INVESTIGATION OF EFFECT OF WATER/CEMENT RATIO- DC CURRENT AND GRAPHENE OXIDE ON POROSITY- MATURITY AND ELECTRICAL CONDUCTIVITY OF HARDENED MORTARS

İSMAİL HOCAOĞLU *
Afyon Kocatepe University, Bolvadin Vocational School, Civil Department, 03300, Afyonkarahisar, Turkey

Today, materials are produced with nanotechnology, which are new products as a result of the development of technology. For cement-based composites, porosity is very important in terms of the strength and durability of the material after the material hardens. Today, with the innovations in technology, new materials are produced in the construction sector. New generation materials are produced on nano-meter scale using nanotechnology. These materials are used in cement-based composites to reduce porosity and improve durability properties. This research is aimed to reduce the porosity of the mortars by adding the nanomaterial graphene oxide (GO) to cement-based mortars whose sizes are 4cm x 4cm x 16cm. To investigate the effect of graphene oxide on porosity, series were produced as water/cement ratios are 0.55, 0.70, 0.90, and 1.00, by substituting 0.025 % GO in the mortars instead of cement. Besides, to investigate the effect of DC stress intensity on porosity, 25 V DC current is applied to all series. Mortar internal temperatures were measured from the beginning of hydration reactions in fresh mortars. Various comparisons have been made by calculating the maturity values of the mortars. Hardened mortars were cured for 7 and 28 days, then current passes on the mortars were measured by using an ampere meter. It has been investigated whether a relationship can be established between flow transfer and porosity. As a result of this study, the porosity of mortars can be reduced and maturity values can be increased by adding GO to cement-based mortars and applying DC current. In addition, porosity of cement-based materials can be estimated by using electrical methods.

Keywords: *Nanomaterial; Graphene oxide; DC current; Porosity; Electrical measurement*

1. Introduction

Cement-based composite materials constitute the most preferred building materials today. Porosity is extremely important in terms of the strength and durability of the cement-based matrix. With the innovations brought by technology, nano-scale materials are used for cement-based materials [1-3]. Some investigations show that; GO is homogeneously distributed in the cement matrix [4]. As a result of this situation, it helps to reduce the porosity of cement-based systems. Jing et al. [5] added a 0.03 % ratio GO to the cement mortar. They concluded that cement hydration can be accelerated and porosity can be reduced with the addition of graphene oxide. Indukuri et al. [6] observed that graphene oxide brought the naturally porous structure of the cement-based composite to a pore structure that would improve mechanical properties. Muthu et al. [7] concluded that when adding up to 0.045 % graphene oxide by weight to cement matrixes, porosity can be reduced and micro-cracks can be closed. In another study, micro-examination analyzes were performed on cement-based composites by substituting GO in different proportions instead of cement. It has been concluded that by adding GO to cement-based composites, porosity can be reduced and compressive strength can be increased [8]. Some researches investigating the electrical properties of cement-based mortars. Cement-based materials are electrically insulating, especially when dry [9]. Therefore, in cement-based composites, electrical conductivity is achieved primarily by ion transport in the porous solution in its fresh state in the cement-based material. It is of great importance to evaluate the hydration process of cement-based materials at an early stage [10,11]. There are limited studies in the literature involving both the use of graphene oxide and the application of current to reduce the porosity of cement-based composite materials. Therefore, this study is of great importance.

In this study, it is aimed to reduce the porosity of cement-based mortars by adding 0.025 % GO instead of cement and applying 25 V DC stress intensity. It is also investigated whether a relationship could be established between current passage and porosity by measuring the currents passing over to mortars which are cured for 7 and 28 days. In addition; The effect of GO and DC current application on the maturity of the mortars has been also investigated.

2. Materials and methods

2.1. The material used and their properties/features

In the preparation of the cement-based mortars, CEM I 42.5 R type cement, which is produced by Afyonkarahisar Cement Industry Factory, in accordance with TS EN 197-1, was used as cement [12]. The proportions of C_3S, C_2S, C_3A, and C_4AF in the cement are 60.11 %, 11.02 %, 6.97%, and 9.95 %, respectively, and are

* Autor corespondent/*Corresponding author*,
E-mail: ihocaoglu@aku.edu.tr

Table 1

Physical and chemical features of cement.

Content, %	CEM I 42.5 R
CaO	63.60
SiO_2	19.60
Al_2O_3	4.72
Fe_2O_3	3.27
MgO	1.91
Na_2O	0.34
K_2O	1.06
SO_3	4.72
Cr_2O_3	0.04
TiO_2	0.41
KK	2.69
Specific weight	3.10
Fineness, cm^2/g	3308
28-day compressive strength, MPa	53.20

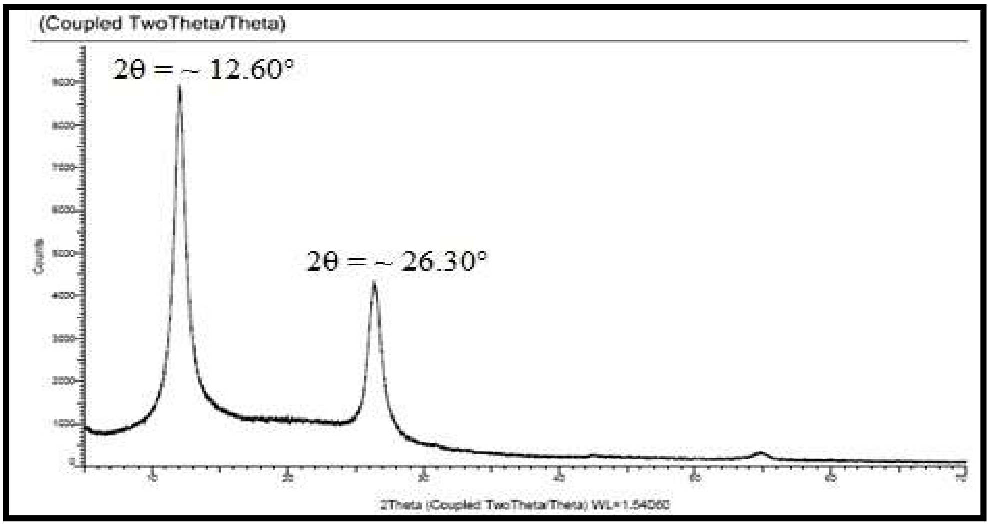


Fig. 1- XRD (X-ray diffraction) spectroscopy analysis of graphene oxide.

Table 2

Component of mortar per cubic meter

	Mortar Mixture Ratio			
W/c	**Cement, kg/m^3**	**Aggregate, kg/m^3**	**Graphene oxide, kg/m^3**	**Water, lt/m^3**
0.55	300	1891.10	-	165.00
0.70	300	1790.40	-	210.40
0.90	300	1631.20	-	270.40
1.00	300	1551.20	-	300.00
0.55	299.92	1891.10	0.075	164.95
0.70	299.92	1790.40	0.075	209.94
0.90	299.92	1631.20	0.075	269.92
1.00	299.92	1551.20	0.075	299.92

shown in Table 1. Potable tap water was used in the mortar mixture.

2.2. Graphene oxide

Graphene oxide production was produced by the method developed by Marcano et al. [13]. XRD (X-ray diffraction) analysis has been performed to investigate whether graphene oxide has been formed and it is shown in Figure 1. The formation of peaks in Figure 1 means that graphene oxide has been formed [14].

(a) (b) (c)

Fig.2- A view of a-cement, b- aggregate, and c- graphene oxide to which has used in experiments.

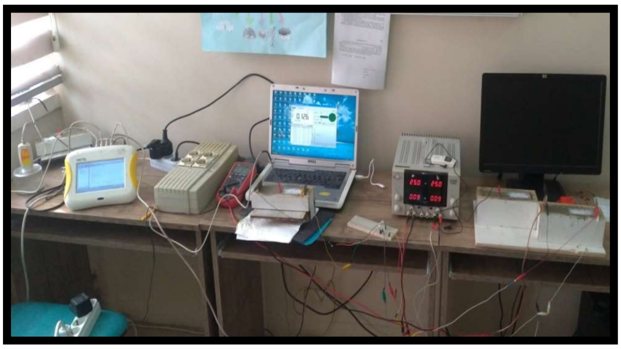


Fig. 3- A view of the test setup.

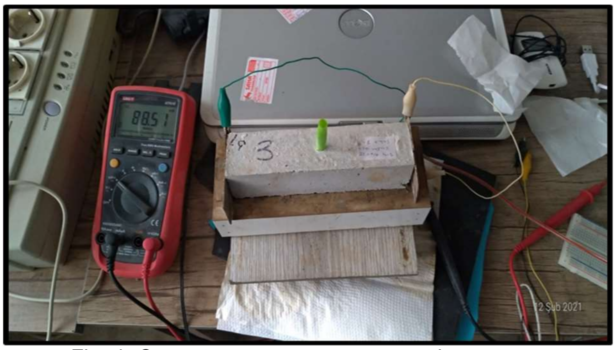


Fig. 4- Current passage measurement in mortars.

2.3. Production of the specimen and the experiments conducted

300 dossaged (300 kg cement in 1 m^3 mortar) mortars were produced as water/cement ratios are 0.55, 0.70, 0.90, and 1.00, by substituting 0.025 % GO in the mortars instead of cement. While the mortar was being produced, first; with cement, aggregate, and graphene oxide the dry mixture was made, and then the admixture was mixed with water for 5 minutes. Cement (OPC), aggregate, and graphene oxide (GO) are shown in Figure 2. The component of mortar per cubic meter is shown in Table 2. The specific gravity of crushed sand was measured as 2.68.

Immediately after the mixture was prepared, the mortars were placed in 4cm x 4cm x 16cm prismatic wooden molds. Steel plates whose sizes are 3.5cm and 5 cm were placed at the ends of the molds. 25 V stress intensity was applied to the mortars for 24 hours through the DC power supply (Figure 3). To examine the effect of graphene oxide on porosity, current passage and, maturity, mortars containing 0.025 % GO were produced in all series. Reference and electric current applied mortars were cured in water saturated with lime for 7 and 28 days. In mortars which are cured for 7 and 28 days, the current passage on the mortars was measured by using an ampere meter (Figure 4).

3. Results and Discussion

3.1. Porosity of Mortars

Mortars to which cured for 7 and 28 days, the saturated surface dry, oven dry, and their weight in water were measured. Then porosity ratios were calculated using the equation (1).

$$Porosity = \left[\frac{W_2 - W_0}{W_2 - W_1} \right] X100 \qquad (1)$$

In equation W_0-W_1 and W_2 are explained below;

W_2= Weight in saturated air (g)

W_1= Weight in water (g)

W_0= weight of the oven-dry (g).

Figure 5 and Figure 6 are prepared to compare the porosity ratios of mortars. Examining the 7-day porosity of the mortars, it is determined that both 0.025 % GO is added and 25 V DC current is applied to the mortars the porosity rate can be reduced (Figure 5). It is observed that the most effective water/cement ratio is 0.70 to reduce the porosity of the mortars to which were cured for 7 days. When the mixtures with a water/cement ratio of 0.70 were examined, it was seen that the void ratio decreased by approximately 37.40 % compared to the reference sample by using both 0.025 % GO instead of cement and applying 25 V DC stress intensity. In general, for all water/cement ratios, the highest porosity values were observed in samples without graphene oxide and without electric current application. In mixtures with a water/cement ratio of 1.00, it has been observed that the DC current application and GO addition to mortars have a negative effect on porosity.

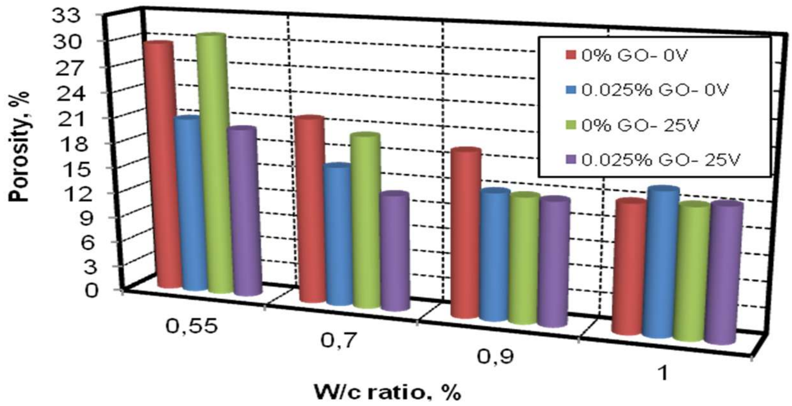


Fig. 5- 7-Day porosity of mortars depending upon GO and DC current.

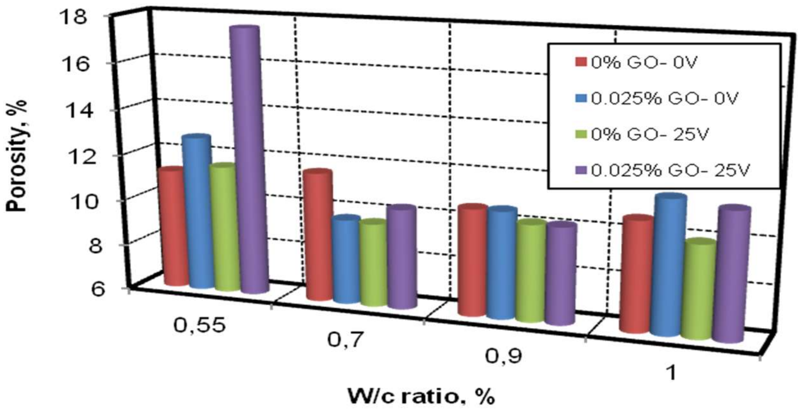


Fig. 6- 28-Day porosity of mortars depending upon GO and DC current.

Table 3

The porosity of mortars according to grapheme oxide ratio and DC current application

Day	GO - Current	Water/cement ratio (%)			
		0.55	0.70	0.90	1.00
7 Day Porosity	0 % GO – 0V	29.63	21.87	19.36	14.94
	0.025 % GO- 0V	20.96	16.51	14.94	16.57
	0 % GO – 25V	30.84	20.31	14.72	15.10
	0.025 % GO- 25V	20.11	13.69	14.51	15.44
28 Day Porosity	0 % GO – 0V	11.23	11.62	10.62	10.71
	0.025 % GO- 0V	12.77	9.69	10.62	11.70
	0 % GO – 25V	11.57	9.61	10.17	9.95
	0.025 % GO- 25V	17.59	10.34	10.17	11.42

When Figure 6 is examined, it was observed that the 28-day porosity of the mortars generally has taken the lowest values in the mortars with 0.70 and 0.90 water/cement ratios. When DC current is applied to the mortars, it has been observed that the porosity decreases.

The highest porosity in mortars with a water/cement ratio of 0.55 is due to insufficient water for hydration reactions. It was observed that the porosity of mortars increases, when adding GO to mortars whose water/cement ratio has 0.55.

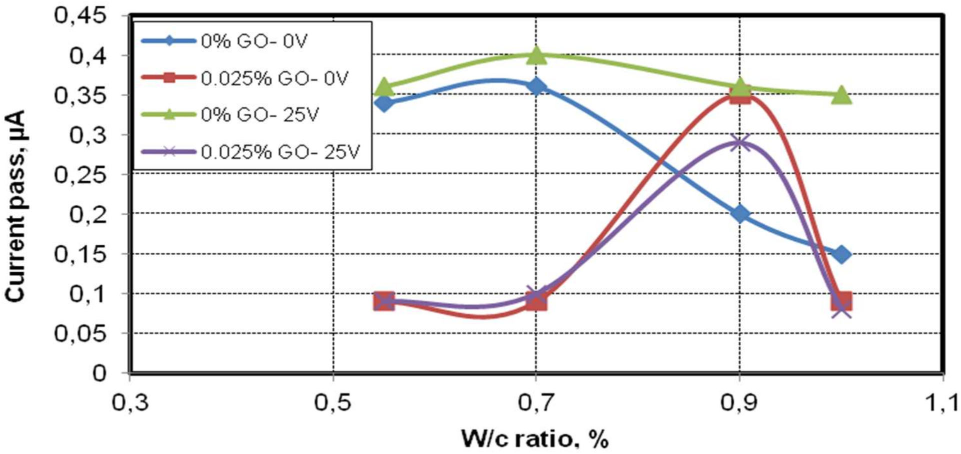


Fig. 7- 7-Day current passage on mortars depending upon GO and current application.

Table 4

Current passage on mortars according to grapheme oxide ratio and DC current application

Day	GO - Current	Water/cement ratio (%)			
		0.55	0.70	0.90	1.00
7 Day Current Passage, Ma	0 % GO – 0V	0.34	0.36	0.20	0.15
	0.025 % GO- 0V	0.09	0.09	0.35	0.09
	0 % GO – 25V	0.36	0.40	0.36	0.35
	0.025 % GO- 25V	0.09	0.10	0.29	0.08
28 Day Current Passage, Ma	0 % GO – 0V	0.40	0.32	0.36	0.39
	0.025 % GO- 0V	0.43	0.41	0.40	0.39
	0 % GO – 25V	0.44	0.34	0.39	0.36
	0.025 % GO- 25V	0.48	0.45	0.42	0.47

This situation can be explained by the absorption of some water by GO. The porosity of the mortars decreased approximately by 11.01 and 4.23 %, compared to the reference samples with the addition of GO and DC current application in the mortars with water/cement ratios of 0.70 and 0.90, respectively (Table 3).

3.2. Current Pass of Mortars

When the 7-day current passage values of the mortars were compared at the rate of 0.55 and 0.70 water/cement, it was observed that the lowest current passage values were obtained as a result of both the use of GO and the DC current application (Figure 7). As a result of this situation, it can be interpreted that these water/cement ratios have a high void ratio. When the water/cement ratio is 0.90, it can be explained by the fact that the current passage is higher than the others, especially in the mortars with DC current applied and GO addition, takes the lowest void ratio at the 0.90 water/cement ratio. According to whether it contains GO in mixtures and whether current is applied or not (0 % GO- 0V, 0.025 % GO- 0V, 0 % GO- 25V, 0.025 % GO-25V) and 7 days cured mortars with 0.90 water/cement ratios, the current passage values have been measured as 0.20, 0.35, 0.36 and 0.29 µA, respectively (Table 4). It has been observed that the mortar that current is applied and with GO, has less electrical conductivity than the mortar that current is not applied and with GO, at this water/cement ratio.

Figure 8 is prepared to compare the 28-day flow passage rate of mortars. With the addition of GO to the mortars, a higher current flow passage was observed to which compared to the reference sample. At the same time, it has been observed that the current flow passage has taken high The high value of the current passage means that the mortars have low porosity. In mortars with water/cement ratios of 0.55, 0.70, 0.90, and 1.00, the current passages were measured as 0.48, 0.45, 0.42, and 0.47 µA, respectively, by substituting 0.025 % GO for cement and

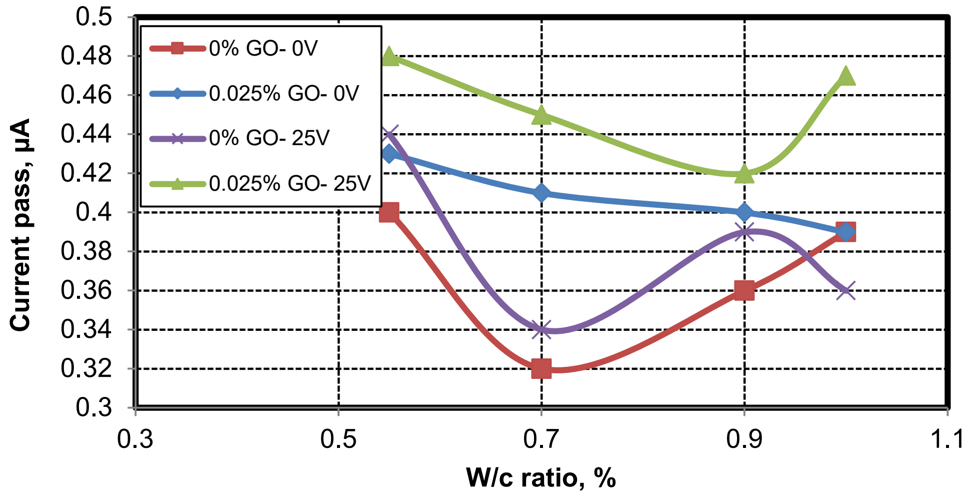


Fig. 8- 28-Day current passage on mortars depending upon GO and current application.

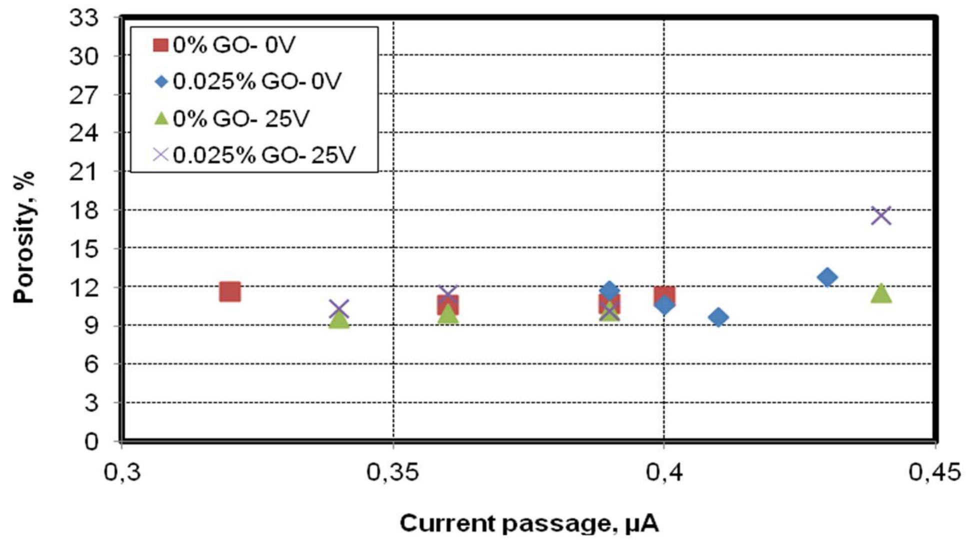


Fig. 9- Relationship between porosity and current passage.

applying 25 V stress intensity (Table 4). In mortars with GO, the highest current passage values were generally observed in mortars to which have 0.70 and 0.90 water/cement ratios. The fact that mortars with a water/cement ratio of 0.55 and adding GO to admixture, have a higher current passage than the other water/cement ratios can be explained by the high electrical conductivity of graphene oxide due to its carbon content.

3.3. Relationship between porosity and current passage

Figure 9 is prepared to investigate whether there is a relationship between porosity and current passage. In general, the optimum porosity for all mixtures was observed in mortars to which have 0.70 and 0.90, water/cement ratios. The lowest porosity values were observed when the current flow rate was between 0.35-0.40 (Figure 9).

Although the current flow between 0.40 and 0.45 takes high values, the increase of the porosity can be explained by the increase of water in the mixture. As the amount of water in the mixture increased, the porosity is increased because the mixture would contain more water than required for hydration.

To establish a relation between current passages and porosity of mortars which are cured for 28 days whose water/cement ratios are 0.55, 0.70, 0.90, and 1.00 graphics have been prepared (Figs. 10 a-b-c-d). In Figs. 10, X-axis represents current passage, and Y-axis represents porosity. In Figure 10, whether the mortars contain GO and whether current is applied or not are examined. As a result of forming a trend line, equations of porosity depending on the GO and DC current application of the mortars have been

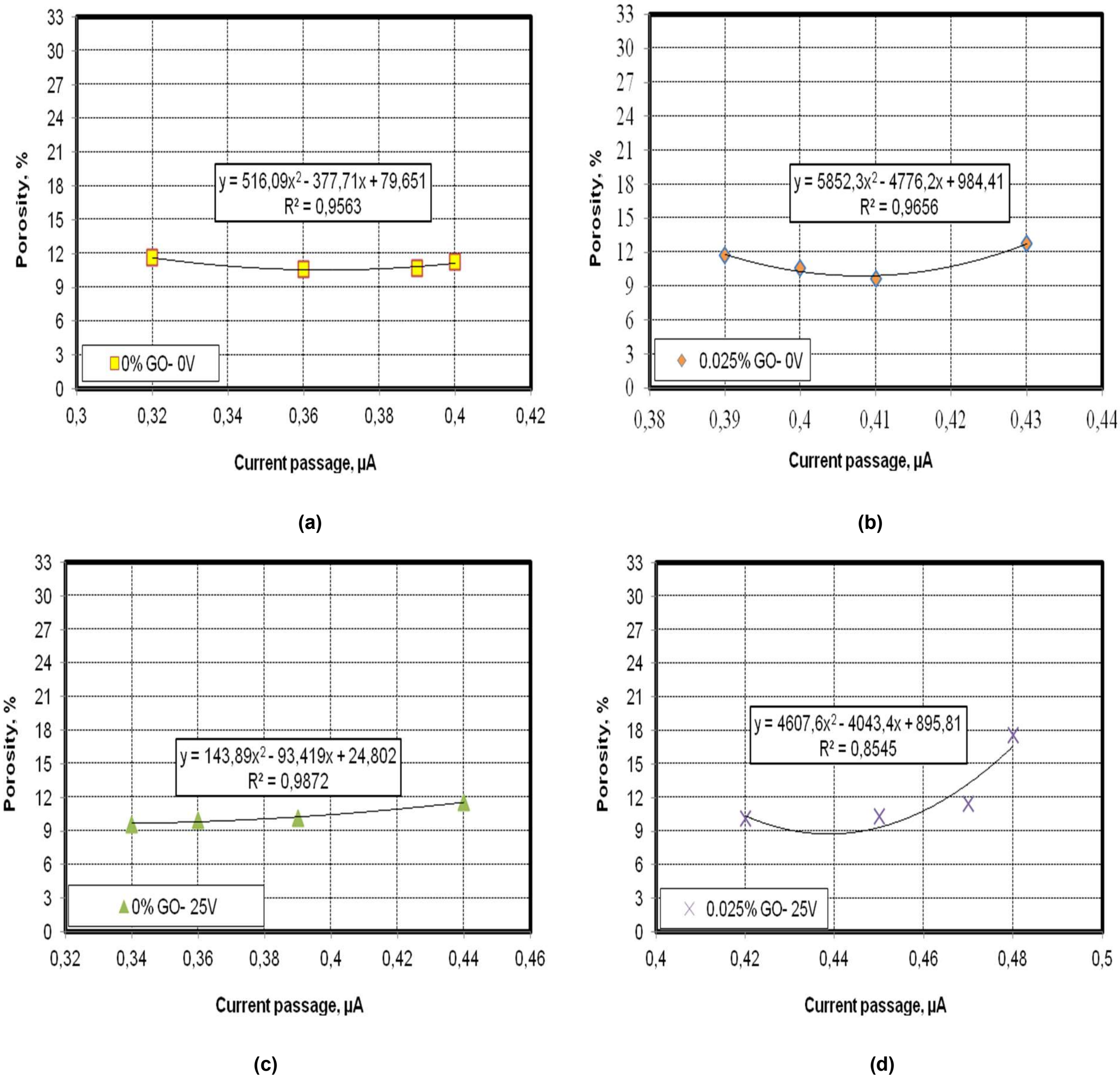


Fig. 10- Relationship between porosity and current passage according to GO and current application (a- 0 V-0 % GO, b- 0 V- 0.25 % GO, c- 25 V- 0 % GO, d- 25 V- 0.025 GO).

Table 5

Equation and correlation coefficient for the relationship between porosity and current passage of mortars

GO - Current	Equation	R^2
0 % GO – 0V	$y = 516{,}09x^2 - 377{,}71x + 79{,}651$	$R^2 = 0{,}9563$
0.025 % GO- 0V	$y = 5852{,}3x^2 - 4776{,}2x + 984{,}41$	$R^2 = 0{,}9656$
0 % GO – 25V	$y = 143{,}89x^2 - 93{,}419x + 24{,}802$	$R^2 = 0{,}9872$
0.025 % GO- 25V	$y = 4607{,}6x^2 - 4043{,}4x + 895{,}81$	$R^2 = 0{,}8545$

determined. It is concluded that the porosity of the mortars can be estimated by measuring the current passage on mortars to which are cured for 28 days.

This study is important because the porosity of cement-based materials directly is related to compressive strength and durability [15]. Hence estimating the porosity of cement-based systems are quite important for a building's service life. It is also aimed in this research decrease of mortar's porosity with GO addition and DC current application. A relationship between porosity and current passage on mortars can be calculated as given in Table 5.

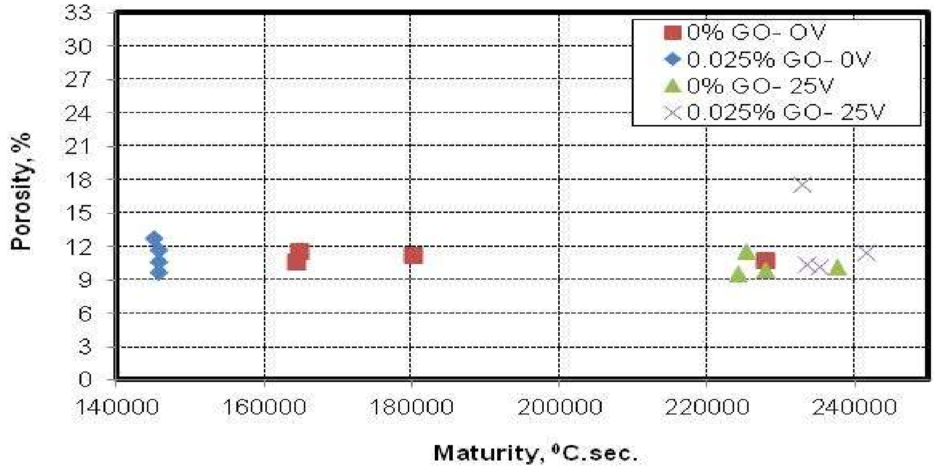
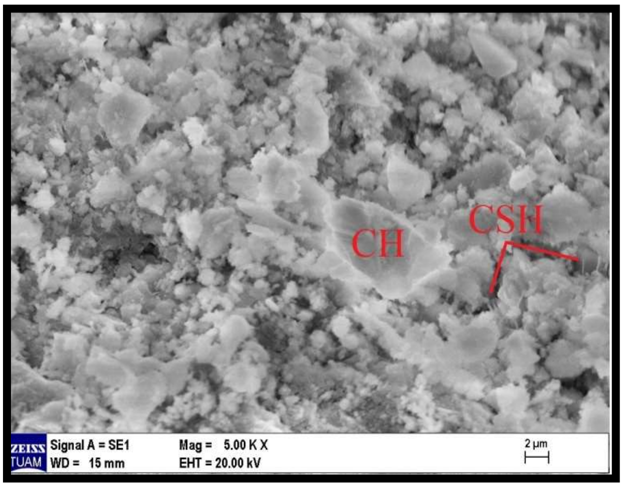
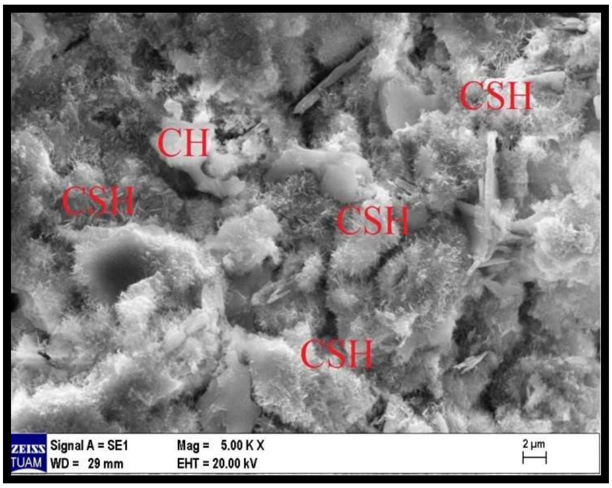


Fig. 11- Relationship between porosity and maturity according to GO and current application.



(a)



(b)

Fig. 12- Microstructure photos of mortars a- 0 V-0 % GO, b- 25 V- 0.025 % GO).

3.4. The relationship between maturity and porosity of mortars

It is important for us to have an idea in terms of maturity, strength and, durability in cement-based composites. Some studies have concluded that the determination of maturity in cement-based materials can be associated non-destructively with compressive strength [16]. In this study, the effect of GO on maturity in the early stages of hydration was investigated. It has been also investigated the effect of DC stress intensity on maturity. On the other hand, it has been investigated whether a relationship can be established between maturity and porosity in cement-based materials. In order to calculate the maturity values of cement-based mortars, the internal temperatures of the mortars from the beginning of the hydration reactions in all mixtures, were recorded in the data logger at 60 second intervals. The maturity values of the mortars were calculated with the help of Formula 2. Figure 11 was prepared to compare the maturity of the mortars after hardened (approximately 11 hours). When Figure 11 was examined, the lowest maturity values were obtained by substituting 0.025% GO for cement. As a result of this situation; It is thought that graphene oxide, which is used instead of cement, slows down the formation time of hydration reactions in the early stages of hydration. It was observed that maturity values are increased noticeably in mortars to which is applied 25 V DC current.

$$M = \sum_{0}^{t}(T - T_o)\Delta t \qquad (2)$$

In this formula; The maturity index M has defined as the average concrete temperature (°C) in the time interval T Dt, the initial temperature T_0, the elapsed time t, and the time interval Dt [17]. The maturity value estimation of the mortars was made according to the ASTM C1074-14 standard [18].

3.5. Micro examination of mortars

The strength of cement-based materials depends on the amount of C-S-H gels. In the first stages of hydration, the hydration of the main component of C_3S takes place faster than the hydration of the C_2S main component, so the contribution of C_3S to the strength increase is higher in the early stages. [19]. The microstructure of the mortar cured for 28 days to which does not contain GO with a 0.70 water/cement ratio is shown in Figure 12a. Figure 12b represents the microstructure of the mortar with both containing 0.025 % GO and 25 V DC stress intensity is applied and 28 days cured water/cement ratio 0.70. It was observed that the hydration reactions started in the mortar to which does not contain GO and current is not applied, CH and CSH products started to form recently. When Figure 12b was examined, it was observed that CSH gels increased on a large scale by substituting a small amount of GO (0.025 %) instead of cement and applying DC current. High CSH gel formation means low porosity.

4. Conclusion

Nanotechnology products such as graphene oxide provide innovation in cement-based mortars and concrete by adding a new vision to building materials.

Several conclusions and suggestions can be drawn from this study:

- As a result of this study, the porosity of mortars can be reduced both by adding GO to cement-based mortars and applying DC current.
- It is seen that the most effective water/cement ratio were 0.70 and 0.90 for 28 days of porosity.
- With the addition of GO to the mortars, a higher current flow passage was observed compared to the reference sample.
- It is determined that the porosity of cement-based materials can be estimated by using electrical methods.
- It was observed that the void ratio was decreased by approximately 37.40 % compared to the reference sample with the addition of 0.025 % GO instead of cement and the application of 25 V DC stress intensity.
- When examined the mortars' maturity-porosity graph (without current application), it is observed that the porosity and maturity had been taken low values in the mortars containing GO. As a result of this situation, by adding GO to cement-based materials, physical properties of mortars can be improved and, GO can be used as a set retarder at the beginning stages of hydration.
- The maturity values of the mortars can be increased without increasing porosity due to adding GO to cement-based materials and applying DC current.
- When the microstructure of the mortars was examined, it was observed that CH and CSH gels, which give strength and durability to the cement-based matrix, were formed more frequently with addition GO and the application of DC current.

It is thought that the study can be developed with the use of GO at different amounts and with the application of different stress intensities.

ACKNOWLEDGEMENTS

A tiny portion of this study was presented as a preliminary study and abstract at the 4th International Istanbul Research Congress.

REFERENCES

[1] K. Sobolev, S.P. Shah, Nanotechnology in construction, Proceedings of NICOM5. Chicag. USA, 2015. https://doi.org/10.1007/978-3-319-17088-6

[2] F. Sanchez, K. Sobolev, Nanotechnology in concrete– A review, Constr. Build. Mater., 2010, **24**(20), 60-71.

[3] X. Li, A. H. Korayem, C. Li, Y. Liu, H. He, J. G. Sanjayan, W. H. Duan, Incorporation of graphene oxide and silica fume into cement paste: a study of dispersion and compressive strength, Constr. Build. Mater., 2016, **123**, 327–335.

[4] S. P. Avanish, M. Monika, C. Amita, S. K. Dhawa, Graphene oxide-ferrofluid-cement composites for electromagnetic interference shielding application, Nanotechnology, 2011, **22**(46), 46-57.

[5] G. J. Jing, Z. M. Ye, C. Li, J. Cui, S. X. Wang, X. Cheng, A ball milling strategy to disperse graphene oxide in cement composites, New Carbon Materials, 2019, **34**(6), 569–577. https://doi.org/10.1016/S1872-5805(19)60032-6

[6] C. S. R Indukuri, R. Nerella, S. R. C Madduru, Effect of graphene oxide on microstructure and strengthened properties of fly ash and silica fume based cement composites Construction and Building Materials, 2019, **229**(11) 63-68. https://doi.org/10.1016/j.conbuildmat.2019.116863

[7] M. Muthu, E. H. Yang, C. Unluer, Resistance of graphene oxide-modified cement pastes to hydrochloric acid attack, Construction and Building Materials, 2021, **273** (90), 12-19. https://doi.org/10.1016/j.conbuildmat.2020.121990

[8] K. Chintalapudi, R. M. R. Pannem, Strength properties of graphene oxide cement composite", Materials Today: Proceedings, 2020, xxxx. https://doi.org/10.1016/j.matpr.2020.08.369

[9] B. Shuya, J. Linhua, J. Yu, J. Ming, J. Shaobo, T. Debiao, Research on electrical conductivity of graphene/cement composites, Advances in Cement Research, 2020, **32**(2), 45-52.

[10] L. Z. Xiao, Z. J. Li, X. S. Wei, Selection of superplasticizer in concrete mix design by measuring the early electrical resistivities of pastes, Cement and Concrete Composites, 2007, **29,** 350-356. https://doi.org/10.1016/j.cemconcomp.2006.12.015

[11] N. Schwarz, M. DuBois, N. Neithalath, Electrical conductivity based characterization of plain and coarse glass powder modified cement pastes, Cement and Concrete Composites, 2007, **24,** 2060-207. https://doi.org/10.1016/j.cemconcomp.2007.05.005

[12] EN 197-1, Cement. Composition, specifications and conformity criteria for common cements, European Standard, 2011.

[13] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, Improved synthesis of graphene oxide, ACS Nano, 2010, **4**(8), pp. 4806-4814. https://doi.org/10.1021/nn1006368

[14] H. Alma, M. Yazici, B. Yildirim, B. Salan, I. Tiyek, Coating and characterization of nano-sized graphene on spunbond nonwoven textile surface by electro drawing method, Textile and Engineer, 2007, **24**(108), 243–253. https://doi.org/10.7216/1300759920172410803

[15] P. Wang, N. Li, L. Xu, Hydration evolution and compressive strength of calcium sulphoaluminate cement constantly cured over the temperature range of 0 to 80 ^{0}C, Cement and Concrete Research, 2017, **45,** 204–213. https://doi.org/10.1016/j.cemconres.2017.05.025

[16] C. Hu, Microstructure and mechanical properties of fly ash blended cement pastes, Construction and Building Materials, 2014, **73,** 618 –625. https://doi.org/10.1016/j.conbuildmat.2014.10.009

[17] A. G. A. Saul, Principles Underlying the Steam Curing of Concrete at Atmospheric Pressure, Magazine of Concrete Research, 1951**, 6**, 127-140.

[18] ASTM International, ASTM C1074-14: Estimating Concrete Strength by the Maturity Method, West Conshohocken, PA, 2011.

[19] T. Y. Erdoğan, Concrete, ODTÜ Geliştirme Vakfı ve Yayıncılık A.Ş. Ankara, 2003, 741.

****