Utilization of Nano-Silica to improve properties of BOF Slag- Cement

Seyed Vahid Hosseini, Mohammad Reza Nilforoushan, Sasan Otroj

Faculty of Engineering, University of Shahrekord, Shahrekord, Iran.
h_seyedvahid@yahoo.com

Abstract: Basic oxygen furnace (BOF) slag is a by-product of the pig iron refining. This paper presents an experimental study on the utilization of nano-silica to improve the setting properties and mechanical strength of pastes and mortars, made from ordinary Portland cement (OPC) by addition of BOF slag. For this reason, some mixtures including different amounts of BOF slag with/without nano-silica were prepared. Initial and final setting times of fresh pastes and compressive and flexural strengths of 3, 7, 28 and 90 days of age hardened mortars were measured. The results have indicated that addition of nano-silica reduces setting time of the pastes and increases mechanical strength of mortars containing large amounts of BOF slag. Microstructural and mineralogical evaluations of hydrated products revealed nano-silica reacts with Ca (OH)2 through a pozzolanic reaction and then, the amount of C–S–H increases. So, this leads to a higher densification of the matrix, which improves the strength and durability of cementitious mixtures containing BOF slag.

[Seyed Vahid Hosseini, Mohammad Reza Nilforoushan, Sasan Otroj. **Utilization of Nano-Silica to improve properties of BOF Slag- Cement.** *Life Sci J* 2018;15(7):73-80]. ISSN: 1097-8135 (Print) / ISSN: 2372-613X (Online). http://www.lifesciencesite.com. 10. doi:10.7537/marslsj150718.10.

Keywords: Nano-Silica, BOF Slag, Cement Mortars, Mechanical Strengths, Setting Time

1. Introduction

Until the present time, most industrial slags are being used without taking full benefits of their properties or disposed rather than used. Basic oxygen furnace slag (BOFS) produced in the process of conversion of pig iron to steel in the basic oxygen furnace. The operating principle of the pig iron refining is to blow oxygen in order to oxidize carbon and then decrease the carbon content. During this operation, lime is added to the furnace in order to fix undesirable elements in the slag and protect the refractory lining. At the end of process, BOF slag is separated from the molten steel by densimetric separation and poured into the casting pits [1]. Depending on the grade of steel produced, 100–200 kg per ton of BOF slag are generated. Thus, about some million tons were produced and piled in worldwide annually [2]. Some investigations were performed on the use of these non-metallic materials in cement and concrete [1-5]. The production and application of cement and concrete containing slag have at least the following advantages [6]:

- It can reduce the cost of cement production as well as decrease amounts of disposed slags at the iron and steel plants.
- The reduction of clinker can decrease air pollution compounds, such as CO_2 and SO_2, during clinker processing at the cement factories.

On the other hand, in recent decade, utilization of nano-particles has received particular attention in many fields of applications to fabricate materials with new functionalities. When ultra-fine particles are incorporated into Portland cement paste, mortar or concrete, materials with different characteristics from conventional materials were obtained [7–10]. Some researchers approved that using of nano-silica can increase mechanical properties of mortars and the appropriate percentage of nano-silica for addition was about 1–5 wt. % [11-17].

Nano-particles of SiO_2 can fill the spaces between particles of C–S–H gel and acting as a nano-filler. Furthermore, nano-silica had a pozzolanic reaction with Ca $(OH)_2$ (calcium hydroxide), and it results to the generation of a compact and dense microstructure by creating calcium silicate hydrate (C-S-H). The higher strengths are attributed to accelerated cement hydration and pozzolanic reactions, reduced pores and improved interface bonding between hardened cement paste and aggregate [10-14]. Nano-silica has also been used to increase early strength of concrete with granulated blast furnace (GBF) slag and fly ash [14, 15, 17].

This paper presents the results of an experimental work on the utilization of BOF slag as a replacement factor in ordinary Portland cement (OPC) in the range of 0-50 wt%, then studied the effects of adding nano-silica on setting time and mechanical strengths of pastes and mortars containing large amounts of BOF slag.

2. Experiments

2.1. Material and methods

The BOF slag was obtained from the Esfahan steel Company of Iran. One kilogram of slag was prepared out of 20 kg samples taken from each batch of slag produced in 24 hours by quarter sampling procedure, for the experiments randomly and mixed completely. The mixed Batch was dried, crashed and milled by various mills such as ball and fast mills, in order to make a powder which pass the #200 mesh sieve (particle size <75 µm). Chemical composition of the starting materials was determined by X-ray fluorescence model Cambridge XR300. The results are given in Table 1. The mineralogical compositions of raw materials was determined by X-ray diffraction, using a Bruker D8-Advance diffractometer with nickel-filtered CuKα1 radiation (=1.5406 Å, 40 kV and 25 mA). The nano-silica used was 30% based on the silica dry powder, it was in the colloidal form. The cement used in this study was Portland type I-325 Esfahan.

Table 1. Chemical composition and physical properties of materials used.

Mineral	OPC	BOF slag	Nano-silica
SiO_2	21.7	10.2	99.8
CaO	63.5	57.1	-
Al_2O_3	5.9	2.1	<0.1
MgO	1.8	1.5	-
$Fe_{(total)}$	3.1	20.5	-
MnO	-	2.6	-
V_2O_5	-	2.2	-
P_2O_5	-	1.2	-
TiO_2	0.6	2.1	-
K_2O	0.7	0.4	-
Na_2O	-	-	0.1
L.O.I	2.7	0.1	-

Figures 1 and 2 have shown the X-ray diffraction patterns of OPC and BOF slag. The main hydraulic compound in OPC is C_3S, C_2S and C_3A. These phases are also present in BOFS with comparable amounts to OPC. This can be an evidence for hydraulic activity of this type of Steel-making slag.

2.2. Testing procedures

Blends of cement, BOF slag and sand were mixed based on the design shown in tables 2 and 3. It was mixed in a rotary mixer for 5 minutes in order to get a uniform powder. The powder then mixed with appropriate amount of water.

The setting time of the pastes were determined by Vicat needle, according to ASTM-C191 [18]. Two distinct stages of setting were recorded in the laboratory for pastes: the initial (time of commencement of setting) and the final set (where the paste stiffens).

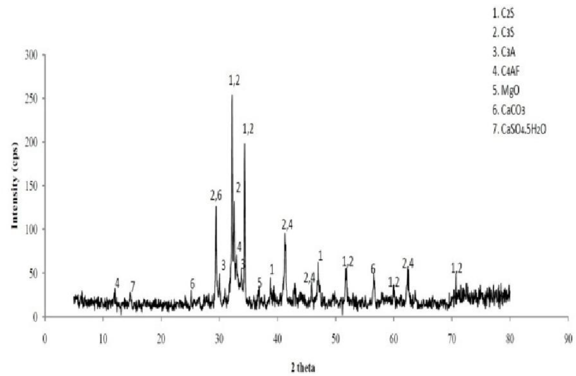


Figure 1. XRD analysis of ordinary Portland cement.

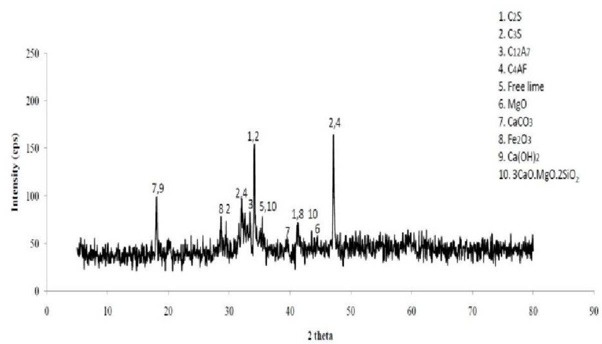


Figure 2. XRD analysis of BOF slag.

Table 2. Mix proportion of mortars containing BOF slag.

Mixture Name	Content (wt. %)			w/cm	Sand (gr)
	OPC	BOF slag	Nano-silica		
OPC	100	-	-	0.6	1350
BOF10	90	10	-	0.6	1350
BOF20	80	20	-	0.6	1350
BOF30	70	30	-	0.6	1350
BOF40	60	40	-	0.6	1350
BOF50	50	50	-	0.6	1350

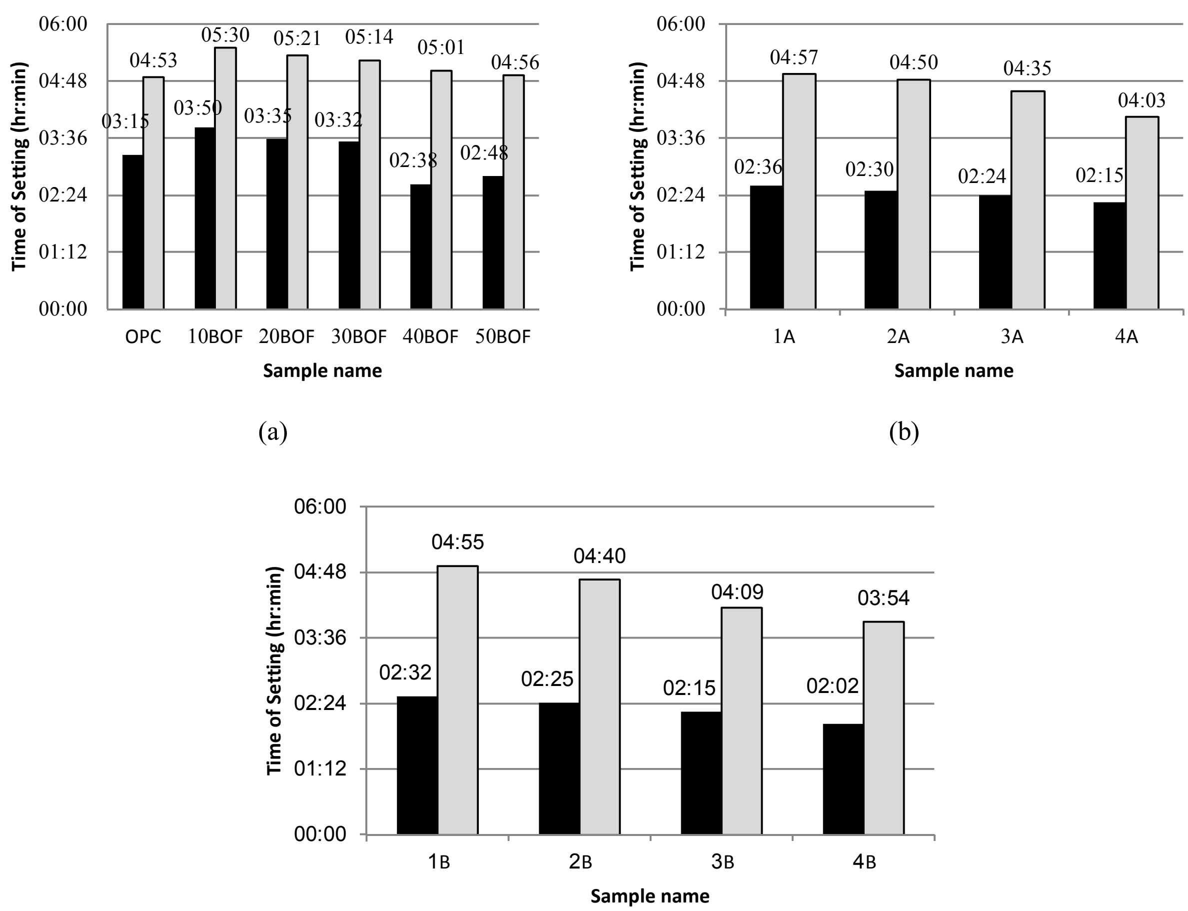
Compressive tests were run on specimens (dimensions of 50×50×50 mm^3) according to ASTM C109 [19]. The other specimens with dimensions of 40 × 40 × 160 mm^3 were also prepared for flexural strength according ASTM C348 [20]. For each mixture, three specimens were made. After being demoulded at the age of one day, all specimens were cured in water at 20 ± 1 ºC for 3, 7, 28 and 90 days. The mechanical strength measurements of the mortars were performed on the Alborz machine with a load rate control regime (10 mm/min).

For the study of hydration products at appropriate ages, pieces of hardened pastes were left in a solution made of acetone and ether for 24 hours and then dried in order to stop further hydration. The samples were kept in a sealed bottle for mineralogical and microstructural investigations. The microstructural study of the hardened pastes at 28 days of age have done with scanning electron microscopy (SEM) model Leo 435-vp, EHT=20 kV.

Table 3. Mix proportion of mortars containing large amounts of BOF slag with different amounts of nano-silica.

Mixture Name	Content (wt. %)			w/cm	Sand (gr)
	OPC	BOF slag	Nano-silica		
A1	59.5	40	0.5	0.6	1350
A2	58.5	40	1.5	0.6	1350
A3	57.5	40	2.5	0.6	1350
A4	56	40	4	0.6	1350
B1	49.5	50	0.5	0.6	1350
B2	48.5	50	1.5	0.6	1350
B3	47.5	50	2.5	0.6	1350
B4	46	50	4	0.6	1350

3. Results and Discussion
3.1. Setting time of pastes



(c)

Figure 3. Setting time of the pastes containing: a) 0-50% BOF slag; b) 40% BOF slag and 0.5-4% nano-silica; c) 50% BOF slag and 0.5-4% nano-silica

The effect of increasing BOF slag on setting time of cement pastes are presented in figure 3-(a). Based on the results, by adding the BOF slag setting time of the paste increased at 10% dramatically. Then, by increasing content of the slag, setting time slightly decreased due to content of lime which exists in BOF slag. The lime (CaO) absorbs water extremely and it caused paste set before the completion its hydration (False set). The effects of increasing nano-silica on setting time of pastes containing 40% and 50% BOF slag are shown in figure 3-(b) and 3-(c), respectively.

3.2. Mechanical strength of mortars

Compressive and flexural strengths of the mortars after 3, 7, 28 and 90 days were measured according to the standards and the results are given in Tables 4, 5 and shown in figure 4. Generally by increasing BOF slag due to reduction of active cementitious phases the mechanical strengths reduced. As be seen in the diagrams, by increasing the nano-silica in the mortars, mechanical strength was increased. It can be seen the mechanical strength of mortars with nano-silica was developed in every case and it was higher than the same samples without nano-silica. Therefore, by addition of nano-silica to the mixtures as an additive their strength improves. This is more effective in the presence of higher amounts of nano-silica. Diagrams of mechanical and flexural strength are shown in fig. 4 respectively (left to right). The addition of nano-silica reduces the setting time and the beginning of the acceleration period of cement hydration. The setting behavior of the pastes was slightly accelerated when content of nano-silica increased because of active particles of nano-silica.

Table 4. Results of mechanical strength (MPa) for the mortars containing BOF slag.

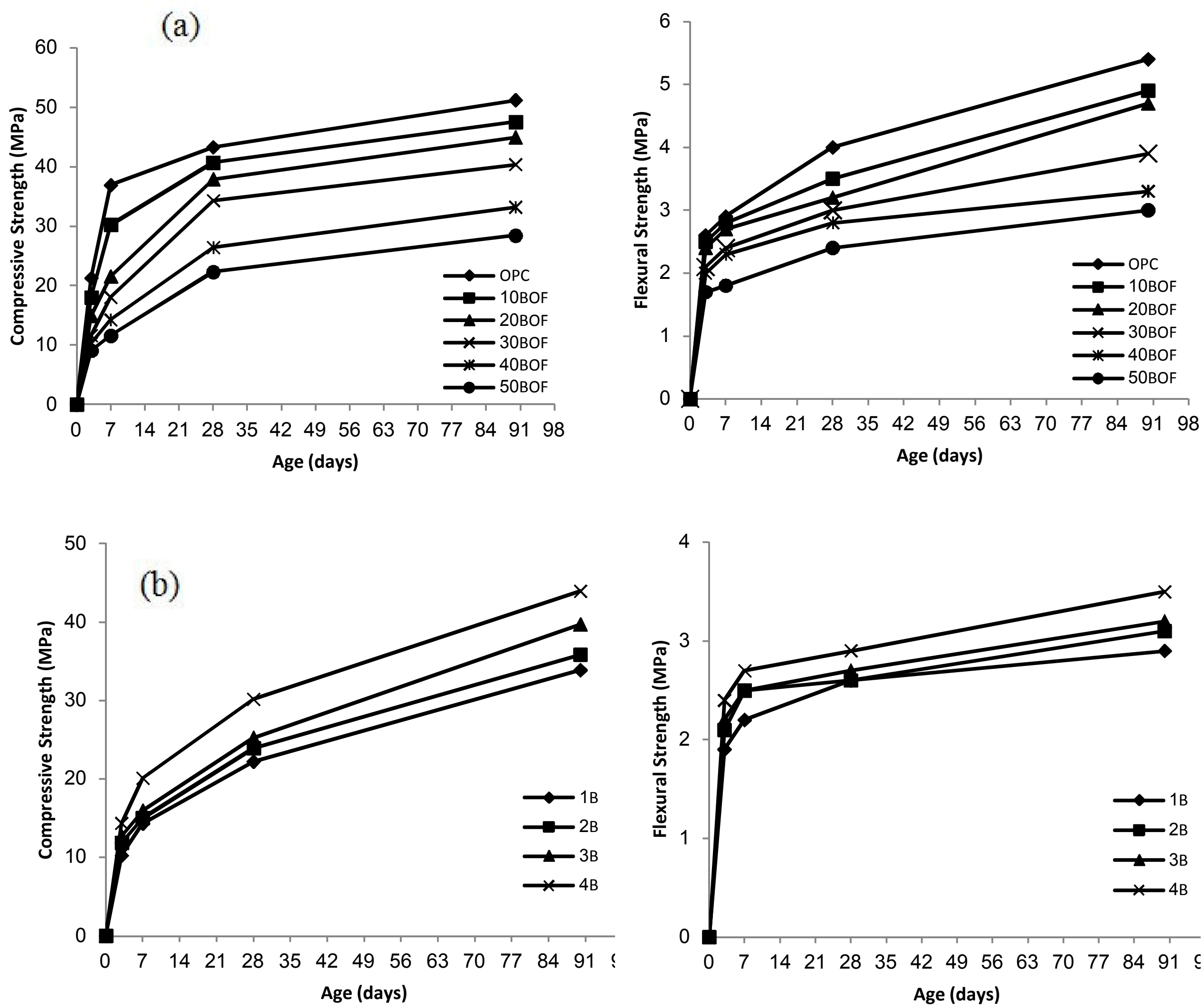
Sample Name	Mechanical Strength (MPa)							
	3 days		7 days		28 days		90 days	
	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
OPC	2.7	21.28	2.9	36.91	4.0	43.29	5.4	51.20
BOF10	2.5	18.03	2.8	30.22	3.5	40.70	4.9	47.56
BOF20	2.4	14.92	2.7	21.54	3.0	37.91	4.7	44.95
BOF30	2.1	11.63	2.4	18.00	3.0	34.32	3.9	40.37
BOF40	2.0	10.32	2.3	14.22	2.8	26.43	3.3	33.21
BOF50	1.7	9.05	1.8	11.56	2.4	22.29	3.0	28.43

Table 5. Results of mechanical strength (MPa) for the mortars containing large amounts of BOF slag with nano-silica.

Sample Name	Mechanical Strength (MPa)							
	3 days		7 days		28 days		90 days	
	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive	Flexural	Compressive
A1	2.1	11.21	2.4	15.32	2.8	23.46	3.4	35.63
A2	2.3	12.56	2.5	16.02	2.9	24.88	3.5	36.76
A3	2.5	15.98	2.8	20.45	3.4	29.98	3.7	41.49
A4	2.6	22.43	3.1	27.76	3.6	35.18	4.3	46.32
B1	1.9	10.24	2.2	14.32	2.6	22.21	2.9	33.87
B2	2.1	11.87	2.5	15.00	2.6	23.92	3.1	35.83
B3	2.2	12.66	2.5	15.97	2.7	25.23	3.2	39.67
B4	2.4	14.33	2.7	20.11	2.9	30.17	3.5	43.93

3.3. Microstructural observations and hydration products

Microstructure of the pastes after 28 days of hydration was investigated by SEM in order to have a clear understanding of the effects of BOF slag and nano-silica on the microstructure (Figs. 5-9). The microstructure of hardened OPC (Figure 5) reveals the compact microstructure with a few porosity and needles like crystals. Accumulation of the Ca $(OH)_2$ crystals on the surface of samples is recognizable by replacing large amounts of BOF slag in the formula (Figs. 6 and 7). It is much higher in the 50% of replacing and due to high amounts of lime in BOF slag composition; needle like crystals is small and more distributed on the surface (Fig. 7). When nano-silica added to the mixture starts to react with lime and portlandite phase, the crystals in the hardened paste becomes lumpy covered with ill platy crystal of tobermorite $[Ca_5Si_6O_{16}(OH)_2]$ and the needle crystals of ettringite (AFt) are rarely present on the broken surface (Figs. 8 and 9). The hydrated phases of OPC, A4 and B4 are specified with XRD analyses as shown in figure 10. Although the crystals of calcium silicate hydrated (C-S-H) and calcium hydrated (C-H) are be seen in all of diagrams, but intensity of it in A4 and B4 are less than pure OPC (Ref). Reduction of portlandite in A4 and B4 is due to presence of the nano-silica and formation of C-S-H. This phase contributed into the performance of mechanical strength of samples. These deductions confirm the results of mechanical strength (table 6). On the other hand, adding of nano-silica increased the density of the cement paste and improved bonding between the cement paste and sand, which might have contributed to the strength development. Moreover, the microstructure of the mixture containing nano-silica revealed a dense and compact formation of hydration products and a reduced lime and portlandite phase.



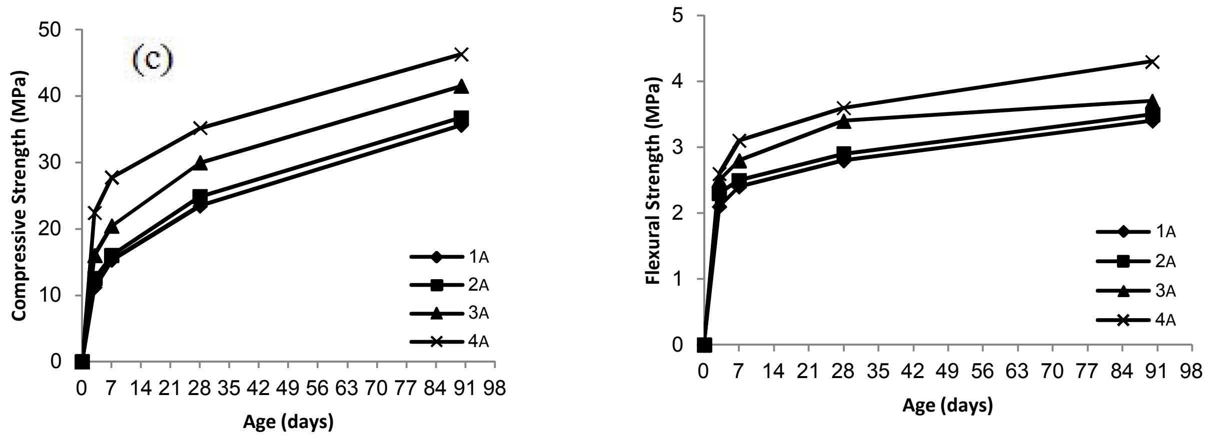


Fig. 4. Diagrams of mechanical strength of mortars containing (Left: Flexural, Right: Compressive):
a) BOF slag without nano-silica
b) 40% BOF slag with nano-silica
c) 50% BOF slag with nano-silica

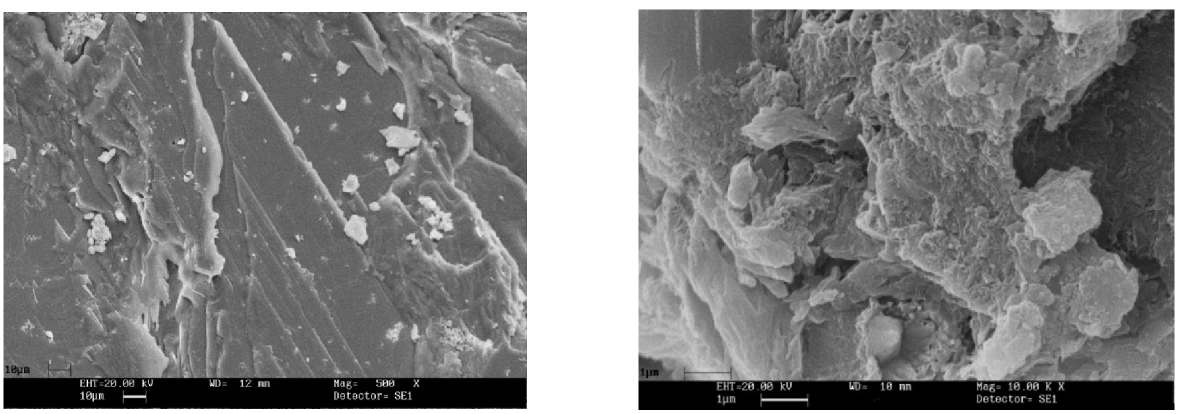


Figure 5. SEM micrographs of OPC at the age of 28 days with different magnifications.

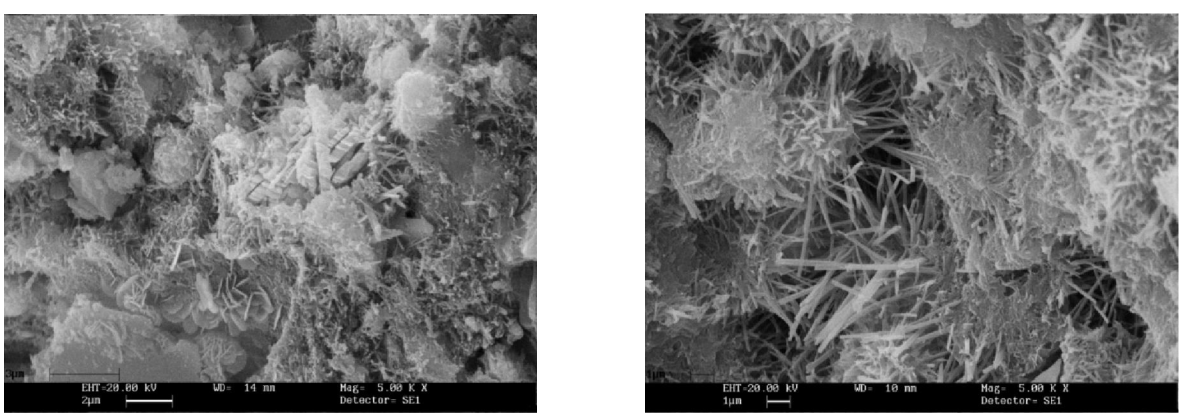


Figure 6. SEM micrographs of BOF40 at the age of 28 days with different magnifications.

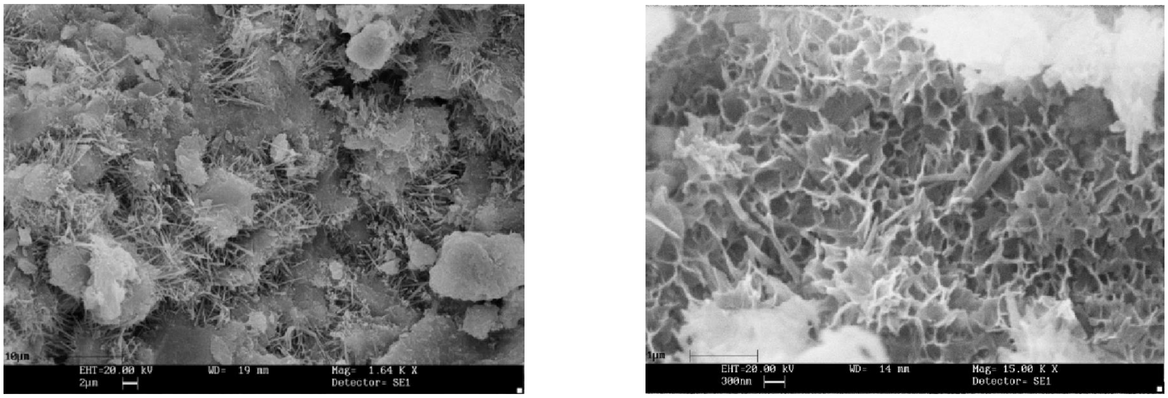


Figure 7. SEM micrographs of BOF50 at the age of 28 days with different magnifications.

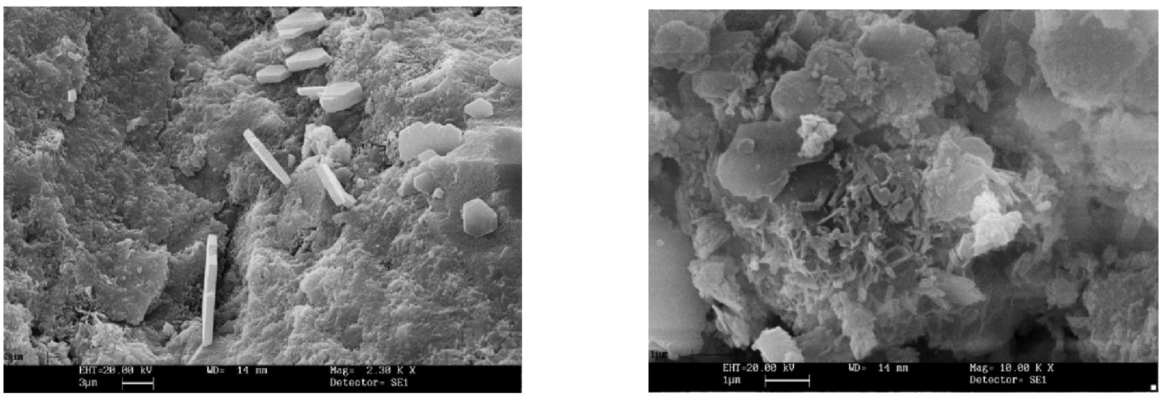


Figure 8. SEM micrographs of A4 at the age of 28 days with different magnifications.

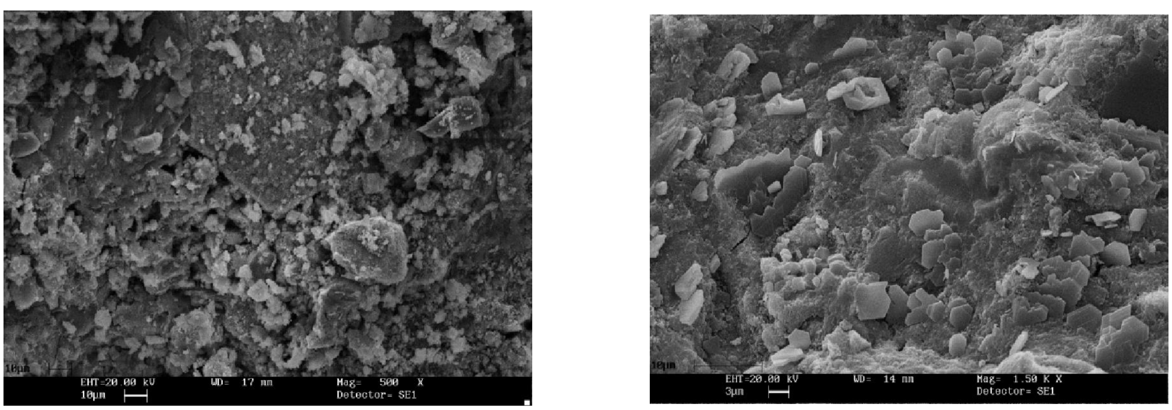


Figure 9. SEM micrographs of B4 at the age of 28 days with different magnifications.

4. Conclusion

The following conclusions can be drawn from the experimental results of this study:

- By addition of BOF slag as a cement replacement, the setting time of mortars increased and mechanical strength reduced. Mechanical behavior of mortars at early ages indirectly relates to the amounts of BOF slag additions, but it recovers at the ages of 28 and 90 days due to the pozzolanic activity of the slag phases.
- Additions of nano-silica, reduces the length of dormant period by reacting as a nucleation site. And, due to the colloidal particle size of nano-silica, it effectively fills capillary pores and it forms C-S-H (calcium silicate hydrated) gel by reacting with the lime and Ca $(OH)_2$ which exist in BOF slag.
- As the content of the nano-silica was increased up to 4 wt %, Because of modifying the microstructure and changing the morphology of crystals from needle like to platy, the mechanical strength of mortars containing large amounts of BOF slag was increased.

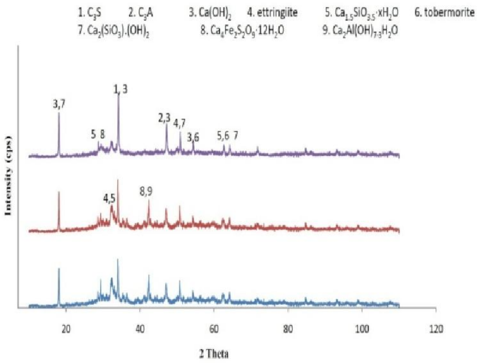


Figure 10. XRD analyses of the hydrated pastes at 28 days.

Corresponding Author:
Seyed Vahid Hosseini
Faculty of Engineering, University of Shahrekord, Shahrekord, Iran.
Email: h_seyedvahid@yahoo.com

Acknowledgment

The authors would like to express their gratitude to Esfahan steel Company, for financial support.

References

1. Belhadj, E., Diliberto, C., Lecomte, A., "Characterization and activation of Basic Oxygen Furnace slag", Cement and Concrete Composites, 34, pp. 34-40, 2012.
2. Mahieux, P. Y., Aubert, J. E., Escadellias, G., "Utilization of weathered basic oxygen furnace slag in the production of hydraulic road binders", Construction and Building Materials, 23, pp. 742-747, 2009.
3. Reddy, A.S., Pradhan, R.K., Chandra, S., "Utilization of basic oxygen furnace (BOF) slag in the production of a hydraulic cement binder", International Journal of Mineral Processing, pp. 98-105, 2006.
4. Kourounis, S., Tsivilis, S., Tsakiridis, P.E., Papadimitriou, G.D., Tsibouki, Z., "Properties and hydration of blended cements with steelmaking slag", Cement and Concrete Research, 6, pp. 815–822, 2007.
5. Qiang, W., Peiyu, Y., "Hydration properties of basic oxygen furnace steel slag", Construction and Building Materials, 24, pp. 1134–1140, 2010.
6. Xuequan, W., Hong, Zh., Xinkai, H., Husen, L., "Study on steel slag and fly ash composites Portland cement", Cement and Concrete Research, 29, pp. 1103–1106, 1999.
7. Li, H., Gang, H., Jie, X., Yuan, J., Ou, J., "Microstructure of cement mortar with nano particles", Composites Part B: Engineering, 35, 185-189, 2004.
8. Older, I., Lea's, "Chemistry of Cement and Concrete", 4th edition, London: Arnold; 1998.
9. Neville, A.M., "Properties of concrete", 4th edition, England: ELBS with Addison Wesley Longman; 1996.
10. Qing, Y., Zenan, Z., Deyu, K., Rongshen, C., "Influence of nano-SiO_2 addition on properties of hardened cement paste as compared with silica fume", Construction and Building Materials, 21, pp. 539–545, 2007.
11. Sanchez, F., Sobolev, K., "Nanotechnology in concrete; a review", Construction and Building Materials, 11, pp.2060–2071, 2010.
12. Porro, A., Dolado, J.S., Campillo, I., Erkizia, E., Miguel, Y.d., Ibarra, Y.S.D., "Effects of nanosilica additions on cement pastes", Applications of nanotechnology in concrete design, London; Thomas, pp. 87–96, 2005.
13. Jo, B.W., Kim, C.H., Tae, G.H., Park, J.B., "Characteristics of cement mortar with nano-SiO_2 particles", Construction and Building Materials, 21, pp. 1351-1355, 2007.
14. Schoepfer, J., Maji, A., "An investigation into the effect of silicon dioxide particle size on the strength of concrete", ACI Special Publication, 267, pp. 45-58, 2009.
15. Li, G., "Properties of high-volume fly ash concrete incorporating nano-SiO_2", Cement and Concrete Research, 34, pp. 1043-1049, 2004.
16. Said, A.M., Zeidan, M.S., "Enhancing the reactivity of normal and fly ash concrete using colloidal nano-silica", ACI Special Publication, 267, pp. 75-86, 2009.
17. Zhang, M.H., Islam, J., "Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag", Construction and Building Materials, 29, pp. 573-580, 2012.
18. ASTM C191-08: Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle.
19. ASTM C109 / C109M - 11b Standard Test Method for Compressive Strength of Hydraulic Cement Mortars.
20. ASTM C348 - 08 Standard Test Method for Flexural Strength of Hydraulic-Cement.

7/25/2018