Juniper Online
Journal Material Science
ISSN: 2575-856X

Research Article
Volume 7 Issue5 - April 2023
DOI: 10.19080/JOJMS.2023.07.555723

JOJ Material Sci

Progress in the Application of Graphene Nanomaterials in the Cement-Based Composites

Jianwei Liu[1,2]*, Xinshuo Cheng[1,2], Zhichao Cui[1,2], Xiaowei Fu[1,2] and Rongyao Chen[1,2]

[1]*School of Petroleum Engineering, Yangtze University, China*

[2]*National Engineering Research Center for Oil and Gas Drilling and Completion Technology, Yangtze University, China*

Submitted: March 23, 2023; **Published:** April 13, 2023

***Corresponding author:** Jianwei Liu, School of Petroleum Engineering, National Engineering Research Center for Oil and Gas Drilling and Completion Technology, Yangtze University, China

Abstract

Graphene nanomaterials are new materials with excellent electrical, thermal and mechanical properties, and the application of graphene to various fields has been a hot topic of research at domestic and abroad. This paper introduces many properties of graphene, especially the mechanical properties on cementitious composites, including the effects on the rheological properties, water loss, thickening time, mechanical properties, and microstructure of cementitious materials, and the research results all show that graphene nanomaterials play a positive role in improving the slurry properties of cement slurry and the comprehensive engineering properties of cement. On this basis, it is investigated whether the application of graphene nanomaterials in oil well cement also has good effect.

Keywords: Graphene; Cement; Nanomaterials; Mechanical properties; Cement paste

Introduction

A sleeve of a certain size is placed down into the borehole of a drilled and completed well and cement is injected into the annular space between the borehole and the casing, the process is called cementing [1]. The cement slurry used for cementing should have good fluid properties and comprehensive engineering properties to adapt to the complex environment in the well and maintain effective long-term sealing performance [2]. However, the inherent brittleness of oil well cementite prevents it from withstanding transient impact pressures of up to 3-4 GPa during oil and gas development, and macroscopic cracks appear in the cement rings due to radial tensile stresses exceeding the ultimate value [3,4]. It has been shown that nanomaterials are applied to cement-based materials. Its cement paste and cementite both exhibit better fluid properties and comprehensive engineering performance [5-8]. Graphene is one of the new nanomaterials. Its application in oil well cement is less studied, and in this paper, we explore the application of graphene nanomaterials in oil well cement under the premise of nanomaterials in cementitious composites and explore a new cement paste system with excellent performance [9].

Graphene

Graphene structure

Graphene is a two-dimensional honeycomb lattice structure of carbon atoms arranged in a single layer, and it is a two-dimensional material with only one carbon atom thickness. This discovery is based on the micromechanical exfoliation method used by British physicists Geim and Novoselovc to separate graphene from graphite fragments [10].

Graphene is currently the hardest and thinnest new material in the world, and also has high strength, high specific surface area, thermal and electrical conductivity, and these excellent properties make it widely used as composite material (Figure 1).

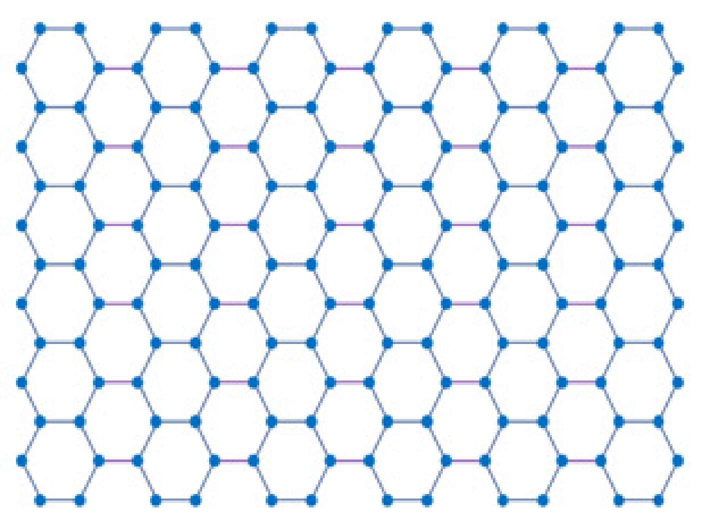

Figure 1: Structure of graphene [10].

Graphene properties

Graphene electrical properties

The excellent electrical conductivity of carbon atoms in graphene is due to its stable lattice structure, and its internal electron transport is highly resistant to interference, with electron mobility exceeding 15,000 $cm^2/(V\text{-}s)$ at room temperature [11]. Graphene has obvious two-dimensional electronic properties, the valence band and conduction band of graphene partially overlap at the Fermi energy level, and it is a two-dimensional semiconductor with zero energy gap, and carriers can move at submicron distances without scattering [12]. Graphene is the smallest resistivity material found so far. The electrical conductivity of graphene can be applied to cementitious composites, and when the incorporation of graphene nanomaterials increases, the resistivity of mortar decreases and the electrical conductivity of cement increases, so that graphene cementitious composites gain crack self-diagnostic capability [13].

Graphene thermal properties

The carbon atoms in graphene have a strong bonding force, and the loss of heat energy during the transfer process is small, so graphene has a high thermal conductivity, which is usually tested using Raman spectroscopy. Depending on the size of the measured graphene sheet, the thermal conductivity of a single layer of suspended graphene can reach 3000-5000 W/(m-K) at room temperature [14], and the thermal conductivity of graphene is twice that of copper and 50 times that of silicon, which are widely used in electronics today.

Graphene mechanical properties

The connections between carbon atoms in graphene are very flexible, and when an external mechanical force is applied, the carbon atomic surface is bent and deformed so that the carbon atoms do not have to be rearranged to adapt to the external force, and the structure is kept stable. Graphene is currently the world's thinnest (thickness of only 0.335 nm) [15] and strongest (elastic modulus of 1.1 TPa, fracture strength of 125 GPa, equivalent to more than 100 times that of steel [16]) new carbon nanomaterial. Using the excellent mechanical properties of graphene, the strength of cementitious composites can be enhanced to adapt to the high-pressure environment in oil wells and to ensure the stability of oil well cement rings.

Progress of Graphene Cementitious Composites

In the past decade, the research on graphene in composites has been mainly focused on polymer matrix. Such as polyethylene, polyaniline, polystyrene, epoxy resin and other matrices. Studies have shown that the incorporation of graphene materials significantly improved the comprehensive performance of composites. In recent years, the research on graphene-modified cementitious composites has also been enhanced. It has been found that cementitious composites modified by graphene present many unique and practical properties, which can change the rheological properties, water loss rate, thickening time and mechanical properties of cement paste and improve the comprehensive performance of cement paste.

Graphene cementitious composite fluidity

Compared to net cement slurry, the rheological properties of cement slurry incorporating graphene nanomaterials are altered and the flowability of cement is reduced. And the greater the graphene dosing, the yield stress and viscosity coefficient of cement paste also increase, and the flowability becomes smaller.

Wang et al. [17] analyzed the rheological properties of cement slurry by partially replacing the silicate cement admixture

How to cite this article: Jianwei L, Xinshuo C, Zhichao C, Xiaowei F, Rongyao C. Progress in the Application of Graphene Nanomaterials in the Cement-Based Composites. JOJ Material Sci. 2023; 7(5): 555723. DOI: 10.19080/JOJMS.2023.07.555723

with graphite micronized powder at different admixtures. The experiments showed that with increasing doping of graphite micro powder. The shear stress of the cement-based functional composites has a tendency to increase significantly. When the shear rate was $100s^{-1}$ and the graphite micro powder addition was 25%, the shear stress increased by 62.83% compared with the reference sample. The dilatancy of cement-based functional composites showed a slow and then sharp decreasing trend.

Jiao Min et al. [18] investigated the effect of graphene oxide on the rheology of just made cement slurry by using Anton Paar Rheolab QC type rotational viscometer and tested the static yield stress, dynamic yield stress and viscosity coefficient of the slurry as well as the thixotropic ring area. It was found that with the increase of graphene oxide admixture. The yield stress and viscosity coefficient of firstly increased. Then decrease. And the composite slurry thixotropic hysteresis ring area first decreases and then increases, and the yield stress and viscosity coefficient reach the highest value when the doping amount of graphene oxide is 0.08%. The slurry thixotropic ring area was the smallest.

Fang Changle et al. [19] studied the effect of rheological properties of graphene oxide (GO) cementitious composites and found that the thixotropic properties of the cement slurry at a doping level of 0.09% GO were the smallest, while its plastic viscosity and yield stress reached the maximum, and when the doping level of GO increased, the thixotropic properties of the cement slurry were first decreasing and then increasing.

Water loss in graphene cementitious composites

As mentioned above the incorporation of graphene nanomaterials reduces the flowability of cement, while graphene is also able to improve the water retention properties of cement and reduce the water loss of graphene cementitious composites.

Jing et al. [20] found that. With the increasing amount of graphene oxide (RGO) admixture. The water retention of mortar increases with the decrease of water loss rate. The water retention effect of RGO on mortar causes the internal structural pores to form a larger radius of the bending moon surface, which decreases the surface tension and reduces the self-contraction ability. At the same time, the increased shrinkage of mortar plasticity is due to the action of RGO which makes the imbalance between the internal water infiltration rate and the evaporation rate of surface water increased. Using X-CT and SEM, it can be observed that RGO plays a role in bridging hydration products across microcracks, dispersing capillary shrinkage stresses and limiting uneven deformation. The positive effect of RGO enhances the crack resistance of the mortar itself and counteracts the negative effect caused by the increased plastic shrinkage.

Wang Qin et al. [21] studied the influence of graphene oxide on the hydration process and hydration products of cement and found that GO incorporation has no significant effect on the hydration process of cement. there is no role of GO in promoting hydration, but GO incorporation can affect the crystallization process and morphology of hydration products, especially calcium hydroxide; GO has an important influence on the characteristics of the gel pores formed after the cement paste hardening, and can make the gel pores contain more free water in order to refine and close the pore structure to a certain extent with the increase of GO admixture; the presence of GO not only has an obvious inhibitory effect on the hexagonal sheet crystals, but also can make the calcium hydroxide in the crystals finer.

Mechanical properties of graphene cementitious composites

The strength of cement has always been a concern for people, cement will crack or even break due to insufficient strength, into the years, there are a lot of experimental data to prove that the graphene admixture can effectively improve the compressive and flexural strength of cement materials, etc. Mahmoud AA et al. [22] investigated the effect of graphite particles on the properties of oil well cements reacting with CO_2-rich solutions at 130°C and 10 MPa for 10d. It was found that the incorporation of graphite significantly improved the compressive and tensile strengths of oil well cements, and the incorporation of 0.2% BWOC graphite resulted in 13.4% and 23.8% higher compressive and tensile strengths of oil well cements than the samples without graphite incorporation, respectively, and when the incorporation of BWOC graphite was increased to 0.3%, the compressive and tensile strengths decreased by 12.6% and 4.5% compared to the incorporation of 0.2%. It can be seen that when BWOC graphite is incorporated at 0.2%. The improvement of tensile strength of oil well cement is the best.

Meng Fei et al. [23] carried out a study on the effect of graphite oxide on the mechanical properties of oil well cement composites. The results showed that graphite oxide could significantly improve the mechanical properties of cementite, and when the graphite oxide doping amount was 0.05%, the graphite oxide enhanced the compressive strength 28d, flexural strength 28d, and splitting tensile strength 28d of cementite, respectively, by 68.63%, 17.44%, and 159.12% compared with the compressive strength of pure cementite; and when the graphite oxide doping amount was increased to 0.07%, the mechanical property enhancement decreased compared to 0.05% graphite oxide admixture, so it's better admixture is 0.05%.

Shenghua Lv et al. [24] The graphene oxide (GO) nanosheet layer dispersion system was prepared by oxidation and ultrasonic dispersion, and the effect of GO nanosheet layer on the mechanical properties of cement matrix composites was investigated. As shown in table 1, the results of the study showed that GO nanosheet layers were blended into cementitious mortar and it was found that GO nanosheet layers were able to increase the tensile and flexural strength of the mortar significantly. Tests

How to cite this article: Jianwei L, Xinshuo C, Zhichao C, Xiaowei F, Rongyao C. Progress in the Application of Graphene Nanomaterials in the Cement-Based Composites. JOJ Material Sci. 2023; 7(5): 555723. DOI: 10.19080/JOJMS.2023.07.555723

conducted when varying the dose of 0.03 wt% GO revealed that there was still 65.5%, 60.7% and 38.9% increase compared to the tensile, flexural and compressive strengths of the cementitious sand at 28d.

Abrishami et al. [25] in conducting experiments on reinforced graphene oxide/cement composites containing NH2 functionalized groups, found that pure graphene oxide/cement composites will improve their flexural and compressive strengths as the amount of graphene oxidation increases. Its optimal graphene oxide incorporation amount was 0.10 wt%. The compressive strength of the sample with 0.10% graphene oxide increased by 8.5% and the flexural strength increased by 23.4% compared to the sample without graphene oxide composites. However, when the graphene oxide concentration increased from 0.10 wt% to 0.25 wt%, the compressive strength decreased from 42.3 to 40 MPa. was due to the decrease in surface energy of graphene oxide nanomaterial sheets due to their agglomeration.

Ming et al. [26] used graphene oxide (GO) reinforced carbon fibers and investigated the mechanical effect of this new graphene oxide modified carbon fiber (GO-cf) on cement. The results showed that this new reinforced cement material had better toughness compared to pure cement. The GO-cf reinforced cement (GOCFRC) exhibited good compressive strength at a BWOC content of only 0.4%. After 14 d of maintenance, the compressive strength of the cement increased to more than 1.18 times that of pure cement. Its flexural tensile strength increased by 38.81% at 3 d maintenance, 38.65% at 7 d maintenance, and 41.76% at 14 d maintenance. In addition, it exhibited excellent triaxial stress-strain toughness compared to pure cement: Young's modulus increased to 150.9%, ultimate stress increased to more than 121%, and ultimate strain increased to approximately 267%. Gong et al. [27] studied the strengthening effect of CNTs and GO on silicate cement, and the compressive and tensile strengths were increased by more than 40% by adding 0.03% of GO to silicate cement.

As shown in table 1, these studies indicate that graphene is beneficial for improving the mechanical properties of cement pastes, depending on the structure of graphene nanomaterials. The use of graphene helps to improve the mechanical properties of cement pastes in different environments.

Table 1: Mechanical properties of graphene cementitious composites.

Reference	Dosage	Flexural Strength	Compressive Strength	Flexural Strength Growth Rate	Compressive Strength Growth Rate
Mahmoud AA et al. [22]	0.02%BWOC	–	97.4 MPa	–	13.4%
Meng et al. [23]	0.05%BWOC	–	–	17.44%	68.63%
Lv et al. [24]	0.03wt%GO	14.21MPa	82.36MPa	60.70%	38.9%
Abrishami et al. [25]	0.10wt%GO	10.20MPa	54.23MPa	38.40%	23.03%
Ming et al. [26]	0.4wt%BWOC	–	–	41.76%	–
Gong et al. [27]	0.03%GO	7.2MPa	63MPa	53.33%	46.5%

Microstructure of graphene cementitious composite

In addition to the impact on the macroscopic properties of cement paste, the microstructure of cement paste can also be changed by graphene.

Xu Yihong et al. [28] observed the microstructure of cement at different graphene oxide doping levels by SEM scanning electron microscopy. The results of the study showed that when the graphene oxide doping amount was 0. The surface of the hydration product is uneven, the internal pores and cracks are large, the structure density is low, and the SEM image shows a complex structure texture with a large fractal dimension of 1.9806; the image of the net cement paste becomes more regular after the graphene oxide doping. The internal pores and fissures are reduced, the texture structure tends to be simple, and the fractal dimension shows a decreasing trend with the increase of graphene oxide.

Yuan et al. [29] investigated the effect law of different doping amounts (0%, 0.03%, 0.06%, 0.09%, and 0.12%, respectively) of graphene oxide GO on the pore size of cementite after hardening in an experiment conducted to investigate the micro mechanism of graphene oxide modified cementitious composites, and it was found that when doped with 0.03% of GO. The net cement paste had the minimum porosity, the doping amount 0.06% of GO in cement net paste also has smaller porosity, but the effect is only second to the sample dosed with 0.03%. The results show that the microstructure inside the cement paste is relatively denser with the dose of 0.03% to 0.06%. This results in excellent mechanical properties of the cement-based composites. When the GO dose is too high, the net cement slurry flow rate becomes low, resulting in the formation of many voids inside the net slurry and the inability of GO to disperse uniformly in the cementitious material, thus the porosity increases significantly.

Lu et al. [30] found in their study of graphene oxide cementitious composites. The graphene oxide GO@Sand hybridization products produced a higher percentage of hydration products (from 43.34% to 80.00%) in the interfacial transition region (ITZ), a higher Ca/Si ratio, and a decrease in microstructural porosity from 43.5% to 30.1%. The enhancement of ITZ resulted in an increase in the oxidation strength of the graphene-based composites.

How to cite this article: Jianwei L, Xinshuo C, Zhichao C, Xiaowei F, Rongyao C. Progress in the Application of Graphene Nanomaterials in the Cement-Based Composites. JOJ Material Sci. 2023; 7(5): 555723. DOI: 10.19080/JOJMS.2023.07.555723

Wang et al. [31] in their study of the effect of graphene oxide addition on the cumulative pore volume distribution of hardened cement paste at 3d, 7d, and 28d found that the cumulative pore volume decreased with increasing age. The pore volume of the hardened cement paste changed significantly with the addition of graphene oxide. That is, the cumulative pore volume (<100 nm) decreases with the increase of graphene oxide admixture. Mixing graphene oxide, the cement slurry accelerates the crystallization hydration products. The orderly arrangement of the crystals changed the pore structure of the cement paste and improved the confinement of the cement paste after hardening.

Shenghua Lv et al. [32] investigated the modulating effect of cement hydration crystal morphology and graphene oxide on mechanical properties in an experiment. It investigated how the oxygen content of 18.65% and 25.53% made GO affect the flexural and compressive strength of cementite, cement hydration products and their microscopic morphology, respectively. It was demonstrated that the cement hydration products of GO containing 25.53% oxygen can form dense flower-like microcrystals, and GO can induce cement crystal hydration, and its toughening effect is greater than the strengthening effect.

Graphene can improve the density of cement slurry, improve the microstructure of cement slurry, and reduce the pore volume of cement paste. These are beneficial for improving the macroscopic properties of cement slurry.

Problems of Graphene Cementitious Composites

a) Current graphene preparation methods are difficult to achieve industrial mass production.

b) Graphene is difficult to disperse in water and easy to agglomerate, so we need to find a suitable dispersant to make it into a stable graphene dispersion.

c) The mechanism of graphene action in cement-based materials is still unclear.

Trends in Graphene Cementitious Composites

a) Preparation of homogeneous and stable graphene dispersions. Select the suitable dispersant, derive the best ratio of dispersant and graphene by experiment, and then prepare a stable dispersion.

b) Using graphene's excellent electrical conductivity and pressure-sensitive properties, intelligent cement materials are prepared for monitoring changes in cement pressure and anticipating in advance the fracture of cement due to pressure changes.

c) The mechanism of the action of graphene in cement-based materials is studied by various means such as molecular dynamics theory and finite element analysis.

Conclusion

Graphene as a material has excellent optical, electrical and mechanical properties. It is able to make up for some shortcomings of cementitious composites. By varying the amount of graphene incorporation, the optimal amount of graphene incorporation is found to modify the cementitious composites to maximize their mechanical properties and comprehensive engineering performance. The new cement with good performance can be subsequently applied in oil and gas well development in order to cope with the complex downhole environment and guarantee the complete sealing effect of the cement ring, so as to guarantee the safety of oil and gas well development.

References

1. Ding S (2002) Current status and development trend of cementing technology at domestic and overseas. Drilling and Completion Fluids 5: 38-42.
2. Zhang X, Gao X, Feng M (2002) Analysis of factors influencing the quality of cementing. Drilling Technology 2: 18-21.
3. Hua S, Yao X (2007) The pathway of oil well cementite brittleness reduction and its mechanism of action. Journal of China University of Petroleum (Natural Science Edition) 1:108-113.
4. Li Z, Su X, Fu B (1999) Experimental study of dynamic fracture toughness of cementite. Mechanics and Practice 1: 41-44.
5. Song J, Xu M, Wang X (2018) Progress in application of nanomaterials in oil cement. Science Technology and Engineering. 18(19): 141-148.
6. Wang Q, Wang J, Lv C, Liu B, Zhang K, Li C (2015) Effect of graphene oxide on the microstructure and mechanical properties of cementitious composites. New Carbon Materials 30(4): 349-356.
7. Du T (2014) Study on the properties of graphene oxide cement matrix composites. Harbin Institute of Technology.
8. Lv SH, Ma YJ, Qiu C, Ju H (2013) Study of graphene oxide reinforced toughened cementitious composites. Functional Materials 44(15): 2227-2231.
9. Mou Y (2006) Research on high-temperature and high-pressure cementing technology. Western Exploration Engineering. 4: 104-106.
10. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, et al. (2004) Electric field effect in atomically thin carbon films 306(5696): 666-669.
11. Zhang Y, Tan YW, Stormer HL, Kim P (2005) Experimental observation of the quantum Hall effect and Berry's phase in graphene. Nature 438(7065): 201-204.
12. Katsnelson MI (2007) Graphene: carbon in two dimensions. Materials Today 10(1-2): 20-27.
13. Sixuan H (2012) Multifunctional graphite nanoplateles (GNP) Reinforced Cementitious Composites.
14. Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, et al. (2008) Superior thermal conductivity of single-layer graphene. Nano Lett 8(3): 902-907.
15. Wang B, Jiang R, Zhao R (2016) Concrete 75(12): 68.
16. Gu Z, Ji G, Lu M (2010) Journal of Nanjing University of Technology, 32(3): 105.

How to cite this article: Jianwei L, Xinshuo C, Zhichao C, Xiaowei F, Rongyao C. Progress in the Application of Graphene Nanomaterials in the Cement-Based Composites. JOJ Material Sci. 2023; 7(5): 555723. DOI: 10.19080/JOJMS.2023.07.555723

17. Wang JP, Li XP, Sun T, Yin W, Yan G, et al. (2020) Effect of graphite micronized powder doping on the rheological and electrical properties of cement-based functional materials. Building Materials World 41(5): 1-5.

18. Jiao M (2021) Effect of graphene oxide on the rheology of fresh cement slurry. Silicate Bulletin 40(07): 2159-2164.

19. Fang C (2018) Effect of graphene oxide on the rheological and hardening properties of cement-based materials and its hardening and strengthening mechanism. Shenzhen University.

20. Jing G (2021) Preparation and performance study of graphene modified cementitious materials. Jinan University.

21. Wang Q, LI S, Wang J, Pan S, Guo Z, et al. (2018) Effect of graphene oxide on the hydration process of cement and its main hydration products. Journal of Silicates 46(2): 163-172.

22. Mahmoud AA, Elkatatny S, Al Majed A, Al Ramadan M (2022) The Use of Graphite to Improve the Stability of Saudi Class G Oil-Well Cement against the Carbonation Process. acs Omega. 7(7): 5764-5773.

23. Meng F, Yuan J, Ding Y, Yang Y, Li M, et al. (2016) Mechanical properties of graphite oxide oil well cement matrix composites. Silicate Bulletin 35(1): 39-43.

24. Lv SH, Sun T, Liu JJ, Ma YJ, Qiu C (2014) Toughening effect and mechanism of action of graphene oxide nanosheet layers on cementitious composites. Journal of Composites 31(3): 644-652.

25. Abrishami ME, Zahabi V (2016) Reinforcing graphene oxide/cement composite with NH_2 functionalizing group. Bull Mater Sci 39(4): 1073-1078.

26. Ming L, Hao W, Chi Z, Shuang D, Kuigang L, et al. (2019) The effect of graphene oxide grafted carbon fiber on mechanical properties of class G Portland cement. Journal of Adhesion Science and Technology 33(22): 2494-2516.

27. Gong K, Pan Z, Korayem AH, Qiu L, Li D, et al. (2015) Reinforcing effects of graphene oxide on Portland cement paste. Journal of Materials in Civil Engineering 27(2): A4014010.

28. Xu Y, Fan Y (2020) Fractal characteristics of mechanical properties and microstructure of graphene oxide cement net paste. Concrete 8:130-134.

29. Yuan X, Yang Y, Zhou C, Zeng J, Xiao G, et al. (2017) Mechanical properties and microscopic mechanism of graphene oxide modified cement mortar. Journal of Chongqing Jiaotong University (Natural Science Edition) 36(12): 36-42.

30. Lu D, Shi X, Zhong J (2022) Nano-engineering the interfacial transition zone in cement composites with graphene oxide. Construction and Building Materials 356.

31. Wang Q, Wang J, Chunxiang LV, Bowei LIU, Zhang K, et al. (2015) Effect of graphene oxide on microstructure and mechanical properties of cementitious composites. New Carbon Materials 30(4): 349-356.

32. Lv SH, Ma YJ, Qiu C, Ju H (2013) The modulating effect of graphene oxide on the hydrated crystal morphology of cement and its influence on mechanical properties. Functional Materials 44(10): 1487-1492.

DOI: 10.19080/JOJMS.2023.07.555723