Effect of olivine nano-silica additions on the fresh and hardened behaviour of cement pastes and mortars

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Introduction

The high demand for sustainable and durable building materials requires profound knowledge on the material properties. In this respect, the phenomena occurring at nano-level are of crucial importance for the design of new building materials. Therefore, all around the world, increasing amounts of funding are being directed to research projects dealing with material properties on nano-level, which is claimed to have tremendous potential for the future. One of the most referred to and used cementitious nano-material is amorphous silica with a particle size in the nano-range, even though its application and effects on concrete have not been fully understood yet. Olivine $(Mg,Fe)_2SiO_4$ is the fastest weathering silicate mineral dissolving easily in acid. During dissolution in acid the metallic ions (Mg^{2+},Fe^{2+}) are replaced by H^+, yielding $Si(OH)_4$ monomers and metallic ions in solution. After cleaning treatments an amorphous nano-silica is obtained. The produced olivine nano-silica (OnS) has a specific surface area between 100 and 400 m^2/g, the size of the primary particles, which are agglomerated in clusters, ranges from 10 to 25 nm and the impurity content is below 5 % /1/. Literature related with the application of OnS in cement based materials is scarce; only one research work performed by Justnes and Ostnor /2/ is available. Thus, the effect of adding OnS in cement based systems has been not studied. Based on this, the present research aims on elucidating the effects of OnS in the fresh and hardened state of cement pastes and mortars.

Materials and experimental methods

The OnS used were produced following the method presented in /1/. OnS wet cakes were dried (105 °C for 24 h) and milled to obtain a powder. The cement used was ordinary Type I Portland cement OPC

(CEM I 52.5N) produced by ENCI Cement, The Netherlands. Standard sand was used according to EN 196-1. In addition, a commercial admixture based on modified polycarboxylic ether (PCE) with 35 % solids content and a density of 1.095 g/cm^3 was used.
To study the effect of OnS and superplasticizer (SP), rheological measurements and the mini spread-flow test were carried out to assess changes of the viscosity caused by the volumetric substitutions of cement (0.5, 1.5, 3.0, 4.5, 7.0 and 10%). The rheological tests were complemented with isothermal calorimetric measurements (cement pastes with w/c of 0.5; and with or without SP). Finally, compressive and flexural strength of standard mortars following the procedure established in EN 196-1 were carried out.

Results and discussion

The obtained flow curves for all tested pastes are displayed in Fig. 1 the experimental data were fitted to the Herschel-Bulkley fluid model using the methodology recommended by /3/. This fluid model was selected as cement pastes show a shear thinning behaviour.

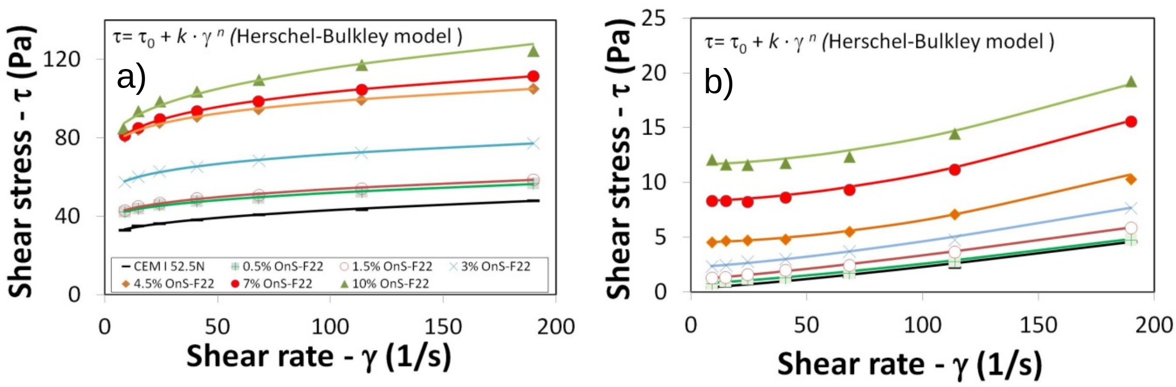

Fig. 1: Flow curves of the cement/OnS paste measured and adjusted to the Herschel-Bulkley fluid model: a) without SP, b) with fixed SP (0.6% bwoc).

The parameters determined by the rheological tests were compared with values obtained on mortar scale using the spread-flow test. It is demonstrated that the yield point of the paste is proportional to the spread flow and the total specific surface area (Fig. 2). The increase in the viscosity and in the yield point of the paste is a result of the increased specific surface are of the paste due to the addition of OnS. In this case it is demonstrated for a fix amount of SP that the workability of the cement paste decreased with increasing OnS content. In addition, it was found that the pastes presented a self-flowing characteristic when the cement paste posses yield point values lower than 9 Pa.
The obtained head flow and total head curves for all tested pastes are

displayed in Fig. 2. For the first system studied, where no SP was added (Fig. 2a), the heat flow curves are close to the reference sample. The main difference observed was in the so called dormant period, which is clearly reduced with increasing volumetric substitution of cement by OnS. In addition, a slight increase in the main hydration peak (C_3S phase) was observed. This increase is produced by the higher reactivity of the OnS (pozzolanic behaviour). In the second system studied (with SP) the retarding effect due to the addition of SP is still evident (Fig. 2b). Nevertheless, the accelerating effect caused by the addition of OnS is also influential. Besides this, an effect on the hydration of aluminates phases (secondary ettringite formation) is displayed for 10% vol. substitution level.

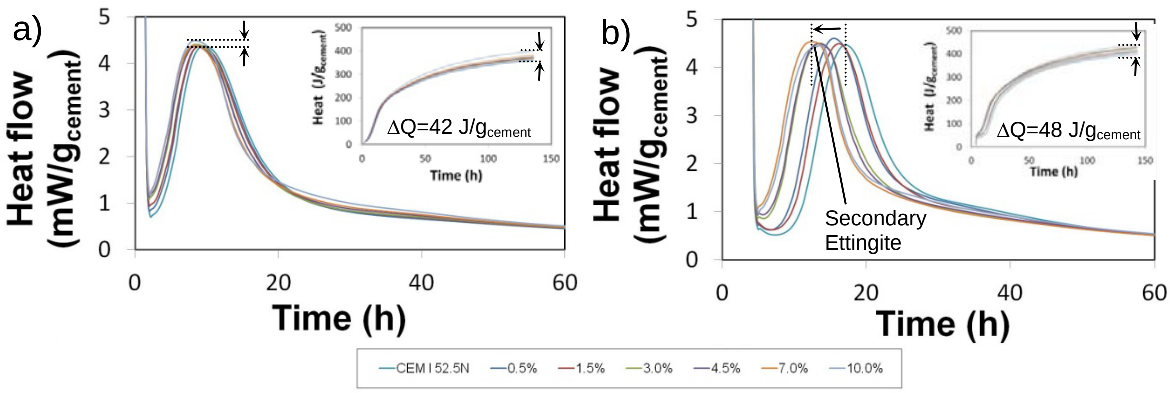

Fig. 2: Heat flow and total heat behaviour of cement/OnS paste: a) without SP, b) with fixed SP (0.6% bwoc).

Finally, the mechanical properties of mortars with different OnS additions and a fixed SP content are shown in Fig. 3.

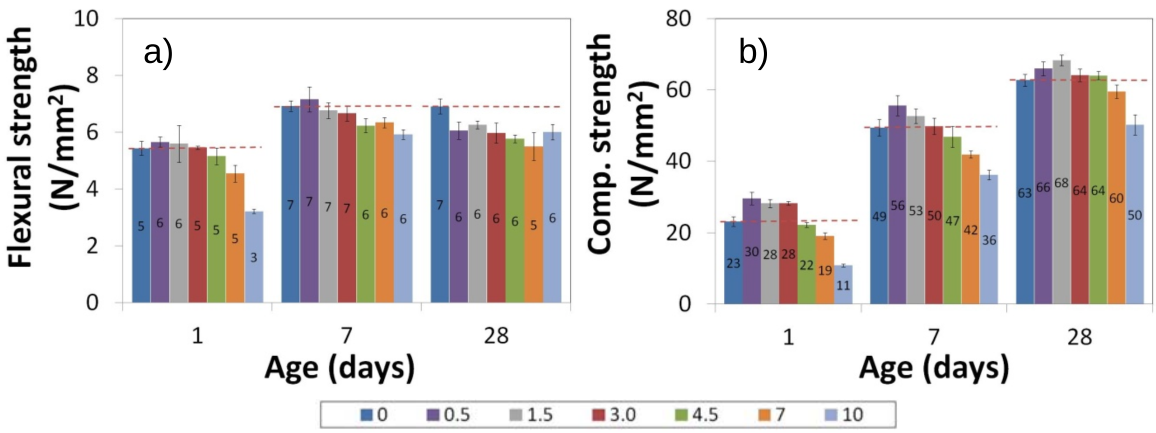

Fig. 3: Mechanical properties of mortars with different content of OnS (w/c=0.5 and 0.6% SP): a) Flexural strength, b) compressive strength.

In general, almost all flexural strength values dropped when OnS was added,. This fact is caused by the high agglomerated state of the OnS, which produced a more porous interparticle transition zone (ITZ). On the contrary, it is possible to observe in Fig. 4b that the compressive strength increases until a maximum that depends on the samples age. Once the maximum is reached the compressive strength dropped. For 28-day the best results was obtained with 1.5 vol% of cement replacement by OnS.

Conclusions

The addition of nano-silica increases the viscosity and the yield point of the cement paste. This holds also for the case in which commercial superplasticizers are applied. The increase in the viscosity and the yield point of the paste is the result of the increased specific surface are of the paste. Based on the isothermal calorimetric measurements and the analysis performed, it is possible to conclude that the OnS acts as an accelerating agent in concrete. The mechanical properties demonstrated that the possible optimum replacement level of OnS would be between 1.5 to 4.5% by vol.

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