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Applications of nano-ingredients in building materials

The overall grading of granular building materials determines the properties of the concrete. The properties in fresh state (flow properties and workability) are for instance governed by the particle size distribution (PSD), but also the properties in hardened state, such as strength and durability, are affected by the mix grading and resulting particle packing. One way to further improve the packing, performance and sustainability, is to increase the particle size spectrum, e.g. by including particles with sizes below 300 nm. Possible materials which are currently available are ground minerals like limestone and silica fines such as silica flour (Sf), micro-silica (mS) and nano-silica (nS). In this paper examples of the application of nS are presented.

Another possibility of rendering building materials more sustainable is functionalizing, e.g. providing them self-cleaning and/or purifying properties. Possible additions are nano zinc sulfide and titania. In the present paper a number of building materials are discussed that have been treated successfully.

1. Building materials¹ for air quality improvement

The initial idea came with the pioneering paper on water splitting by Fujishima and Honda [1], which paved the way to thousands of manuscripts and patents aiming at utilization of semiconductor photocatalysts for water splitting, water/air purification and self-cleaning surfaces [2]. Nowadays, titanium dioxide (TiO₂), a semiconductor photocatalyst, is one of the most commonly used materials for the implementation of the photocatalytic property into various materials [3-9]. TiO₂ has been tested by many researchers in order to take an advantage of its surface oxidation-reduction processes upon the irradiation by appropriate light [6][10-13]. These processes can result in a reduction or complete degradation of pollutants, in a solid [14, 15], liquid [16, 17] or in a gas phase [6, 10, 18, 19].

Several building materials have been used as carriers for the application of photocatalytic materials, for example concrete [20, 21], mortar [6, 22], clay [23], glass, polymers [5, 7], [24-26]. It can be concluded that the application of photocatalytic materials is more beneficial while applied as a top layer rather than in the entire volume of the product, where most of the photocatalytic materials are hindered, not exposed to the environment and thus not effective.

Indoor environment conditions, such as pollution concentration, pressure, temperature, or light irradiation differ from the outdoor conditions. The biggest differences are: (a) pollution concentration indoors being very often higher than the ambient concentration and (b) type of irradiation which is mostly limited to the visible range indoor in contrast with ultraviolet range present outdoors. Despite that the air treatment is mainly studied through "*active photocatalytic products*", such as ventilation system containing embedded filter or an electrostatic precipitator with photocatalyst and its own light source [2], the application of "*passive photocatalytic products*" is promising due to the fact that no additional energy is required. These "*passive photocatalytic products*" are in this context photocatalytic building materials.

The testing of the materials/products for the air purification is initially carried-out in a laboratory scale level by applying various reactors and experimental conditions [6, 27-

¹ Building materials for an air improvement are meant here in the context of materials possessing photocatalytic oxidation (PCO) property

29]. The application of passive photocatalytic products shows promising results [3, 4, 6], which allow us to understand the factors that affect the photocatalytic efficiency and the degradation mechanisms [11, 30] of the model pollutants. However, some of the tests do not clearly represent the ability of the photocatalytic materials/products to clean the air in a realistic environment since the experimental conditions are far from being realistic.

Lorencik et al. [5] investigated the possibility of incorporation of a visible light responsive photocatalyst – carbon-doped titanium dioxide (C-TiO₂) – into a water based top coating applied on wall covering. The result showed that stabilized nano-suspension of C-TiO₂ was more suitable for the incorporation due to better distribution of the photocatalyst within the matrix of the polymer. However, an additional step was found to be necessary in order to “activate” the developed product by exposing the photocatalytic particles to environment. Ultraviolet (UV) irradiation pre-treatment was found to be an efficient method for the “activation” since the degradation of NO_x, tested according to ISO 22197-1 under modified conditions (visible light irradiation, lower pollutant concentration and various flow rates), came from inactive material to 10% (after 5 hours of pre-treatment) and later on to 18% (after 10 hours pre-treatment).

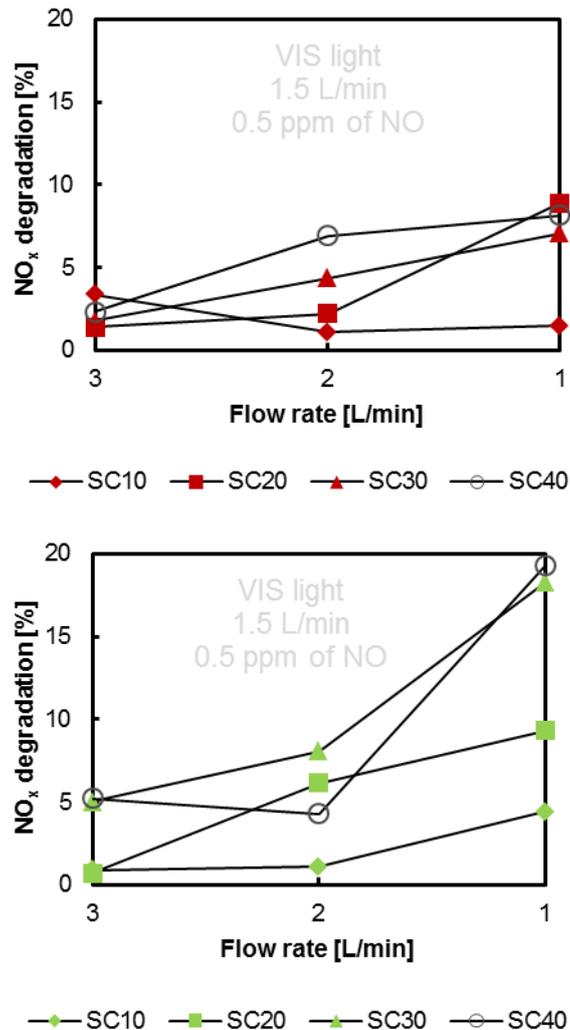


Figure 1. NO_x degradation efficiencies of SC10-40 pre-treated for 5 hours (left) and 10 hours (right) tested under various flow rates.

The effect of the UV pre-treatment was further investigated on coatings containing only by C-TiO₂ in nano-suspension form and incorporated nano-silica applied on the wall covering in various dosages (layers). The results showed that dosage and the silica incorporation has a great effect on the “activation” and final PCO efficiency of the product.

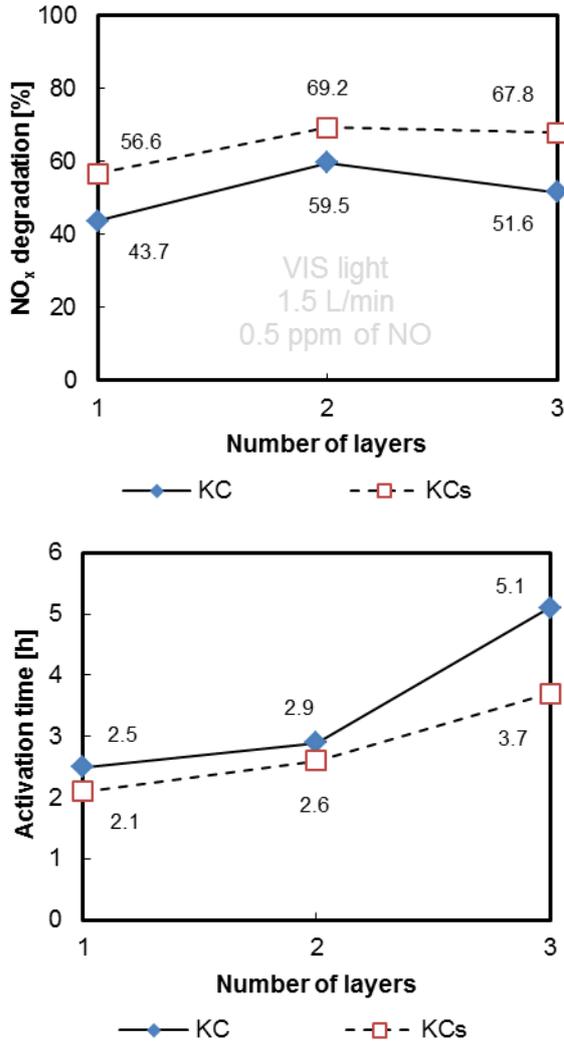


Figure 2. NO_x degradation results (left) and activation times (right) of the developed coatings.

Another work by Lorencik et al. [31] aimed to design an air purifying lightweight concrete with incorporated visible light responsive photocatalyst and zeolite as an adsorption additive to further improve the photocatalytic efficiency. Various experimental conditions, such as flow rate, pollutant concentration and type of irradiation, were applied in this study to investigate their effect.

Table 1. Experimental conditions

	ISO	UV1	UV2	UV3	VIS1
Flow rate [L/min]	3.0	1.5	3.0	1.5	1.5
NO [ppm]	1.0	1.0	0.5	0.5	0.5

The results showed that all the developed samples possessed excellent NO_x removal efficiency tested under ISO standard conditions (over 50 % degradation in overall). Zeolite addition showed a positive effect on the photocatalytic efficiency leading to enhanced de-NO_x efficiencies. A sample, which contained a combined low amount of lightweight aggregates together with zeolite led to the highest degradation efficiency. The developed samples demonstrated excellent air pollutants removal efficiency under realistic outdoor conditions (e.g. 94% NO_x removal by Mix 5). The developed concrete also possessed very good air purifying performance under realistic indoor conditions (e.g. 37% NO_x removal by Mix 5).

There are several examples of full scale demonstration carried out in order to assess the impact of the developed photocatalytic products on the air pollution [20, 32, 33]. Ballari and Brouwers [20] performed a full scale demonstration of a developed air purifying concrete pavement in Hengelo, The Netherlands.

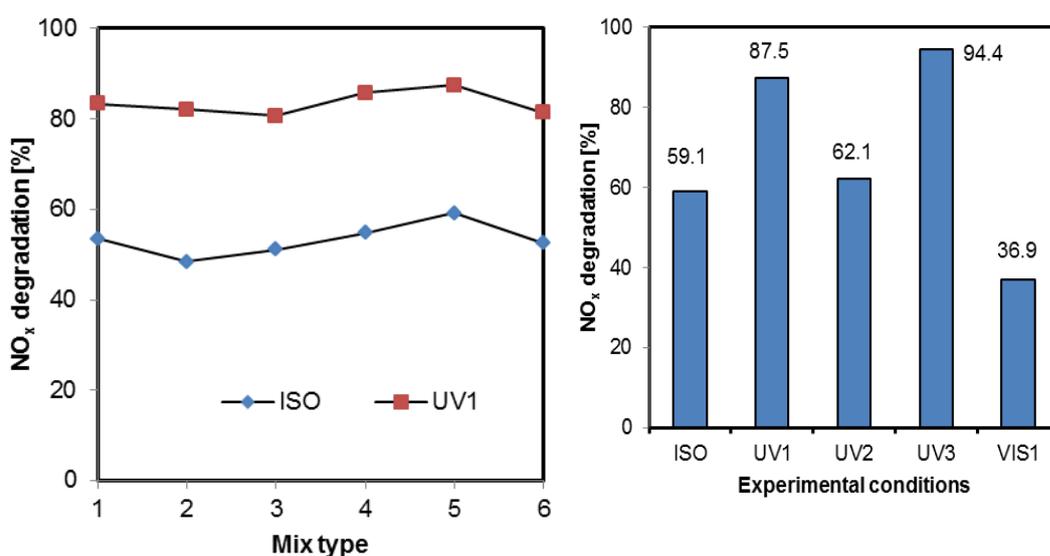


Figure 3. NO_x degradation results under ISO/UV1 conditions (left); NO_x degradation results of the best performing sample under all tested conditions (right).

Ballari and Brouwers [20] monitored traffic intensity, NO, NO₂ and ozone concentration along with temperature, relative humidity, wind speed, wind direction and light (UV/VIS) irradiance on two streets, one paved with the photocatalytic pavement and another one without photocatalytic pavement which was used as a reference. The measurements were performed in the heights of 5, 30 and 150 cm. The results showed that the photocatalytic efficiency is strongly dependent on the conditions, degrading 19% of NO_x in average during the whole day. However, in average, 28% of NO_x was degraded in the afternoons and even 45% of NO_x degradation was observed under ideal conditions (high irradiation and low relative humidity). These results were rather consistent with the lab-scale experiments performed on the same samples where 38% of NO_x was degraded under standard (ISO 22197-1) conditions.

2. An alternative method: the olivine nano-silica (OnS) process

Nanotechnology and nanomaterials have attracted great attention in the previous years as can be seen from the fact that the number of patents has increased by 600% from 1992 to 2002 [34] and the annual global turnover is estimated to increase up to € 1.5

trillion by 2015 [35]. Nano-silica is one of the compounds that is boosting the field of nanomaterials with an annual rise of 5.6% to reach a projected 2.8 million metric tons in 2016 [36]. Likewise, the market is estimated to grow by 7.5% to \$6.4 billion [36]. 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.

Process description

An alternative synthesis route to the commercial production methods of amorphous nano-silica is the dissolution of silicate minerals in acid. The raw materials employed in this method are olivine ((Mg,Fe)₂SiO₄) and acid (in the present case sulfuric acid). Olivine is a solid solution between forsterite (Mg₂SiO₄) and fayalite (Fe₂SiO₄). The crystalline structure of forsterite is represented in Figure 4. Olivine is the fastest weathering silicate due to the absence of Si-O bonds in its structure. In addition, olivine is the most common mineral in the upper mantle and a common mineral in the earth's crust, which makes it a low-price commodity.

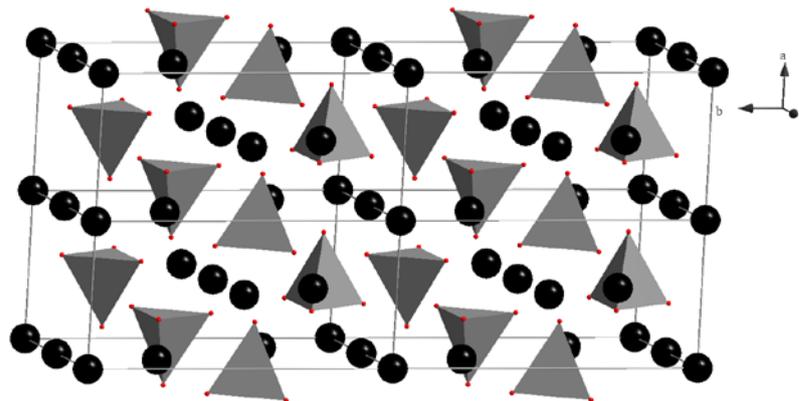
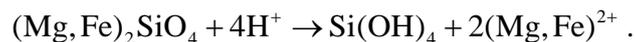


Figure 4. Crystalline structure of forsterite, Mg₂SiO₄.

Where the tetrahedrons are SiO₄ particles with four oxygen atoms at the vertex, and the spheres next to the SiO₄ tetrahedrons are magnesium ions.

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 5. 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 [37]. The energy generation during the olivine nano-silica (OnS) process for the hypothetical case of an adiabatic reactor is shown in Table 2.

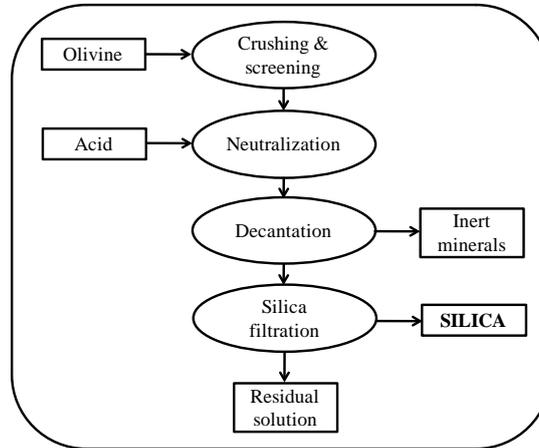


Figure 5. Flow chart of the production of nano-silica by the dissolution of olivine.

When 1.5 moles of olivine react with 1L solution of sulfuric acid 25%, the temperature of the mixture will increase 79 °C. Therefore, the reaction generates more than enough energy to keep the system at the desired temperature (between 50 and 90 °C) provided the reactor is sufficiently insulated. In addition, the dissolution of concentrated sulfuric acid also generates a considerable amount of heat.

Table 2. Energy generation during the olivine nano-silica process.

ΔH_r (kJ/mol)	$V_{H_2SO_4}$ (L)	$m_{H_2SO_4}$ (g)	n_{ol} (mol)	m_{du} (g)	X (%)	Q (kJ)	ΔT (°C)
223	1	1186	1.5	242	100	333.5	79.3

ΔH_r is the enthalpy of reaction, X the conversion degree of the reaction and Q is the heat generated. Heat capacities of 25% sulfuric acid and forsterite are 3.38 [38] and 0.83 [39] J·g⁻¹·°C⁻¹, respectively. The heat capacity of dunite has been approximated as the one of forsterite.

Properties of the olivine nano-silica

The olivine nano-silica prepared following the previous production route has a specific surface area between 100 and 500 m²/g. The silica particles are agglomerated in clusters forming a material with micropores (pores below 2nm), mesopores (pores between 2 and 50 nm) and macropores (pores above 50 nm). The purity content is above 99 % and can be further cleaned by performing additional washing steps (more details can be found in [40]). A TEM photograph of this type of silica is presented in Figure 6. The process conditions (i.e., the impurity content, reaction conversion degree,

pressure of filtration) of the olivine nano-silica production have a strong influence on the final SSA_{BET} of this material. In addition, the specific surface area can also be modified by performing post-treatments such as hydrothermal treatments to this material.

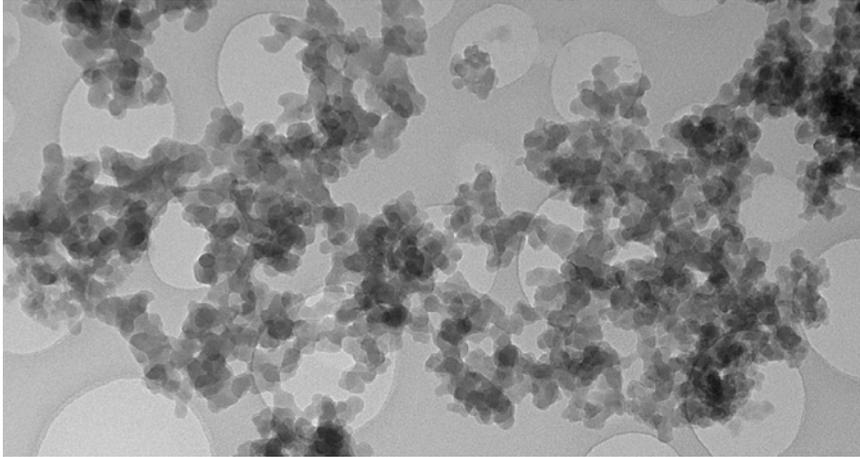


Figure 6. TEM picture (89 kx) of the olivine nano-silica [41].

Thus, modifying the process conditions or performing hydrothermal treatments, nano-silicas with different SSA_{BET} can be synthesized. The process conditions and the hydrothermal treatment influence the properties of nano-silica in different ways:

- 1) The cleaner the nano-silica is, the higher its specific surface area is, reaching values between 300 and 400 m^2/g for olivine silicas with low content of salts or silica purities above 99%. The sulfate salts are located in the pores of the silica clusters, blocking them and drastically reducing the SSA_{MP} .
- 2) The higher the filtration pressure is, the higher the surface area will be. This is due to a reduction of the pore volume. However, if the applied pressure is too high, the pores of the material drastically collapse, reducing the SSA_{BET} drastically.
- 3) The smaller the conversion degree of the dissolution of olivine is, the higher the SSA_{BET} is. Silicas with surface areas above 500 m^2/g were produced at slow kinetics (50 °C) and conversions of 38% (see sample NS-50-S3).
- 4) The hydrothermal treatment process diminishes the specific surface area of nano-silica by 75%. In addition, this treatment removes the microporous surface area of the samples almost completely.

Summarizing, the SSA_{BET} of olivine nano-silica (OnS) can be tailored to meet the requirements of different possible applications. This tailoring can be done by changing the filtration pressure, controlling the conversion degree and/or performing ripening treatments after the production process has been completed. Thus, the typical SSA_{BET} for a clean nano-silica ($\sim 350 m^2/g$) can be modified in the range 90 to 500 m^2/g . Furthermore, the high purity and low energy requirements of this type of silica makes this process a very interesting alternative to the current existing production methods.

3. Application of nano-silica in concrete

One of the most referred to and used cementitious nano-materials is amorphous silica with a particle size in the nano-range, even though its application and effect in concrete has not been fully understood yet. It has been reported that nano- SiO_2 addition

increases the compressive strength and reduces the overall permeability of hardened concrete due to its pozzolanic properties, which are resulting in finer hydrated phases (C-S-H gel) and densified microstructure (nano-filler and anti-Ca(OH)₂-leaching effects) [42-44]. These effects may enhance the durability of concrete elements and structures. There are different commercial types of nano-SiO₂ additives available on the market, which are produced in different ways such as precipitation, pyrolysis, sol-gel and others [44]. These processes are expensive due to the price of the raw materials and the energy requirements involved. As a result of this a more economical method to produce nano-silica has been developed, based on dissolution of olivine (OnS) in acid [41, 45]. In this method, olivine and sulfuric acid are combined, whereby precipitated amorphous silica with high fineness and purity but agglomerated form is synthesized (nano-sized particles between 6 to 30 nm), and even greener (lower CO₂ foot print) than contemporary micro- and nano-silica [41, 45].

Several procedures and material characterization techniques have been applied to obtain the main physical-chemical properties of different commercial-type nano-silica materials. In this context, Quercia et al. [46] studied the morphology and texture of amorphous micro- and nano-silica manufactured by different routes, such as precipitation from waterglass, olivine dissolution in acids, flame hydrolysis and condensation of silica fume. The results elucidate the implications of the silica characteristic towards the fresh and hardened properties of concrete. It was concluded that the morphology (particle shape) and texture (specific surface area, pore diameter and pore-size distribution) of nano-silica depends on the production route. The production route also determines the nature (chemical composition, density and amount of surface and internal silanol groups) and the ratio of agglomeration of silica nano-particles. In addition, the effects on the slump-flow test (Figure 7) and the mechanical properties of mortars formulated with the nano-silica samples were also analyzed in [46].

Based on this experimental assessment, a potential relationship between the total surface area of the mix (cement, sand and nano-silica) and the slump-flow of mortars with different types of amorphous silica nanoparticles was established. It was observed that the higher the total surface area of the mortar, the smaller the mortar slump-flow (Figure 7).

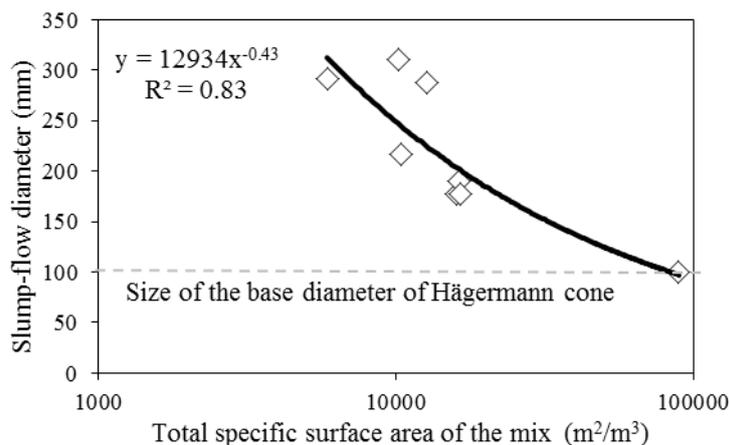


Figure 7. Relationship between the slump-flow diameters of standard mortars after 15 strokes in the flow-table and the total specific surface area of the mix (cement, sand and silica) [46].

It was also found that the final slump-flow can be affected by the state of aggregation of the primary silica particles that leads to the presence of microporosity (with a high water retention capacity) in nano-silica samples. Furthermore, the slump-flow showed an exponential relationship with the micropore volume of the nanoparticles. Even though the nano-silicas studied had different textural properties, the main parameters that influence the slump-flow diameter (workability) and final mechanical properties were the specific surface area, the micropore volume (which defines the water adsorption capacity) and the state of agglomeration. These parameters controlled the filling capacity, pozzolanic activity and rate of hydration of cement. It was suggested that the silica should be dispersed as good as possible to obtain the intended improvement of mortar or concrete properties.

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The effect of nano-silica characteristics on the water demand of cement paste and mortars were also addressed in [47], where the mini spread-flow test was used for the determination of water demand, water film thickness and the impact on the workability of cement paste and mortars. It was concluded that decreasing the primary particle size of nano-silica and, consequently increasing specific surface area (SSA), increases the mix sensibility to water change (deformation coefficient E_p defined by Hunger [48]) and the agglomerates produce higher water demand (β_p) than plain cement pastes. This leads to a linear relationship between the agglomeration ratio (d_{agg}/d_{BET}) and the water demand (Figure 8) and indicates that water has a stronger influence on the workability of the hydrating system containing nano-silica with high surface area. A similar thickness of the water layer of nano-silica particles (24.8 nm), as reported in [48] for micro-sized powders, was also confirmed by Quercia [49]. These values allow an initial estimation of the water demand of a given amorphous silica sample with a known specific surface area.

The effect of additions of olivine nano-silica (OnS) on the fresh and hardened cement paste, standard mortars, normal vibrated concrete (NVC) and self-compacting concrete was also elucidated by Quercia [49]. Different effects were derived in terms of granulometric properties of the mixes and OnS characteristics. Some of them were confirmed by literature, while others were new. OnS addition to cement paste, increases the viscosity, yield point and hydration degree of the system as a result of the increased specific surface area (nucleation and filler effect) of the mix. This holds also for the case in which fixed amounts of superplasticizer were applied. Based on the isothermal calorimetry tests it was demonstrated that OnS acts as an accelerating agent in cement-based systems. OnS affects the rate of hydration and can increase the compressive strength of the concrete and oilwell cement compositions at early age.

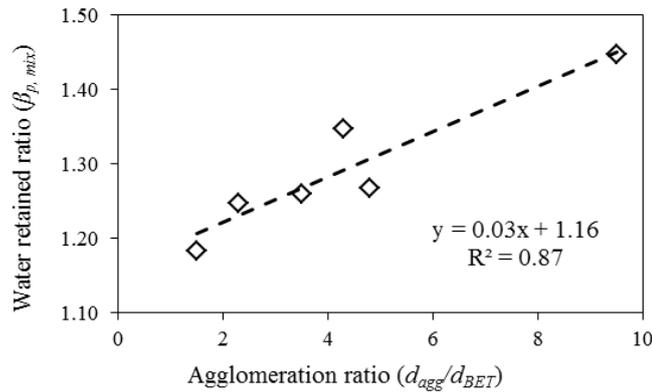


Figure 8. Variation of the water retention ratio (β_p , mix) for silica addition of 1.5% bwoc with agglomeration ratio (d_{agg}/d_{BET}) determined in [49].

It was suggested that the early strength improvement and higher degree of hydration are caused by changes in the rate of hydration of the calcium silicates (mainly C_3S) and aluminates phase hydration of the clinker components. This also holds when slag/fly-ash particles were added in the system and generate a higher heat of hydration (Figure 9).

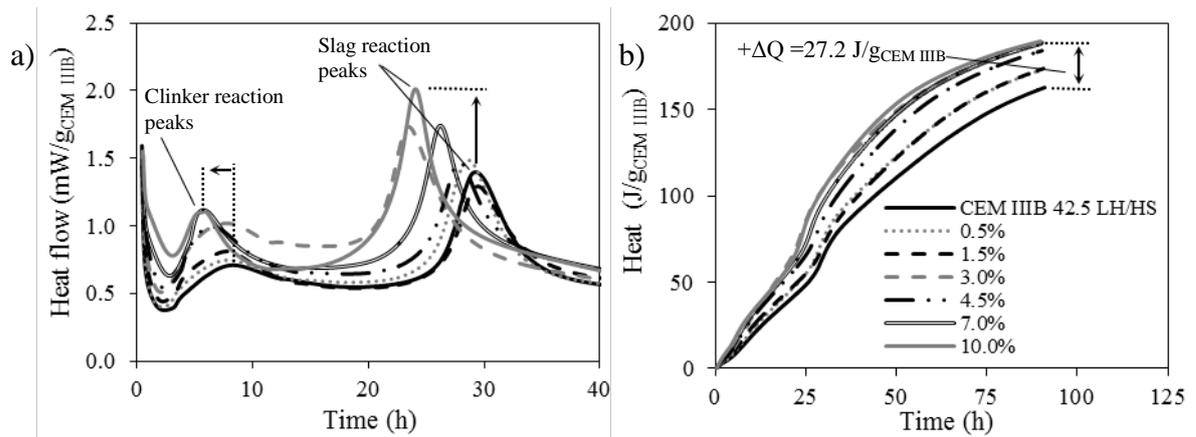


Figure 9. Results of the calorimetric measurements on CEM III/B 42.5 LH/HS pastes with OnS, a) Normalized heat flow, b) Normalized total heat evolution (Q) [49].

Additionally, Quercia [49] demonstrated that the replacement of cement with OnS influenced the amount and type of hydration phases formed and thus, the volume, porosity and finally the durability of the tested mortars. The major changes consider the amount of chemically bound water (C-S-H gel formed) and the consumption of portlandite. Furthermore, the results showed that the properties of mortars containing OnS depended on the concentration and form of addition (powder vs. wet dispersion), which determines the agglomeration state of the nano-silica particles in the cement matrix. It has been also confirmed that the increasing SSA due to the addition of incremental amounts of OnS decreases potentially the final spread-flow of the mortars with the same SP content. Similarly, the compressive and flexural strength was influenced by the method of addition (dried or dispersed). A mortar with higher

compressive strength was obtained with 1.5 vol.% of cement replacement by OnS in powder form. It was concluded that to increase or avoid the reduction of the flexural strength and to increase the replacement level of this type of nano-silica, it should be added as dispersion. This type of nano-silica can be classified as a pozzolanic material with activity index in the range of 100 to 108 [46].

The recent developments [45, 49] in the field of OnS showed significant promise in addressing many of the challenges to produce an environmentally friendly concrete. For example, it was demonstrated that the combined use of OnS and optimized particle packing using the ideas of the mix design tool developed by Hüsken and Brouwers [50] can be used to increase the quality and overall properties of normal vibrated (NVC) and self-compacting concretes (SCC). This allowed the use of lower binder content and finally a lower amount of concrete to be used for the same functionality. Quercia [49] illustrated that the replacement of 5% cement (by volume) with olivine nano-silica in NVC results in higher mechanical properties (strength) with a decrease in the estimated CO₂ footprint of 3%. The high compressive strength of NVC carries loads more efficiently than normal-strength concrete, which also should reduce the total amount of material placed and lower the overall cost of the structure. Additionally, the same authors [51] in other study demonstrated that all durability indicators of SCC (conductivity, chloride migration and diffusion coefficients, freeze-thaw resistance and permeability) were significantly improved by the addition of 3.8% of different types of the nano-silica (Figure 10). Due to longer service life, the use of nano-silica in concrete will reduce repair and maintenance costs to a great extent.

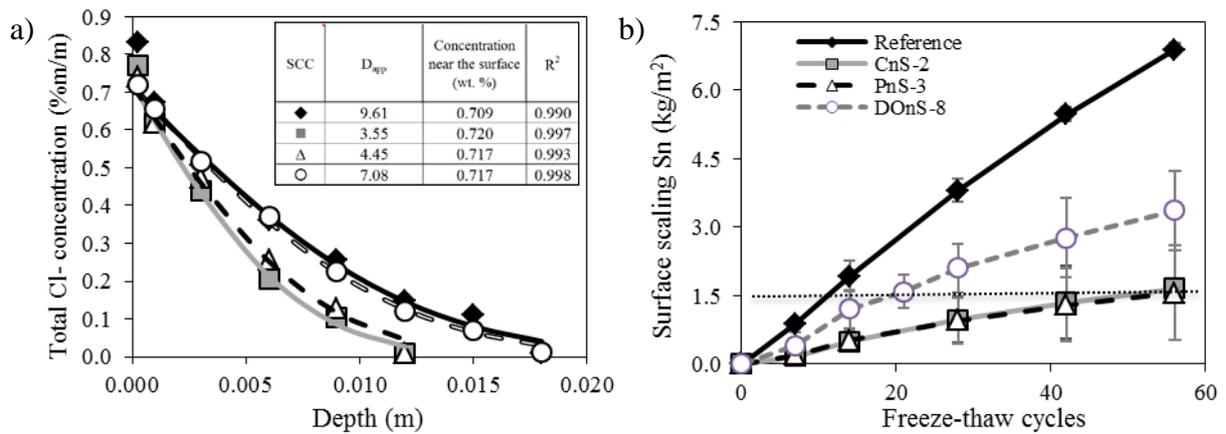


Figure 10. a) Chloride diffusion profiles of the tested SCC mixes (◆ Reference, ■ CnS-2: colloidal nano-silica, △ PnS-3: pyrogenic nano-silica and ○DOnS-8: olivine nano-silica dispersed), b) cumulative scaling factor (Sn) after 56 freeze-thaw cycles (3% NaCl solution) [49].

Similarly, using the same amount of OnS mentioned before (3.8% bwoc) at laboratory and pilot scale tests, Quercia [49] demonstrated that is possible to decrease the binder content of eco-SCC to a greater extent (13 kg/m³ less), maintaining similar 28-day compressive strength as conventional SCC. As a consequence, a more green and ecological SCC was produced with a decreased CO₂ foot-print (18% less) owing to the reduced amount of cement (Figure 11). The reduction in cement will help in protecting the environment to a large extent. In addition, the use of nano-silica will reduce the cement consumption for a specific grade of concrete. These results confirmed that addition of nano-silica enhances the use of other supplementary cementitious materials such as fly ash and granulated blast furnace slag. This also opens the incorporation of

other waste materials and recycling products in concrete, which normally reduces the mechanical properties.

Another contribution to the sustainable development of building materials is the application of nano-silica sludge coming from the photovoltaic industry. This is considered to be a waste material and which is an alternative source of nano-silica. The results shown in [52] demonstrate that if the chloride content of this type of nano-silica can be decreased, it can be used as a potential supplementary cementitious material to partly replace cement in concrete, thereby decreasing the CO₂ footprint of concrete and the environmental impact associated with the landfill of waste.

In summary, the newly developed olivine nano-silica can be produced in large quantities and for low price, so the mass application in concrete is within reach. It may replace cement in the mix, which is the most environmentally unfriendly component in concrete. The use of nano-silica makes the produced concrete financially more attractive and reduces the CO₂ footprint of concretes produced thereof. The application of nanotechnology will improve the concrete properties enabling the development of high performance concretes for various constructions. This results in concrete with better performance, lower costs and improved ecological footprint.

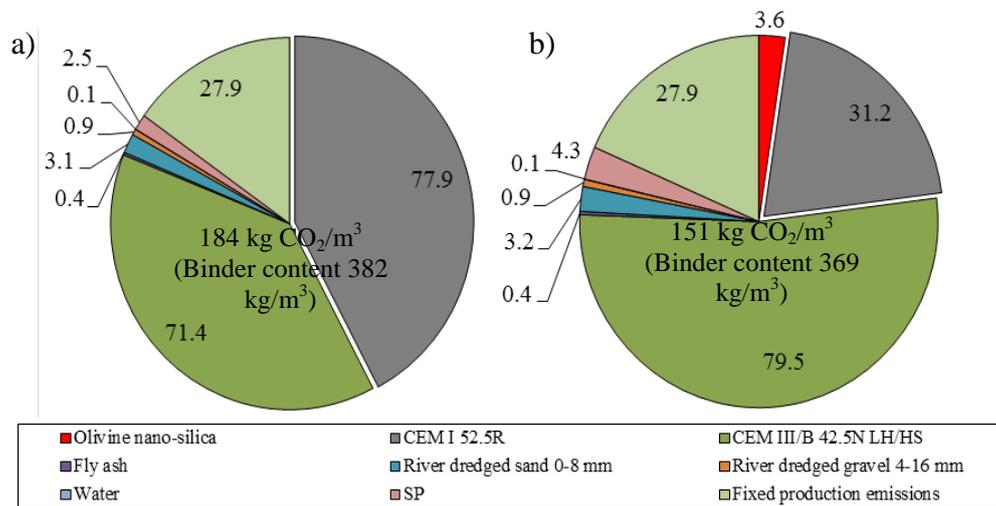


Figure 11. Estimated CO₂ footprint per cubic meter of eco-SCC, a) reference SCC mix and b) optimized eco-SCC (3.8% OnS and 60% less CEM I 52.5R) [49].

Conclusions

The current paper presented examples of effectively rendering building materials ecological and/or functional by applying nanomaterials, particularly nS and nT. The effect is even more pronounced when the nanomaterial as such is produced in a sustainable way as well, as is the case with the presented OnS. And finally, the photocatalytic effectiveness of nT can be enhanced by combining it with nS, research that is in progress.

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