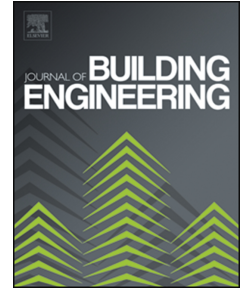


Journal Pre-proof



Microstructural, durability and colorimetric properties of concrete coated with a controlled application of graphene oxide

Andrea Antolín-Rodríguez, Daniel Merino-Maldonado, María Fernández-Raga, José Miguel González-Domínguez, Julia M, Morán-del Pozo, Julia García-González, Andrés Juan-Valdés

PII: S2352-7102(24)00488-1

DOI: <https://doi.org/10.1016/j.jobe.2024.108920>

Reference: JOBE 108920

To appear in: *Journal of Building Engineering*

Received Date: 5 December 2023

Revised Date: 9 February 2024

Accepted Date: 23 February 2024

Please cite this article as: A. Antolín-Rodríguez, D. Merino-Maldonado, Marí. Fernández-Raga, José.Miguel. González-Domínguez, J. M, Morá.-del. Pozo, J. García-González, André. Juan-Valdés, Microstructural, durability and colorimetric properties of concrete coated with a controlled application of graphene oxide, *Journal of Building Engineering* (2024), doi: <https://doi.org/10.1016/j.jobe.2024.108920>.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2024 Published by Elsevier Ltd.



Microstructural, durability and colorimetric properties of concrete coated with a controlled application of graphene oxide

Andrea Antolín-Rodríguez^a, Daniel Merino-Maldonado^a, María Fernández-Raga^b, José Miguel González-Domínguez^c, Julia M^a Morán-del Pozo^a, Julia García-González^a and Andrés Juan-Valdés^a

^aINMATECO Research Group, Department of Agricultural Engineering and Sciences, University of Leon, Spain

^bDepartment of Chemistry and Applied Physics, University of Leon, Vegazana Campus S/N, 24071 Leon, Spain

^cInstituto de Carboquímica (ICB-CSIC), Group of Carbon Nanostructures and Nanotechnology (G-CNN), C/Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Abstract

The present work analyzes how an aqueous suspension of graphene oxide (GO), as a surface treatment, can influence the properties of conventional concrete. The results show that the application of a GO surface coating on concrete improves its resistance to carbonation and chloride ion penetration, and also increases its electrical resistivity. In the best case, the GO coating can reduce carbonation by 40% and chloride ion diffusion by 75%. An increase of up to 75% in concrete resistivity was also achieved. The application of GO promotes the hydration process and densifies the microstructure of the concrete surface, and this is verified by scanning electron microscopy analysis. In addition, no color modification occurred after application of the treatment.

Keywords: concrete; coating; graphene oxide; carbonation; chloride migration; color change

1. Introduction

Over the last century, concrete has been the most successful building material; its unique properties have made it a very efficient and adaptable asset. However, in recent decades there has been a growing interest in the preservation of this material, with the aim of increasing its performance. Specifically, there is a global concern on guaranteeing the long-term performance of this material in structures exposed to aggressive environments or subjected to severe service conditions and, consequently, to reducing the high cost that repair and maintenance tasks can entail.

The deterioration of concrete is enhanced by physical and/or chemical processes that directly affect its durability. The durability of concrete is subjected to the structure of its pores, and more specifically to their distribution, shape and size. Therefore, the pore structure of concrete establishes the transport properties for the main harmful agents that cause concrete deterioration (ions, gases and water) [1,2].

Numerous methods and strategies have been studied to extend the service life of concrete structures. Therefore, in the construction field, one of the main approaches that have been adopted is the use of high-performance concrete (HPC). This type of concrete uses various types of admixtures and low water/cement (w/c) ratios in its formulation, which characterizes them as having low permeability and high strength [3,4]. Another of the most commonly used strategies is the use of coatings or surface treatments. These have been applied for the consolidation and protection of existing and even new structures. The main characteristics of

such coatings are their barrier properties and high hydrophobicity [5,6]. The commonly employed treatments present different mechanisms of action depending on their composition, their main objective being the formation of a thin layer or film that serves as a barrier, filling and sealing the pores that are present on the concrete surface, a fact that prevents the transport of water and of any other harmful agent [7,8]. Recently, studies have been conducted using nanoparticles as a surface treatment material to increase the durability of cement-based composite materials [9–12]. Hou et al. [9] investigated how the application of a nano-SiO₂ colloidal coating could influence hardened cement pastes and determined that this type of coating was able to reduce the water transport properties of the samples by modifying the porous structure. On the other hand, Franzoni et al. [10] studied a nanosilica-based coating to determine whether it could serve as a protection for concrete floors. Through an evaluation in terms of morphology and microstructure, they concluded that the coating was effective for the protection of concrete structural elements. Scarfato et al. [12] studied two polymer resins as coatings to which they incorporated nanoclays to enhance their protective action. The results obtained indicated that the incorporation of nanoclays significantly improved the efficiency of the coating. They were able to reduce the diffusion properties of the polymeric matrices and improve the blocking of the concrete pores, all thanks to the laminar nanofilling effect produced by the nanoclays.

According to the current literature, the vast majority of surface treatments that have been investigated consist of composites or nanocomposites; however, the direct application of nanomaterials on the surface of concrete as a protective surface treatment has been scarcely explored [13–16]. In this line, future research directions arise based on the use of new surface treatments formed composed only by 2D nanomaterials. Currently, one of the most promising 2D materials in many technological applications is graphene oxide (GO), a nanomaterial obtained from the chemical exfoliation of graphite, with a high and homogeneous colloidal stability in aqueous media. Thanks to its atomic thickness and lamellar structure, providing GO with a high surface area, and rich oxygen surface chemistry providing good dispersibility in water, it can be a potential alternative for the protection of building materials [16–18].

In recent years, in order to respond to the challenges associated to the conservation of construction materials, some previous studies have been performed on the application of GO for such purpose. These pioneering studies focus their research on the use of GO as an additive to be included in the mix with the aim of improving the mechanical [19–22] and durability [23] properties of cement pastes. Lv et al. [19] investigated the incorporation of GO nanosheets into cement composites to improve their hardness, as they showed that the nanosheets were able to control the formation of cement hydration crystals and this resulted in a significant increase in cement hardness. Pan et al. [20] also investigated the incorporation of GO in the cement paste, achieving an increase in concrete strength of 15-30% in compression tests and 40-60% in flexural tests. Another study, authored by Saafi et al. [21], studied the transport characteristics of concrete with GO reinforcement in its composition. Their experimental results showed that the incorporation of GO effectively prevented the penetration of chloride ions and improved water sorption. In summary, all these studies concluded that when GO is incorporated into the mix, both durability and mechanical properties of cement-based composites can be significantly improved. However, the use of this nanomaterial as an additive in concrete mixing and batching is still far from being a proven and effective technique. Recent studies [24,25] have confirmed that the incorporation of GO as an additive in the mix can cause workability problems due to the agglomeration of the GO nanoparticles by the marked

alkaline character of the cement mixture and the possible occurrence of undesired chemical reactions that could involve the destabilization of the GO suspension.

Considering that reports addressing the application of GO as a protective coating for the surface of concrete are certainly rare, and considering that GO is the most affordable graphene derivative, from the economic point of view it allows for large-scale coatings. Therefore, a study on the effectiveness of surface treatment with GO for the protection of construction materials is herein proposed. If the application of GO as a coating provides actual protection, it would represent a new line of improvement in the resistance of concrete, which could be applied in situ in areas with special requirements. More specifically, the present study used GO as a surface treatment to determine the resistance to the carbonation process and to chloride diffusion. The effectiveness of the treatment was evaluated by physical, morphological, and colorimetric analyses.

2. Materials and methods

2.1. Experimental materials

2.1.1. Conventional concrete

Natural aggregates, siliceous gravel as coarse aggregate and siliceous sand as fine aggregate, are used for the manufacture of the concrete mix. The aggregates used were previously studied to check their suitability in accordance with the specifications established in the EN 12620:2003+A1 [26] and EN 1992-1 [27] standards. Figure 1 shows the particle size distribution of the aggregates established according to European standard EN 933-1. The binder used for the mix is blast furnace slag cement type CEM III/A 42.5N/SR, which complies with the standards established in EN 197-1 [28].

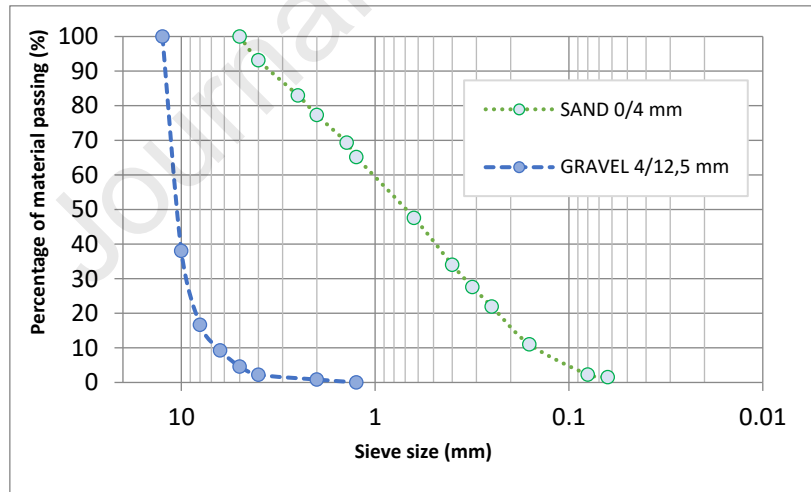


Figure 1. Particle size distribution of natural aggregates

Table 1 shows the dosage followed for the production of the concrete. This dosage complies with the mechanical and durability conditions set out in the European standards (EN) governing the manufacture of hardened concrete.

Table 1. Batching of the concrete mixture

Materials (Quantity/m ³)	Conventional concrete
4/12.5 mm Gravel (kg)	1030.7

0/4 mm Sand (kg)	650.5
CEM III/A 42.5 N/SR (kg)	390.0
Water (L)	198.0

The w/c ratio used is 0.51, selected on the basis of the expected exposure to which the concrete will be exposed. The expected exposure will be XC, corresponding to an exposure to corrosion induced by carbonation. The Spanish Structural Code [29] establishes that, for this type of exposure, the w/c ratio can reach up to a maximum value of 0.60.

The manufactured conventional concrete specimens were cured for 90 days at a temperature of (20 ± 2) °C and relative humidity (>95%).

2.1.2. Graphene oxide

Graphene oxide (GO) is the material of choice to protect concrete. To this end, its synthesis is performed through the exfoliation of graphitic oxide in water after the application of mild ultrasound. In turn, the graphitic oxide was obtained by applying the Hummers oxidation method to the graphite. In their study, González-Campelo et al. [15] reported in detail all the information about the synthesis and the complete characterization of GO.

Figure 2 shows an image of freshly exfoliated GO obtained by transmission electron microscopy (TEM). This image illustrates the thin and two-dimensional nature of GO, as well as its physical adaptability and flexibility (judging by its observed folds and wrinkles). It confirms that GO is a suitable material at the microscopic level to act as a protective coating for surface.

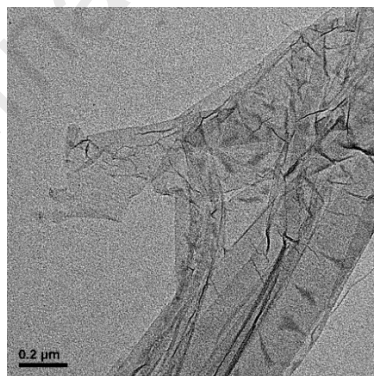


Figure 2. TEM image of a GO flake (Microscope JEOL-200FXII)

2.2. Concrete surface treatment

A GO dispersion in water with a concentration of 0.5 mg/ml is used to protect the surface of the concrete. Before starting the treatment of the concrete surface, the GO dispersion is subjected to a gentle sonication process for about 3 minutes, until a homogeneous colloid is obtained. Sonication is a very efficient technique to disperse graphene-based materials in liquids, the main rationale of which is to exfoliate stacked graphene sheets by cavitation forces and keep them stable against re-aggregation, and thus to achieve a homogeneous distribution [30]. After the sonication process, it can be observed that there is no deposition of the GO particles on the bottom for at least several hours, and consequently, it is a homogeneous dispersion [31]. Once the GO dispersion is ready, it is applied to the surface of the concrete. The application process consists of spraying the GO dispersion with an airbrush. When several

applications are made, a drying time of 1 hour is always maintained between applications. It is important to consider that the application of the treatment is always performed at a slow and constant speed with a horizontal movement, thus controlling the amount of treatment deposited on the surface of the concrete ($26.2 \mu\text{g}/\text{cm}^2$ per application). After complete application of the treatment, the samples are left to dry at a temperature of $(20 \pm 2) ^\circ\text{C}$ and a relative humidity of $(45 \pm 15) \%$. The treatment was applied 48 hours prior to testing.

Six groups of concrete samples were studied. Five of the groups received surface treatment of GO dispersion, with different surface concentrations. Up to a total of 5 applications of the GO suspension were performed. Thus, the amount of the GO deposited on the concrete was $26.2 \mu\text{g}/\text{cm}^2$, $52.4 \mu\text{g}/\text{cm}^2$, $78.6 \mu\text{g}/\text{cm}^2$, $104.8 \mu\text{g}/\text{cm}^2$ and $131.1 \mu\text{g}/\text{cm}^2$, respectively. The last group that remains to be specified corresponds to concrete samples to which no Surface treatment was applied, this group being considered the control. Table 2 shows all the information on each type of application and the related amount of GO deposited on each concrete sample.

Table 2. Treatment on the concrete surface

Surface treatment (application)	Amount of GO ($\mu\text{g}/\text{cm}^2$)
C	0.0
GO1	26.2
GO2	52.4
GO3	78.6
GO4	104.8
GO5	131.1

2.3. Tests and methodology

2.3.1. Resistance to carbonation

The chemical process of carbonation is the reaction in which the calcium hydroxide present in the concrete mix reacts with the carbon dioxide present in the air, leading to the formation of calcium carbonate. This chemical process promotes the reduction of the pH of the concrete, which can lead to a carbonation-induced corrosion causing the deterioration of concrete [32].

The natural method established in EN 12390-10 standard [33] is used to study the resistance to carbonation. This method consists of placing the concrete sample specimens ($100 \times 100 \times 100 \text{ mm}^3$) in an enclosure that is exposed to the natural environment but protected from the direct action of rain. During the test, parameters such as temperature, relative humidity and CO_2 concentration are considered. Thus, after defined exposure periods (90, 180, and 365 days), the depth of the carbonation front is determined. For this purpose, the concrete samples are broken in half and a phenolphthalein solution is sprayed on them (revealing the alkaline parts by color change). Subsequently, the penetration front was measured using a caliper, taking 12 readings for each sample.

Finally, the carbonation speed is calculated, which is the parameter defining the concrete's susceptibility to carbonation. The carbonation speed is calculated from the exposure time to which the concrete samples are subjected, known as the effective time. Therefore, the average carbonation depth calculated above (y-axis) is plotted against the square root of the effective time in years (x-axis) and a linear regression is plotted through the points. The slope of the regression corresponds to the speed of carbonation produced in the concrete in $\text{mm}/\text{year}^{0.5}$.

2.3.2. Electrical resistivity

The electrical resistivity of concrete is a property that quantifies the strength with which this material opposes the flow of electric current. In addition, it is established as an indirect measure of porosity and the distribution and quantity of pores contained in the hardened concrete [34].

To establish the electrical resistance of hardened concrete, readings were taken according to the protocol established in the EN 12390-19 standard [35]. This established that a uniform electric field is applied to cylindrical specimens (100 mm diameter and 200 mm height) of saturated concrete by means of two electrodes, one placed at each base of the specimen. To ensure that there is a correct electrical connection, two wet sponges about 5 mm thick were placed between the electrodes and the bases of the specimen, whose electrical resistance is previously known. The electrical resistivity of the concrete specimens is recorded, which is defined by the voltage applied and the electrical current passing through the specimen.

2.3.3. Chloride ion diffusion. Multi-regime method

One of the main causes of concrete deterioration is the possible ingress of ions from the environment. It is important to know the transport of ions through concrete, thus studying its diffusion characteristics. The test performed to establish the diffusion coefficient of chloride ions in concrete is regulated by the EN 83987 standard [36]. In this case, the multi-regime method is applied, which is a method that allows to know the diffusion coefficient of chloride ions in concrete in two states, stationary and non-stationary.

The basis of the method is to calculate the migration of chloride ions. For this purpose, the test is performed on three cylindrical concrete specimens (75 mm diameter and 25 mm height), which serve as a barrier between two solutions, an ion source solution (1 M NaCl) and an ion-free solution (distilled water). To accelerate the migration process, a potential difference of 12 V is applied. The migration of chloride ions in the two states, steady state (D_s) and non-steady state (D_{ns}), which are defined by the electrical voltage and conductivity, are calculated.

2.3.4. Colorimetric analysis

The possible variation of aesthetic properties produced by the application of a surface treatment on concrete is an important aspect. It is well known that the main objective of any surface treatment is to prolong the durability of the concrete, but if it also maintains or improves the visual appeal of the concrete, it would be improving its aesthetic properties. For this reason, a colorimetric analysis is performed on the concrete samples, both with and without GO surface treatment. The Konica Minolta Chroma Meters CR-200 colorimetric is used for this analysis.

The test is performed on three test specimens for each type of treatment, taking five measurements on each one. The final result is the mean value of fifteen measurements, which makes it possible to verify the reproducibility of the result obtained. The colorimetric analysis is based on the color changes evaluated using the L^* , a^* , b^* system (ASTM D-1925, CIE 1976). The L^* coordinate is the surface brightness with values between 0 (black) and 100 (white). The a^* coordinate is the deviation of the chromatic point towards red if a^* (+), or towards green if a^* (-). Similarly, the b^* coordinate is the deviation towards yellow if b^* (+), and towards blue if b^* (-). The total color variation (ΔE) is calculated by means of the following equation (2):

$$\Delta E = \sqrt{\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}} \quad (2)$$

2.3.5. Surface characterization

It is important to perform a surface characterization of concrete samples when a coating or surface treatment is performed. Therefore, the concrete samples were observed by scanning electron microscopy (SEM). The microscope chosen to perform the surface analysis is the Hitachi S-4800 device with a tungsten X-ray source, a Si/Li detector and a Bruker XFlash 5030 EDS analyzer. Prior to microscopic observations, the samples are coated with gold. The resulting microscopies of the samples are taken without any test on the surface of the concrete.

3. Results and discussion

3.1. Resistance to carbonation

Figure 3 presents the carbonation depth of the various concrete samples studied, after defined exposure periods. Thus, it can be observed that the carbonation depth decreases significantly in the samples that present surface applications of GO. If the maximum exposure time, 365 days, is analyzed, samples GO1, GO2, GO3, GO4 and GO5 decreased their carbonation depth by 21%, 26%, 30%, 36% and 37%, respectively, compared to the control samples (without any surface application).

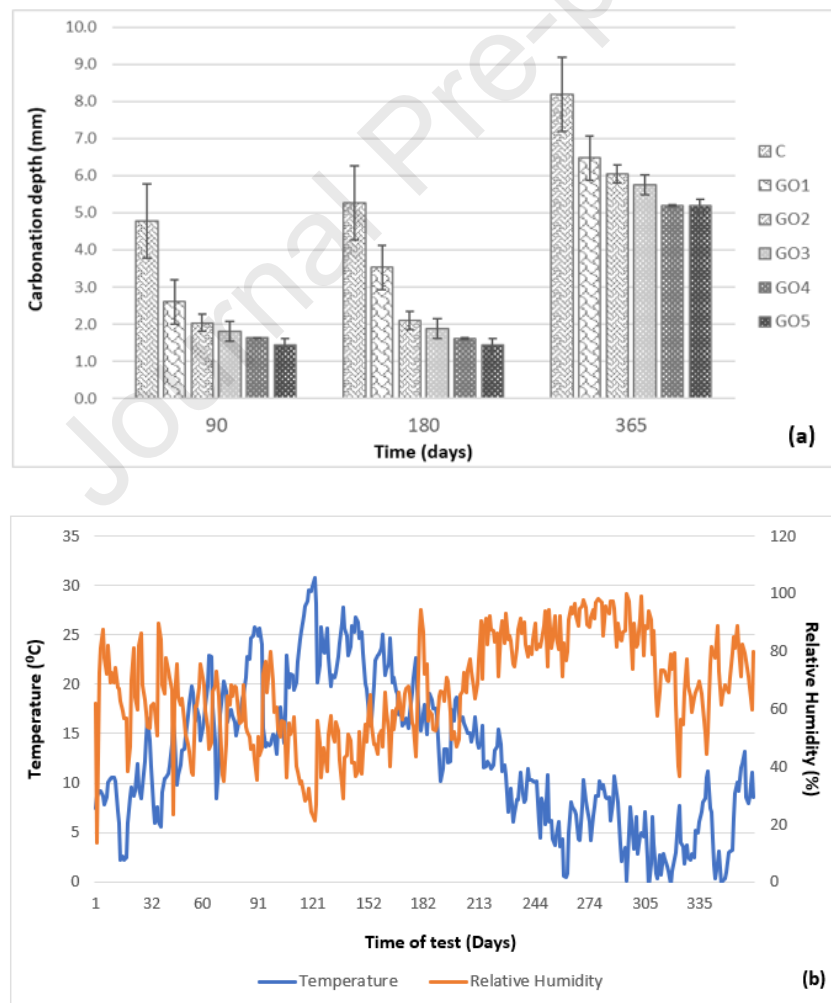
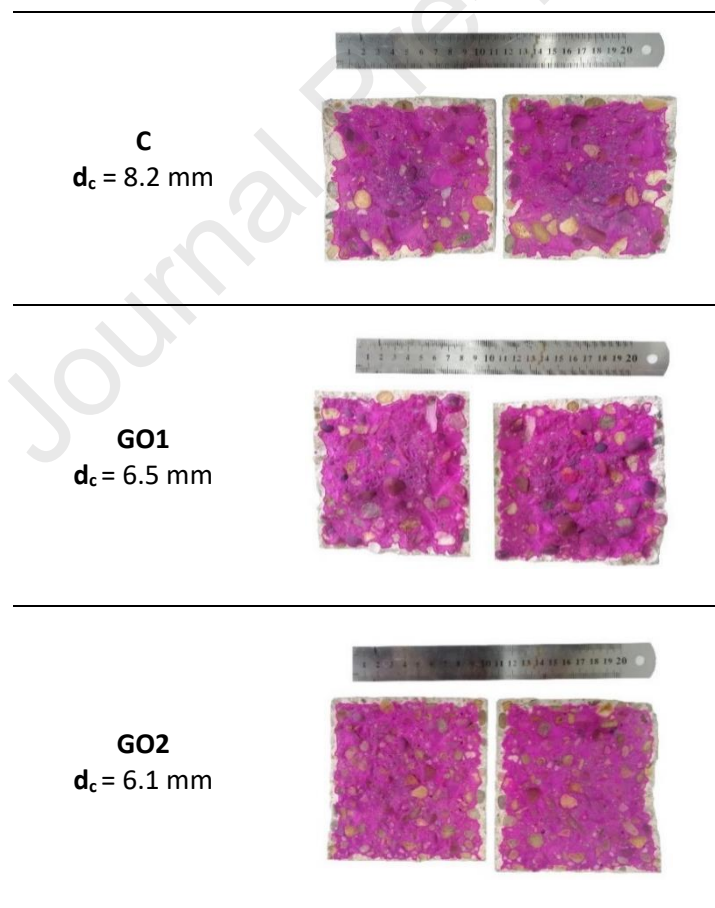


Figure 3. Carbonation depth of concrete samples (a). Average temperature and relative humidity record during the exposure time of the test (b).

For all the exposure times analyzed, the carbonation depth is significantly reduced after increasing the number of GO applications on the surface of the concrete samples. It is worth noting that, depending on the exposure period, the extent of the reduction in each application of GO is different. Thus, GO1 and GO2 have a lower carbonation depth in the first exposure, showing a considerable increase after 90 days of exposure. However, GO3, GO4 and GO5 have an almost constant carbonation depth during the 180 days of exposure. After the longest exposure period, 365 days, all concrete samples show an increase in carbonation depth compared to the rest of the exposure periods. Even so, it is observed that with increasing GO applications, the carbonation depth decreases.

The pronounced increase in carbonation depth during the longest exposure period in all the samples tested is mainly due to the environmental conditions to which the samples were subjected. At the beginning of the test there are medium-high temperatures and medium relative humidity. However, at the end of the second exposure period the temperatures are much lower, and the relative humidity is high, which translates into worse environmental conditions to which the concrete samples are subjected. Therefore, it is normal for the penetration depth to increase sharply.

Figure 4 shows the results of the pH determination performed on the various concrete samples belonging to the maximum exposure period of the test (365 days).



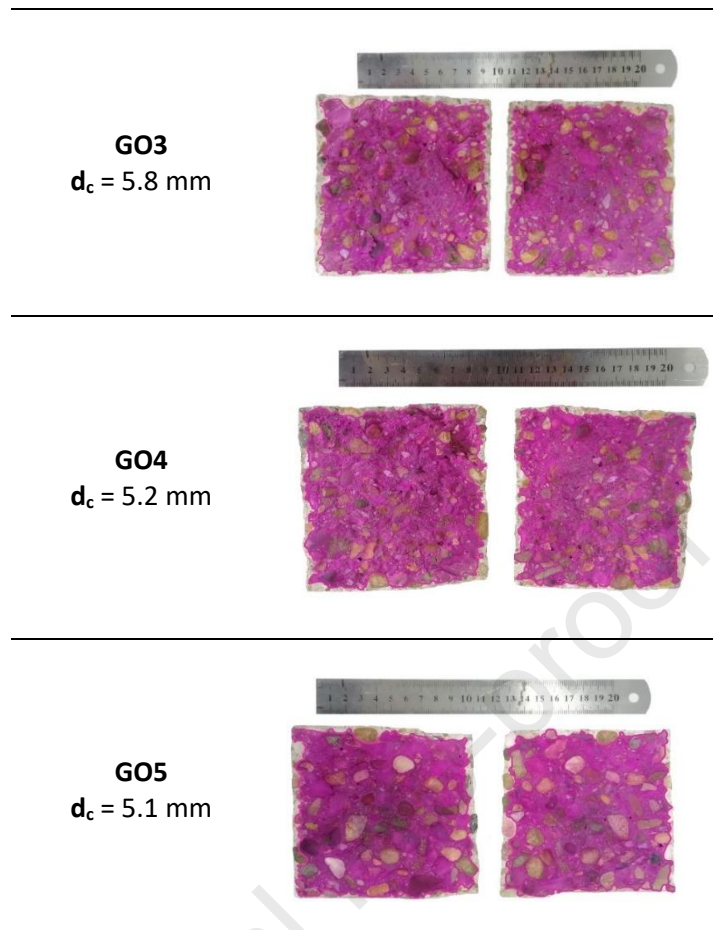


Figure 4. Depth of carbonation in concrete after 365 days of exposure (d_c = average depth of carbonation)

In order to have more information about the carbonation resistance of the concrete samples studied, the carbonation speed is calculated (

Figure 5). The concrete samples with GO applications on their surface achieve a considerable reduction in the carbonation speed, when compared to the control samples. The results achieved coincide with what happened with the depth parameter, which is logical, since it depends directly on it. Comparing the samples with GO application with the control samples, the carbonation speed decreased by 22%, 31%, 35%, 41% and 42%, for samples GO1, GO2, GO3, GO4 and GO, respectively. Considering the results achieved, the advantages of GO surface treatment on concrete are evident.

The creation of a dense GO layer that adapts and adheres perfectly to the surface of the concrete is one of the possible mechanisms that justifies the improvement in carbonation resistance. The spraying of the GO dispersion allowed the GO sheets to be spread evenly over the surface of the concrete samples [37,38], creating an increasingly dense layer as the number of applications of the treatment increased. Previously published studies revealed that the presence of oxygen functional groups in GO films can react with $\text{Ca}(\text{OH})_2$ or CSH [39], which means that the GO layer is firmly bonded to the concrete surface. Due to this strong bond, the size and number of microcracks and pores on the concrete surface can be significantly reduced. Therefore, the entry of gases into the concrete is hindered, increasing the resistance to carbonation.

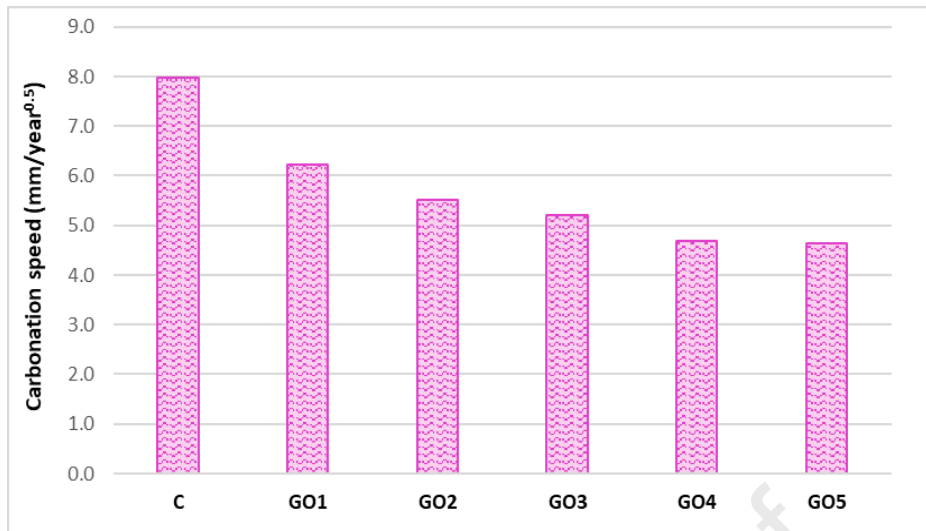


Figure 5. Carbonation speeds of concrete samples

The application of GO coating effectively increased the resistance to carbonation, results that coincide with those achieved in other studies that apply other type of nanoparticles as coatings [40–42]. Li et al. [40] investigated coatings for concrete (chlorinated rubber, aliphatic polyurethane and epoxy resin) mixed with nano-SiO₂ particles; reaching a 44% increase in carbonation resistance. Fajardo et al. [41] examined that the application of silicon nanoparticles on cement-based materials reduced the carbonation depth by 67%, due to pore blocking. Similarly, Franzoni et al. [42] found that the application of two types of dispersions, aqueous nanosilica dispersion with and without the addition of sodium silicate, reduced the carbonation depth by 46% and 17%, respectively. The difference in the results obtained is due to the fact that sodium silicate is able to penetrate deeper into the concrete, making it possible the occlusion of the pores and, consequently, hindering their permeability.

3.2. Electrical resistivity

The distribution of pores in concrete is closely linked to its electrical resistivity. The electrical resistivity of a concrete increases when its pore network is finer and the interconnection between the pore is smaller [43,44]. Therefore, it is important to carry out a study on the behavior of concrete with respect to the electrical resistivity parameter.

Figure 6 shows the electrical resistivity results obtained for each type of concrete samples analyzed. As it can be seen, the electrical resistivity of the concrete increased significantly after the application of GO on its surface. Thus, increases of 49%, 59%, 66%, 68% and 75% were achieved for samples GO1, GO2, GO3, GO4 and GO5, respectively, when compared to the control samples.

The different applications of GO on the surface of the concrete effectively promoted the concrete's own resistivity, which boosted its intrinsic corrosion resistance. ASTM C876-91 standard [45] was used to evaluate the increase in corrosion protection provided by the GO applications to the concrete on the basis of electrical resistivity measurements. Following the limit ranges established in the aforementioned standard, one and two applications of GO implied that the concrete presented a moderate corrosion risk, the same as the risk presented by the control samples, although it is worth highlighting that, when these applications of GO were made, the risk value obtained was very close to the low corrosion risk limit. From the third application of GO onwards, the concrete presents a low corrosion risk.

In relation to the results obtained, the advantages that the application of GO on the surface of the concrete can provide in terms of protection against corrosion are notable. It has already been said that resistivity is a parameter that is directly related to the structure and porosity of the concrete. Therefore, a reduction in the porosity of the concrete is expected to result in higher electrical resistivities [46]. The reduction in porosity could be explained by the bonding between the GO coating layer and the concrete surface. Presumable chemical interactions of the CSH or $\text{Ca}(\text{OH})_2$ of concrete with the oxygen functional groups present in the GO could produce advantageous chemical and physical bonds [39]. These interactions could decrease the amount of free pores on the concrete surface and block the interconnectivity between them, thus increasing the electrical resistivity.

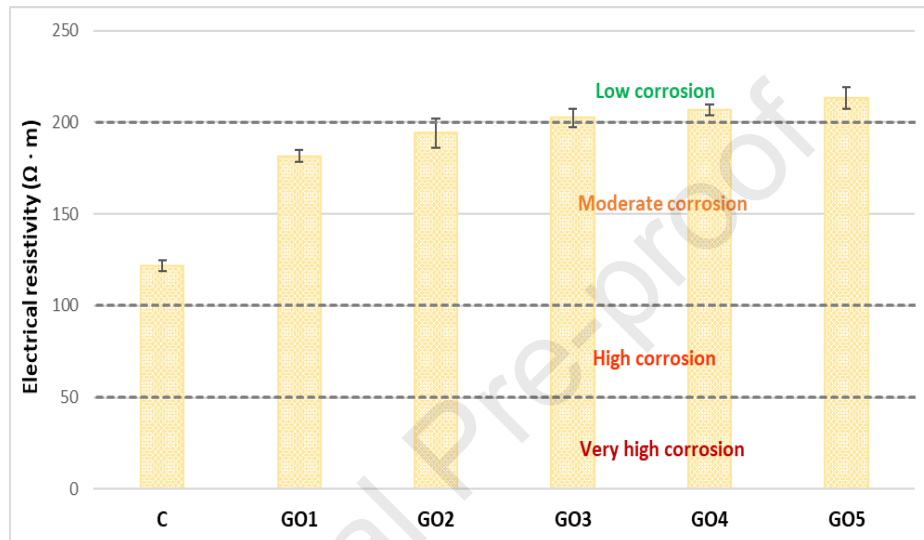


Figure 6. Electrical resistivity of concrete samples and their corrosion risk

Previous works obtained by other researchers have also pointed out that the application of other nanoparticles on the surface of concrete produces an increase in its electrical resistivity, in agreement with the results herein presented in the case of GO. Fajardo et al. [41] determined that the electrical resistivity increased up to 1.5 times in concrete samples with silicon nanoparticles on their surface, with respect to untreated samples. They attributed the increase in resistivity to possible pore blockages and decreased pore interconnections. Thus, the results obtained by us are comparable to those of those researchers, suggesting that the application of GO on the surface of concrete might exert a similar effect to the application of silicon nanoparticles.

3.3. Chloride ion diffusion

The results obtained in the multi-regime test to determine the diffusion of chloride ions are shown in Figure 7. Two phases can be distinguished in the development of this test. The first phase is the non-steady state, in which the arrival of chlorides into the vessel (which is initially free of chloride) is indistinguishable. During this phase, chloride ions pass through the thickness of the concrete specimen and react with the hydrated phases of the cement. Immediately after this, the second phase of the test, which is the steady state, takes place. In this second phase, chloride ions already start to appear in the collection vessel and gradually increase in concentration.

Figure 7 shows that GO1 and GO2 have a short non-stationary phase, as occurs with sample C (control), detecting the arrival of chloride ions in the vessel earlier than in the rest of the

samples. The opposite occurs in samples GO3, GO4 and GO5, which have a longer non-stationary phase, which lengthens in time as the number of GO applications increases. As for the second or stationary phase, it is observed that as the number of GO applications increases, the concentration of chloride ions decreases, demonstrating the protective effect of GO on the concrete surface.

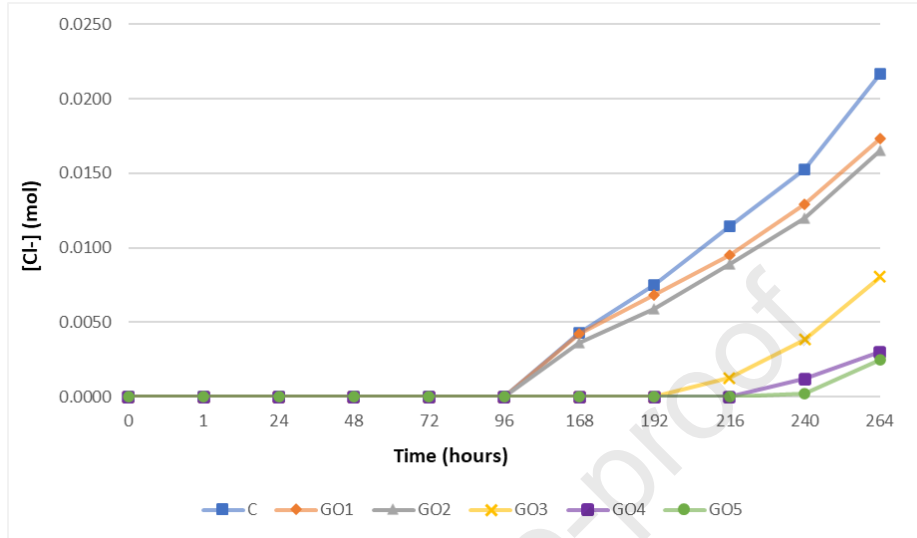


Figure 7. Variation of chloride concentration with time in concrete samples

The diffusion coefficients for the stationary phase and for the non-stationary phase of the various concrete samples analyzed are shown in Figure 8. In general, in both phases, the diffusion coefficients decrease after the application of GO on the surface of the concrete. Thus, the larger the GO surface concentration, the lower the diffusion coefficient of such concrete. Analyzing each of the phases separately, and in comparison with the control samples, it is determined that the non-steady-state diffusion coefficient (D_{ns}) decreased by 3%, 7%, 36%, 41% and 51% for samples GO1, GO2, GO3, GO4 and GO5, respectively. Similarly, the steady-state diffusion coefficient (D_s) decreased by 6%, 13%, 31%, 64% and 75% for samples GO1, GO2, GO3, GO4 and GO5, respectively.

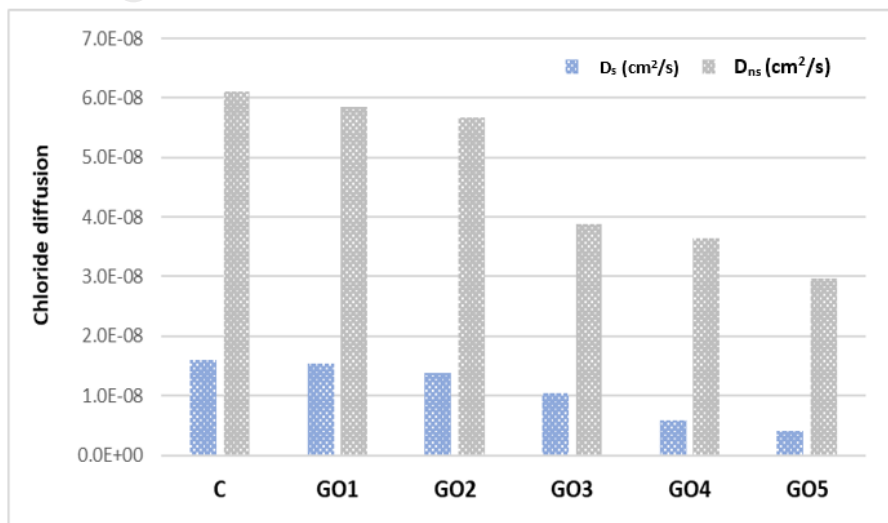


Figure 8. Diffusion coefficients of chloride ions on steady-state and non-steady-state phases

To study in more detail the resistance of concrete to chloride ion diffusion, the diffusion coefficients of each of the phases are analyzed in relation to the surface treatment of the concrete samples (Figure 9). As previously specified, in both phases studied, the diffusion coefficient of chloride ions decreases after increasing the number of GO applications (i.e. upon higher GO concentration) on the concrete surface, there being a linear relationship.

Analyzing the results achieved, it is determined that the application of GO on surface brings significant advantages against concrete protection. Due to the GO network formed, the surface of the concrete that is exposed to chlorides is smaller, which means less ion penetration. The GO network formed on the surface may have some defect, which could allow more aggressive ions to penetrate into the concrete. However, because some oxygenated functional groups (epoxy, carboxylic acids and hydroxyl) are present on the surface of GO [47], they could cause a negative charge that repels chloride ions, thus preventing their penetration into the concrete. This chloride ion repulsion mechanism has been studied in detail in an investigation of water and alkali ion purification in GO membranes [48–50]. The repulsion mechanism would involve blocking the ions as they pass through the GO layers, reducing the number of chloride ions that manage to enter the concrete pores.

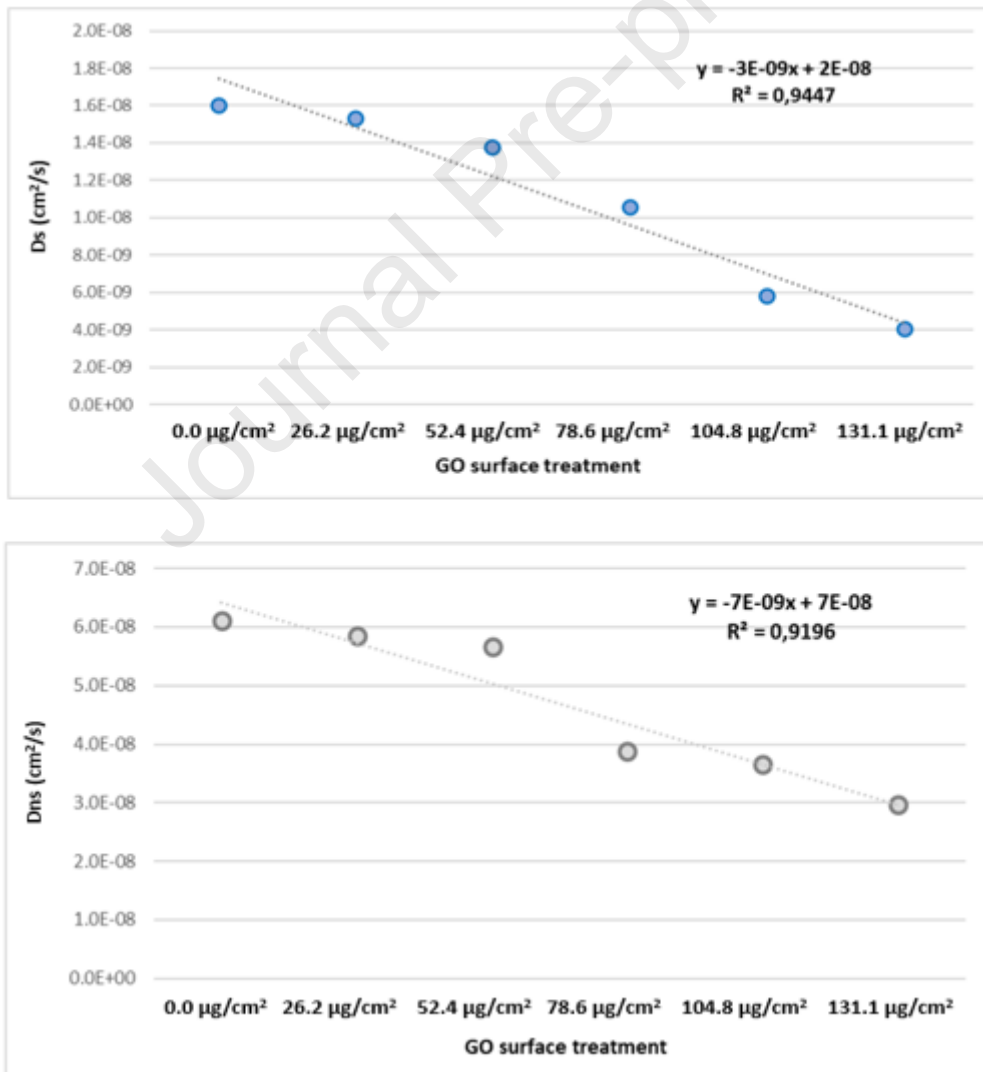


Figure 9. Stationary (D_s) and non-stationary (D_{ns}) diffusion coefficients for each type of surface application

The results showed that the application of GO on the surface of concrete effectively promoted its resistance to chloride ion diffusion. Similarly, results achieved by other researchers show that the use of nanoparticle-based coatings promoted the resistance to chloride ion penetration [51–54]. Li et al. [51] applied a cementitious coating that they had previously modified with polymers by adding 0.5% nano-SiO₂ or nano-TiO₂, achieving improved chloride resistance. This improvement in resistance was linked to the filling effect and reduction of porosity produced by the coating. Similarly, Li et al. [52] applied polymeric coatings (polyurethane, epoxy resin and chlorinated rubber) which they modified by incorporation nano-TiO₂ at 2 wt%. They succeeded in decreasing the chloride ion penetration by 60%, 62% and 77%, respectively.

On the other hand, Hou et al. [53] applied as surface treatment silane films previously modified with GO, achieving a decrease in the transport rate of chloride ions by almost 70%. The application of this surface treatment implied an increase in concrete protection and greatly alleviated concrete degradation. Guo et al. [54] performed the application of a surface treatment based on epoxy resin modified with 0.5% TiO₂ – graphene, which allowed reducing the penetration depth and the diffusion coefficient of chloride ions. Thus, they achieved a 77% reduction in the samples to which they applied the surface treatment.

The results achieved by all these researchers are comparable to the results achieved in this investigation. Such high values of chloride ion diffusion reduction are achieved when a fourth or fifth application of GO is performed. Therefore, the application of GO on the concrete surface can exert a similar effect to the application of the treatments used by all these researchers. It is notable, however, that the treatments employed in those studies entail nanoparticles as a filler for the actual protective material, not as the sole surface treatment. Conversely, our approach, not only fully exploits the benefits of using a single nanomaterial with an easy application methodology, but it is also entirely based on an organic composition (GO is mainly made of carbon and oxygen). Altogether, our approach is more practical, and economically and environmentally more appealing.

3.4. Colorimetric Analysis

After the application of the coating treatment, the surface of the concrete is analyzed for possible color changes (Figure 10). For this purpose, a colorimetric analysis is performed, which is based on the CIE 1976 color system coding. Figure 11 shows a summary table of the color analysis performed, detailing the possible color changes that may have occurred on the surface of the concrete. If we observe it, to the naked eye no color changes can be observed.

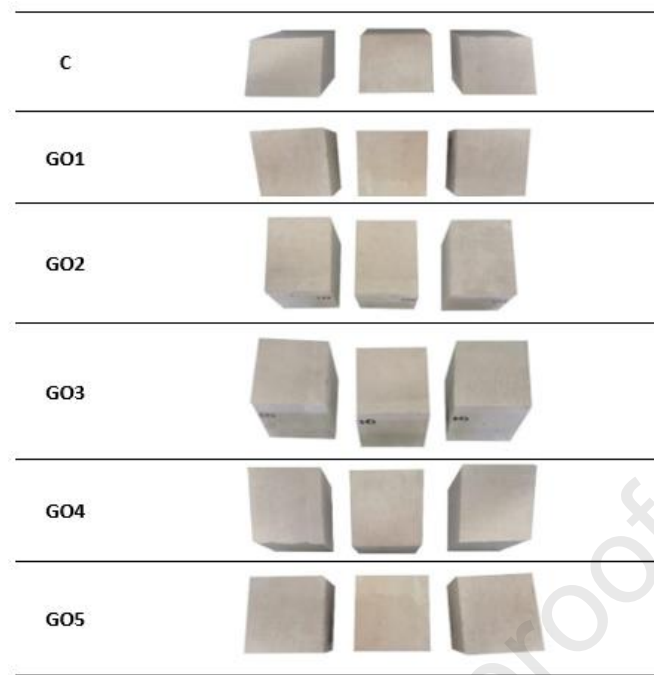


Figure 10. Concrete samples on which colorimetric analysis is performed

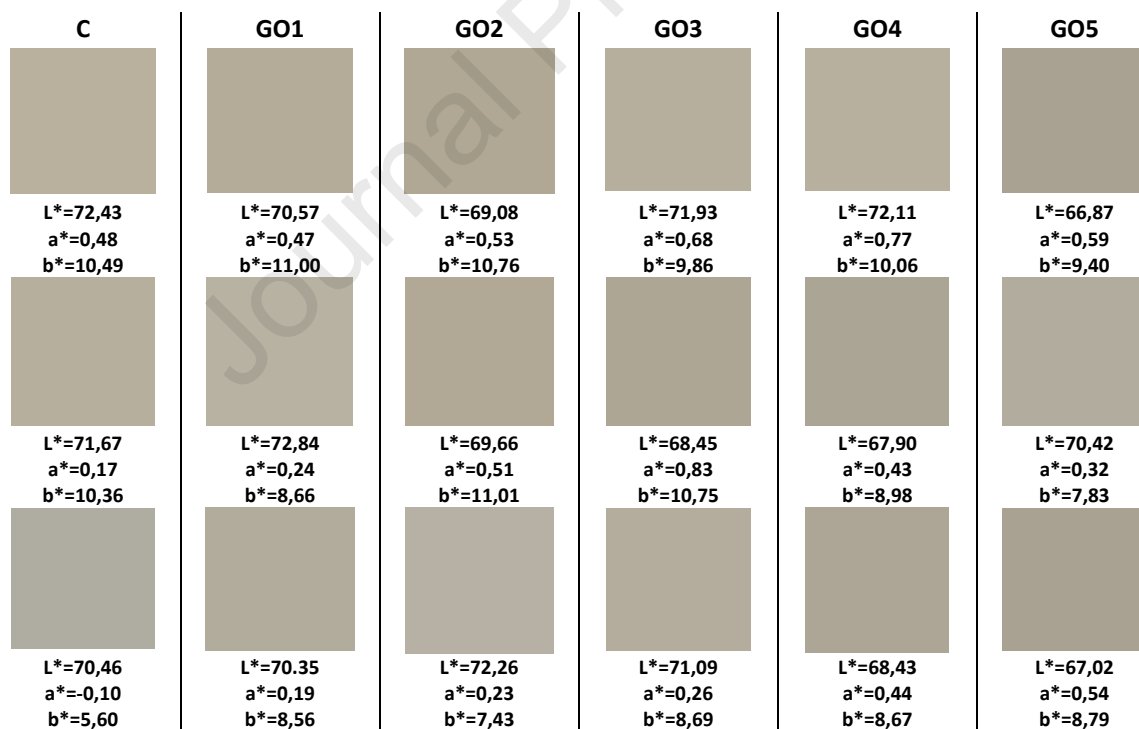


Figure 11. Color charts based on CIE coding

The color changes obtained are analyzed in more depth, for this purpose a study is made of the chromatic variation (ΔE) that exists between the samples that have received GO applications and the control samples. Table 3 shows the parameters (ΔL^* , Δa^* , Δb^*) defining the chromatic variation.

Table 3. Color variation with respect to uncoated concrete samples

Specimens	ΔL^*	Δa^*	Δb^*	ΔE
GO1	0.27	-0.11	-0.59	0.66
GO2	1.19	-0.24	-0.92	1.52
GO3	1.03	-0.41	-0.95	1.46
GO4	2.04	-0.36	-0.42	2.11
GO5	3.42	-0.30	0.14	3.44

Once the color variation results have been obtained for each of the concrete samples studied, they are analyzed considering the tolerance thresholds for color variation. These tolerance thresholds are set out in ISO 12647-2, which is the standard in charge of printing requirements. This standard established that if ΔE is less than 3, it is referred to as JND or “just noticeable difference”. Taking this into account, the results obtained show that up to the fourth application of GO, the surface of the concrete shows a barely perceptible color difference. From the fifth application of GO onwards, the color changes start to be observable. Therefore, the application of GO on the surface of the concrete hardly modifies its final color, maintaining its initial appearance, thus being a material that hardly influences the aesthetic properties of the concrete. Thanks to the fact that GO does not cause a drastic color change it can help the fact that it can be applied in areas where extra reinforcement is necessary due to the fact that they may suffer greater wear. It is therefore possible to locally reinforce a part of the structure without incurring a large aesthetic cost.

3.5. SEM Analysis

In order to analyze in a more detailed way what morphological changes can occur on the surface of the concrete samples after the application of the GO surface treatment, SEM observations are performed. Figure 12 shows the SEM images (magnification x500) of the Control (C), GO1, GO3 and GO5 samples. As can be seen in the Control sample (C), there is no type of coverage on the surface, and numerous microcracks and pores of different sizes can be seen in the cement hydration products. Therefore, all of them are easily accessible for the penetration of any type of substance. After the first application of GO, it can be observed that there is a thin coating on the surface of the concrete, it is beginning to be appreciated that there are not so many microcracks or pores and also these are of smaller size, if we compare it with the Control samples (C). As the number of applications with GO increases, it can be observed that the surface of the concrete presents a denser coating layer, as occurs in samples GO3 and GO5. In these samples there are no microcracks and the pores are tiny. The decrease of microcracks and pores in the cement hydration products implies the formation of a denser microstructure of the concrete surface, which would result in the formation of a barrier against the penetration of any type of substance harmful to the concrete. The improvement observed in the microstructure of the GO3 and GO5 samples indicates that the surface treatment with GO may have facilitated the cement hydration process, and therefore, the densification of the concrete microstructure.

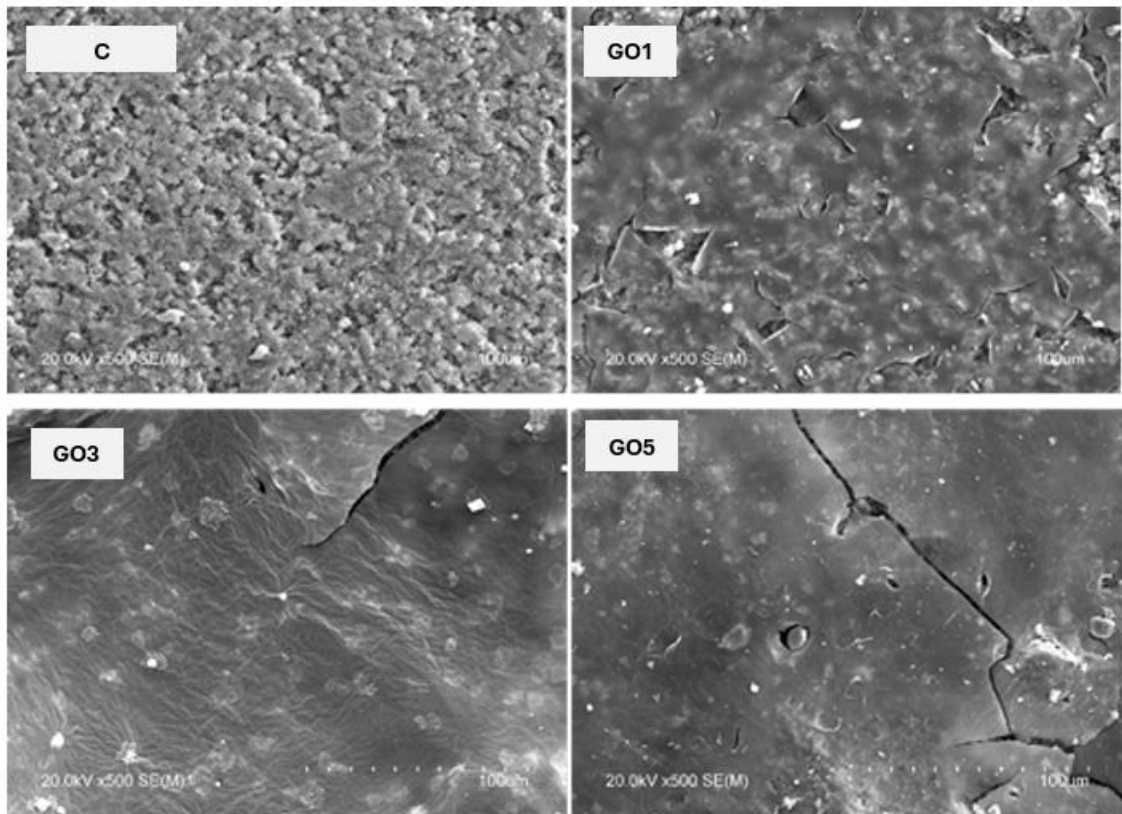


Figure 12. SEM images of the concrete surface of the specimens studied (Control, GO1, GO3 and GO5)

In the first instance, just a quick consideration on the fact that a GO coating as a protective treatment for the concrete surface may seem contradictory, since a simple aqueous dispersion of such a hydrophilic nanomaterial can endow concrete with aqueous impermeability. This mechanism suggests that the main driver of protection is the barrier properties of GO. Previous studies [55] established that the membranes that form the GO act as a selective screen, making it a barrier. Selective screening is one of the most relevant properties of 2D GO assemblies. Some metal ions (Al^{3+} , Ca^{3+} , Mg^{2+} , etc.) are able to act as cross-linking agents for the GO membranes, which is what forms the assemblies and endows it with the selective screening capability. Some of the alkaline earth cations described above are key components of the cement used in the manufacture of concrete, such as Ca^{3+} , Mg^{2+} and Al^{3+} . This could lead to a chemical bonding of GO with the above-mentioned cations present on the concrete surface [56]. However, further studies, such as the present research, are needed to learn more about the selective screening effect of GO membranes and to establish the specific mechanisms (physical and chemical) that allows GO to adhere to the surface of concrete, making it a good sealant for cement-based materials. Consequently, the application of GO as a surface treatment will imply that the number and size of pores will decrease and that the surface of the concrete exposed to aggressive actions will be effectively reduced, since GO would be creating a preventive shield against the entry of any type of substance, but mainly against the entry of salts and ions.

4. Conclusions

This work reports on the controlled application of graphene oxide (GO) as a surface treatment for concrete protection. For this purpose, an aqueous suspension of GO is sprayed as a

protective coating layer and its influence on the durability, microstructural and colorimetric properties of concrete surfaces is studied. To ascertain the durability of concrete, the following tests were performed: resistance to carbonation, resistance to chloride ion diffusion and electrical resistivity measurements. For the study of the microstructural and colorimetric properties of concrete, SEM and colorimetric analyses were performed, respectively. The results determined that the application of GO improved the carbonation resistance of the concrete, effectively reducing the carbonation speed. The best results were obtained after applications of $104.8 \mu\text{g}/\text{cm}^2$ and $131.1 \mu\text{g}/\text{cm}^2$ of GO, which decreased the carbonation speed by approximately 40% compared to samples without any surface treatment. Regarding electrical resistivity, the results specified that the surface coating with GO implied an increase in this parameter. Thus, the best results were obtained with the application of $131.1 \mu\text{g}/\text{cm}^2$ GO, as it increased the electrical resistivity of the concrete by up to 75%, meaning that the concrete presented a very high level of protection against corrosion. In addition, the results also showed that the application of GO effectively reduced the diffusion of chloride ions. Thus, the application of $131.1 \mu\text{g}/\text{cm}^2$ GO showed the best results, reducing the diffusion of chloride ions by up to 75% compared to samples without any surface treatment. The SEM analysis showed that the surface of the concrete was modified after the application of GO. The GO flakes are able to adhere to the surface of the concrete and modify its microstructure and porosity. The greater the amount of GO deposited on the surface, the greater the reduction in the number and size of pores; and therefore, the smaller the surface exposed to the aggressive actions of the environment. Finally, the results obtained in the colorimetric analysis determined that, although the amount of GO deposited on the surface of the concrete increased, there was no perceptible difference in colour, which has important implications for the aesthetic cost. Only small colour changes begin to be observable after applications of $131.1 \mu\text{g}/\text{cm}^2$ GO.

These findings shed light on the promising use of GO aqueous suspension as a surface treatment of concrete by mitigating the penetration of any kind of substance; inducing strong resistance to wear and deterioration; thus, preserving the mechanical properties of concrete and thereby increasing its durability. Similarly, the direct application of this nanomaterial (without other additives or components) is the consequence of the excellent results achieved on an already formed surface, being more practical at an operational level, and more suitable in environmental and economic terms.

Acknowledgements

Andrea Antolín-Rodríguez and Daniel Merino-Maldonado would like to thank the Junta de Castilla y León for the support granted through the “Ayudas para financiar la contratación predoctoral de personal investigador”, cofinanced by the European Social Fund and resulting in ORDEN EDU/875/2021 and ORDEN EDU/601/2020.

José Miguel González-Domínguez and María Fernández-Raga greatly acknowledge the Spanish Ministry of Science and Innovation (MICINN) for the funded project “Nanoshield” (PID2020-120439RA-I00)

Conflict of interest

None.

Funding Resources

Not applicable.

References

- [1] F.P. Glasser, J. Marchand, E. Samson, Durability of concrete — Degradation phenomena involving detrimental chemical reactions, *Cem Concr Res* 38 (2008) 226–246. <https://doi.org/10.1016/J.CEMCONRES.2007.09.015>.
- [2] A. Goyal, H.S. Pouya, E. Ganjian, P. Claisse, A Review of Corrosion and Protection of Steel in Concrete, *Arab J Sci Eng* 43 (2018) 5035–5055. <https://doi.org/10.1007/s13369-018-3303-2>.
- [3] A. Dushimimana, A.A. Niyonsenga, F. Nzamurambaho, A review on strength development of high performance concrete, *Constr Build Mater* 307 (2021) 124865. <https://doi.org/10.1016/J.CONBUILDMAT.2021.124865>.
- [4] F. Tittarelli, G. Moriconi, The effect of silane-based hydrophobic admixture on corrosion of reinforcing steel in concrete, *Cem Concr Res* 38 (2008) 1354–1357. <https://doi.org/10.1016/J.CEMCONRES.2008.06.009>.
- [5] A.P.F. Pinto, J.D. Rodrigues, Stone consolidation: The role of treatment procedures, *J Cult Herit* 9 (2008) 38–53. <https://doi.org/10.1016/J.CULHER.2007.06.004>.
- [6] C.D. Vacchiano, L. Incarnato, P. Scarfato, D. Acierno, Conservation of tuff-stone with polymeric resins, *Constr Build Mater* 22 (2008) 855–865. <https://doi.org/10.1016/J.CONBUILDMAT.2006.12.012>.
- [7] F. Altmann, V. Mechtcherine, Durability design strategies for new cementitious materials, *Cem Concr Res* 54 (2013) 114–125. <https://doi.org/10.1016/J.CEMCONRES.2013.08.008>.
- [8] M. Safiuddin, K.A. Soudki, Sealer and coating systems for the protection of concrete bridge structures, *International Journal of Physical Sciences* 6 (2011) 8188–8199. <https://doi.org/10.5897/IJPSX11.005>.
- [9] P. Hou, X. Cheng, J. Qian, R. Zhang, W. Cao, S.P. Shah, Characteristics of surface-treatment of nano-SiO₂ on the transport properties of hardened cement pastes with different water-to-cement ratios, *Cem Concr Compos* 55 (2015) 26–33. <https://doi.org/10.1016/J.CEMCONCOMP.2014.07.022>.
- [10] E. Franzoni, B. Pigino, C. Pistolesi, Ethyl silicate for surface protection of concrete: Performance in comparison with other inorganic surface treatments, *Cem Concr Compos* 44 (2013) 69–76. <https://doi.org/10.1016/J.CEMCONCOMP.2013.05.008>.
- [11] M.M. Hassan, H. Dylla, L.N. Mohammad, T. Rupnow, Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement, *Constr Build Mater* 24 (2010) 1456–1461. <https://doi.org/10.1016/J.CONBUILDMAT.2010.01.009>.
- [12] P. Scarfato, L. Di Maio, M.L. Fariello, P. Russo, L. Incarnato, Preparation and evaluation of polymer/clay nanocomposite surface treatments for concrete durability enhancement, *Cem Concr Compos* 34 (2012) 297–305. <https://doi.org/10.1016/J.CEMCONCOMP.2011.11.006>.

- [13] A.A. Shirzadi Javid, P. Ghoddousi, M. Zareechian, A. Habibnejad Korayem, Effects of Spraying Various Nanoparticles at Early Ages on Improving Surface Characteristics of Concrete Pavements, *International Journal of Civil Engineering* 17 (2019) 1455–1468. <https://doi.org/10.1007/s40999-019-00407-4>.
- [14] K. Gordon, K. Kupwade-Patil, H.E. Cardenas, K. Gordon, L.S. Lee, Corrosion Mitigation in Reinforced Concrete Beams via Nanoparticle Treatment Article in *Aci Materials Journal*, 2012. <https://www.researchgate.net/publication/257023432>.
- [15] D. González-Campelo, M. Fernández-Raga, Á. Gómez-Gutiérrez, I. Guerra-Romero, J.M. González-Domínguez, Extraordinary Protective Efficacy of Graphene Oxide over the Stone-Based Cultural Heritage, (2021). <https://doi.org/10.1002/admi.202101012>.
- [16] A. Habibnejad Korayem, P. Ghoddousi, A.A. Shirzadi Javid, M.A. Oraie, H. Ashegh, Graphene oxide for surface treatment of concrete: A novel method to protect concrete, *Constr Build Mater* 243 (2020). <https://doi.org/10.1016/j.conbuildmat.2020.118229>.
- [17] R. Martínez-García, D. González-Campelo, F.J. Fraile-Fernández, A.M. Castañón, P. Caldevilla, S. Giganto, A. Ortiz-Marqués, F. Zelli, V. Calvo, J.M. González-Domínguez, M. Fernández-Raga, Performance Study of Graphene Oxide as an Antierosion Coating for Ornamental and Heritage Dolostone, *Adv Mater Technol* (2023). <https://doi.org/10.1002/admt.202300486>.
- [18] A. Antolín-Rodríguez, D. Merino-Maldonado, Á. Rodríguez-González, M. Fernández-Raga, J.M. González-Domínguez, A. Juan-Valdés, J. García-González, Statistical Study of the Effectiveness of Surface Application of Graphene Oxide as a Coating for Concrete Protection, *Coatings* 13 (2023) 213. <https://doi.org/10.3390/coatings13010213>.
- [19] S. Lv, Y. Ma, C. Qiu, T. Sun, J. Liu, Q. Zhou, Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites, *Constr Build Mater* 49 (2013) 121–127. <https://doi.org/10.1016/J.CONBUILDMAT.2013.08.022>.
- [20] Z. Pan, L. He, L. Qiu, A.H. Korayem, G. Li, J.W. Zhu, F. Collins, D. Li, W.H. Duan, M.C. Wang, Mechanical properties and microstructure of a graphene oxide–cement composite, *Cem Concr Compos* 58 (2015) 140–147. <https://doi.org/10.1016/J.CEMCONCOMP.2015.02.001>.
- [21] M. Saafi, L. Tang, J. Fung, M. Rahman, J. Liggat, Enhanced properties of graphene/fly ash geopolymeric composite cement, *Cem Concr Res* 67 (2015) 292–299. <https://doi.org/10.1016/J.CEMCONRES.2014.08.011>.
- [22] D. Kang, K.S. Seo, H.Y. Lee, W. Chung, Experimental study on mechanical strength of GO-cement composites, *Constr Build Mater* 131 (2017) 303–308. <https://doi.org/10.1016/J.CONBUILDMAT.2016.11.083>.
- [23] A. Mohammed, J.G. Sanjayan, W.H. Duan, A. Nazari, Incorporating graphene oxide in cement composites: A study of transport properties, *Constr Build Mater* 84 (2015) 341–347. <https://doi.org/10.1016/J.CONBUILDMAT.2015.01.083>.
- [24] Q. Wang, G.D. Qi, Y. Wang, H.Y. Zheng, S.H. Shan, C.X. Lu, Research progress on the effect of graphene oxide on the properties of cement-based composites, *Xinxing Tan Cailiao/New Carbon Materials* 36 (2021) 729–750. [https://doi.org/10.1016/S1872-5805\(21\)60071-9](https://doi.org/10.1016/S1872-5805(21)60071-9).

- [25] C. Liu, X. Huang, Y.Y. Wu, X. Deng, Z. Zheng, Z. Xu, D. Hui, Advance on the dispersion treatment of graphene oxide and the graphene oxide modified cement-based materials, *Nanotechnol Rev* 10 (2021) 34–49. <https://doi.org/10.1515/ntrev-2021-0003>.
- [26] EN 12620+A1, Belgium, Brussels, 2003.
- [27] UNE-EN 1992-1-1:2013. Eurocode 2: Design of concrete structures - Part 1-1: General rules and rules for buildings., Madrid, n.d.
- [28] EN 197-1. Cement. Part 1: Composition, Specifications and Conformity Criteria for Common Cements, Belgium, Brussels, 2011.
- [29] Structural Code, Madrid, 2021.
- [30] A.H. Alateah, Graphene concrete: Recent advances in production methods, performance properties, environmental impact and economic viability, *Case Studies in Construction Materials* 19 (2023) e02653. <https://doi.org/10.1016/J.CSCM.2023.E02653>.
- [31] V. León, J.M. González-Domínguez, J.L.G. Fierro, M. Prato, E. Vázquez, Production and stability of mechanochemically exfoliated graphene in water and culture media, *Nanoscale* 8 (2016) 14548–14555. <https://doi.org/10.1039/c6nr03246j>.
- [32] T.P. Hills, F. Gordon, N.H. Florin, P.S. Fennell, Statistical analysis of the carbonation rate of concrete, *Cem Concr Res* 72 (2015) 98–107. <https://doi.org/10.1016/J.CEMCONRES.2015.02.007>.
- [33] CEN. EN 12390-10 Determination of the carbonation resistance of concrete at atmospheric carbon dioxide levels., Brussels, Belgium, 2019.
- [34] R.B. Polder, W.H.A. Peelen, Characterisation of chloride transport and reinforcement corrosion in concrete under cyclic wetting and drying by electrical resistivity, *Cem Concr Compos* 24 (2002) 427–435. [https://doi.org/10.1016/S0958-9465\(01\)00074-9](https://doi.org/10.1016/S0958-9465(01)00074-9).
- [35] UNE 83988-1. Concrete durability test methods. In Determination of the Electrical Resistivity. Part 1: Direct Test (Reference Method), Madrid, Spain, 2008.
- [36] UNE 83987. Determination of chloride ion diffusion coefficients in hardened concrete. Multi-rate method., Madrid. Spain., 2014.
- [37] S. Lv, Y. Ma, C. Qiu, T. Sun, J. Liu, Q. Zhou, Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites, *Constr Build Mater* 49 (2013) 121–127. <https://doi.org/10.1016/J.CONBUILDMAT.2013.08.022>.
- [38] R. Martínez-García, D. González-Campelo, F.J. Fraile-Fernández, A.M. Castañón, P. Caldevilla, S. Giganto, A. Ortiz-Marqués, F. Zelli, V. Calvo, J.M. González-Domínguez, M. Fernández-Raga, Performance Study of Graphene Oxide as an Antierosion Coating for Ornamental and Heritage Dolostone, *Adv Mater Technol* 8 (2023). <https://doi.org/10.1002/admt.202300486>.
- [39] Z. Pan, L. He, L. Qiu, A.H. Korayem, G. Li, J.W. Zhu, F. Collins, D. Li, W.H. Duan, M.C. Wang, Mechanical properties and microstructure of a graphene oxide–cement composite, *Cem Concr Compos* 58 (2015) 140–147. <https://doi.org/10.1016/J.CEMCONCOMP.2015.02.001>.

- [40] G. Li, W. Hu, H. Cui, J. Zhou, Long-term effectiveness of carbonation resistance of concrete treated with nano-SiO₂ modified polymer coatings, *Constr Build Mater* 201 (2019) 623–630. <https://doi.org/10.1016/J.CONBUILDMAT.2019.01.004>.
- [41] G. Fajardo, A. Cruz-López, D. Cruz-Moreno, P. Valdez, G. Torres, R. Zanella, Innovative application of silicon nanoparticles (SN): Improvement of the barrier effect in hardened Portland cement-based materials, *Constr Build Mater* 76 (2015) 158–167. <https://doi.org/10.1016/J.CONBUILDMAT.2014.11.054>.
- [42] E. Franzoni, B. Pigino, C. Pistolesi, Ethyl silicate for surface protection of concrete: Performance in comparison with other inorganic surface treatments, *Cem Concr Compos* 44 (2013) 69–76. <https://doi.org/10.1016/J.CEMCONCOMP.2013.05.008>.
- [43] P.J. Tumidajski, A.S. Schumacher, S. Perron, P. Gu, J.J. Beaudoin, On the relationship between porosity and electrical resistivity in cementitious systems, *Cem Concr Res* 26 (1996) 539–544. [https://doi.org/10.1016/0008-8846\(96\)00017-8](https://doi.org/10.1016/0008-8846(96)00017-8).
- [44] Z. Liu, Y. Zhang, Q. Jiang, Continuous tracking of the relationship between resistivity and pore structure of cement pastes, *Constr Build Mater* 53 (2014) 26–31. <https://doi.org/10.1016/J.CONBUILDMAT.2013.11.067>.
- [45] ASTM C876-91. Standard test method for half-cell potentials of uncoated reinforcing steel in concrete. , 1999.
- [46] G. Andreu, E. Miren, Experimental analysis of properties of high performance recycled aggregate concrete, *Constr Build Mater* 52 (2014) 227–235. <https://doi.org/10.1016/J.CONBUILDMAT.2013.11.054>.
- [47] F. Mouhat, F.X. Coudert, M.L. Bocquet, Structure and chemistry of graphene oxide in liquid water from first principles, *Nat Commun* 11 (2020). <https://doi.org/10.1038/s41467-020-15381-y>.
- [48] P. Sun, M. Zhu, K. Wang, M. Zhong, J. Wei, D. Wu, Z. Xu, H. Zhu, Supporting Information Selective Ion Penetration of Graphene Oxide Membranes, n.d.
- [49] P. Sun, F. Zheng, M. Zhu, K. Wang, M. Zhong, D. Wu, Z. Xu, H. Zhu, Supplementary Information Selective Trans-membrane Transport of Alkali and Alkaline Earth Cations through Graphene Oxide Membranes Based on Cation- π Interactions, n.d.
- [50] P. Sun, K. Wang, H. Zhu, Recent Developments in Graphene-Based Membranes: Structure, Mass-Transport Mechanism and Potential Applications, *Advanced Materials* 28 (2016) 2287–2310. <https://doi.org/10.1002/adma.201502595>.
- [51] G. Li, Y. Ding, T. Gao, Y. Qin, Y. Lv, K. Wang, Chloride resistance of concrete containing nanoparticle-modified polymer cementitious coatings, *Constr Build Mater* 299 (2021) 123736. <https://doi.org/10.1016/J.CONBUILDMAT.2021.123736>.
- [52] G. Li, H. Cui, J. Zhou, W. Hu, Improvements of Nano-TiO₂ on the Long-Term Chloride Resistance of Concrete with Polymer Coatings, (2019). <https://doi.org/10.3390/coatings9050323>.
- [53] D. Hou, C. Wu, B. Yin, X. Hua, H. Xu, X. Wang, S. Li, Y. Zhou, Z. Jin, W. Xu, H. Lu, Investigation of composite silane emulsion modified by in-situ functionalized graphene

- oxide for cement-based materials, *Constr Build Mater* 304 (2021) 124662. <https://doi.org/10.1016/J.CONBUILDMAT.2021.124662>.
- [54] S.Y. Guo, H.H. Luo, Z. Tan, J.Z. Chen, L. Zhang, J. Ren, Impermeability and interfacial bonding strength of TiO₂-graphene modified epoxy resin coated OPC concrete, *Prog Org Coat* 151 (2021) 106029. <https://doi.org/10.1016/J.PORGCOAT.2020.106029>.
- [55] Z. Wang, F. He, J. Guo, S. Peng, X. Quan Cheng, Y. Zhang, E. Drioli, A. Figoli, Y. Li, L. Shao, Cite this: *Mater. Adv.*, 2020, 1, 554 Inorganic Chemistry in 2011 from Nanchang University and her PhD in Chemical Engineering and Technology in 2017 from Open Access Article, 1 (2020) 554. <https://doi.org/10.1039/d0ma00191k>.
- [56] G.Y. Li, P.M. Wang, X. Zhao, Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes, *Carbon N Y* 43 (2005) 1239–1245. <https://doi.org/10.1016/J.CARBON.2004.12.017>.

Highlights

- Graphene oxide (GO) surface coating is used as a new surface sealer for concrete.
- GO could physically and chemically adhere to the concrete surface creating a dense layer on its surface.
- GO effectively attenuated the carbonation process and the penetration of chloride ions.
- GO is proposed as a surface coating for concrete to increase its durability and prolong its useful life.

Journal Pre-proof

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof