Tailoring the properties of olivine nano-silica and its application in concrete

A. Lazaro[1], G. Quercia[1,2], H.J.H. Brouwers[1]

[1]Eindhoven University of Technology, Eindhoven, NL
[2]Materials innovation institute (M2i), Delft, The Netherlands

Abstract

The dissolution of olivine in acid is an interesting alternative route to produce nano-silica because of the low cost of raw materials and the low energy requirements. 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 CO_2 emission reduction of 3 %.

Production of olivine nano-silica

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.
The dissolution of olivine in acid, see Eq. (1), is carried out at low temperatures and represents a convenient alternative for producing amorphous silica because of the high quality of the silica and the low energy requirements (more information about the properties of olivine nano-silica can be found in /1,2/):

$$(Mg,Fe)_2SiO_4 + 4H^+ \rightarrow Si(OH)_4 + 2(Mg,Fe)^{2+} \qquad (1)$$

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. Table 1 summarizes the properties of olivine nano-silicas /1,3/.
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 /4/. When 1.5 moles of olivine react with sulfuric acid, the temperature of the mixture will increase 84 °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 large and well insulated.

Parameters	Pyrogenic	Precipitated	Olivine nano-silica	Olivine nano-silica
Purity, SiO_2 (%)	>99.8	>95	>95	>99
SSA_{BET} (m^2/g)	50-400	30-500	100-300	300-500
d (nm)	5-50	5-100	10-25	5-20
d_p (nm)	None	>30	>10	-
Reference	/5/	/5/	/1/	/3/

Table 1: Summary of the properties of different amorphous nano-silicas

Tailoring the properties of olivine nano-silica

The properties of nano-silica can be tailored by the Ostwald ripening process, which consists of a hydrothermal treatment at basic pH in order to modify the equilibrium of the solubility of silica. The solubility of silica depends on the solution pH, the temperature, the radius of curvature of the silica particles and the content of impurities. Regarding the pH and temperature, the solubility of silica increases when these parameters rise /6/. The influence of the pH on the specific surface is illustrated in Figure 1, where the SSA_{BET} of the ripened samples at room temperature are plotted.

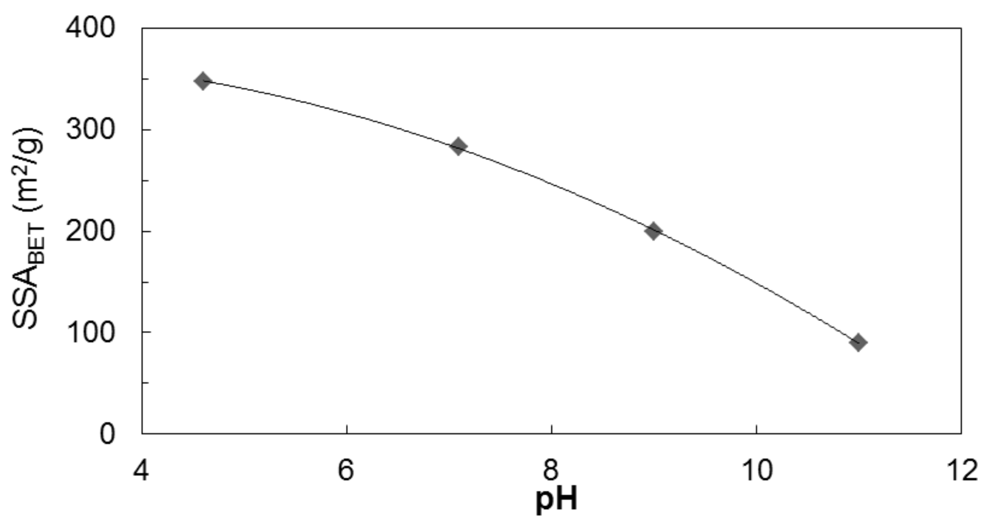

Fig. 1: Reduction of the SSA_{BET} after the Ostwald ripening treatment

Application of olivine nano-silica in concrete

The effect of olivine nano-silica (ONS) in conventional vibrated concrete (CVC) was investigated by casting three mixes with different substitution levels of CEM I 52.5N with olivine nano-silica. The mix designs were based on a commercial recipe, see Table 2, (more details in /7/). The compressive strengths of the CVC are depicted in Figure 2. The best result was obtained after 28 days for the mix with 5 % replacement resulting in a rise of 20 % for the compressive strength. Figure 3 presents the estimated CO_2 footprint per cubic meter of reference CVC with and without 5 % replacement. The reduction of CO_2 emissions for CVC with 5 % replacement was 3 % with respect to the reference concrete. This could be further improved by tailoring the properties of olivine nano-silica so less SP would be necessary to maintain the same rheological properties.

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 (% bwob)	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

Table 2: Mix designs of CVC with/without replacement of cement for ONS

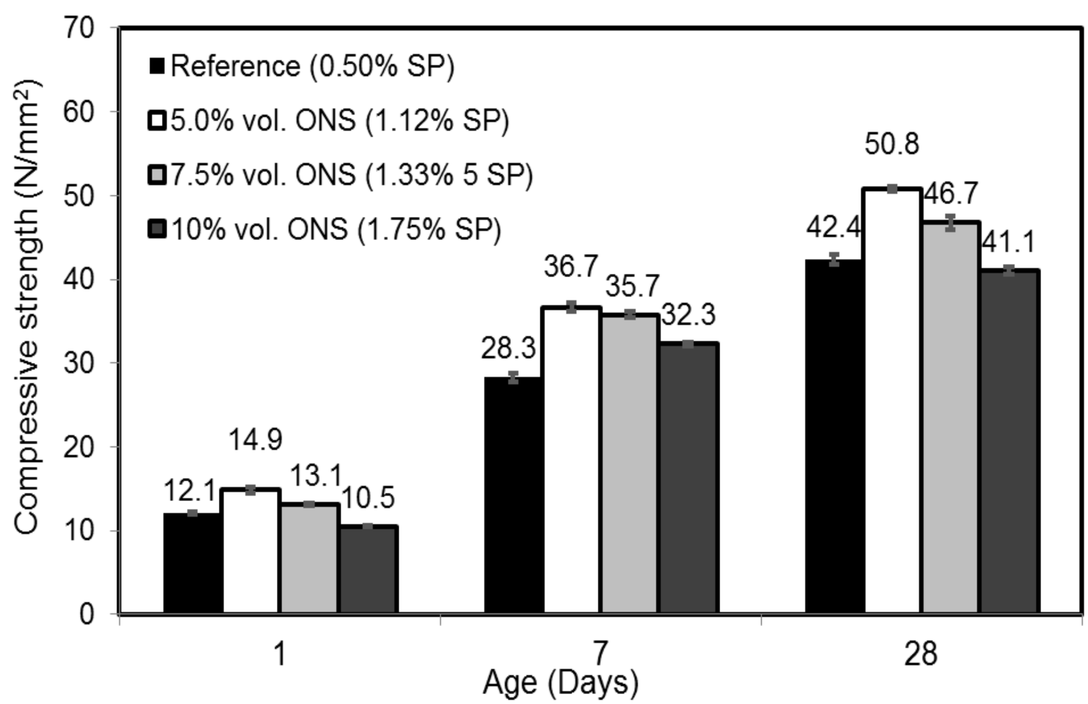

Fig. 2: Compressive strength development of CVC at different replacement levels of cement with ONS

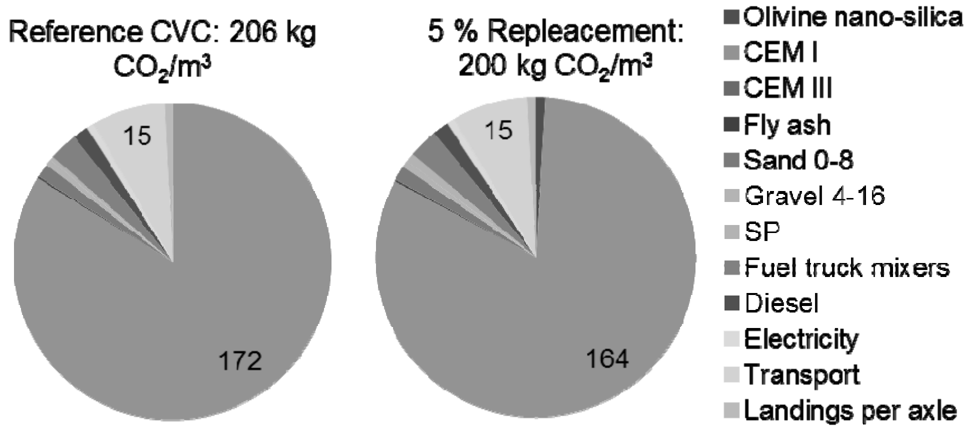

Fig. 3: CO_2 footprint of CVC with/without replacement of cement for ONS

Conclusions

The optimum replacement level of olivine nano-silica in CVC is around 5% by volume resulting in: 1) a compressive strength increase of 20 %; 2) a CO_2 emission reduction of 3 %.

Acknowledgments

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