UHPC Containing Nanoparticles Synthesized by Sol-gel Method

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Sol-gel technology is an alternative method for producing nanoparticles. This paper deals with preparing UHPC mixes by using amorphous silicium dioxide nanoparticles specially synthesized by applying the sol-gel method. Grading of used micro and nano components was carried out by Dynamic Light Scattering (DLS) method. The studied micro and nanoparticles have dimensions in the range from 30 to 600 nm. Proportions of filler components were selected by taking into account optimal packing models. Experimental part of research includes preparation of the mix containing traditional UHPC ingredients (Portland cement, quartz filler, silica fume) and nanoparticles synthesized by sol-gel technology in amount up to 1% of cement. Influence of nanoparticles on concrete properties was studied. Mineralogical composition of UHPC matrix was examined by X-ray method. After summarizing the results it may be concluded that incorporation of the small amount of nano sized silicium dioxide nanoparticles synthesized by sol-gel technology slightly decreases compressive strength in early hardening period (7 days in normal conditions) and increases strength after intensive curing (+90 ºC for 3 days).

Keywords: UHPC, nanoparticle, sol-gel method

1 Introduction

It is necessary to ensure ultra-dense particle packing at macrostructure and microstructure levels in order to obtain the UHPC concrete. The concrete mix particles should be within a wide range of particle size distribution. Ground mineral materials and amorphous silica fume (as pozzolanic admixture) are normally used as micro fillers. Particle size of the commercially used silica fume is in range of 0.1 – 1 μm. A new generation of UHPC concrete provides the use of special nano sized amorphous nanoscale pozzolanic particles [1, 2] with the dimensions less than 100 nm. Nano silica allows achieving more dense structural packing and better physical and mechanical properties. Nowadays, pyrogenic nano silica products as an effective filling agent are commercially available.

Sol-gel technology is an alternative method for production of silica nanoparticles. The first silica sol-gel synthesis carried by J.J. Ebelmens was described 150 years ago. He proved that silicon esters are slowly hydrolyzed in the presence of hydrated silica. The term "sol-gel process" refers to chemical reactions between the colloidal particles and/or connections between the polymers in solution leading to a gelatine type structures. The liquid phase (or solvent) is removed by drying thereby obtaining a porous dry gel or xerogel, which can be sintered to a dense amorphous (or crystalline) solid. Metal alcoxides, which easily react with water, are often used as reagents for sol-gel chemistry. Silicate alcoxides, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), are most widely used, as well as liquid glass - sodium hydrous. Sol-gel process is also used for other additives which provide the possibility to obtain particles with the required composition and structure [3, 4]. Sol-Gel synthesis is the chemical method carried out at a moderate temperature and by using moderate reagents. The method is based on molecular synthesis of nanoparticles [5]. The scheme of the used sintering method is shown in Figure 1. The synthesis of oxide nanoparticles in aqueous is based on the hydrolytic ion condensation process that leads to formation of extremely small primary particles. The further aging process in nanodispersed system leads to a sol - gel or settlings formation.

Change of aging conditions (temperature, pH, constituent relations, their concentrations, etc.) allows regulating the phase compositions, created nanoparticle size and shape within a wide range [6].

2 Used Materials, Mix Composition and Methods

Raw Materials

Experimental UHPC concrete mixtures were produced by using commercially available binding agents, pozzolanic admixtures and local mineral fillers.

White, rapid hardening Portland cement CEM I 52.5 R was used as a binding agent. Undensified commercial silica fume product (SF) Elkem microsilica 971U was used as pozzolanic micro filler. Nanosilica (NS1) applied in reference mix is a high-purity pyrogenic silica industrial product in the form of powder with a high specific surface of 50 m^2/g.

Other silica materials were specially synthesized in the laboratory in accordance with the scheme shown in Figure 1. NS2 is synthesized non-calcined nano silica. NS3 material was calcined at the temperature 500^{o}C and additionally ground for 1 hour in a laboratory ball mill. NS4 material was calcined at the temperature 650°C and additionally ground for 1 hour. The last type of nanosilica NS4 was used in the form of sol (silicon dioxide particle concentration 25%). Nanosilica materials were incorporated in concrete as water suspension by mixing with water and superplasticiser. Characteristics of used pozzolanic materials are summarized in Table 1. Micro and nanoparticle size distribution were determined in water environment by the Dynamic Light Scattering (DLS) method, using Brookhaven Instrument (USA). Grading diagrams of used fillers and cement are shown in Figure 2.

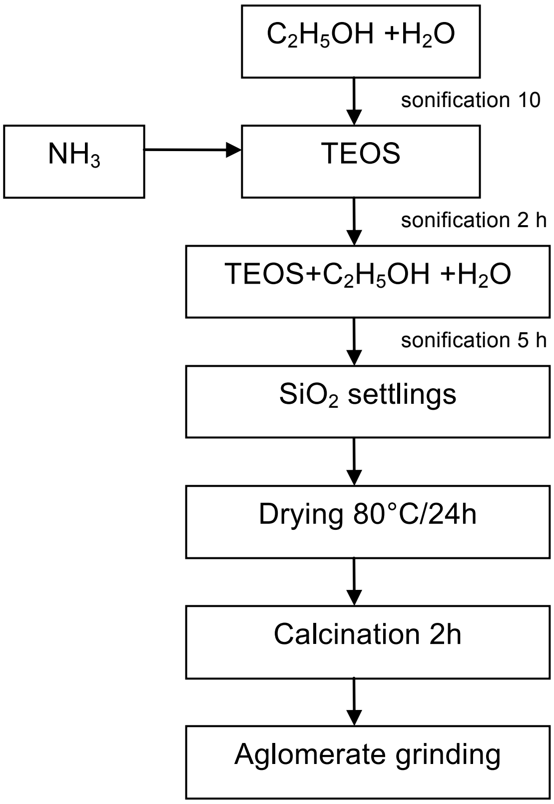

Figure 1: Method of synthesizing SiO_2 nanoparticle.

Table 1: Characteristics of cement, micro and nanosilica.

Parameter		CEM I 52.5 R	SF	NS1	NS2	NS3	NS4
Loss of ignition	%	<1	0.8	<0.01	<1	<1	<1
Particle effective diameter	μm	1-50	<1	0.184	0.099	0.600	
Density	kg/m³	3150	2200	2200	2200	2200	2200
Bulk density	kg/m³	1100	200	100	100-150	150-200	150-200
SiO_2 content	%		>97	99.9	99.9	99.9	99.9
Calcination temp.	°C				-	500	650

Three types of local fractionated quartz sand (fractions 0/0.5 mm, 0.3/0.8 mm and 0/0.3 mm as micro filler) act as mineral aggregate fillers. The content of quartz is about 97%.

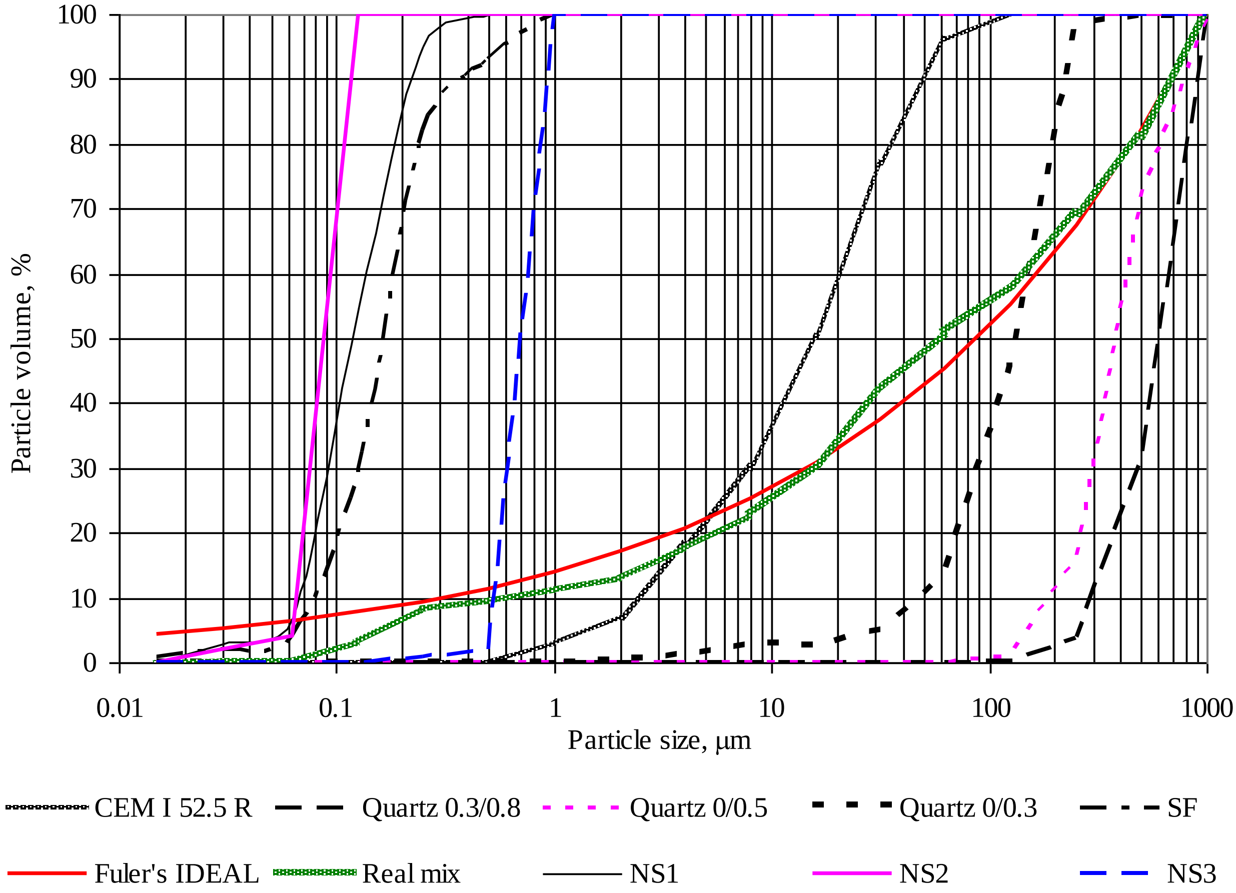

Figure 2: Particle size distribution.

Mix composition

Typical fine graded UHPC mix composition was selected as the basic (reference) mix. Proportions of the components are the same for all mixes, while the types of nanosilica vary. Cement content is 950 kg per cubic meter and nanosilica content of 10 kg/m^3 was assumed. Concrete mix compositions are summarized in Table 2. Water content and water/cement ratio (0.19) are kept constant for all mixes. The first mix (SF) was prepared without nanosilica (the corresponding amount was replaced by the additional content of microsilica). The second mix NS1 contains standard commercial nanosilica. The rest mixes were prepared by using specially synthesized nanosilica (NS2, NS3, NS4 and NS5 correspondingly).

Table 2: UHPC concrete mix compositions (kg/m^3).

Materials	SF	NS1	NS2	NS3	NS4	NS5
Portland cement CEM I 52.5 R	950	950	950	950	950	950
Quartz sand 0.3/0.8 mm	470	470	470	470	470	470
Quartz sand 0/0.5 mm	200	200	200	200	200	200
Quartz filler 0/0.3 mm	340	340	340	340	340	340
Silica fume 971U	150	140	140	140	140	140
Nanosilica Elkem	-	10	-	-	-	-
Nanosilica NS2 (non-calcined)	-	-	10	-	-	-
Nanosilica NS3 (500ºC)	-	-	-	10	-	-
Nanosilica NS4 (650ºC)	-	-	-	-	10	-
Nanosilica NS5 (sol)	-	-	-	-	-	10
Superplasticiser	30	30	30	30	30	30
Steel fibre 13 mm/0.16 mm	30	30	30	30	30	30
Water	180	180	180	180	180	180
Mix properties:						
Cylinder flow, mm	220	223	200	208	230	255
Concrete density, kg/m^3:	2400	2390	2370	2370	2370	2360

Methods

Concrete compositions were mixed in the high speed paddle mixer according to the following procedure: dry components were mixed for 1 minute, 2/3 of water amount was added and mixed for 1 minute. During the second step of mixing the remaining water was incorporated together with superplasticiser and nanosilica suspension. This mixing method was applied to achieve a more effective usage of the superplasticiser (otherwise superplasticiser can be absorbed by the dry aggregate thus reducing the plasticising effect). The mixing time was determined with the purpose to provide a homogenous mixture (approximately for 5 min).

Mix flowability was determined by means of cylinder flow test. Cylinder with the internal diameter 50 mm and height 100 mm was filled with UHPC concrete mix and lifted up. The diameter of the cylinder flow was measured after 1 minute.

Concrete cube specimens (10x10x10 cm) were made by using steel moulds. There were prepared 6 specimens for each composition. The specimens were cured in the water environment. The compressive strength was determined in accordance with the standard [7] at the age of 7 days in normal curing conditions (+20^{o}C), then additionally in accelerated curing conditions (in 90^{o}C hot water) for 3 days. Thus, the curing time of the specimen series are 7 and 10 days accordingly.

X-Ray analysis was carried out for hardened specimens by using the equipment with Rigaku Optima Plus diffractometer with $Cu_{K\alpha}$.

3 Results and discussions

It should be stressed that addition of nano silica into the mix has no particular effect on the flowability of the mix (Tab. 2); at the same time, mixes with nano silica were more plastic and homogeneous. The mixture with not calcined sol-gel nano silica N2 was with the lowest consistency.

Compressive strength results within the age of 7 days of the mixes with only silica fume and standard nano silica (NS1) were similar. The results for the mixes with nano silica that was synthesized by sol-gel method were even slightly lower.

It should be noted that the specimens with sol-gel nano silica were also marked by lower density (Table 2). It can be explained by insignificant air entraining effect, which can be caused by residue of some organic solvents from sol-gel process. The lower strength results were registered by the mix NS5 containing nano silica sol. The mix had the highest cylinder flow (hence the amount of water could be reduced). Weak influence of this nanosilica sol may be explained by considerable amount of organic solvents.

After intensification of the hardening process (aging in hot water for 3 days) the results were completely different. Mixes with calcined sol-gel nano silica showed more increase in strength compared to the reference configurations SF and NS1. The highest result was for the mix with nano silica calcined at 500 °C. The hardening effect of these compositions may be explained by activation of the pozzolanic reactions between silica and calcium hydroxide. Superdisperse particles of sol-gel nanosilica could be as initiating centres of formation of new concrete minerals.

It must be emphasized that statistically proved effect of nano particles cannot be discussed taking into account the values of standard deviation. In spite of obtained tendencies of strength development, the differences between strength results are low (within 5%). In order to obtain objective results it is necessary to conduct further research with more amounts of nanoparticles as well as number of specimens.

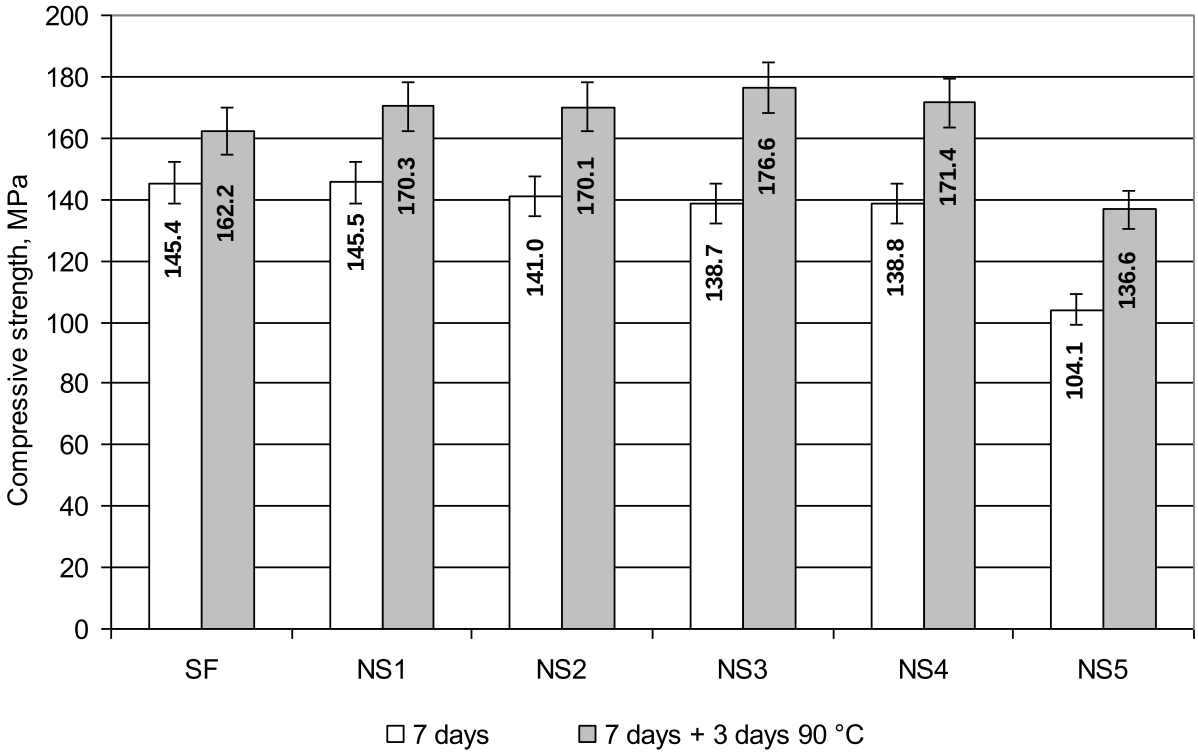

Figure 3: Compressive strength results.

X-Ray analysis was carried out for 3 mixes containing standard nanosilica (NS1), not calcined nanosilica (NS2) and calcined in 500°C nanosilica (NS3). Obtained results (Fig. 4) do not indicate any significant difference in mineralogical composition among those 3 specimens. The following minerals were recorded in the course of analysis of X-Ray diagrams. One of them is Quartz, which is the main component of aggregate. Minerals Hatrurite (also is known as Alite) and Larnite (also is known as Belite) are non-hydrated part of cement. The last recorded mineral is Portlandite (calcium hydrate) is the products of cement hardening. It should be mentioned that X-Ray analysis indicates only minerals in crystalline form while amorphous phases of material are not visible. It is possible to obtain more detailed results by using other methods of examination, for example SEM-microscopy.

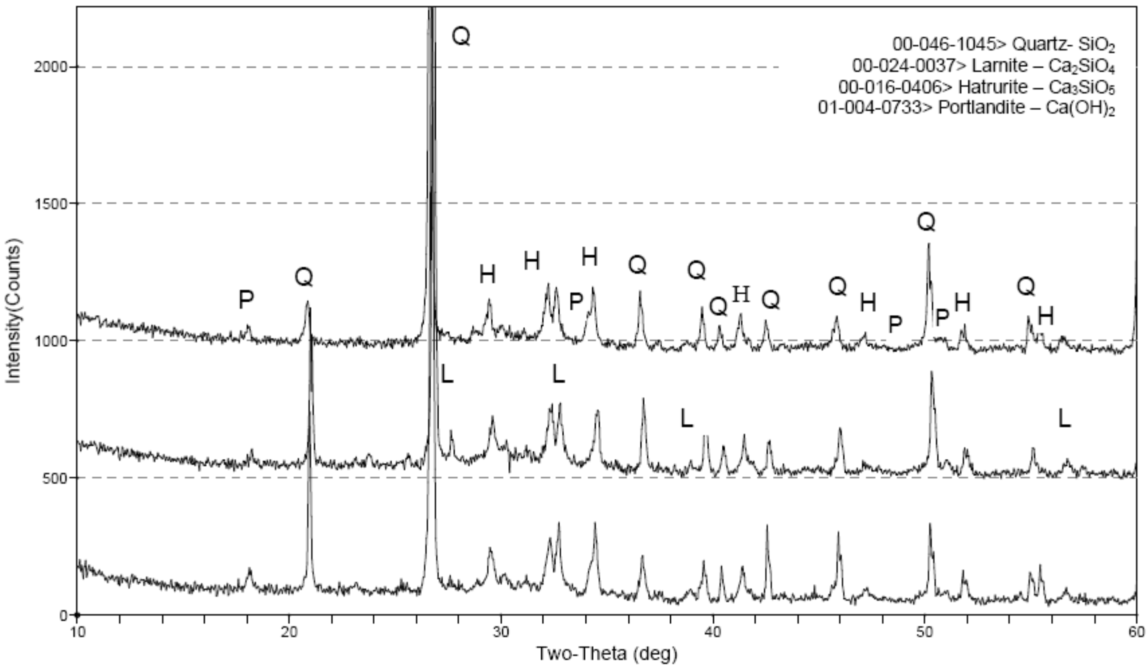

Figure 4: X-Ray analysis results (above: NS3, on the middle: NS2, below: NS1).

4 Conclusions

The effect of incorporation of nano silica particles synthesized by sol-gel method in UHPC mix has been examined in this study. Experimental results indicate that strength for mixes with synthesized nano silica was even slightly lower compared to the reference mix based on standard micro and nano silica in the early age concrete. It was found that mixes with sol-gel nano silica after accelerated hardening in hot water showed slightly increase in strength of up to 4 % compared to the reference mix. The highest result was achieved for the mix with calcined nano silica at 500°C. The hardening effect can be explained by activation of pozzolanic reactions between nanosilica and calcium hydroxide. It must be emphasised that effect of adding nano-particles, obtained by sol-gel method, is insignificant since strength characteristic of concrete mix differs only by some per cents (about 3-5 %). Ranges of standard deviation are overlap.

Synthesized nano silica produced by the sol-gel method may have some benefits compared to standard micro and nano silica:

1) the regulation of the parameters of sol-gel process makes it possible to provide the definite particle sizes in accordance with required the grading composition (thus, it becomes possible to achieve the optimum particle packing);

2) sol-gel technology can be implemented in a simple way since this process does not require very high temperatures compared to traditional pyrogenic nanosilica.

Initial investigation showed positive impact of non-traditional synthesised nano admixture by sol – gel method. In further studies it is worthwhile: 1) to synthesize particles with defined sizes; 2) to solve the problem of nano particles uniform dispersion and, 3) to perform detailed examination of microstructure and mineralogical composition of concrete specimens.

5 Acknowledgement

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