THE ASSESSMENT OF NANOSILICA INFLUENCE ON SELECTED CEMENT COMPOSITES PROPERTIES WITH DIFFERENT PLASTICIZERS

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At world-wide production over 30 billion of tones, concrete is one of the most popular construction materials, at the same time the amount of carbon dioxide derived from cement industry is estimated to 5-7% of world annual CO_2 emissions. By enhancing concrete's properties, the application of nanoparticles to cement composites production could diminish the carbon footprint of the industry. Nanosilica is researched with an aim to enhance mechanical properties and durability of concrete. The aim of this study is to assess the influence of nano-silica on compressive strength, density and water absorption of cement paste with an addition of two plasticizers with different chemical base. The consistency of fresh cement paste with plasticizers was measured. The dosage of nanosilica was 1%, 2% or 3% of binder mass. The addition of nano-silica severely reduced the consistency of cement paste. The enhancement of early compressive strength was observable.

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INTRODUCTION

United States Geological Survey estimated the worldwide production of cement in 2014 to 4,2 billion tones [1]. At this levels of production the global cement industry is responsible for 5-7% of CO_2 emissions [2]. Half of that amount derives directly from carbonates thermal breakdown that are inseparable stage of clinker production. This part of emission can only be reduced through enhancing the properties of concrete and therefore reducing designed cross-sections [3] .

Nanotechnology is an emerging field of science, that studies and modifies the materials at nanometric dimensions. In concrete technology the dimensions of less than 500 nm are considered nanometric. Nanoparticles are the most promising application of nanotechnology in concrete industry. Cement matrix by itself is a material that can be considered a nanostructured material. The quality of concrete's nanostructure and microstructure influence the properties of the material in macroscale. There is a growing interest in modifying the nano-sized and micro-sized structure of cement composites through utilizing nanoadditions. Nanosilica, nano-titanium dioxide, carbon nanotubes and nano-alumina are the most popular in research [4]. Due to small dimensions, nanoadditions tend to have high values of their specific surface, which influence the reactivity through the process of cement binding, thus the cement matrix can be denser. Aside from enhancing mechanical properties and durability nanoparticles can give new properties to the material. Nano-TiO_2 particles have photocatalytic properties. Photocatalysis can chemically decompose organic substances in present of UV light. Concrete with this addition can exhibit self-cleaning and air-cleaning properties. Nano-Fe_2O_3 and carbon nanotubes can relate the stress-levels in the materials to electric resistivity, providing a material that has self-sensing properties [4, 5].

Nanosilica is a material used widely in other industries, for example to create hydrophobic surfaces. It is a synthesized form of silica with small particle diameter (5-150 nm) and with significant chemical purity (95-99%) [6]. Nanosilica is produced through eg. Strober method (in koloid form) or pyrolysis (in powder form). Modification of production parameters result in different properties of final product. The particles' ability to agglomerate, their diameter and chemical purity can be affected by production method. All of those properties have an impact on the properties of cement composite properties with added nanosilica [7, 8].

Nanosilica similarly to other nanoadditions enhances the properties of concrete through modification of its nano- and microstructure. High specific surface of the additive provides an effective nucleation site for the cement hydration. Nanosilica changes the proportion of silicon in the cement matrix which reduces its chemical permeability. Thus modified material can exhibit higher mechanical properties and durability [6, 9].

A problematic issue concerning the application of nanoadditives is their dispersion. Agglomerated particles can become local weak spots in cement matrix and influence the compressive and flexural strength of the material. Fine dispersed sol of nanosilica may not provide sufficient dispersion in fresh mixture due to different chemical nature of both liquids [8, 10].

The aim of this paper was to assess the influence of nanosilica on selected properties of cement composites with different plasticizers. The experiment program consisted of compressive strength, density and water absorption tests.

MATERIALS, PREPARATIONS AND TEST METHODS

As a binder material a commercial CEM I 42,5R cement was used. The material conformed to the requirements of the PN-EN 197-1 standard. Nanosilica was added in form of white powder, its properties are provided in table 1. Destiled water was used. Two different superplasticizers were used – first superplasticizer (spA) had a polycarboxylate ethers base, and the second (spB) a naphthalene sulfonates base.

6 series of cement pastes were prepared with constant value of water/binder ratio (w/b) equal 0,35. The differed in dosage of nanosilica (nk) and superplasticizer (spA or spB). The dosage of nanosilica was either 1%, 2% or 3% mass of binder (% m.b.). The amount of superplasticizer was determined by consistency tests. Each series characterized similar consistency of fresh mixture equal to 200 mm ± 10 mm. The compositions of cement pastes are presented in table 2.

Table 1 – Properties of nanosilica

	Values declared by the producer
SiO_2 content (%)	99,85%
pH (-)	3,6-4,3
Specific surface (m^2/g)	300
Bulk density (g/dm^3)	50

Table 2 – Composition of cement pastes

	Series with superplasticizer A			Series with superplasticizer B		
Series number	S1	S2	S3	S4	S5	S6
Series description	nk=1%, spA	nk=2%, spA	nk=3%, spA	nk=1%, spB	nk=2%, spB	nk=3%, spB
Cement (g)	495	490	485	495	490	485
Nanosilica (g)	5	10	15	5	10	15
Binder (g)	500	500	500	500	500	500
Water (g)	174,5	172	168,5	170	163	152
Super-plasticizer (g)	0,5	3	6,5	5	12	23

Cement binder was prepared in high-speed mixer. The preparation started from spoon mixing cement with nanosilica for 90 s. Homogenization proceeded in the mixer, the binder was mixed with 167 Hz for 180 s. Finally, binder was spoon mixed for additional 90 s. Cement paste preparation started with adding cement to water with addition of superplasticizer. In less than 10 s the mixture was transferred to the mixer and was mixed with 1,7 Hz for 90 s. The mixing was stopped for 30 s of spoon mixing and homogenization of paste left on the side of the bowl. Additional 90 s of mixing was performed with frequency of 1,7 Hz.

The samples of cement paste were prepared in form of cubes with dimensions: 20x20x20 mm or cylinders with diameter and height of 420 mm. Each 6 cube samples were dedicated to different compressive strength or density and water absorption test. The compressive strength tests were performed after 7, 28 and 56 days from mixing. The density and water absorption tests were performed after 28 days on cylinder samples.

The consistency test were performed with a flat cone form of 345 cm^3 volume. The measurement was the mean value of two perpendicular diameters. The compressive strength test were performed by flipping the cubes on the back and measuring the force by which they were destroyed. By dividing it through the surface of the cube's back the value of compressive strength was calculated. The water absorption was calculated by measuring the maximum mass of absorbed water and dividing it through the dry mass of the cube.

RESULTS AND DISCUSSION CONSISTENCY TESTS RESULTS

With growing nanosilica dosage the amount of superplasticizer needed to maintain equal consistency results was also growing. Different dosages of both superplasticizers were needed at the same dosage of nanosilica. The change in dosage of admixture was bigger in the group of series with superpasticizer spB. With addition of 3% of nanosilica the dosage of superplasticizer spA was equal 1,3% m.b. (series S3). Mixture of the series S6, with the same dosage of nanosilica, needed 4,6% m.b. of superplasticizer spB (table 3).

Table 3 – The results of consistency tests

Series numer	Series description	Superplasticizer dosage (% of binders mass)	Consistency (mm)
S1	nk=1%, spA	0,1	205
S2	nk=2%, spA	0,6	195
S3	nk=3%, spA	1,3	200
S2	nk=1%, spB	1	198
S5	nk=2%, spB	2,4	205
S6	nk=3%, spB	4,6	203

Similar influence of nanosilica dosage on the consistency and the amount of superplasticizer was observed in other research [10, 11]. With growing dosage of nanosilica the consistency of cement composite mixture is reduced and additional amount of plasticizer is needed. The different dosage of both plasticizers shows that the plasticizer base might have an influence on the ability to disperse nanosilica particles. Chemical nature of this phenomena was suggested [10].

COMPRESSIVE STRENGTH TESTS RESULTS

The results of compressive strength tests enabled to show the development of compressive strength up to 56 day from mixing. The development of compressive strength of series with admixture spA was similar (Figure 1). The results of series with 3% addition of nanosilica (S3) had up to 6% higher compressive strength results on 28 day compared to 1% and 2% dosage of nanosilica (S1 and S2).

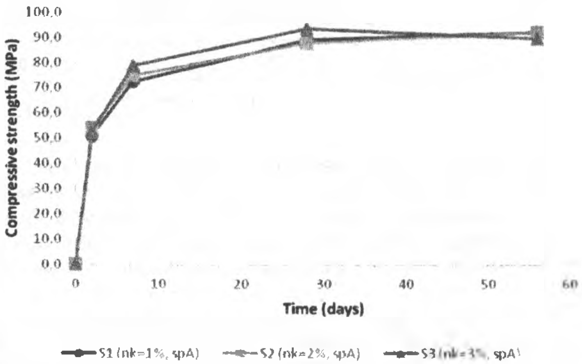

Figure 1 – The influence of nanosilica on compressive strength of cement paste with addition of superplasticizer spA

In the results of series with admixture spB the differences between series with different nanosilica dosage was observable (Figure 2). The highest results of compressive strength tests were measured on the samples of the series with 3% addition of nanosilica (S6). The most prominent enhancement was noted after 2 days and 7 days from mixing. The results were higher up to 16% comparing to series with 1% and 2% addition (S4 and S5). The lowest results were noted in the series with 2% addition of nanosilica. Different dynamics of compressive strength development was observed between 7 days and 28 days results with spB admixture. The results of tests performed after 7 days was similar to 28 days and 7% smaller than 56 days.

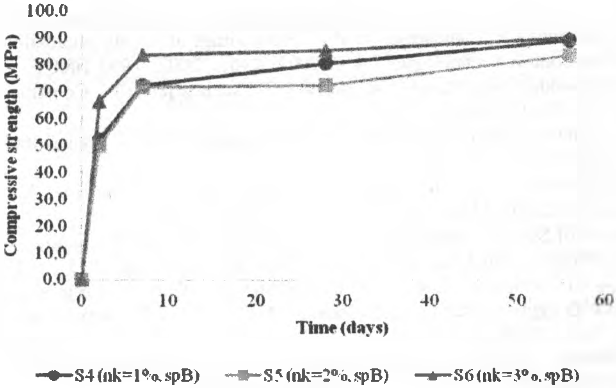

Figure 2 – The influence of nanosilica on compressive strength of cement paste with addition of superplasticizer spB

Considering the trend-less influence of nanosilica addition on the results, the admixture spB could work less effectively in dispersing the addition. The results of the group of series with admixture spA suggest that widening the dosages of nanosilica might result in more visible influence of the addition. The differences in the development of compressive strength in both groups could suggest different influence of plasticizer's base on the dispersion of nanosilica.

WATER ABSORPTION AND DENSITY TESTS RESULTS

The results of water absorption and density tests present small changes of values between series (Table 4). Probably neither plasticizer or nanosilica had influence on both properties. The water absorption of all series was about 20%. The mean density of cement pastes was about 1,70 g/cm^3.

Table 4 – The results of water absorption and density tests

Series numer	Series description	Water absorbtion (%)	Density (g/cm^3)
S1	S1 (nk=1%, spA)	20,68	1,73
S2	S2 (nk=2%, spA)	22,47	1,70
S3	S3 (nk=3%, spA)	21,46	1,67
S4	S1 (nk=1%, spB)	19,55	1,69
S5	S2 (nk=2%, spB)	19,68	1,69
S6	S3 (nk=3%, spB)	18,93	1,70

CONCLUSIONS

The addition of nanosilica as a cement replacement in cement paste has some influence on characteristics of the material. The consistency of fresh cement paste was reduced with growing dosage of nanosilica addition. The differences in compressive strength tests results was observable, but plasticizer might have been more influential. Some influence on early compressive strength was observed in case of series with the admixture spB. The compressive strength after 7 days was similar to 28 days results. No influences of superplasticizer or nanosilica were noted in the results of water absorption and density test.

Additional research is needed in the dispersion of nanosilica and rheology of cement paste with this addition.

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