Challenge Journal of Concrete Research Letters

Research Article

Effect of nano silica on cement mortars containing micro silica

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ABSTRACT

The use of cement and concrete is becoming increasingly widespread all over the world. However, the high energy consumption required for the production of clinker and the greenhouse gas emissions generated during production negatively affect both the economy and the environment. In the studies conducted for many years, researchers have found that the substitution of various pozzolans with cement provides both technical advantages and environmental benefits. The use of pozzolans in cementitious composites provides advantages such as the improvement of the physical and mechanical properties of the material, the conservation of the environment and the economy in terms of the evaluation of industrial wastes. In recent years, studies on the use of nanoparticles in cementitious composites are positively. In this study, it was aimed to investigate the properties of fresh and hardened cement mortars using micro silica as pozzolan and nano silica as nanoparticle. For this purpose, four different cement pastes and mortars mixtures were prepared by substituting 0%, 1%, 2%, 3% nano SiO_2 (silica) cement in mortar mixtures containing 5% micro silica. The effects of the nano silica on the micro silica-containing cement paste on the consistency and setting time were investigated. The mortar mixtures produced were subjected to flexural and compressive strength tests on days 7, 28 and 90th. SEM images of mortar mixtures were taken. As a result, it was found that 2% nano silica admixture of 5% micro silica containing cement admixture affects the flexural and compressive strength positively, whereas 2% nano silica admixture increased the flexural strength by 13% and compressive strength by 7%.

ARTICLE INFO

Article history:
Received 17 May 2019
Revised 15 June 2019
Accepted 26 June 2019

Keywords:
Mortar
Micro silica
Nano silica
Strength

1. Introduction

In the World, studies for discovering new areas with respect to nano technologies applications in all science and engineering branches have gone on. In construction sector, researches on using carbon nano tubes and nano particles in concrete, ceramics and glass production have been made. Specifically in cement based composites, strength and durability enhancing through nano material usage is at the top ranks among expected returns (Özbora et al., 2013; Bozoğlu and Arditi, 2012). Additionally, today scientists doing research about nano technology in concrete and cement concentrate on hydration reaction and effects of nano particles over concrete features (Özbora et al., 2013).

Concrete is a composite material and includes hydration products in nano and micro scale. Particle sizes and specific surface areas of concrete constituents are seen in Fig. 1. Although it is resulting from the Fig. 1 that conventional concrete doesn't contain nano particle, chemical additives, water in gel spaces and as a hydration product C-S-H gels are indeed nano scale substances.

In concrete sector, researches for nano technology usage is going on but, it is known that applications are limited. However, improvement of physical and mechanical characteristics in cement-based materials are certain according to obtained results. Some developments obtained in cement-based composites through nano particles usage are summarized below (Özbora et al., 2013):

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ISSN: 2548-0928 / DOI: https://doi.org/10.20528/cjcrl.2019.02.003

- Adherence between aggregate and cement paste strengthens.
- Micro crack generation decreases, and these cracks heals by their self.
- Concrete permeability declines.
- Shrinkage generation diminishes.
- Negative effect of aggregates involving clay lessen.
- Elasticity module increases.
- Resistance of concrete to heat rises.
- Durability features like alcali silica reaction, corrosion, freezing-dissolution improve.

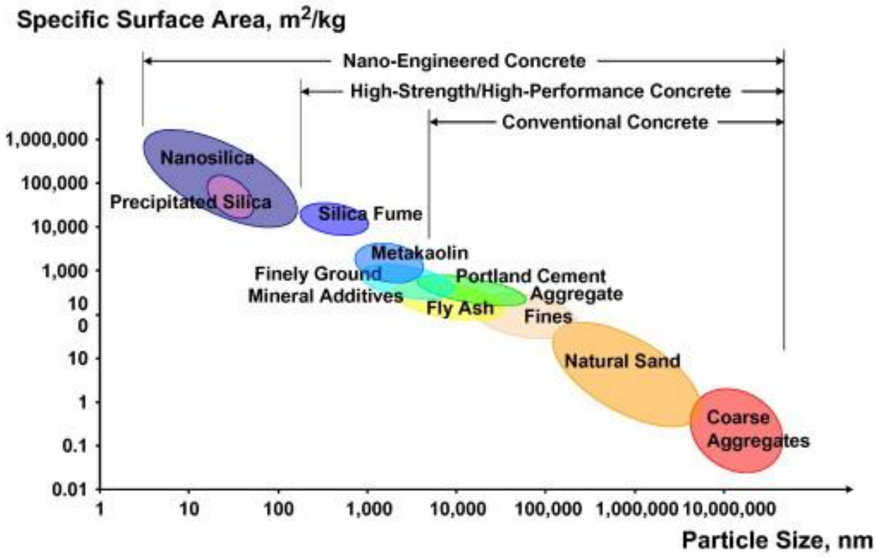

Fig. 1. Particle sizes and specific surface areas of concrete materials.

The most commonly used nano particles in cement and concrete are nano SiO_2, nano Al_2O_3 and nano TiO_2. Studies about nano particle usage over hydration, rheological structure, micro pattern, strength, elasticity module features of cement and concrete have been in literature. Some results of these studies are:

- Compressive strength of cement mortar increases 111.2% on 7th day and 108.6% on 28th day via adding 1% nano $CaCO_3$ to cement mortar by weight, while compressive strength of concrete mortar rises 14% on 7th day and 16.7% on 28th day via adding 1% nano Al_2O_3 to concrete mortar by weight (Zhang et al., 2015).
- When water/cement ratio is 0.40 and 0.60, the highest compressive strength in both water/cement ratios on 28th day is given by mortars involving 5% nano TiO_2 among 0%, 1%, 3% and 5% of TiO_2 usage ratios (Lee et al., 2013).
- In a study about self-compacting concrete that is blended with nano SiO_2 and fly ash, the highest compressive strength on 28th day is in self compacting concrete samples containing 0% fly ash and 4% nano SiO_2 (Güneyisi et al., 2015).
- According to another study that nano SiO_2, $Cu_{0.5}Zn_{0.5}Fe_2O_3$ ve $NiFe_2O_4$ powders are used, optimum dosage is 3% in concretes produced with nano SiO_2, while it is 2% in the other concretes using $Cu_{0.5}Zn_{0.5}Fe_2O_3$ and $NiFe_2O_4$ powders. Concrete samples involving nano SiO_2 give better results than samples containing $Cu_{0.5}Zn_{0.5}Fe_2O_3$ and $NiFe_2O_4$ (Amin and Abu El-Hassan, 2015).

Pozzolana usage is commonly used in cement-based composites. Through adding silica fume to concrete, compressive strength increases, shrinkage decreases, abrasion resistance rises, adherence grows and permeability diminishes. Economical and ecological benefits of silica fume should not be overlooked in addition to its positive contribution over concrete features (Topçu and Canbaz, 2002). It is well known that the addition of micro silica can improve the strength and durability of concrete and the addition of nano silica can also improve certain properties of concrete (Li et al., 2017). In literature context, micro and nano silica usage in both cement mortars and concrete is seen to be extensive.

The aim of this study is to determine usability of 2 materials that have micro and nano sizes together in cement mortars. Silica fume and nano silica are preferred respectively as a micro material and nano particle. Moreover, nano silica's effects over mechanical characteristics of silica fume added cement mortars are investigated.

2. Materials and Method

2.1. Materials

In the study, the CEM I 42,5 R cement supplied from Akcansa Cement Plant, micro silica, nano silica, CEN standard sand and mains water are used. Chemical, physical and mechanical properties of the cement are given in the Table 1 (TS EN 197-1 2012).

Micro silica that has a 2.32 g/cm³ particle density is supplied from Antalya Eti Electro-Metallurgy Plant. Its chemical features are seen in the Table 2.

Table 1. Chemical, physical and mechanical properties of the CEM I 42,5 R cement.

Analysis	Oxide	Value	Analysis	Tests	Value
Chemical (%)	CaO	62.64	Physical	Blaine, cm²/g	3269
	Al_2O_3	4.56		Volume expansion, mm	2.0
	Fe_2O_3	3.36		Intensity, g/cm³	3.12
	SiO_2	19.05		Setting start time, min.	150
	SO_3	2.88		Setting finish time, min.	210
	MgO	2.98	Mechanical	Day	MPa
	Na_2O	0.15		2. day	32.5
	Ignition loss	3.02		7. day	43.4
	Insoluble residue	0.30		28. day	53.6

Table 2. Micro silica's chemical features.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Micro silica	81.40	4.47	1.40	0.82	1.48	1.30

Nano silica's average particle size is 30 nm and has a 99.9% purity. B.E.T. surface area is 440 m²/g, its color is white. Nodular nano SiO_2 has a density between 2.2-2.6 g/m³. Binding materials used during the study are seen in the Fig. 2.

CEN standard sand in conformity with TS EN 196-1 supplied from Kırklareli Limak Cement Plant is used in mortar admixtures. Its sieve analysis is given the Table 3.

In the study, cement pastes and mortar admixtures are produced in four different groups and defining codes are given to the samples. The codes are shown in the Table 4.

On the prepared cement pastes, consistency experiments and determination tests for initial and final setting time are done according to the TS EN 196–3.

According to the TS EN 196-1 mass ratios of mortar constituents are prepared in the way of 1 portion cement (450 gr), 3 portions standard sand and 0,5 portion water (225 gr). In this study, 4 different mortar admixtures are prepared with cement, micro silica, nano silica, standard sand and water. Material quantities for the mortar admixtures are seen in the Table 5.

Samples belonging to the mortar admixtures 5S, 5S+1NS, 5S+2NS and 5S+3NS are subjected to flexural strength test on 7th, 28th, 90th days. The experiment carried out with 3-point method. Prismatic samples that have 40 mm x 40 mm x 160 mm sizes (TS EN 196–1, 2016).

Fig. 2. a) Micro silica; b) Nano silica; c) Cement.

Table 3. Standard sand sieve analysis.

Square aperture size (mm)	Cumulative retaining at sieve (%)
2.00	0
1.60	7±5
1.00	33±5
0.50	67±5
0.16	87±5
0.08	99±1
0.00	0

Table 4. Codes of the mortar samples.

Sample Name	Code
Cement pastes or mortar with 5% micro silica substitution	5S
Cement pastes or mortar with 5% micro silica + 1% nano silica substitution	5S+1NS
Cement pastes or mortar with 5% micro silica + 2% nano silica substitution	5S+2NS
Cement pastes or mortar with 5% micro silica + 3% nano silica substitution	5S+3NS

Table 5. Material quantities for the mortar admixtures.

Sample Code	Cement, gr	Micro silica, gr	Nano silica, gr	Standard sand, gr	Water, gr
5S	427.5	22.5	0	1350	255
5S+1NS	423.0	22.5	4.5	1350	255
5S+2NS	418.5	22.5	9.0	1350	255
5S+3NS	414.0	22.5	13.5	1350	255

Compressive strength experiments are made on the 6 samples with 40 mm x 40 mm x 40 mm size resulting from flexural strength. Compressive strength device is arranged at appropriate capacity and loading speed (2400±200) N/s for the experiment. Semi-prisms obtained after flexural test are located without overflowing not more than ±5 mm between plates of the device by centering. Loading to the device are made until it is cut at (2400±200) N/s speed. The result of compressive strength experiment are stated as arithmetical mean of 6 results that are assigned from 3 prism sets (TS EN 196–1, 2016).

3. Results and Discussion

In the study, by being put in nano silica substitution in the ratios respectively 0%, 1%, 2% and 3% to the 5% micro silica added cement pastes and mortar samples, admixtures are prepared. Consistency- setting time determination tests are made on cement pastes belonging to 5S, 5S+1NS, 5S+2NS and 5S+3NS admixture, whereas on mortars, compressive- flexural experiments are done on 7th, 28th and 90th days.

The results obtained from the consistency test over the cement pastes with micro silica (5%) and nano silica (0%, 1%, 2%, and 3%) substitution are seen in the Fig. 3. Nano silica substitution slightly effects water necessity. Water quantity increased by 0.65% for 1% and 2% substitution rates according to the 5% micro silica substitution (0% nano silica substitution). 3% nano silica substitution increased the water requirement by 3%.

The results obtained from setting time experiments over the 5% micro silica and nano silica substituted (with different rates) cement pastes are seen in the Fig. 4.

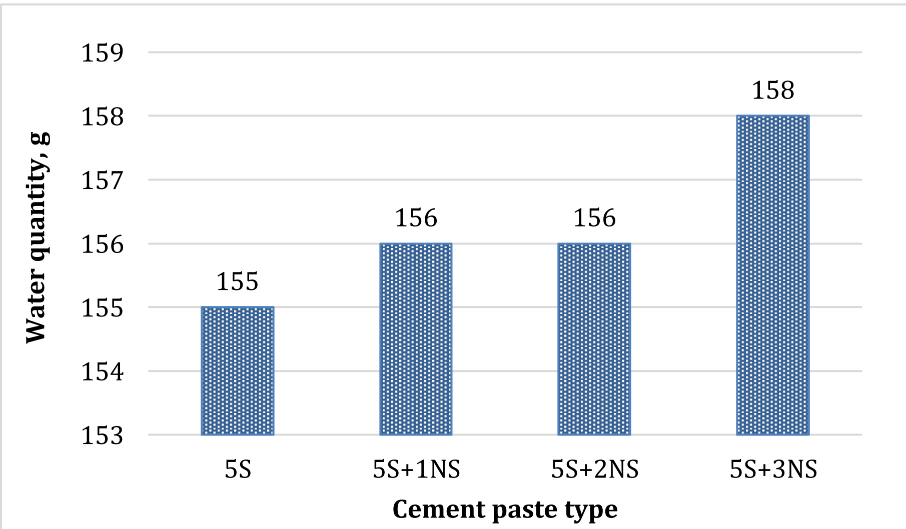

Fig. 3. Water necessities of cement pastes with micro and nano silica substitutions.

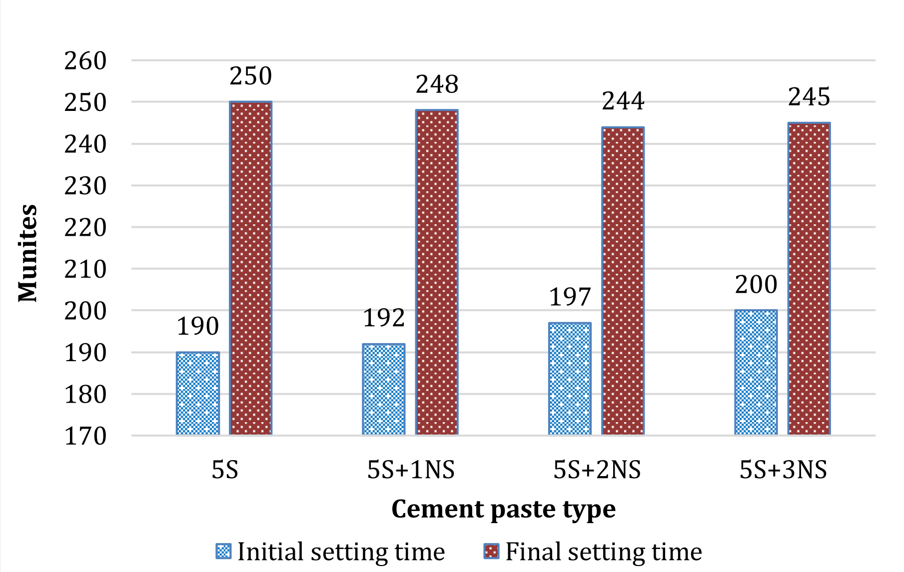

Fig. 4. Initial and final setting times of cement pastes with micro and nano silica substitutions.

When initial and final setting times of the 5S, 5S+1NS, 5S+2NS and 5S+3NS cement pastes are analyzed, it is seen that initial setting time extends whereas final setting time decreases in condition that nano silica substitution increases. Cement mortar containing 5% micro and 3% nano silica have more initial setting time. 3% nano silica substitution increases initial setting time by 5% compare to cement paste without nano silica. This result is parallel with literature. Kumar and Singh (2018) studied the effect of nano silica on setting times and observed that initial setting time increases with the addition of nano silica (Kumar and Singh, 2018).

Cement technology and industry that developed fast in the end of 19th century has gradually shown progress from the point of quality. Cement enters the hardening (setting) process by starting reaction when it gets in touch with water. This process stays in certain limits. Standards define at least 1 hour and 10 hours respectively for setting starting and setting finishing time. If setting starting process is fast, carrying and placing of fresh concrete is very difficult. If hardening becomes late, concrete can't obtain its strength in desired time and formwork removal time lingers. So, concrete is affected from out climate conditions (Çelik et al., 2004).

Cement pastes belonging to mixtures that produced in study progress, don't exceed the rule "initial setting time can't be less than 1 hour" defined in the standard (TS EN 197-1, 2012).

Çelik et al. (2001), researched silica fume's effect over Portland cement's setting time through 5%, 10% and 15% silica fume substituted to Portland cement and found that the mixture with 5% silica fume had no effect to setting time while the mixtures with 10% and 15% silica fume clearly delays setting times.

Findings obtained from flexural strength tests over the 5% micro silica and nano silica substituted (with different rates) mortar samples that were done on 7th, 28th and 90th days are given in the Fig. 5.

Changes of flexural strengths when substituting nano silica to micro silica added mortars are concluded at the Table 6. At all ages, the best flexural strength value belongs to 5S+2NS mortar admixtures.

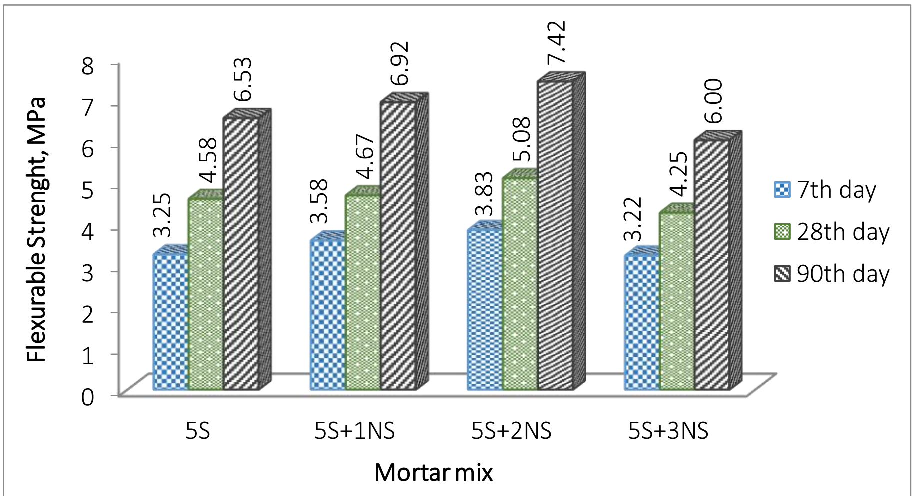

Fig. 5. Flexural strength results of mortar mixtures.

Table 6. According to 5% micro silica added mortars, the effect of nano silica substitution over flexural strength (+, increases; -, decreases).

Substitution Rate	7th day	28th day	90th day
%1 NS	+10.0	+2.0	+6.0
%2 NS	+17.0	+10.0	+13.0
%3 NS	-1.0	-7.0	-8.0

Among the mortar samples whose flexural strength studied, the highest strength values on 7th, 28th and 90th days are obtained from 5S+2NS mortar mixtures. According to 5% micro silica added mortars 1% and 2% nano silica substitution increases flexural strength respectively 6% and 13% on 90th day, while 3% nano silica substitution decreases flexural strength.

Findings obtained from compressive strength tests over the 5% micro silica and nano silica substituted (with different rates) mortar samples that were done on 7th, 28th and 90th days are given in the Fig. 6.

Changes of compressive strengths when substituting nano silica to micro silica added mortars are concluded at the Table 7. At all ages, the best compressive strength value belongs to 5S+2NS mortar admixtures. On 90th day, 2% nano silica substitution increases compressive strength 7%.

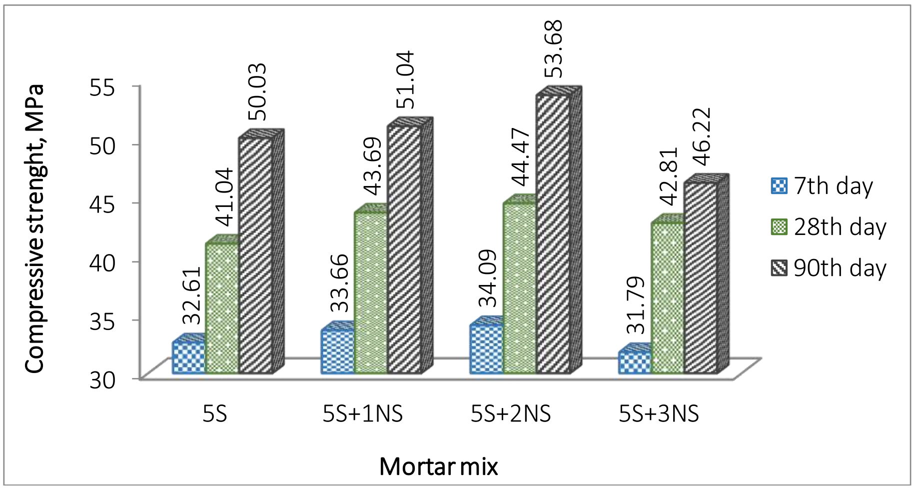

Fig. 6. Compressive strength results of mortar mixtures.

Table 7. According to 5% micro silica added mortars, the effect of nano silica substitution over compressive strength (+, increases; -, decreases).

Substitution Rate	7th day	28th day	90th day
%1 NS	+3.0	+6.5	+2.0
%2 NS	+4.5	+8.0	+7.0
%3 NS	-2.5	+4.0	-7.5

Li et al. (2017) determined micro and nano silica using increases cube strength, sulphate, carbonation and chlorine resistance. However, it is found that based on powder type and combination, nano powders usage in mortars containing micro silica has an upper limit. In a study, this limit is specified as 1.25% and it is ascertained that when it is surpassed, quantity of space grow because of coagulation (Oltulu and Şahin, 2013). In this study, it is found nano silica usage with a ratio of 3%, decreases both flexural and compressive strength. In this context, it is thought that coagulation happened with a 3% ratio and due to the spaces, this coagulation affects strengths negatively.

Jo et al. 2007 explored that in nano SiO_2 is a filler material developing microstructure and the more silica fume and nano SiO_2 quantities increase, the more compressive strength of mortar increases (7th and 28th day). Also it is known that the compressive and flexural strength of the cement mortars with nano SiO_2 were higher than that of the plain cement mortar (Li et al., 2004).

The authors (Haruehansapong et al., 2014) investigated on the cement composite with silica fume and with 9% of nano SiO_2. It was found that the microstructure of control cement paste and cement paste with silica fume was similar. The silica fume has lesser pozzolanic activity and filling ability compared to nano SiO_2.

Li et al. (2018) demonstrated that with both micro silica and nano SiO2 added together, the compressive strength and elastic modulus could be increased to higher than those achievable with only MS added or only NS added.

SEM images obtained from the mortar samples 5S, 5S+1NS, 5S+2NS and 5S+3NS are seen in the Fig. 7. According to the SEM images of all the cement mortars, C-S-H phase which is intensively prevalent to the structure is seen. Formless gel constitutes prevalent phase in the all structure, forms a linkage between hydration products and tries to fill spaces. The phase tries to fill the spaces in the 5S cement paste, but the 1-2 micron length sporadic spaces are encountered even though they are very few. Additionally, cracks are run across even if they have very small sizes.

Besides, it is seen that 5S+1NS and 5S+2NS coded cement pastes have a more solid and stable structure. Abd El-Baky et al. (2013) determined that cement mortar containing nano silica have more homogeneity binder, less pores, more adhesion at interfacial zone in SEM analysis. However, it is found that as per the other samples, 5S+3NS cement paste has a more porous structure that is up to 3 micrometer. It is known that excessive dosage of NS would result in more serious agglomeration of nano particles, with decline in nano effect (Zhanga et al., 2018).

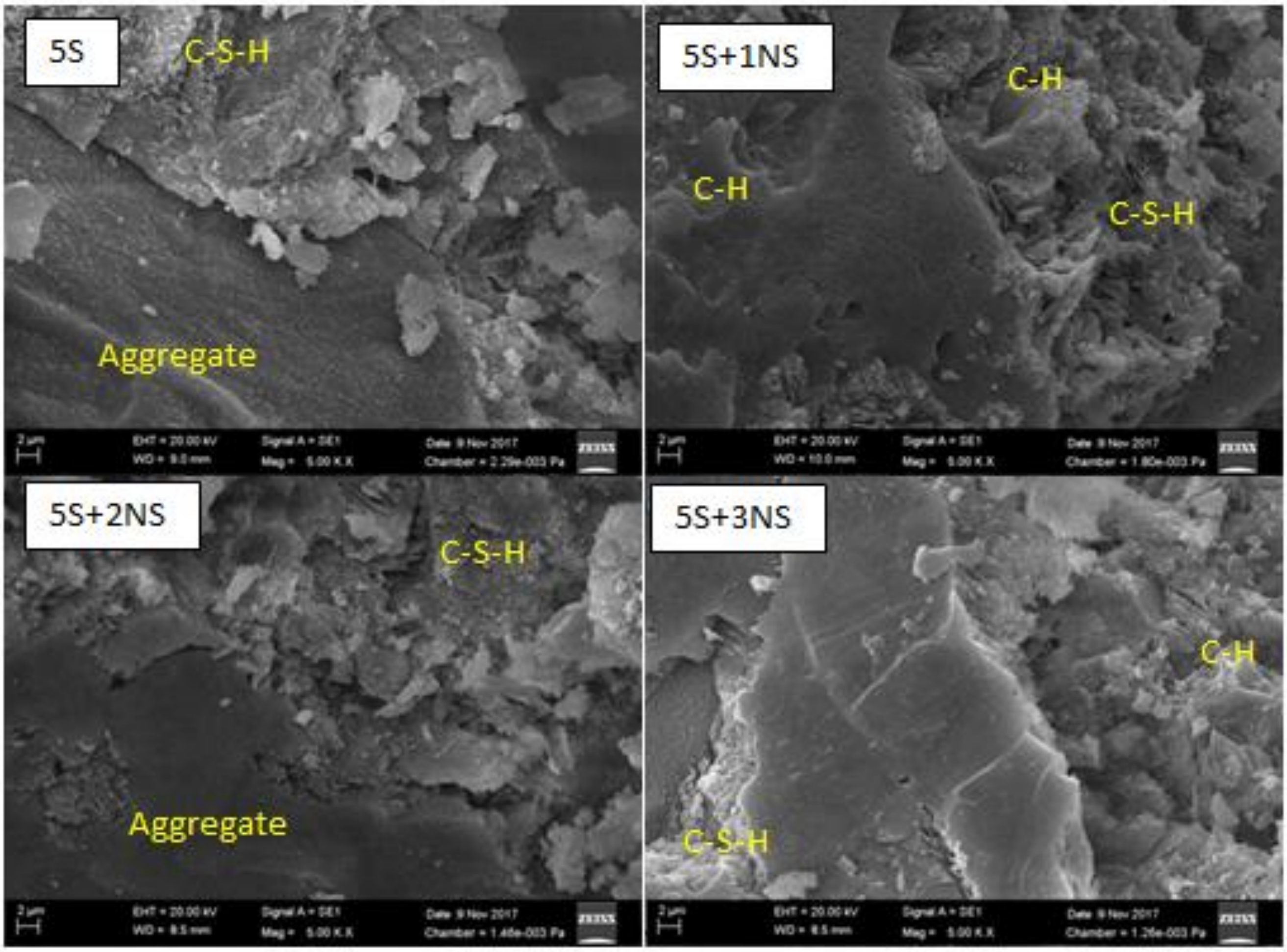

Fig. 7. SEM images of the mortar admixtures.

4. Conclusions

According to consistency, initial and final setting time experiments over the cement pastes of 5S, 5S+1NS, 5S+2NS and 5S+3NS mixtures, it is found that 3% nano silica substitution somewhat increases water necessity and all the nano silica substitutions extend initial setting time whereas they shorten final setting time as per mortar mixture containing 5% micro silica.

With regard to flexural and compressive strength tests on 7^{th}, 28^{th} and 90^{th} days over the cement pastes of 5S, 5S+1NS, 5S+2NS and 5S+3NS mixtures, in comparison with mortar samples containing 5% micro silica, it is detected 1% and 2% nano silica substitutions increases flexural and compressive strength, whereas 3% nano silica substitution decreases these strengths.

It is established that 2% nano silica substitution to 5% micro silica added cement mortars affects flexural and compressive strength positively. On 90^{th} day, 2% nano silica substitution increases flexural strength 13% and compressive strength 7%.

On the other hand, 3% nano silica substitution decreases 8% flexural strength and compressive strength 7.5% in comparison with mortar mixture containing 5% micro silica.

Acknowledgements

This research has been supported via 2016.F94.02.02 numbered Project by Artvin Çoruh University Scientific Research Projects Fund. The authors gratefully acknowledge the financial support provided by Artvin Çoruh University.

Publication Note

This research has previously been presented at International Civil Engineering and Architecture Conference (ICEARC'19) held in Trabzon, Turkey, April 17-20, 2019. Extended version of the research has been submitted to Challenge Journal of Concrete Research Letters and has been peer-reviewed prior to the publication.

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