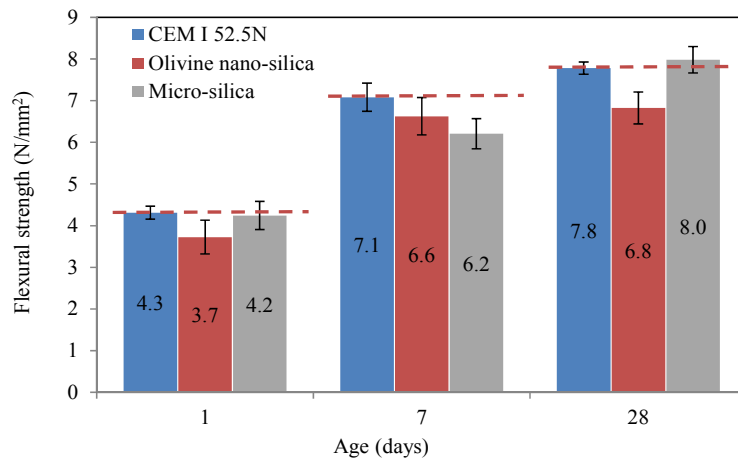


Figure 5. Flexural strength development of the tested mortars.

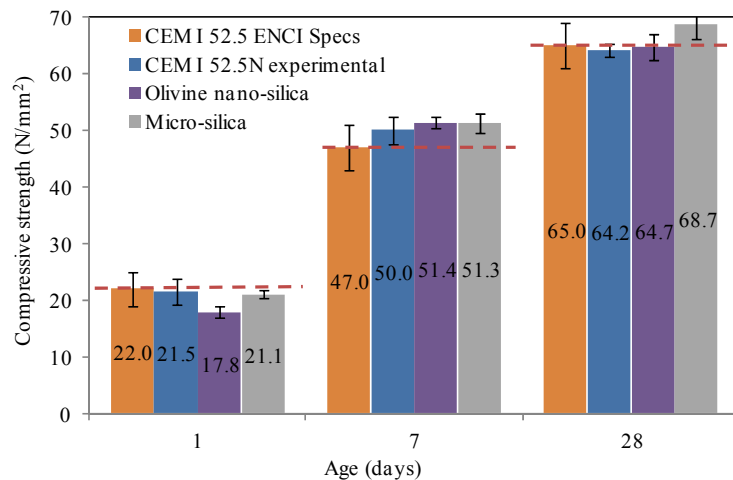


Figure 6. Compressive strength development of the tested mortars.

strength at 28 days of the nano-silica mortar was the lowest. The compressive strength of the nano-silica mortar at 28 days showed higher values than the standard mortar, but lower than the micro-silica mortar.

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

The pozzolanic index shows that olivine nano-silica has a high pozzolanic reactivity (101%). Therefore, olivine nano-silica can be classified as a pozzolanic material [29]. Nevertheless, the 28-day activity index was lower than the activity index of micro-silica (107%). This was probably due to the higher specific surface area and the agglomerated state of the nano-silica, which means that the maximum wet packing was not achieved, resulting in a lower compressive strength. Despite the positive results that were obtained, further research is needed to understand the strength development of the olivine nano-silica.

3.5. Application of Olivine Nano-Silica in Concrete

The effect of olivine nano-silica in conventional vibrated concrete (CVC), which is the most commonly used concrete, was investigated by casting three mixes with different substitution levels of CEM I 52.5 N with olivine nano-silica. The mix designs were based on a commercial recipe (see **Table 11**); eighteen cubes were casted using a vibrating table and were tested for their slump and compressive strength after 1, 7 and 28 days. The SP used was Ha-BE 100 (PCE type). **Table 11** also presents the values 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 the 5% replacement, it was not

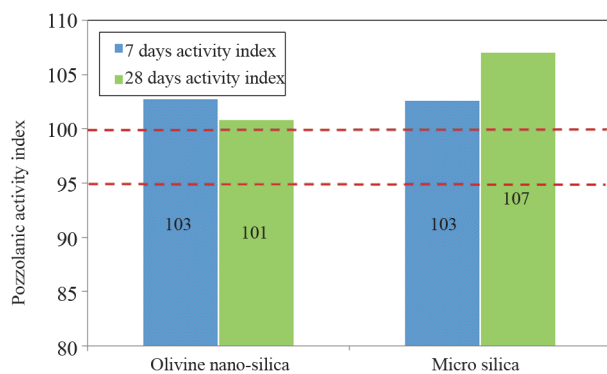


Figure 7. Pozzolanic activity index of the different mortars tested.

possible to obtain the desired slump class. Therefore, when the specific surface area of the mix was raised 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 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 after 1, 7 and 28 days of the CVC are depicted in **Figure 8**. This figure shows that the strength after one day was not completely 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%

Table 11. Mix designs of CVC with and without replacement of cement with olivine nano-silica

Materials (kg/m ³)	Reference	5% vol.	7% vol.	10% vol.
Olivine NS	0.0	6.9	10.3	13.7
CEM I 52.5 N	210	200	194	189
Fly-Ash	88.2	88.2	88.2	88.2
Sand 0-4	781	781	781	781
Gravel 4-16	1086	1086	1086	1086
Water	159	159	158	158
SP (b wob)	0.50	1.12	1.33	1.75
w/f (%)	0.54	0.54	0.54	0.54
Slump class	S2	S2	S1	S1
Slump diam. (mm)	60	60	40	40

*Where f refers to fine materials below 125 μm .

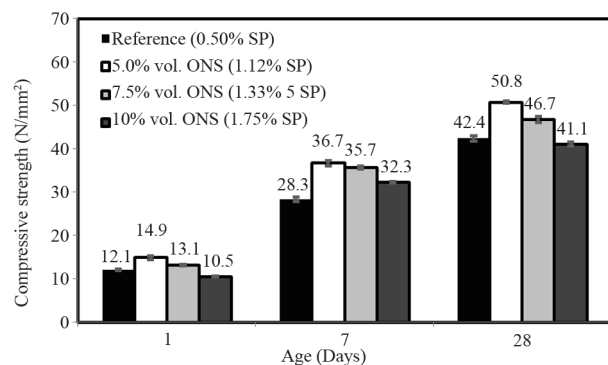


Figure 8. Compressive strength development of CVC at different replacement levels of cement with ONS. (ONS refer to olivine nano-silica).

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 rose by 20% compared to the reference mix. This suggests that the optimum substitution of olivine nano-silica should be around this value.

Figure 9 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 (VOBN). 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 concrete used while maintaining the same compressive strength as the reference material, therefore minimizing CO₂ emissions.

4. 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 SiO₂ purity can be increased by employing additional cleaning steps to fulfill the sulfate requirements of the norm NEN – EN 13263-1 + A1. The olivine nano-silica process is: more sustainable because it requires less fuel (so fewer CO₂ emissions), and it is possible to use waste materials as a silica source.

Waste dunite rocks with a low content of olivine can be beneficiated by dense media separation to produce a material with an olivine content of 75%. The beneficiated material can be satisfactorily used for nano-silica production as long as the content of olivine is equal to or higher than 75%, and the contents of carbonates, calcium and talc are low.

The compressive strength of the standard mortar is affected when cement is replaced with olivine nano-silica by 7% bwoc. This material can be classified as a pozzolanic material with activity indexes of 101%. Further research is needed to obtain the optimum replacement level of cement for the olivine nano-silica.

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 reduce CO₂ emissions. This green nano-silica can also be used in any other applications where the high specific surface area is required.

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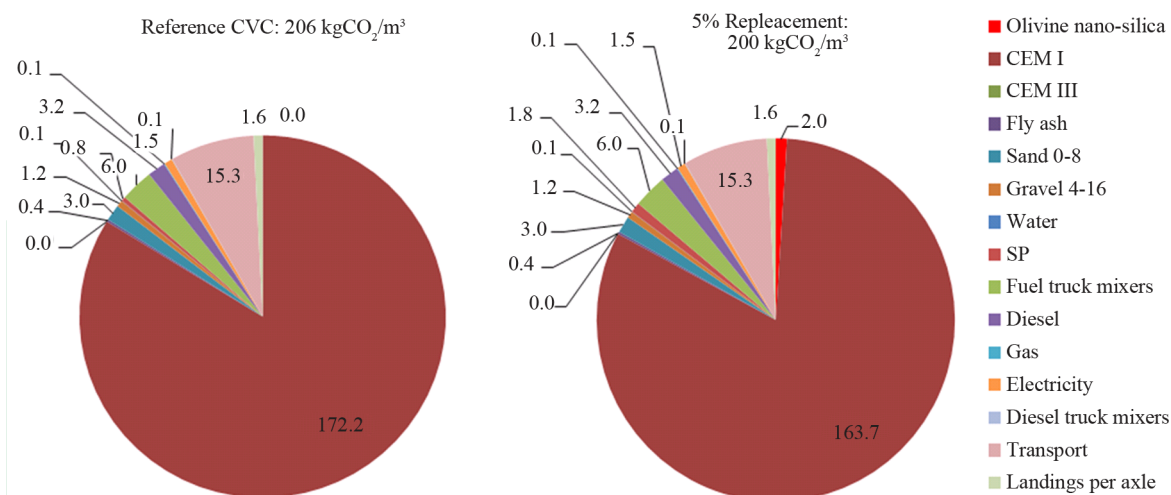


Figure 9. CO₂ footprint of CVC and of CVC with 5% replacement of cement with ONS.

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