Application of nano-silica (nS) in concrete mixtures

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Abstract

Concrete is the most common used material for construction and their design consumes almost the total cement production in the world. The use of large quantities of cement produces increasing CO_2 emissions, and as a consequence the green house effect. A method to reduce the cement content in concrete mixes is the use of silica fines. One of the silica fines with high potential as cement replacement and as concrete additive is nano-silica (nS). However, the commercial nS is synthesized in a rather complex way, resulting in high purity and complex processes that make them non-feasible for the construction industry. Furthermore, the application of nS and its effect in concrete is not fully understood yet.

In a recent research project a new nano-silica [1-4] is produced from olivine. This nS, as well as commercially available nS, will be applied and tested. In addition, a mix design tool used for self compacting concrete (SCC) [5] [6] will be modified to take into account particles in the size range of 10 to 50 nm. This paper aims to present the state of the art of nS application in concrete, focusing on the nS properties to render it suitable to be applicable in concrete. It includes the nS production process, their addition effect and their application in concrete. Also an overview of the experimental setup and further research is presented.

1. Introduction

The construction industry uses concrete to a large extent. About 14 bln ton were used in 2007 [7]. Concrete is used in infrastructure and in buildings. It is composed of granular materials of different sizes and the size range of the composed solid mix covers wide intervals. The overall grading of the mix, containing particles from 300 nm to 32 mm determines the mix properties of the concrete [8-10]. The properties in fresh state (flow properties and workability) are for instance governed by the particle size distribution (PSD), but also the properties of the concrete in hardened state, such as strength and durability, are affected by the mix grading and resulting particle packing [11]. One way to further improve the packing is to increase the solid size range, e.g. by including particles with sizes below 300 nm. Possible materials which are currently available are limestone and silica fines likes silica flavor (Sf), silica fume (SF) and nano-silica (nS) [12]. However, these products are synthesized in a rather complex way, resulting in high purity and complex processes that make them non-feasible for the construction industry [11]. In this PhD project a new developed nano-silica [1-4] produced from olivine will be applied and tested. In addition to this, a design tool used for the mix design of SCC [5][6][11] is extended to account for particles in the nano range, whereby special effects may occur. The aim of this research is to create a practical application method and a model to apply newly developed nS in concrete.

2. Production method of nS

Nowadays, there are different methods to produce nS products. One production method is based on a *sol-gel process* (organic or water route) at room temperature. In this process, the starting materials (mainly Na_2SiO_4 and organometallics like TMOS/TEOS) are added in a solvent, and then the pH of the solution is changed, reaching the precipitation of silica gel. The produced gel is aged and filtered to become a xerogel [13]. This xerogel is dried and burned or dispersed again with stabilized agent (Na, K, NH_3, etc.) to produce a concentrated dispersion (20 to 40% solid content) suitable for use in concrete industry [14][15].

An alternative production method is based on *vaporization of silica* between 1500 to 2000 °C by reducing quartz (SiO_2) in an electric arc furnace. Furthermore, nS is produced as a byproduct of the manufacture of silicon metals and ferro-silicon alloys, where it is collected by subsequent condensation to fine particles in a cyclone [3][12]. Nano-silica produced by this method is a very fine powder consisting of spherical particles or microspheres with a main diameter of 150 nm with high specific surface area (15 to 25 m^2/g).

Estevez et al. [16] developed a *biological method* to produce a narrow and bimodal distribution of nS from the digested humus of California red worms (between 55nm to 245nm depending of calcination temperature). By means of this method, nanoparticles having a spherical shape with 88% process efficiency can be obtained. These particles were produced by feeding worms with rice husk, biological waste material that contain 22% of SiO_2.

Finally, nS can also be produced by *precipitation method.* In this method, nS is precipitated from a solution at temperatures between 50 to 100 °C (precipitated silica) [2][14][17]. It was first developed by Iller in 1954. This method uses different precursors like sodium silicates (Na_2SiO_3), burned rice husk ash (RHA), semi-burned rice straw ash (SBRSA), magnesium silicate and others [2][13][17-19].

In addition, nano-silica (nS) is being developed via an *alternative production route*. Basically, olivine and sulphuric acid are combined, whereby precipitated silica with extreme fineness but agglomerate form is synthesized (nano-size with particles between 6 to 30 nm), and even cheaper than contemporary micro-silica [2]. The feasibility of this process has been proven in two preceding PhD theses and published data [1-3][20]. Currently, parallel PhD project [4] focuses on the process to produce nS on industrial scale in large quantities for concrete production. Furthermore, the combination of raw materials and process parameters on production will be examined.

3. Effect of nS addition in concrete and mortars

In concrete, the micro-silica (Sf and SF) works on two levels. The first one is the chemical effect: the pozzolanic reaction of silica with calcium hydroxide forms more CSH-gel at final stages. The second function is physical one, because micro-silica is about 100 times smaller than cement [12]. Micro-silica can fill the remaining voids in the young and partially hydrated cement paste, increasing its final density [13]. Some researchers [11][12][21][22] found that the addition of 1 kg of micro-silica permits a reduction of about 4 kg of cement, and this can be higher if nS is used. Another possibility is to maintain the cement content at a constant level but optimizing particle packing by using stone waste material to obtain a broad PSD [11]. Optimizing the PSD will increase the properties (strength, durability) of the concrete due to the acceleration effect of nS in cement paste [14][22]. Nano-silica addition in cement paste and concrete can result in different effects. *The accelerating effect* in cement paste is well reported in the literature [21-23]. The main mechanism of this working principle is related to the high surface area of nS, because it works as nucleation site for the precipitation of CSH-gel. However, according to Bjornstrom et al. [24] it has not yet been determined whether the more rapid hydration of cement in the presence of nS is due to its chemical reactivity upon dissolution (pozzolanic activity) or to their considerable surface activity. Also the accelerating effect of nS addition was established indirectly by measuring the viscosity change (rheology) of cement paste and mortars [22][25]. The viscosity test results shown that cement paste and mortar with nS addition needs more water in order to keep the workability of the mixtures constant, also concluded that nS exhibits stronger tendency for adsorption of ionic species in the aqueous medium and the formation of agglomerates is expected. In the latter case, it is necessary to use a dispersing additive or plasticizer to minimize this effect.

Ji [26] studied the effect of nS addition on *concrete water permeability and microstructure*. Different concrete mixes were evaluated incorporating nS particles of 10 to 20 nm (s.s.a. of 160 m^2/g), fly ash, gravel and plasticizer to obtain the same slump time as for normal concrete and nS concrete. The test results show that nS can improve the microstructure and reduce the water permeability of hardened concrete. Lin et al. [23] demonstrated the effect of nS addition on permeability of eco-concrete. They have shown with a mercury porosimetry test that the relative permeability and pores sizes decrease with nS addition (1 and 2% bwoc). Decreasing permeability in concrete with high fly ash content (50%) and similar nS concentrations (2% of nS power) was reported by [27]. Microstructural analysis of concrete by different electronic microscope techniques (SEM, ESEM, TEM and others) [21-27] revealed that the microstructure of the nS concrete is more uniform and compact than for normal concrete. Ji demonstrated [26] that nS can react with $Ca(OH)_2$ crystals, and reduce the size and amount of them, thus making the interfacial transition zone (ITZ) of aggregates and binding cement paste denser. The nS particles fill the voids of the CSH-gel structure and act as nucleus to tightly bond with CSH-gel particles. This means that nS application reduces the calcium leaching rate of cement pastes and therefore increasing their durability [21][28].

The most reported effect of nS addition is the impact on the *mechanical properties of concrete and mortars*. As it was explained before, the nS addition increases density, reduces porosity, and improves the bond between cement matrix and aggregates [12][14][15][21][23][25][27][29]. This produces concrete that shows higher compressive and flexural strength [30][31]. Also, it was observed that the nS effect depends on the nature and production method (colloidal or dry powder). Even though the beneficial effect of nS addition is reported, its concentration will be controlled at a maximum level of 5% to 10% bwoc, depending on the author or reference [14][23][25][27-29]. At high nS concentrations the autogenous shrinkage due to self-desiccation increases, consequently resulting in higher cracking potential. To avoid this effect, high concentration of superplasticizer and water have to be added [12][24] and appropriate curing methods have to be applied.

4. Applications of nS

At present Sf, SF and nS, because of their price, are only used in the so-called high performance concretes (HPC), eco-concretes and self compacting concretes (SSC) [12][14][15][32]. For the last types of special concretes (eco-concrete and SCC) [11][23][27][32-36], the application of these materials is a necessity. Also, some explorative applications of nS in high performance well cementing slurries [37], specialized mortars for rock-matching grouting [29][38], and gypsum particleboard [39] can be found, but nS is not used in practice yet. The application of these concretes can be anywhere, both in infrastructure and in buildings. Nano-silica is applied in *HPC and SCC concrete* mainly as an anti-bleeding agent. It is also added to increase the cohesiveness of concrete and to reduce the segregation tendency [29-32]. Some researchers found [35] that the addition of colloidal nS (range 0 to 2% bwoc) causes a slight reduction in the strength development of concretes with ground limestone, but does not affect the compressive strength of mixtures with fly ash or ground fly ash (GFA). Similarly, Sari et al. [32] used colloidal nS (2% bwoc) to produce HPC concrete with compressive strength of 85 MPa, anti-bleeding properties, high workability and short demolding times (10 h). Another application of nS well documented and referred in several technical publications [23][32-36], is the use as additive in *eco-concrete mixtures* and tiles [38]. Eco-concretes are mixtures where cement is replaced by waste materials mainly sludge ash, incinerated sludge ash, fly ash or others supplementary waste materials. One of the problems of these mixtures is their low compressive strength and long setting period. This disadvantage is solved by adding nS to eco-concrete mixes to obtain an accelerated setting and higher compressive strength [32-36]. Roddy et al. [37] applied particulate nS in oil well cementing slurries in two specific ranges of particles sizes, one between 5 to 50 nm, and a second between 5 and 30 nm. Also they used nS dry powders in encapsulated form and concentrations of 5 to 15% bwoc. The respective test results for the slurries demonstrate that the inclusion of nS reduces the setting time and increases the strength (compressive, tensile, Young's modulus and Poisson's ratio) of the resulting cement in relation with other silica components (amorphous 2.5 to 50 µm, crystalline 5 to 10 µm and colloidal suspension 20 nm, types silica) that were tested.

5. PhD project plan and further research

The following subproject in the application of nS in concrete will be performed:

1) Literature review of nS specification for its applicability in concrete and selection of commercial nS materials as references.

2) Characterization of the main properties of nS and micro-silica collected using difference techniques like laser granulometry, SEM, TEM and BET measurements. The characterization of the new nS will result in recommendations for the production conditions of this material.

3) Determination of water requirements and admixture needs (superplasticizer types and concentration) of nS, applying the spread flow test to assess workability of pastes and mortars. Existing silica and the new silica will be tested experimentally and theoretically verifying if the existing theoretical models also holds for submicron particles.

4) Design and testing of mortars and concrete mixes with nS (low cement, self compacting and high compressive strength) and optimization of the simulation tool for PSD in order to incorporate nano sized particles.

5) Concrete design and testing using principles described in [5] and [6], where a previous developed/modified simulation tool, will include nS, superplasticizer, cement, sand and gravel, so covering a particle size range from 3 nm to 32 mm (comprising seven ranges of particles sizes distributions).

6) Properties prediction and practical application. Finally the experimental and theoretical results will be used to relate knowledge on raw material properties, the mix design tool and the experiments with the full scale testing. The outcome will be a methodology to design concrete and a practical framework which will yield the optimum way of applying new developed nS in concrete, given the available raw materials and the desired properties of the end-product.

6. Conclusions

A new nano-silica (nS) can be produced in high quantities and for low prices that allows for a mass application in concrete. It may replace cement in the mix, which is the most costly and environmentally unfriendly component in concrete. The use of nS makes concrete financially more attractive and reduces the CO_2 footprint of the produced concrete products. The nS will also increase the product properties of the concrete: the workability and the properties in hardened state, enabling the development of high performance concretes for extreme constructions. That means that a concrete with better performance, lower costs and an improved ecological footprint can be designed. Also further research is required to modify the production methods of nS in order to avoid the formation of agglomerates (such as the development of nS products in liquid state, application of surfactants, ultrasonification and microwave drying), and to achieve better dispersion of developed nS from olivine dissolution. Additional work is necessary to investigate the effect of synthesized nS on the hydration of Portland cement based systems, as differential calorimetric analysis, adiabatic temperature measurements, pore solution analysis and mathematical modeling.

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