21st International Research/Expert Conference
”Trends in the Development of Machinery and Associated Technology”
TMT 2018, Karlovy Vary, Czech Republic, 18th – 22nd September, 2018

EFFECT OF NANOSILICA ON EARLY STRENGTH OF CEMENT MORTAR

Adnan Mujkanović[1], Nevzet Merdić[2], Marina Jovanović[1],
[1]University of Zenica, Faculty of Metallurgy and Technology
Travnička cesta 1, Zenica
[2]Cement plant “Kakanj”, Kakanj
Bosnia and Herzegovina

ABSTRACT

This paper presents the effect of nanosilica on the early strength of cement mortars. Three series of samples were investigated: one with ordinary Portland cement CEM I 52,5 N and two with siliceous and calcareous fly ashes as a partial cement replacement (25 wt. %). The results reveal that by using small amount of nanosilica (2 and 4 wt. % of binder) water demand of all tested cement pastes increases proportionally to nanosilica content, while the setting time is not significantly influenced. Compared to the reference samples, the addition of 2 % nanosilica increased two-days strengths, while addition of 4 % nanosilica reduced two-days strengths of the mortar samples.

Keywords: nanosilica, cement composites, fly ash, early strength

1. INTRODUCTION

Since recently, the use of nano scale-size particles increased in many fields of applications, which lead to creating materials with novel functionalities. It is known that ultra-fine particles incorporated into cementitious composites results in dramatically improved characteristics compared to conventional materials. One of the most widely used addition in cementitious composites is silica fume (microsilica). It is a very fine powder mostly composed of amorphous silicon dioxide, and it used as a mineral addition in cement composites since the mid-20th century. It reacts in pozzolanic reaction with calcium hydroxide to produce calcium silicate hydrates (C-S-H). Thus, the amount of binder is increased, which both increases the strength and reduces the permeability by densifying the matrix of the concrete [1]. Also, submicroscopic silica fume particles served as nucleation sites for crystallization during the early hours when it existed as chemically inert filler which promote hydration of cement phases [2]. It is known that the rate of the pozzolanic reaction is proportional to the fineness of addition. Nanosilica (nS) denotes colloidal particles consisting of an amorphous SiO_2 core with a hydroxylated surface, insoluble in water. Compared to silica fume, nS have higher specific surface areas and activities. Also, particles of amorphous silica appear to considerably impact the process of silicate minerals hydration. Nowadays a substantial investigation effort has been paid on illuminating their effect on the properties of cementitious composite. [3-6]. The objective of this study is to investigate the effect of nS on water demand, setting time and early strength of cement mortars in which part of the cement is replaced by fly ash, the most common supplementary cementitious material.

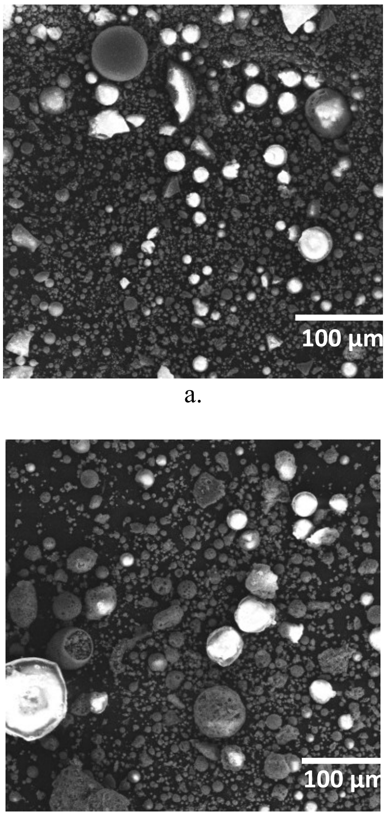
2. MATERIALS AND EXPERIMENTAL METHODOLOGY

2.1. Materials

The cement used in this study is ordinary Portland cement (OPC) CEM I 52.5 N, with Blaine specific surface 3460 cm^2/g, provided by Cement plant “Kakanj“. Two types of unprocessed fly ash were used as a partial cement replacement: calcareous fly ash from Powerplant “Kakanj”, and siliceous fly ash from Powerplant “Tuzla”. The main physical and chemical characteristics of fly ashes, as well as standard criteria for fly ash usage in concrete, are shown in Tab. 1. Mira Tescan FESEM (20keV) scanning electron microscope (SEM) is used for mineral admixtures (fly ashes and nS) particle morphology analysis. SEM images of mineral admixtures are shown in Fig. 1 and Fig. 2. Chemical characteristics of fly ashes were tested according to EN 196-2 [7], except free CaO content which is determined according to HRN B.C8.020 [8]. Fractions of reactive SiO_2 and reactive CaO were calculated from chemical analysis results in accordance to EN 197-1 [9]. Density of fly ashes were tested according to ASTM C-188-16 [10], specific surface according to EN 196-6 [11] and activity index according to EN 450-1 [13]. Fly ashes properties are shown in Tab. 1.

Table 1. Fly ashes properties

Properties	Fly ash Kakanj	Fly ash Tuzla
Loss on ignition, %	0.11	3.98
Chlorides, %	0.006	0.004
SO_3, %	1.96	0.55
Total SiO_2, %	39.60	52.60
Total CaO, %	26.39	9.40
Reactive CaO, %	23.06	8.60
Free CaO, %	4.96	1.53
Reactive SiO_2, %	36.55	44.7
Al_2O_3, %	17.85	18.64
Fe_2O_3, %	9.26	9.50
MgO, %	2.71	2.79
Na_2O, %	0.33	0.26
K_2O, %	1.28	1.21
CO_2, %	0.00	0.44
Na_2O_{eq}, %	1.17	1.06
28 days activity index, %	87.4	86.9
Blaine specific surface area, cm^2/g	2490	2080
Density, g/cm^3	2.57	2.26



a.

b.

Fig. 1. SEM images of fly ash Kakanj (a) and fly ash Tuzla (b)

Precipitated silica Ultrasil 7005 provided by Evonik Industries was used in experimental work. Ultrasil 7005 is highly dispersible powder mainly used as reinforcing filler in tire production. It is almost 100 % pure amorphous silica powder, with primary particle size 20-30 nm and BET specific surface area greater than 200 m^2/g. Primary particles are agglomerated during synthesis process to enable low-dust handling, which can be seen in the SEM image shown in Fig. 2. Measurements of particle size distribution were obtained by laser diffraction method using a Mastersizer 2000, (Malvern Instruments Co.) and results are presented in Fig. 3. This method enables to determine only the particle size distribution of the nS agglomerates, since the primary particles are too small to detect.

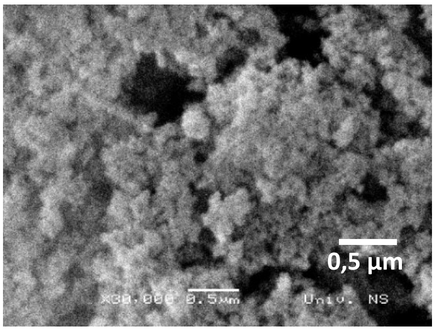


Fig. 2. SEM images of Ultrasil 7005

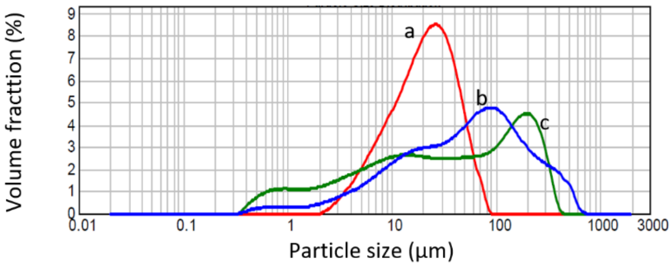


Fig. 3. Particle size distribution of nS agglomerates (a), fly ash Tuzla (b), fly ash Kakanj (c)

2.2. Experimental methodology, results and discussion

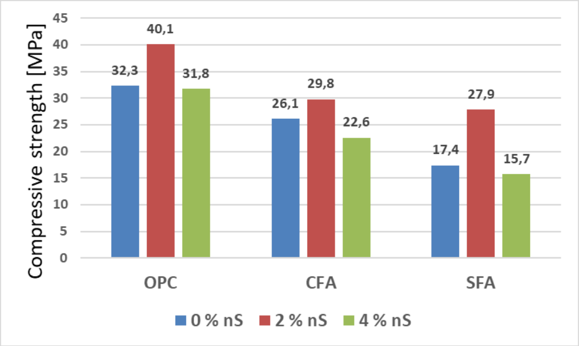
In order to make sure that nS was dispersed thoroughly, water and silica were premixed for 10 minutes with commercial blender. Standard consistency and setting time were determined on the cement paste samples according to EN 196-3. Nine series of samples were investigated: three with pure ordinary portland cement CEM I 52,5 N (OPC1, OPC2, OPC3), and three with fly ash Kakanj (CFA1, CFA2, CFA3) and three with fly ash Tuzla (SFA1, SFA2, SFA3) as a partial cement replacement. The cement, nS and fly ashes mixing proportions are shown in Tab. 2, as well as results of testing carried out on cement pastes.

Table 2. Paste composition and testing results

Sample	CEM I 52,5 N (%)	Fly ash Kakanj (%)	Fly ash Tuzla (%)	nS (%)	Standard consistency (%)	Initial setting time (min)	Final setting time (min)
OPC1	100.0	-	-	-	27.2	160	185
OPC2	98.0	-	-	2.0	30.4	155	200
OPC3	96.0	-	-	4.0	34.4	165	205
CFA1	75.0	25.0	-	-	23.0	185	245
CFA2	73.5	24.5	-	2.0	26.8	180	235
CFA3	72.0	24.0	-	4.0	30.4	185	240
SFA1	75.0	-	25.0	-	27.4	245	295
SFA2	73.5	-	24.5	2.0	32.4	245	290
SFA3	72.0	-	24.0	4.0	36.4	230	280

Results of standard consistency test reveal that partial replacement of cement with calcareous fly ash led to the reduction in mixture water demand. In contrary, using of siliceous fly ash led to the increasing in water demand. SEM images of both fly ashes shown in Fig. 1. explains this behaviour of tested cement pastes. Calcareous fly ash particles are spherical and have relatively smooth surface, which has favourable effect on paste water requirement. On the other hand, siliceous fly ash contains a significant amount of irregularly shaped and porous particles. Because of that standard consistency of pastes containing this type of fly ash is increased. An increasing in the amount of nS increases the standard consistency in all tested cement pastes. This is since the specific surface of nS is much larger than the specific surface of the cement and both types of ash. So, by replacing the part of the binder with nS, a larger amount of water is adhered to the surface of the particles, thus increasing the water demand. The mixing of nS into the composition of cement pastes has not led to a notable change in the setting time.

Mortar specimens of dimensions 40×40×160 mm were made according to EN 196-1 in order for compressive/flexural strength testing to be undertaken. Water-cement ratio in all samples was 0,45, and aggregate-binder ratio 3:1. Mixing proportions of cement, nS and fly ashes were same as in prepared pastes (Tab. 2). Standard sand EN 196-1 was used as an aggregate for mortar. Samples were demolded after 24 hours and tested after another 24 hours curing in water. The results of compressive and flexural strength are shown in Fig. 4 and Fig. 5. As expected, the strengths of samples with pure cement as a binding agent (the samples of OPC series) are higher than the strengths of the samples containing fly ash (the samples of CFA and SFA series). Unlike cement, fly ash has no cementitious properties on its own, but it reacts with calcium hydroxide formed via cement hydration. Therefore, in the first days, the samples in which part of the cement is replaced by fly ash act as they contain less binder. The partial replacement of the cement with siliceous fly ash caused much greater reduction in early strength caused than cement replacement with calcareous fly ash. Regardless of the fly ash type, an addition of 2% nS resulted in increasing, and an addition of 4% nS in decreasing of two-day strength. The highest strength increase (62,4% for compressive strength and 58,7% for flexural strength) was observed in mortars containing siliceous fly ash and 2 % nS. Strengths reduction in mortars containing 4 % nS wasn't expected. However, during the preparation of the samples it was observed that at the water-binder ratio of 0,45 all mixtures containing 4% nS had severely reduced workability and this is a probable reason of recorded strength loss. The increase in the water-binder ratio or the adding superplasticizer into the mixtures would probably have resulted in a favorable effect of the addition of 4% nS.



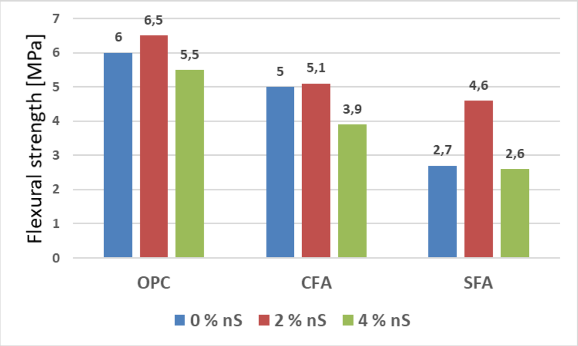


Fig. 4. Compressive strength test results

Fig. 5. Flexural strength test results

3. CONCLUSION

Partial replacement of cement with fly ash extends both initial and final setting times, as well as decreases early strength of mortar. These effects are particularly manifested in samples containing siliceous fly ash. An increasing in the amount of nS increases the standard consistency, while setting time isn't significantly influenced. An addition of 2% nS resulted in early strengths increasing of all tested mortars. The highest strengths increase was observed in mortar containing siliceous fly ash, and the lowest strengths increase in mortars containing calcareous fly ash. At water-binder ratio 0,45 workability of mortars with 4 % nS is severely worsened and this is probable cause of strength reduction.

4. REFERENCES

[1] Hewlett P., Lea's Chemistry of Cement and Concrete, Elsevier, 2003.
[2] J. A. Larbi, A. L. A. Fraay, and J. M. J .M. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems cement and concrete research, Vol: 20, pp. 506-516, 1990
[3] Sing, L.P. et al, Beneficial role of nS in cement based materials – A review, Construction and Building Materials 47 (2013) 1069–1077
[4] Yu R., Spiesz P., Brouwers H.J.H. Effect of nano-silica on the hydration and microstructure development of Ultra-High Performance Concrete (UHPC) with a low binder amount, Construction and Building Materials 65 (2014) 140–150
[5] Hou P, Kawashima S, Wang K, Corr DJ, Qian J, Shah SP. Effects of colloidal nS on rheological and mechanical properties of fly ash–cement mortar. Cem. Concr. Compos. 2013;35(1):12–22.
[6] Land G, Stephan D. The influence of nano-silica on the hydration of ordinary Portland cement. J Mater Sci 2011;47(2):1011–7.[6] Björnström J, Martinelli A, Matic A, Börjesson L, Panas I.
[7] EN 196-2, Method of testing cement. Chemical analysis of cement
[8] HRN B.C8.020, Portland cements. Sampling and methods of chemical analysis
[9] EN 197-1, Cement - Part 1: Composition, specifications and conformity criteria for common cements
[10] ASTM C-188-16 Test Method for Density of Hydraulic Cement
[11] EN 196-2 Methods of testing cement. Determination of setting times and soundness
[12] EN 450-1:2012, Fly ash for concrete - Part1: Definitions, specifications and conformity criteria