EFFECT OF MAGNETITE NANOPARTICLES ON CEMENT BASED COMPOSITE

AYLIN AKYILDIZ *
Tekirdag Namık Kemal University, Corlu Engineering Faculty, Civil Engineering, Corlu, Tekirdag, Turkey

There has been a rapid increase in interest in nanotechnology and nanoparticles. Nanotechnology has been increasingly brought into the study of cement-based materials in the recent years. Adding nanosized particles in small amounts as materials can affect their properties significantly. In this study, the effect of nano magnetite Fe_3O_4/humic acid mixture (used as addition of 0.1, 0.5, 1, 1.5, 2, 3, 4 and 5% in mass of the cement) on the microstructural development and mechanical properties of cement composites has been investigated. Hence, samples size of 40•40•160 mm were produced using obtained cement based composites. After 28th days, flexural and compressive strength and water absorption experiments were implemented for cement based mortar samples. The microstructural analysis of mixtures nanoparticles were performed by scanning electron microscopy. Results were compared with the reference composite. As a result, 1% substitution nanoparticles with cement supplied best performance in terms of strength, water absorption.

Keywords: *Compressive strength; Fe_3O_4/humic acid nanoparticles; Mortar; Nanoparticles*

1. Introduction

Nanotechnology is a new and expanding technology, its main applications are the development of innovative methods to fabricate new products, to formulate new chemicals and materials [1, 2]. It has been more than 20 years since there has been research going on in the field of nanotechnology. Nanotechnology can be defined as the engineering of examining, monitoring, and modifying behaviors and performance of materials at nanoscale [3]. There has been a rapid development in interest in nanotechnology and using nanoparticles in commercial applications [4, 5]. Nanotechnology has been common brought into the study of cement based composite technology in recent years [6-10]. Nanoparticles are increasingly being used in cement-based composites for their properties improving [11-14].

The production of cementitious composites (cement mortars and concretes) is one of the most significant branches in building materials. Concrete is the most used material in construction world. It is a heterogeneous, nanostructured, multi-phase building material with various sizes of small crystals. It is widely used in nearly all construction activities. The use of nanomaterials in cement, cement based composites and concrete can lead to improvements of building materials [15]. Nanomaterials in cement based composite enable the improvement of properties, since the mechanical strength of concrete structures are determined by its microstructure [16, 17].

The nanomaterials used in the building materials industry include silicon dioxide, titanium dioxide, and zinc oxide. These nanomaterials, together with silver nanoparticles, carbon nanotubes, and nanofibers, are most often used for the production of the commercially available building products containing nano-objects [18-23]. There are many studies on the evaluation of the influence of nanomaterials on the mechanical properties of cement based material but the effects of some nanomaterials are not yet been fully defined. Among the undefined nanomaterials are iron oxides (nano-Fe_3O_4) [24, 25]. The literature on this subject is limited so it is one of the aims of this study to investigate the effect of this nanoparticle on composites.

Humic acid (HA) is one of the most common natural organic matters. It is neutral in aqueous solutions and environmentally friendly. Chemically, it could be a heterogeneous compound that has different containing carboxyl and hydroxyl bunches as its predominant functional bunches. Humic acids help to diminish the surface tension of water, resulting in an improved utilization of solid particles in concrete. Earlier research work in the usage of humic acid as replacement for cement shows to improve the strength of reinforced concrete [26]. The strength development characteristics containing HA solidified with cement and Fe_3O_4 have not been investigated.

Table 1

Composition of Cement

Component	CaO	Al_2O_3	SiO_2	MgO	Fe_2O_3	K_2O	Na_2O	SO_3	Loss of ignition
Cement, %	62.62	5.23	20.84	0.85	3.60	0.74	0.58	3.23	0.96

* Autor corespondent/*Corresponding author*,
E-mail: aakyildiz@nku.edu.tr

This study aims to characterize the effectiveness of Fe_3O_4/humic acid nanoparticles as admixture on physical, mechanical and microstructural characteristics of cement based mortar. Furthermore, the impact of nanoparticles on the microstructure of cement based mortars will also be determined.

2. Materials and Methods

2.1. Materials

2.1.1. Cement

Cement used was type CEM I 42.5 R. Its gravity was 3.16 g/cm^3. The composition is shown in Table 1.

2.1.2. Magnetite nano-Fe_3O_4/humic acid

Fe_3O_4/humic acid nanoparticle mixture was prepared according to the literature [27]. Firstly, 0.5 ratio of $FeCl_3$ $6H_2O$ and $FeCl_2 4H_2O$ salts were distributed in 50 ml of deionized water using magnetic stirring. 0.2 g of humic acid (HA) was added under constant stirring. The material was separated magnetically, washed with deionized water to eliminate impurities. Finally, a black powder product was obtained, which was dried at 80°C for 4 h. Fe_3O_4/humic acid nanoparticles were shown in Figure 1.

Fig. 1 - Fe_3O_4/humic acid nanoparticles.

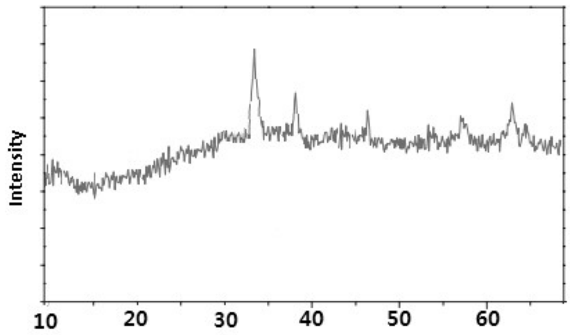


Fig. 2 - XRD pattern Fe_3O_4/humic acid magnetic nanocomposites.

Phase composition of the magnetite was characterized by using XRD analysis recorded at 2θ from 10° to 70° at a scanning rate of 1° min^{-1} Fe_3O_4/humic acid showed diffraction peaks at 2θ = 34.2° (Figure 2).

2.1.3. Sand

The used standardized sand was produced by Trakya Cement Plant of Limak Western Cement. The grading of sand is shown in Table 2.

2.2 Mixture

The Fe_3O_4/humic acid nanoparticles from mortar mixtures was varied namely 0.1%, 0.5%, 1%, 1.5%, 2%, 3%, 4% and 5% by weight of the cement. The mix amounts of mortars are seen in Table 3. Water/binder ratio is 0.50. Firstly, the nanoparticles were sonicated in mixing water for 1 min. Afterwards the cement was added and blended 30 s and subsequently the sand was poured into the mortars composition, and mixed for 30 s with high speed. The flow table experiment was applied to fresh mortar. The mortars were placed into 40•40•160 mm molds. After 28 days water absorption, compressive, flexural strengths of the samples were determined.

Table 2

Grading of sand

Sieve, mm	2.00	1.60	1.00	0.50	0.16	0.08
Percentage, %	0	7 ± 5	33 ± 5	67 ± 5	87 ± 5	99 ± 1

Table 3

Mix amounts of mortar

Name	Cement, g	Water, g	Sand, g	nano-Fe_3O_4/humic acid, g
F0	450	225	1350	0
F0.1	450	225	1350	0.45
F0.5	450	225	1350	2.25
F1	450	225	1350	4.50
F1.5	450	225	1350	6.75
F2	450	225	1350	9.0
F3	450	225	1350	13.5
F4	450	225	1350	18.0
F5	450	225	1350	22.5

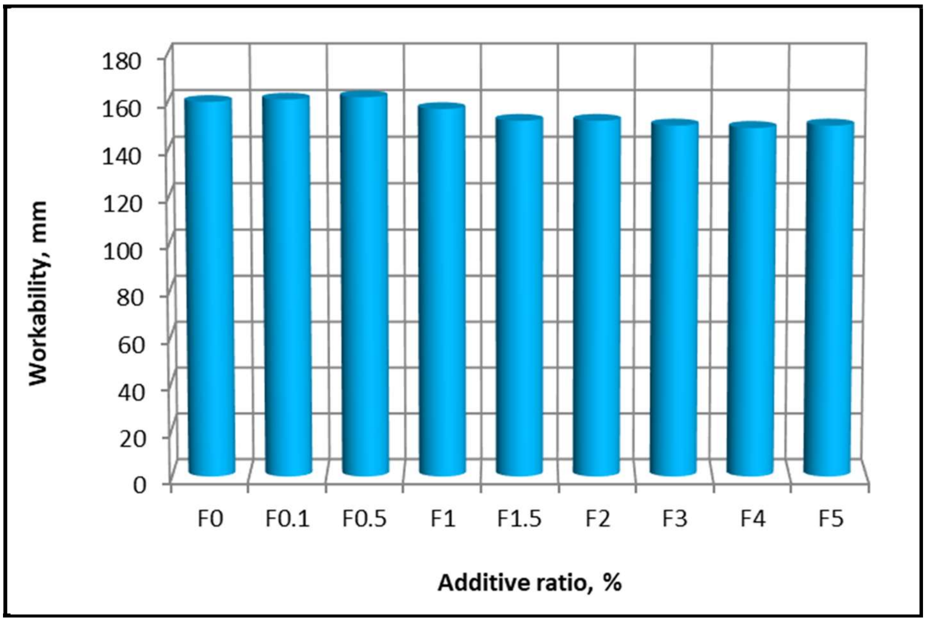


Fig. 3 - Workability of the fresh mortars.

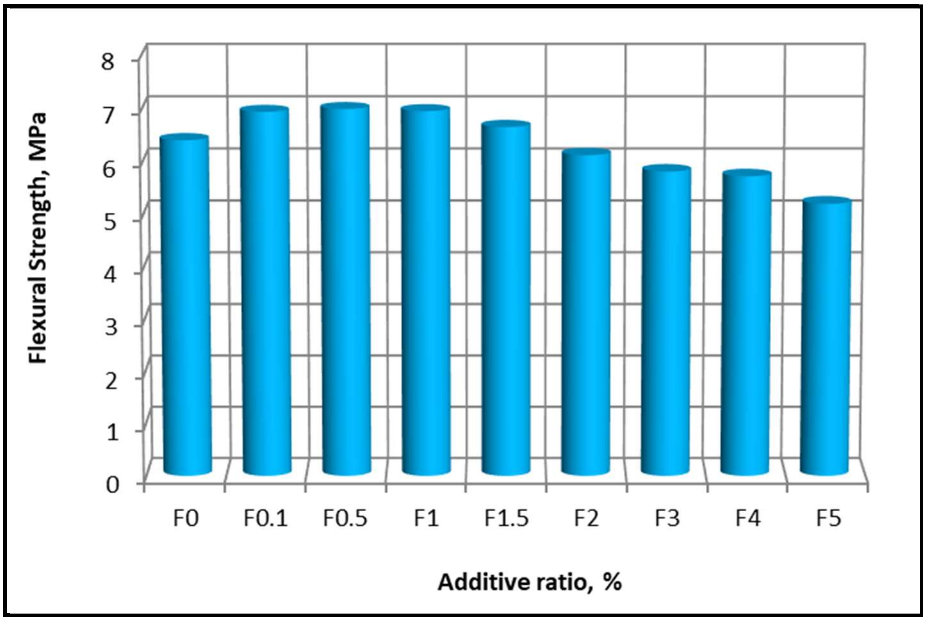


Fig. 4 - Flexural strength of the cement mortar containing Fe_3O_4/humic acid.

2.3. Methods

2.3.1. Flow table experiment

In order to test the workability of the samples, flow table experiments were applied to fresh mortar according to the TS EN 12350-5 [28].

2.3.2. Flexural strength

The flexural test was performed according to TS EN 196-1 [29]. The flexural strength was calculated using Equation 1, given below:

$$R_f = 1.5 \times F_f \times \ell)/b^3 \quad (1)$$

R_f is the flexural strength (MPa); F_f is the load applied to the middle of the prism (N); b is the side of the square section of the prism (mm); ℓ is the distance between the supports (mm).

2.3.3. Compressive strength

In order to perform compressive strength test, the two mortar specimens chunk resulted after the flexural test with 40x40x80 mm sizes were used. Compressive strength test were performed in accordance with TS EN 196-1 [29] and calculated according to Eq. (2):

$$R_c = F_c / 1600, \quad (2)$$

R_c is compressive strength (MPa); F_c is the max. load (N) and 1600 is the area of the face (mm^2) .

2.3.4. Water absorption

After 28 days, water absorption experiments were implemented for composite mortar samples. The specimens were dried in oven for 72 h at 105 ◦C. The initial weight was measured then specimens were put in the water for about 72 h. The final weight was measured and calculated according to Eq. (3).

$$W_A=((W_w - W_d)/W_d)x100, \quad (3)$$

In the equations above W_A is the water absorption percentage (%), W_d is the water absorption percentage (dry weight) (%) and W_w is the water absorption percentage (wet weight) (%).

2.3.5. Microstructure

Scanning electron microscopy (SEM) microstructural studies of mortar specimens with and without nanoparticles have revealed the mechanisms for improved performance with nanoparticles. SEM analyses were made in Tekirdag Namık Kemal University Laboratories, by using FEI Quanta FEG 250 microscope. For this purpose, a small part of composite, from each mortar mixture, was removed around the sand and analyzed in term of microstructure.

3. Results and Discussion

3.1. Workability

The workability of the fresh mortars was determined by the flow table method, and the results are presented in Figure 3.

As can be noticed, the addition of Fe_3O_4/HA did not greatly influence the consistency of the fresh mortars. Slump and slump flow are often used for the assessment of the workability of cementitious composites. A decrease in the flow with increasing nanoparticles content in the composite has been observed in studies [18,30, 31]. This is connected to the small size effect of the nanostructures.

3.2. Flexural strength

Flexural strength values of cement-based mortars are presented in Figure 4. After 28 days, strength values of the samples were in the range 5.2-6.99 MPa.

The highest strength of sample was 6.99 MPa (0.5%). Samples 0.1%, 0.5%, 1% and 1.5% exhibited a slight improvement in flexural strength in comparison to control samples. 0.5% exhibited the highest improvement in flexural strength; by 10%. The results prove that flexural strength results are almost close with that of reference mortar up to cement replacement of 1.5%.

Composite is a mixture of the sand, cement and other components and the interface between these materials. The increase in strength of cement based mortar containing nanomaterials play an important role in improving the sand-paste bond through the transition zone and formation of more calcium silicate hydrate (C-S-H). Thus, Fe_3O_4/humic acid nanoparticles, presents a better contribution to achieve adequate interfaced to the strength.

3.3 Compressive strength

Compressive strengths were given in Figure 5. After 28 days, strength values of the samples were in the range 25.00-34.00 MPa. The specimen containing 0.1% nanoparticles showed the best strength and the one with 1% nanoparticles exhibited a 12% improvement in strength in comparison to the control sample. However, 2 %, 3%, 4% and 5% increase in the content of

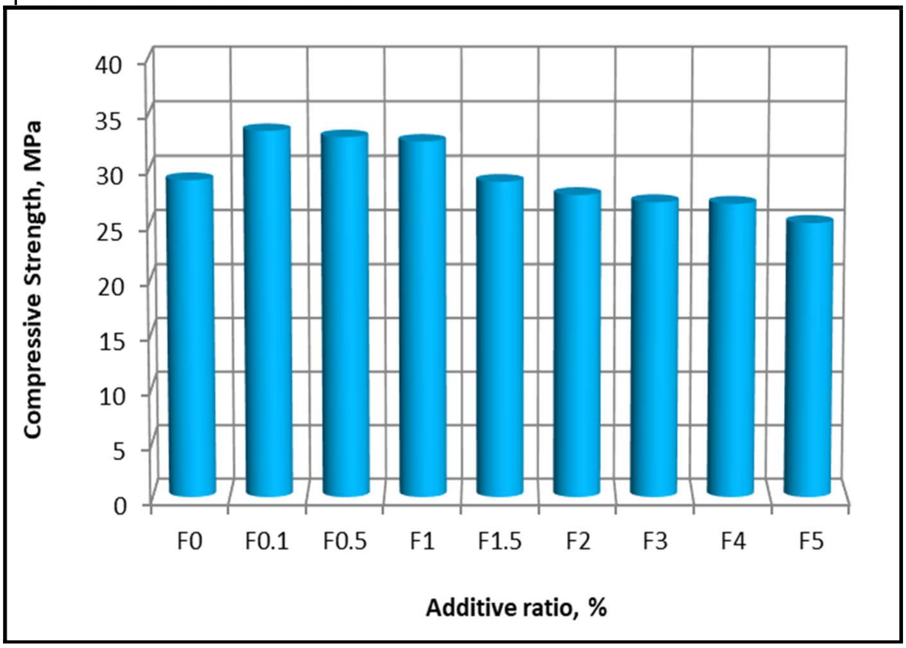


Fig. 5 - Compressive strength of the cement mortar containing Fe_3O_4/humic acid.

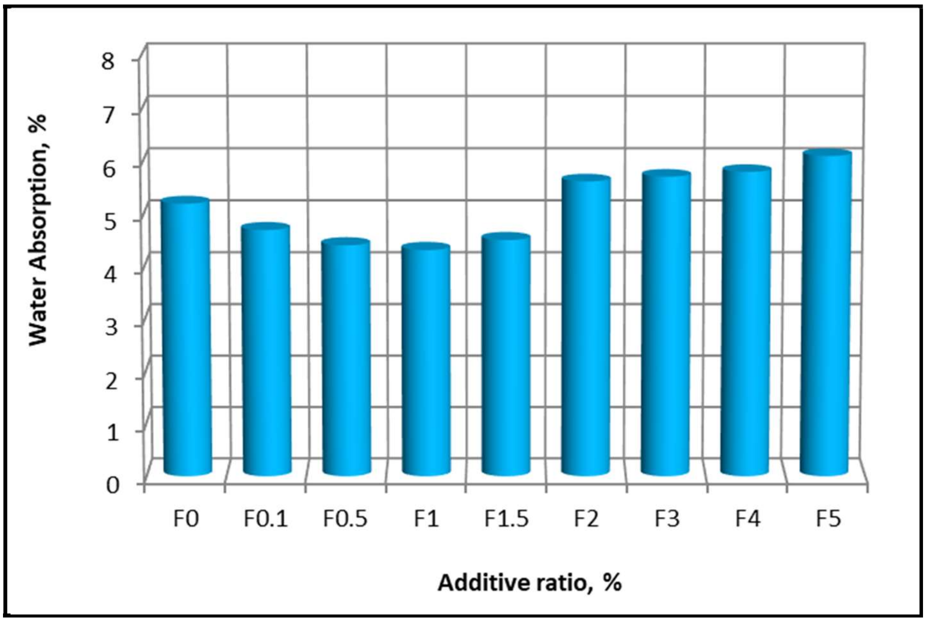


Fig. 6 - Water absorption of the cement mortar containing Fe_3O_4/humic acid.

Fe_3O_4/humic acid nanoparticles, caused a decrease in the sample strength to a level comparable with the control sample. The lowest compressive strength was 25 MPa for the mortar specimen with 5% nanoparticles addition. The strength improvement at the optimal amount of incorporated nanomaterial (0.1%) was attributed to the nucleation and filling effects of iron oxide nanoparticles, leading to the formation of denser and more compacted microstructures [32].

The results showed that compressive strength of samples with different proportions of nanoparticles was significantly increased as compared to the control sample. The presence of Fe_3O_4/humic acid nanoparticles contributed to improvement of compressive strength values (0.1%, 0.5%, 1%, 1.5%), as a result of the nano-filling effect, causing for emerging denser and more compacted microstructures.

3.4. Water absorption

The test was given in Figure 6. It shows that 5% nanoparticles had the highest absorption rate compares to other mixes and 1% nanoparticles exhibited the 18% improvement in water absorption in comparison to the control sample. When the results are compared with control sample value, the effect of nanoparticles amount in mortars mixture in terms of water absorption were positive for 0.1, 0.5, 1, and 1.5% of Fe_3O_4/humic acid nanoparticles content. This occurred due to the micro filler effect. Water absorption properties can be related to the decrease in the amount of pores in the cement paste, because of the addition and homogeneous dispersion of the nanomaterial particles. According of Li et al. [33] the nanoparticles tend to favor the growth of C-S-H crystals, increasing the density of interface transition zone (ITZ) and have a filler effect in concrete. These features allow obtaining a cement paste with a homogeneous microstructure, which may have better physicochemical and mechanical performance [33].

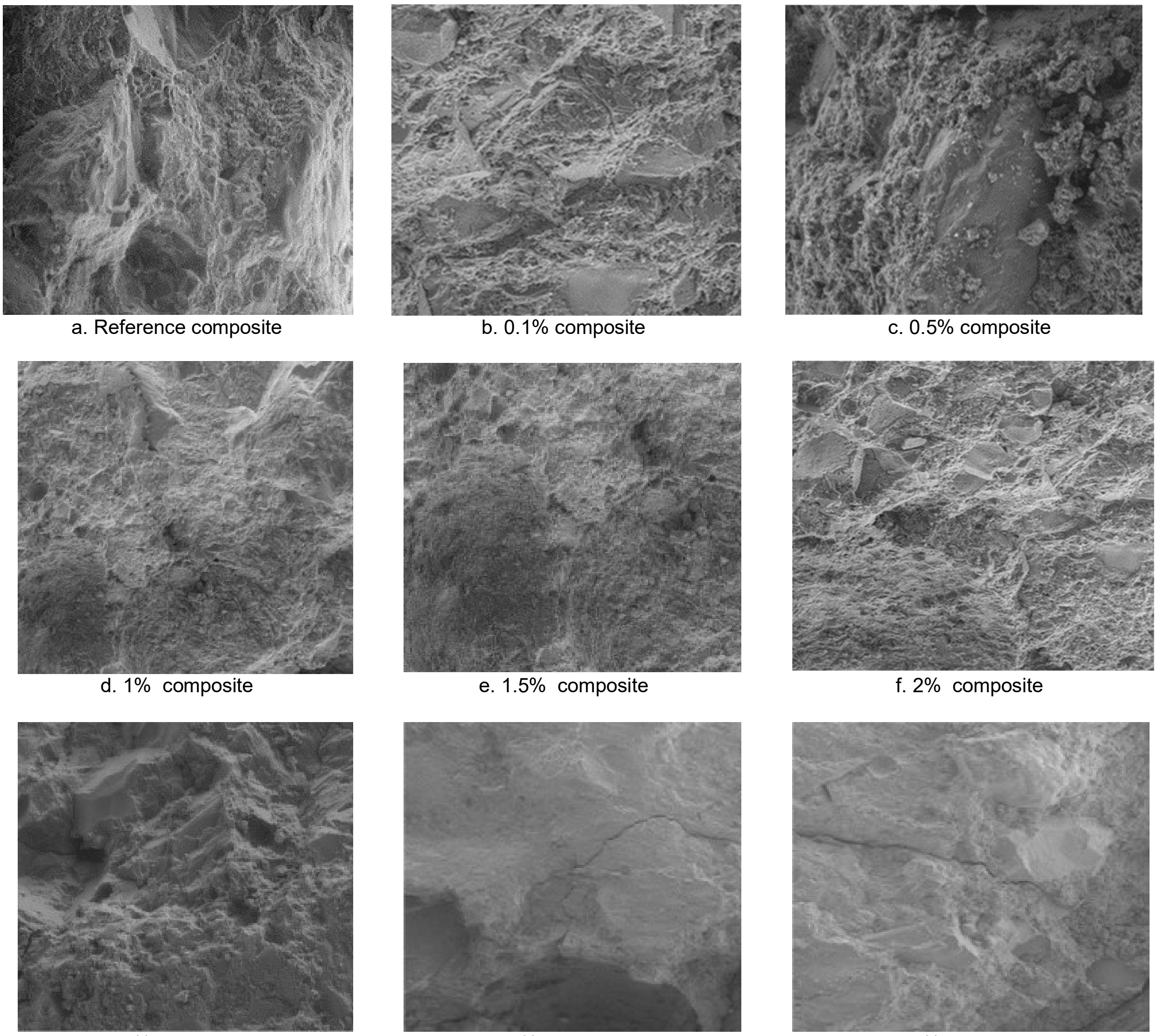
3.5. Microstructure

After 28 days, the microstructure of the different cement mortars specimens was analyzed using SEM. Figure 7b - e corresponds to the mortar specimens with 0.1, 0.5, 1 and 1.5% Fe_3O_4/humic acid nanoparticle content for which the large voids or holes are not observed compared with the reference specimen (Figure 7a). This could be attributed to structure densification after 28 days of curing which indicates a rapid formation of C-S-H gel in the presence of available nanoparticles. Nanoparticles filled the cement pores increasing the strength.
Sikora et al. [32], attributed the increase in compressive strength to the role of magnetite nanoparticles.

It can be appreciated that with the growth of Fe_3O_4/humic acid nanoparticles, the positive effect on properties can be mostly associated with filling impression of the nanoparticles. The SEM analyses results are in good correlation with the water absorption results. In Figure 7f and g, small voids and pores are contained in mortar specimens. As could be seen in Fig. 7h and i, the presence of cracks is obvious which could be explained by the highest content of nanoparticles which leads to poor adhesion between cement matrix and sand particles.

4. Conclusions

This research presented the impact of using Fe_3O_4/humic acid nanoparticles on the



a. Reference composite | b. 0.1% composite | c. 0.5% composite

d. 1% composite | e. 1.5% composite | f. 2% composite

g. 3% composite | h. 4% composite | i. 5% composite

Fig. 7 - SEM analysis.

properties of cement based composite structures. Conclusions were obtained from the overall test results.

- The specimen containing 0.1% nanoparticles showed the best compressive strength, with an increase of about 16% with respect to the control sample. In this regard the Fe_3O_4/humic acid nanoparticles addition likely enabled the cement matrix to have a better microstructures. However, 2 %, 3%, 4% and 5% increase in the content of Fe_3O_4/humic acid nanoparticles, caused a decrease in the sample strength to level comparable with control sample.
- The highest flexural strength of sample was 6.99 MPa. Flexural strength results are almost close with that of reference mortar up to cement replacement of 1.5%. The flexural strength value of cement based mortar with 0.5% of Fe_3O_4/humic acid nanoparticles indicated that the increase of flexural strength was 10% higher than control mixture. It can be concluded that the nanoparticles had a pronounced impact on flexural strength and compressive strength.
- The mortar specimen with 5% nanoparticles addition had the highest absorption rate compares to other mixes and 1% nanoparticles exhibited the 18% improvement in water absorption in comparison to the control sample. The addition of 0.1, 0.5, 1 and 1.5% of Fe_3O_4/humic acid reveals a positive effect on water absorption of cement based composite compared with control mixture.
- The microstructure of mortar specimens with 0.1, 0.5, 1 and 1.5% Fe_3O_4/humic acid nanoparticles was much denser and more compact due to the role in structure densification of iron oxide nanoparticles by nucleation and filling effect.

REFERENCES

[1] G. Schmid, Nanotechnology volume I: principles and fundamentals, Environmental Engineering Management Journal, 2008, **7**(6), 871-873.

[2] S. C. Paul, A. S. van Rooyen, G. P. van Zijl, F. Petrik, Properties of cement-based composites using nanoparticles: A comprehensive review, Construction and Building Materials, 2018, **189**, 1019-1034.

[3] A. K. Rana, S. B. Rana, A. Kumari and V. Kiran, Significance of nanotechnology in construction engineering. International Journal of Recent Trends in Engineering, 2009, **1**(4), 46-48.
[4] P. Casey, Nanoparticle technologies and applications, Nanostructure Control of Materials, 2006, 1-36.
[5] P. Christian, Von der Kammer, M. Baalousha and T. Hofmann, Nanoparticles: structure, properties, preparation and behavior in environmental media, Ecotoxicology, 2008, **17**(5), 326-43.
[6] K. Sobolev, F. Sanchez and I. F. Vivian, The Use of nanoparticle admixtures to improve the performance of concrete. Conference: 12th International Conference on Recent Advances in Concrete Technology and Sustainability Issues, 2012, 455-469.
[7] F. Sanchez and K. Sobolev, Nanotechnology in concrete – A review, Construction and Building Materials, 2010, **24**, 2060–2071.
[8] N. B. Singh, M. Kalra and S. K. Saxena, Materials Today: Proceedings, Nanoscience of Cement and Concrete, 2017, **4**(4), 5478-5487.
[9] S. A., Alyasri, I. S. Alkroosh and P. K. Sarker, Feasibility of producing nano cement in a traditional cement factory in Iraq, Case Studies in Construction Materials, 2017, **7**, 91-101.
[10] I. Hincapie, A. Caballero, G. D. Hiltbrunner and B. Nowack, Use of engineered nanomaterials in the construction industry with specific emphasis on paints and their flows in construction and demolition waste in Switzerland, Waste Management, 2015, **43**, 398–406.
[11] J. Silvestre, N. Silvestre and J. de Brito, Review on concrete nanotechnology, European Journal of Environmental Civil Engineering, 2015, **20**(4), 1-31.
[12] J. Lee, S. Mahendra and P. J. J. Alvarez, Nanomaterials in the construction industry: A review of their applications and environmental health and safety considerations, ACS Nano 2010, **4**, 3580–3590.
[13] A. Slosarczyk, A. Kwiecinska and E. Pelszyk, Influence of selected metal oxides in micro and nanoscale on the mechanical and physical properties of the cement mortars, Procedia Engineering, 2017, **172**, 1031-1038
[14] N. Elahi, M. Kamali and M. H. Baghersad, Recent biomedical applications of gold nanoparticles: a review, Talanta, 2018, **184**, 537-556.
[15] M. Krystek and M. Gorski, Nanomaterials in Structural Engineering, 2018, Publisher: IntechOpen
[16] M. S. M. Norhasria, M. S. Hamidah and A. M. Fadzil, Applications of using nano material in concrete: A review, Construction and Building Materials, 2017, **133**, 91-97.
[17] L. Wang, H. Zhang and Y. Gao, Effect of TiO_2 nanoparticles on physical and mechanical properties of cement at low temperatures, Advances in Materials Science and Engineering, 2018, Volume 2018, Article ID 8934689.
[18] E. Horszczaruk, Properties of cement-based composites modified with magnetite nanoparticles-a review. Materials, 2019, **12**(2), 1-34.
[19] W. Jones, A. Gibb, C. Goodier, P. Bust, M. Song and J. Jin, Nanomaterials in construction – what is being used, and where? Proceedings of the Institution of Civil Engineers: Construction Materials, 2016, https://doi.org/10.1680/jcoma.16.00011.
[20] The Royal Society & The Royal Academy of Engineering, Nanoscience and nanotechnologies: opportunities and uncertainties, Publisher: Royal Society, 2004.
[21] G. Q. Bianchi, Application of nano-silica in concrete, PhD Thesis Eindhoven University of Technology Netherlands, 2014.
[22] J. M. Makar and J. J. Beaudoin, Carbon nanotubes and their application in the construction industry, Nanotechnology in Construction, 2003, **57**, 331 – 341.
[23] S. Jahangir and S. Kazemi, Effect of nano-alumina (n-al) and nanosilica (ns) as admixtures on concrete behavior, International Conference on Advances in Agricultural, Biological & Environmental Sciences (AABES-2014) Dubai (UAE), 2014, 37-41.
[24] B. Han, S. Ding, J. Wang and J. Ou, Nano-Engineered Cementitious Composites Principles and Practices, 2019, Publisher:Springer
[25] M. Bolhassani and M. Sayyahmanesh, A study on mechanical properties of cement paste using magnetite-silica nano-composites, Advances in Cement Research, 2015, **27**(10), 571-580.
[26] K. S. Prabha and A. K. Thajudeen, Experimental Study on Properties of Concrete USNG Humic Acid, International Journal of Scientific and Research Publications, 2015, **5**(8), 1-4.
[27] M. Amir, S. Güner, A. Yıldız and A. Baykal, Magneto-optical and catalytic properties of Fe_3O_4@ HA@ Ag magnetic nanocomposite, Journal of Magnetism and Magnetic Materials, 2017, **421**, 462-471.
[28] TS EN 12350-5:2010 Testing fresh concrete - Part 5: Flow table test, Turkish Standard, Turkey.
[29] TS EN 196-1:2016 Methods of testing cement - Part 1: Determination of strength, Turkish Standard, Turkey.
[30] Y. Reches, Nanoparticles as concrete additives: Review and perspectives, Construction and Building Materials, 2018, **175**, 483-495
[31] M. Berra, F. Carassiti, T. Mangialardi, A.E. Paolini, M. Sebastiani, F. Carassiti, T. Mangialardi, A. E. Paolini, M. Sebastiani, Effects of nanosilica addition on workability and compressive strength of Portland cement pastes. Construction and Building Materials, 2012, **35**, 666–675.
[32] P. Sikora, E. Horszczaruk, K. Cendrowski, and E. Mijowska, The Influence of Nano-Fe_3O_4 on the Microstructure and Mechanical Properties of Cementitious Composites, 2016, Nanoscale Research Letter, **11**, 182.
[33] H. Li, H. Xiao, J. Ou, A Study on Mechanical and Pressure-Sensitive Properties of Cement Mortar with Nanophase Materials. Cement and Concrete Research, 2004, **34**, 435-438.

****