

Effect of Inorganic SiO₂ Nanofibers in High Strength Cementitious Composites

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Abstract. The paper deals with the verification of the effect of the addition of inorganic SiO₂ nanofibers to cement composites. In the first stage, a stable suspension of SiO₂ nanofibers was prepared in an aqueous medium. It is important to distribute nanofibers so that the nanofibers do not appear in the form of clumps and at the same time do not get damaged during the dispersion process. The ultrasonification process was used for dispersion. The dispersed suspension of SiO₂ nanofibers and water was dosed together with the superplasticizing admixtures into the dry components of the cement composite and the components were homogenized. The properties of the cement composite with SiO₂ nanofibers have been tested – compressive strength, flexural strength, density. Composites with the addition of SiO₂ nanofibers at a dose of 0.008 % by weight of cement exhibited an increased compressive strength of up to 33 % and a 19 % greater flexural strength at doses of 0.016 and 0.032 % of cement weight than the reference sample without nanofibers. The presence of SiO₂ nanofibers in the composite was monitored by scanning electron microscopy (SEM).

1 Introduction

Concrete is the most widely used building material worldwide. Concrete is quasi-brittle material with high compressive strength, low tensile strength and low toughness, which in the end can result in cracks, especially in the stretched areas of concrete structures. This can largely be prevented by the application of fibers that act as dispersed reinforcement in the cement matrix and, if the fibers have a greater modulus of elasticity than the matrix, they capture a portion of internal stress [1-4]. Although macro and micro fibers can slow the development of cracks, they cannot prevent them from forming. The application of nanoparticles, especially nanofibers can theoretically achieve greater control over the distribution of internal stress at the nanoscale, thus preventing the forming of the cracks [5-6]. However, the use of nanofibers has its own disadvantages over macro and microfibers. Due to their small dimensions and the large ratio between the length and the diameter, large aggregates are formed, which have to be disassembled before being used in the matrix. Another condition without which nanofibers would not fulfil their purpose is the strength of the fiber-matrix transit zone (ITZ – interfacial transition zone). This zone is analogous to the transit zone at the aggregate-matrix interface and, as is known, that is the weakest place in the concrete structure. Other problems the application of nanofibers

is facing are the inability of nanofibers to „attach“ in portlandite crystals and also the relatively large porosity of ordinary concrete. It is possible that a great deal of these pitfalls can be circumvented by at least suppressing the use of ultraviolet concrete due to its dense structure, lower content of portlandite, higher content of C-S-H gel and better transit zone properties. Another reason to use ultra high strength concrete is purely economic. In ordinary concrete technology, we generally try to reduce the production costs and use of waste materials, which does not correspond to the potential use of expensive nanofibers. Conversely, ultra high strength concrete is an advanced high-tech material in which the use of nanofibers makes sense [7]. Therefore, the research work focused on the use of nanofibers for high strength cement composites.

2 The objective of the experimental work

The aim of the experimental work was to verify the efficiency of the addition of inorganic SiO₂ nanofibers in the cement composite.

In the first stage of preparation, it was necessary to create a stable suspension from SiO₂ nanofibers so that the nanofibers did not form clumps and it was possible to disperse nanofibers in the entire volume of the cement composite. The simple addition of nanofibers

without dispersion into the cement matrix does not produce a positive effect [8-9]. The ultrasonification process was used for dispersion. The dispersed suspension of SiO₂ nanofibers and water was dispensed together with superplasticizing admixtures into the dry components of the cement composite. The properties of the cement composite with SiO₂ nanofibers have been tested – compressive strength, flexural strength, density. Using the scanning electron microscopy (SEM), the presence of SiO₂ nanofibers in the composite was monitored.

3 Mix design and materials used

The proposed mix design contained standard components for high strength composite, namely CEM I 52.5 N cement, microsilica, siliceous powder, silica sand, superplasticizing admixtures and water. The ratio of cement, siliceous powder and microsilica was 100:50:25. The water-cement ratio w/c was 0.28. As a residual porosity, 2 % was chosen for the design of the mixture [10].

The composition of the cement composite per 1 m³ is given in Table 1.

Table 1. Mix design of cement composite per 1 m³

Component	Weight [kg]
Cement CEM I 52.5 N C3A frei	690
Siliceous sand 0.1-0.4	927.5
Siliceous powder QuarzwerkeGruppe	345
MicrosilicaElkem 940 Undensified	172.5
BASF MasterGlenium ACE 430	31
BASF MasterSure 911	13.8
BASF MasterFinish DF 370	1
Water	160.5
SiO ₂ nanofibers (dose from the weight of cement)	0.004, 0.008, 0.016, 0.032, 0.064 %

3.1 Nanofibers

Inorganic nanofibers from SiO₂ produced by Pardam were used. Nanofibers from silica are a type of ceramic material. The fibers consist only of amorphous silicon dioxide, with a small proportion of porous particles of the same chemical composition [11]. Amorphous silicon dioxide nanofibrous material is represented by fine fibrous structure and high specific surface area. This material is produced by Centrifugal Spinning technology which enables to produce very thin fibers 100 – 300 nm in diameter with narrow distribution of fiber diameters.

Table 2. Selected parameters of SiO₂ fibres NnF CERAM® produced by Pardam, Czech Republic [11].

Fiber structure	Amorphous nanofiber
Typical fiber diameter	100 - 300 nm
Fiber length	2 to hundreds of μm (can be modified by milling)
Specific area	50-500 m ² /g
Crystal phase	Amorphous SiO ₂
Physical form	White powder
Melting point	1665 °C
Thermal conductivity	1.3 W/m·K

3.2 Cement

Cement CEM I 42.5 N C3A frei Mannersdorf, producer company Lafarge was used for experimental work. The cement has low amount of C₃A. The C₃A, is connected to the initial setting and hardening of cement, and hydration heat release. Another important aspect is the fact that the C₃A is linked to sulphate attack resistance when the sulphate is coming from the environment. Properties of cement are in Table 3.

Table 3. Properties of cement CEM I 42.5 N C₃A-frei [12].

Properties	Guide values	Standard requirement EN 197-1
Density [kg/dm ³]	3.14	-
Compressive strength [N/mm ²]	1 day	-
	2 days	≥ 10
	7 days	-
	28 days	≥ 42.5 ≤ 62.5
Tensile strength [N/mm ²]	28 days	-
Grinding fineness [cm ² /g]	3200	-
Bleeding [cm ³] after 120 minutes	15	-
Heat development [J/g] after 15 hours	200	-
Initial setting time [min]	160	≥ 60

3.3 Microsilica

ElkemMicrosilica® Grade 940 U (Undensified) is microsilica supplied in a undensified form. The microsilica behaves physically as microfiller and chemically as a strongly reactive pozzolan. The properties of microsilica are shown in Table 4.

Table 4. Chemical and physical properties of Elkem Microsilica® Grade 940 Undensified [13].

Properties	Specification
SiO ₂ [%]	> 90
Retention on 45µm sieve [%]	< 1.5
H ₂ O (when packed) [%]	< 1.0
Bulk Density [kg/m ³]	200 - 350

3.4 Siliceous powder QuarzwerkeGruppe

Table 5. Properties of siliceous powder QuarzwerkeGruppe [14].

Properties	Specification
Density [kg/m ³]	2650
Retention on 45µm sieve [%]	19
Retention on 63µm sieve [%]	3
SiO ₂ content	97
Al ₂ O ₃ content	1.6

3.5 Silica sand

Siliceous sand of 0.1-0.4 mm fine particle was used as filler, resulting in a high homogeneity of the mixture.

3.6 Superplasticizing admixtures

A combination of 3 chemical admixtures - BASF MasterGlenium ACE 430, BASF MasterSure 911 and BASF MasterFinish DF 370 were used to prepare the UHPC.

3.6.1 BASF MasterGlenium ACE 430

It is a superplasticizing admixture based on polycarboxylate ethers. It allows a high flow rate and greater initial strength. The recommended dosage is 0.2 – 3 % by weight of cement. In our case, a dosage of 4.5 % by weight of cement was used due to the high content of microsilica and silica powder [15].

3.6.2 BASF MasterSure 911

It is a polycarboxylate ether based plasticizer with delayed effect used to maintain consistency. The effect starts after approximately 15 – 25 minutes; the effect lasts at least 90 minutes. It is used in combination with a conventional superplasticizing admixture [15].

3.6.3 BASF MasterFinish DF 370

Liquid admixture with a strong bleeding action, the recommended dosage is in the range of 0.75 – 1 kg/m³ of fresh concrete. When used with the MasterGlenium

superplasticizing admixture, it improves the flow rate even though it does not have the liquefying properties itself [15].

4 The process of preparing cement composite with SiO₂ nanofibers

The first step was the dispersion of nanofibers. Perfect and stable dispersion of nanoparticles in aqueous solution and then in the concrete mix is a prerequisite for the successful use of nanofibers for the transfer of tension across the matrix.

The process of preparing the dispersion of nanofibers was designed based on our experience in preparing nanoparticle suspensions, in particular carbon nanoparticle suspensions [8-9, 16, 17]. The nanofibrous suspension was prepared by ultrasonication; the ultrasonic cavitator performance was 100 W. SiO₂ nanofibers were centrifuged for 1 minute. The nanofibers were dosed at concentrations of 0.004, 0.008, 0.016, 0.032 and 0.064 % by weight of cement. The suspension was then filled with liquid admixtures - BASF MasterGlenium ACE 430, BASF MasterSure 911 and BASF MasterFinish DF 370.

The dry components of the mixture (cement, silica sand, siliceous powder and microsilica) were weighed on laboratory scales with 0.1 g accuracy. The dry mixture was homogenized for a minute using a cordless drill with a stirrer extension at 400 rpm. After the 10 seconds of mechanical mixing of the liquid components, a liquid portion was added while stirring the dry mixture at a rate of 400 rpm. The time of application of the liquid portion was 30 – 40 s, for the best possible homogeneity. The total stirring time at 400 rpm was 1 minute. Higher speed was not used due to turbulence of the dry mix at higher speeds. After 1 minute, the dry and liquid portions of the mix water were homogenised to the extent that higher rates of 1300 rpm could be used. This speed was maintained for the next 2 minutes. The resulting mixture was then filled into moulds and test specimens were made.

5 Experiment results and discussion

5.1 Characteristics of cement composites with SiO₂ nanofibers

The properties of the cement composites with SiO₂ nanofibers were verified after 28 days – compressive strength, flexural strength, density. Cement composites with SiO₂ nanofibers showed virtually identical values of bulk weights as composites as reference samples without nanofibers. However, the differences were reflected in the mechanical properties of the composites with SiO₂ nanofibers that increased in flexural strength by up to 19 % at 0.016 and 0.032 % concentrations and a compressive strength of 33 % at a concentration of 0.008% of the fiber by weight of the cement. The results are shown in the following Table 6 and in Fig. 1 and Fig. 2.

Table 6. Changes in compressive and flexural strength after 28 days relative to the strength of the reference sample without the addition of SiO₂ nanofibers.

SiO ₂ nanofibers content of weight of cement [%]	Changes in compressive strength after 28 days [%]	Changes in flexural strength after 28 days [%]
0	--	--
0.004	12	1
0.008	33	9
0.016	19	19
0.032	-4	18
0.064	-13	-6

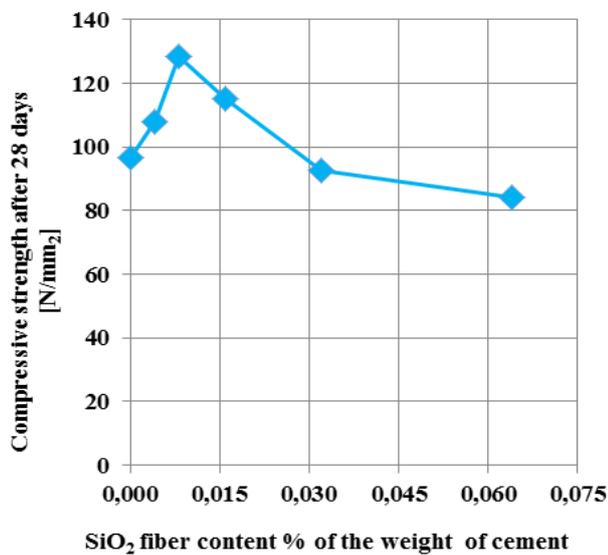


Figure 1. Compressive strength of cement composites with SiO₂ nanofibers after 28 days.

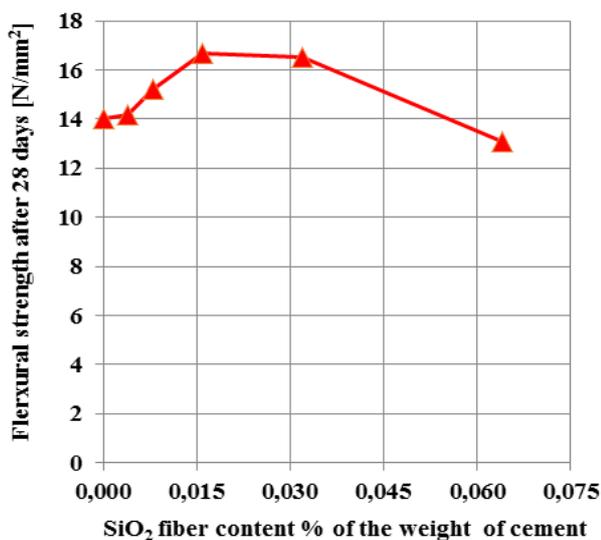


Figure 2. Flexural strength of cement composites with SiO₂ nanofibers after 28 days.

The bulk density of the reference cement composite without nanofibers was 2240 kg.m⁻³. The bulk density of composites with nanofibers ranged between 2240 and 2250 kg.m⁻³.

The reference mixture without nanofibers had a tensile strength of 14.0 MPa. For composites with SiO₂ nanofibers, a flexural strength of 16.7 MPa at a 0.016 and 16.5 MPa concentration at 0.032 % was achieved, then dropped to 13.1MPa at a concentration of 0.064 %. Even in the case of compressive strength (Fig. 4), some dependence on the concentration of nanofibers can be seen. Compared to a reference mixture with strength of 96.6 MPa, it progressively increased to 108.6 MPa at a concentration of 0.004 % and 128.3 MPa at a concentration of 0.008 %. With increasing concentration, the strength gradually decreased to 84.2 MPa.

5.2 Direct observation of nanofibers with SEM

The presence of SiO₂ nanofibers in the composite was monitored using scanning electron microscopy (SEM). Sample fragments of cement composites with SiO₂ nanofibers at a concentration of 0.064 % after the compression strength test were subjected to direct observation of nanofibres in the structure. There samples were chosen because of the high concentration of nanofibers, allowing their easier finding. The scanning electron microscope FEI was used for observation. After initial unsuccessful attempts to find them, the specimens were treated so that they were immersed in 5% HCl solution for 3 minutes due to breakage of the cement matrix on the surface and eventual detection of nanofibers. This procedure proved to be successful. The SiO₂ nanofiber in the cement matrix is shown in Fig. 3.

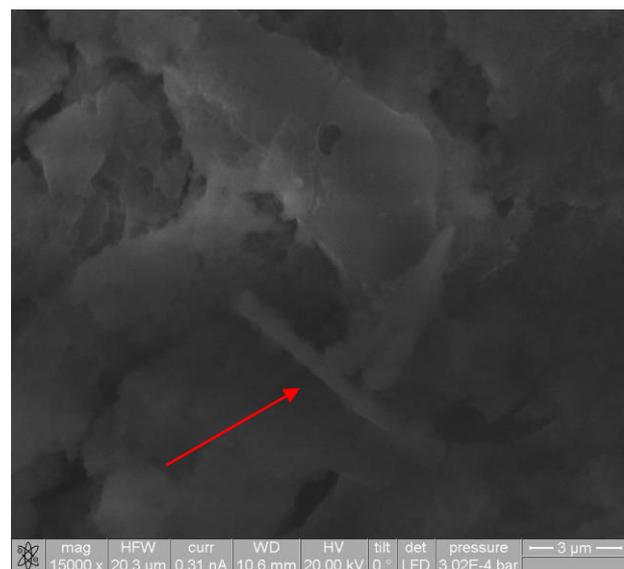


Figure 3. Image of SiO₂ nanofibers in a cement matrix, Scanning Electron Microscopy [10].

6 Conclusions

The aim of the research was to verify the possibility of using inorganic SiO₂ nanofibers in high strength cement composites.

Our previous researches in this area [9, 16-17] were mainly focused on inert carbon nanofibers and nanotubes, the verification of the effect of inorganic nanofibers from silica is a new direction of our research.

The experiments carried out confirmed the successful application of SiO₂ nanofibers to the cement composite

Different concentrations of SiO₂ nanofibers were tested. Concrete density, compressive strength and flexural strength were determined. The positive effect of SiO₂ fibers in certain concentrations on the resulting mechanical properties of cement composites was found. SiO₂ nanofibers in the cement composite were detected using a scanning electron microscope.

As a further direction of the research, a suspension with SiO₂ nanofibers for the production of ultra high strength concrete (UHPC) will be tested. Nanofibers are a currently relatively expensive material, so its use is useful in special types of concrete such as HPC and UHPC. Any further significant improvements to the HPC and UHPC properties may be justified even if the price increases.

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