



The Impact of Water Dispersed Graphene Oxide on Physical Properties of Cement Paste

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Abstract. Nanomaterials, especially carbon-based products, have long been a cutting-edge research topic in the realm of concrete and cement. Among these, graphene along with its related compounds stand out as the most widely studied nano-additives for cementitious materials. Although some of this topic has been covered in the literature, more research is still necessary to completely comprehend the physical properties of cement composites containing graphene oxide (GO).

In order to investigate the impact of water-dispersed GO on the paste properties of physical cement, this study compares a typical paste. Using a 7-day curing period, six graphene oxide percentages (0.01%, 0.03%, 0.05%, 0.1%, 0.3%, and 0.5%) were studied. Setting time decreased to 0.05% graphene content, increased up to 0.3%, and plateaued thereafter. Workability reduced due to graphene oxide's high specific surface, affecting water absorbency. Electrical resistivity increased to 0.05% graphene content, decreasing afterward due to ion diffusion. Optimal Ultrasonic Pulse Velocity was observed at 0.3% graphene oxide. Lower values are attributed to voids and bubbles in graphene oxide-containing mixtures.

Keywords: Graphene oxide, Cement paste, Hydration, Setting time, Electrical resistivity, Workability, Heat of hydration, Nanotechnology.

1 Introduction

Nanotechnology has emerged as a transformative force in various engineering domains, offering solutions to challenges in electronics, biomedicine, and material science. Nanomaterials, characterized by enhanced properties such as thermal, mechanical, rheological, and electrical attributes, play a pivotal role in advancing material performance [1]. Notably, the utilization of nanotechnology in cementitious materials has demonstrated significant improvements in cement properties [2].

GO, a modified form of graphene known for its exceptional strength—it is 200 times more stronger than the steel [3], has emerged as a promising nanomaterial for enhancing cementitious composites. GO is oxidized from graphite, featuring oxygen molecules on

its planes and basal edges. The hydrophilic nature of GO, attributed to its oxygen-rich functional groups, facilitates its dispersion in composites [4]. The unique structural strength and high surface area of GO.

2 Importance of Study

Prior studies have indicated that the performance of GO incorporation in cement-based composites is highly dependent on the quantity of GO included in the mix design. It is significant to note that the majority of research in the aforementioned field has concentrated on particular traits alone. A thorough and methodical study employing a standard cementitious mixture is still required to assess the overall efficacy of GO and its impact on different properties. Furthermore, depending on its concentration, the influence of GO on the properties of cementitious binders varies, indicating a need for more research. This work aims to meticulously examine the physical properties of cementitious composites containing GO at concentrations of 0.01%, 0.03%, 0.05%, 0.1%, 0.3%, and 0.5% .

Three main types of nanomaterials can be identified based on their form and spatial arrangement: two-dimensional sheets, one-dimensional fibers, and zero-dimensional particles. The latter group includes GO nanosheets, which have shown to significantly alter cement's properties [5]. GO is said to have a Young's modulus of 1 TPa and an intrinsic strength of 100 GPa, indicating significant reinforcing potential in cement composites. Researchers have put forth a number of models that clarify how GO affects cement microstructure modification. [6] found that GO influences the morphology of hydration crystals by encouraging the growth of flower-like crystals. [7] illustrated how the denser microstructure that GO produces has an impact on the development of C-S-H gels. Additionally, [8] suggested a strong connection between GO and C-S-H, serving as a platform for the nucleation of C-S-H gel during the cement reaction.

While GO's oxygen content enhances its dispersibility, an optimal oxygen content is crucial to avoid structural defects that diminish thermal and electrical conductivity. Hydroxyl, carbonyl, and epoxy functional groups aid in the dispersion of GO in water, stable single-layered sheets were generated that contribute to improved bonding with cement products.

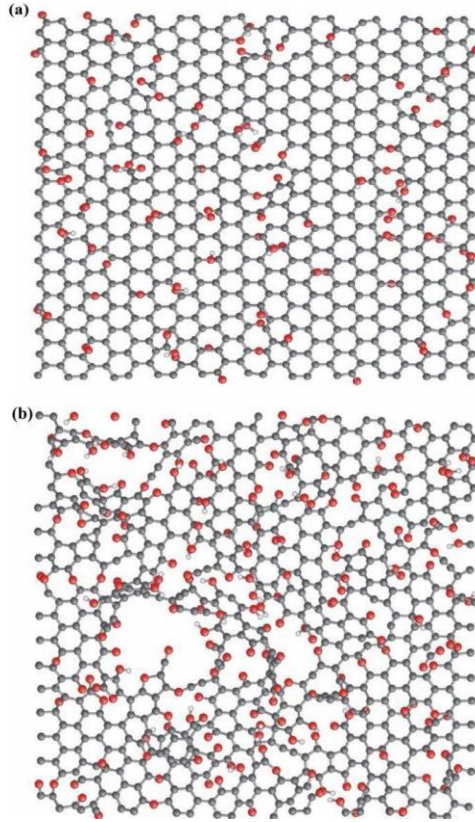


Fig. 1(a). The structure of GO featuring a content of 20% oxygen (Mattevi C. et al., 2010).

Fig. 2(b). The structure of GO featuring a content of 33% oxygen (Mattevi C. et al. 2010).

By examining the physical characteristics of cement pastes with varying graphene oxide concentrations, this study aims to identify the ideal graphene oxide content for maximum performance. The need to look into the physical properties of cement-based composites containing GO is the primary focus of this study. Graphene incorporation has been shown by several researchers to improve the physical properties of cement composites. [9] noted how GO nanosheets in contact with cement and water form GO agglomerates, which affect the lateral size and thickness. [10] revealed that adding graphene oxide to cement increased its rate of hydration. A seeding effect was proposed by the authors in [11] because GO agglomerates provide more nucleation sites.

Surface morphology analysis revealed wrinkled surfaces and cringed sheets of GO nanosheets with interlocked Van Der Waals forces. Fourier Transmission Infrared spectra confirmed the presence of hydroxyl, carbonyl, and alkenic bonds. Workability challenges in graphene- incorporated cement pastes were evident, with significant reductions reported by [12] and [13]. The hydrophilic nature of GO and its strong water-absorbing capacity reduced the presence of free water, which enhances frictional resistance between cement particles.

Water-reducing admixtures proved effective for improving the dispersibility of graphene oxide in cementitious composites [10]. However, despite various methods for dispersion enhancement, challenges remain due to economic and practical considerations.

Because functional groups cause conjugated bonds to break, the electrical resistivity of cementitious composites containing graphene oxide increased as the graphene content increased. Researchers highlighted the dependence of conduction on the amount of nano-carbon materials, indicating a threshold for percolation between 1 wt% and 5 wt%. Sonic velocity reduction in cementitious composites with graphene oxide suggested higher void content and embedded air bubbles, correlating with a decrease in density and workability.

3 Methodology

This section presents methodology adopted.

3.1 Materials

GO-enhanced cement composites were made using Bastion general purpose (GP) cement, which complies with AS3972 [66]. A fine aggregate that is used in cement mortar is river sand. It has a 50 μm to 4.75 mm particle size range and is derived from natural sources. To ensure consistent dispersion, distilled water and GO powder were combined to create an aqueous suspension by sonicating the mixture.

3.2 Mixture Preparation

The preparation of an GO aqueous suspension came before mixing the mortar. Table 1's mixture ratios were used to calculate the appropriate amounts of GO to add to distilled water. The ultrasonic cell crusher chamber held a 200 ml flask that was filled with water and GO nanosheet powder. The sonication process took two minutes, after which the flask was taken out. Throughout the experiment, a consistent water-to-cement (w/c) ratio of 0.45 was upheld.

Graphene oxide (GO) was added to the Hobart mortar mixer used to prepare the cement mortars. The necessary volumes of cement and sand, as listed in Table 1, were first mixed dry in the mixer for 30 seconds. After that, the remaining water and the sonicated GO solution were added and stirred for five minutes to get a homogenous consistency. The prepared mortar was poured into molds and vibrated for 30 seconds on a vibration table to ensure proper compaction and eliminate air bubbles. The molds were covered with polyethylene sheets to prevent water loss and cured in a water bath for a maximum of 28 days prior to testing. Following that, they were kept at room temperature (23 ± 2 oC) for a full day.

Numerous experiments, such as those measuring flowability loss, setting time, electrical resistivity, and ultrasonic pulse velocity (UPV), were conducted to evaluate the cement mortar's characteristics. While the other tests were carried out on different

samples measuring 285x75x75 mm, the setting time and flowability decrease tests were carried out on the fresh mortar sample.

. The molds used for the setting time and flowability loss tests had a total volume of 1375 cubic centimeters. For these tests, a mixture containing 1500 grams of cement and 2250 grams of sand were used in the testing. The water quantity was determined based on the 0.45 w/c ratio, resulting in 675 ml of water. The amount of graphene oxide varied according to its percentage in the mix, as outlined in Table 1.

Table 1. Graphene Oxide amount in Mix Design

Cement (grams) with percentage of Graphene Oxide in terms of	Graphene Oxide amount (grams)
1500x0.01%	0.15
1500x 0.03%	0.45
1500x 0.05%	0.75
1500x 0.1%	1.50
1500x 0.3%	4.50

In the concrete lab at Swinburne University, the required amounts of materials were thoroughly mixed using a hand mixer. The cement and sand were first mixed for five minutes, and GO was then dissolved in water using a sonicator for two minutes. After adding the required amount of water and the dispersed GO solution to the dry mixture, everything was thoroughly combined. After repeating this process, various graphene oxide percentages were obtained, and the mortar was then poured into molds according to those results..

4 Testing

4.1 Cement Mortar Flow and Flow Loss

Fresh cement mortar's flowability and flow loss were examined, and this was conducted using a flow table, as illustrated in Figure 2.

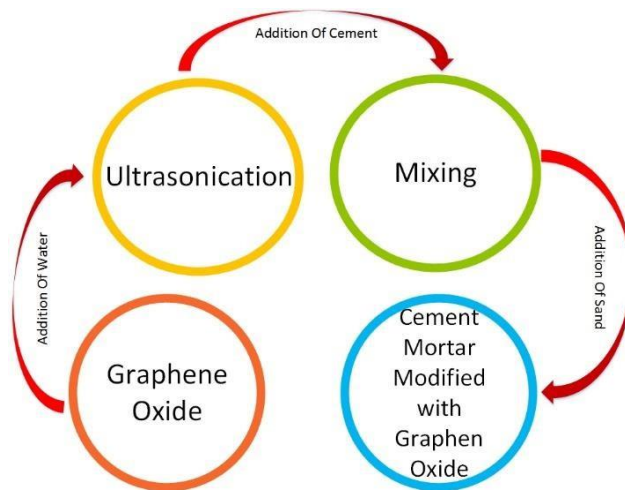


Fig. 2. Schematic diagram of the casting process

This test, according to ASTM C1437, determines the consistency and transportable moisture limit of the cement mortar. Consistency is crucial for achieving the desired strength and qualities after the setting time. The fresh mortar was poured into a truncated cone positioned on a flow table. Each layer was tamped 20 times, after which the cone was carefully lifted. The mortar spread was measured in three distinct directions, and the average of these measurements was calculated. Afterward, the mortar received 25 blows, and the flow of the mortar was computed by using the subsequent mathematical formula:

$$Flow = \left[\frac{(D_{avg} - D_o)}{D_o} \right] * 100 \quad (1)$$

D_o = The specimen's initial average diameter before receiving 25 blows

D_{avg} = The specimen's initial average diameter before receiving 2 blows

This process was repeated at 30-minute intervals until a constant flow was achieved.

4.2 Setting Time

The mortar's first setting time was determined in accordance with ASTM C191-19 criteria by means of the Vicat Needle Test. This test identifies when the cement paste begins to lose its plasticity. The prepared mortar mix was placed into a mold positioned on a non-porous glass plate, with the Vicat needle's plunger gently touching the mold's surface. After that, the plunger was allowed to go through the mixture, and the first setting time was determined by timing how long it took the needle to descend 25 mm from the mold's top. Results and Conclusions

4.3 Setting Time

Using fresh mortar, the Vicat Needle Test was used to measure the setting time while keeping an eye on the needle's penetration. Every 15 minutes, measurements were taken, and when the needle penetrated 25 mm below the surface, that was when the cement's initial setting time was indicated. The outcomes for different GO concentrations were contrasted with those of the control mortar, which was devoid of graphene. The Vicat needle test results were obtained in compliance with ASTM C191-19 guidelines..

Table 2. Setting Time of Mortars

Percentage of Graphene Oxide	Setting Time
0.01%	300 Minutes (5 Hours)
0.03%	270 Minutes (4 Hours 30 Minutes)
0.05%	255 Minutes (4 Hours 15 Minutes)
0.1%	270 Minutes (4 Hours 30 Minutes)
0.01%	300 Minutes (5 Hours)

4.4 Heat of Hydration

There are contradictory findings in the literature from the ongoing research on graphene oxide's impact on the heat of hydration. According to Zhao et al. in [14], graphene oxide increases cement hydration's maximum exothermal rate., introducing an accelerated heat generation process. However, [15] presents contradictory findings, suggesting an opposing effect. The temperature development of distinct mortar compositions is visually represented in figure 3 below.

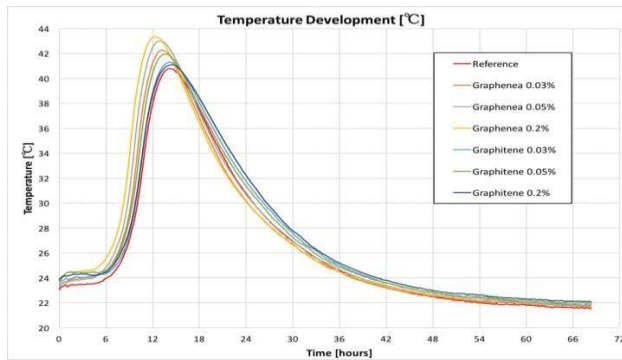


Fig. 3. Temperature Development of Different Mortar Compositions

The influence of graphene oxide on exothermal heat development in various mortar compositions is a subject of investigation. Notably, [14] and [16] present insights into the heightened exothermal heat generation associated with the presence of graphene oxide.

In the study by [14], diverse mortar compositions exhibited increased exothermal heat development, potentially attributed to the interaction between cement mortar and graphene oxide. Peak temperatures of various mixtures were compared with a reference mortar. [14] further differentiated between water-dispersed graphene oxide (Graphenea) and powdered graphene oxide (Graphitene), noting that temperature development for water-dispersed graphene exceeded that of powdered graphene. For instance, at a 0.05% graphene oxide an increase of 5.4% in temperature was observed for water-dispersed graphene and 2.9% for powdered graphene following the addition of the additive.

[16] carried out tests using various graphene oxide percentages to illustrate the development of hydration heat. Different samples, such as normal cement paste (G), 0.02% graphene oxide (CG2), and 0.04% graphene oxide (CG4), showed different temperature development patterns that were similar to those of ordinary Portland cement (OPC) paste. The curves displayed five stages: the initial reaction, induction period, acceleration period, deceleration period, and decline period. When graphene oxide was added, the peaks' intensities altered.

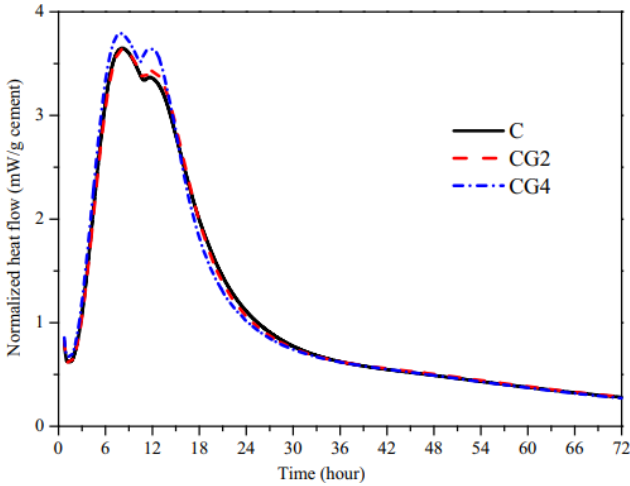


Fig. 4. Comparison of Temperature Development for Different Mortar Compositions

4.5 Heat Flow and Hydration Characteristics

Notable changes have been observed in the heat flow and hydration properties of cementitious materials following the incorporation of GO. The findings indicate a 6.8% increase in heat flow with the addition of graphene oxide. Interestingly, adding GO increased the heat flow at the end of the induction phase rather than lengthening the induction period. Furthermore, samples containing 0.04% GO reached the main hydration peak 3.5% earlier, indicating an acceleration of the induction and acceleration phases of cement hydration. Heat flow and duration during the induction phase are significantly influenced by the rate at which ions diffuse from the mineral phase into the aqueous phase.

While GO nanosheets adsorbed on cement particle surfaces may slow down the rate of diffusion, the findings show that the induction period is accelerated. The minimal adsorption of GO onto cement particle surfaces is responsible for this acceleration.

In terms of the acceleration time, the quantity of hydrated nuclei in the mixture affects the rate of hydration. By encouraging the quick nucleation and growth of hydrates, graphene oxide (GO) is added, which raises the hydration rate as well as the peak of hydration. This effect is due to the enhanced availability of nucleation sites for hydration product formation, attributed to the seeding effect caused by GO's small particle size and large surface area.

These findings align with the results presented in the current research, as summarized in Table 2. The data shows that the setting time decreased with increasing dosages of GO up to 0.05%. Beyond this concentration, the setting time began to increase with higher GO percentages. This trend can be attributed to the seeding effect and the increased number of nucleation sites within the mixture.

4.6 Flow Characteristics and Flow Loss

Flowability and loss of flow in mortars with dissimilar amounts of graphene oxide were the flowability and flowability loss of mortars containing diverse proportions of graphene oxide were evaluated using the Flow Table Test. Measurements were taken at 30-minute intervals, capturing both the initial spread and the spread after 25 blows. Based on these readings, flowability and flowability loss were calculated. The results, including the numerical data and graphical representations, are provided in the tables and graphs below for the 0.01% graphene oxide sample.

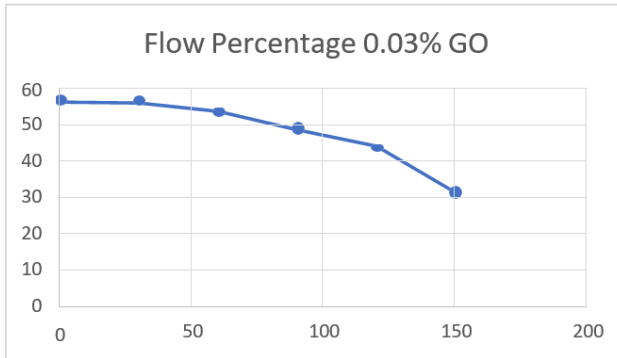


Fig. 5. Flow Percentage 0.03% GO

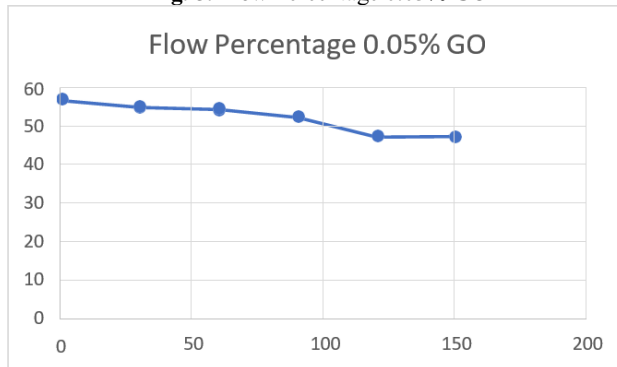


Fig. 6. Flow Loss 0.03% GO

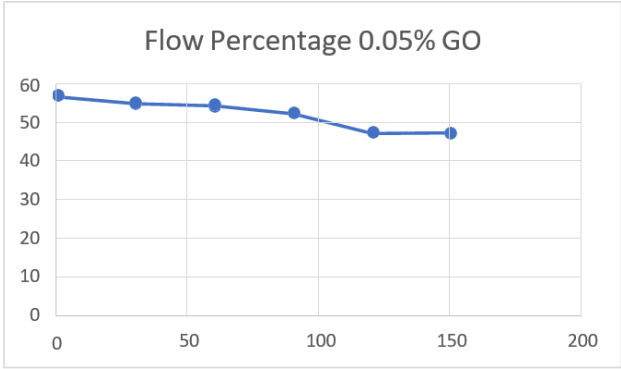


Fig. 7. Flow Percentage 0.05% GO

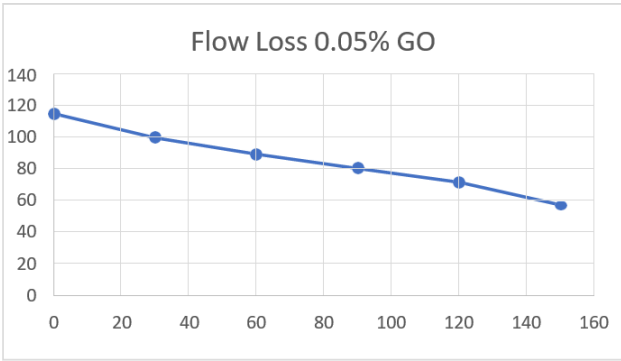


Fig. 8. Flow Loss 0.05% GO

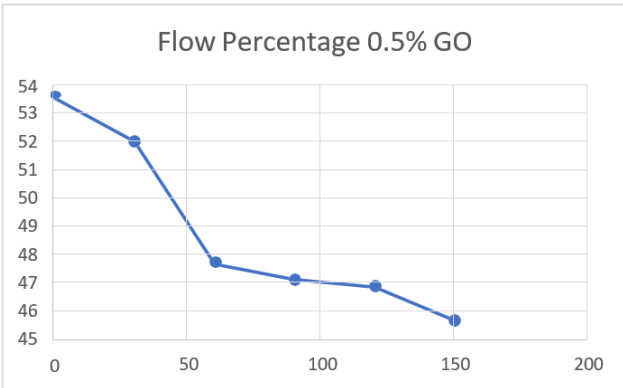


Fig. 9. Flow Percentage 0.5% GO

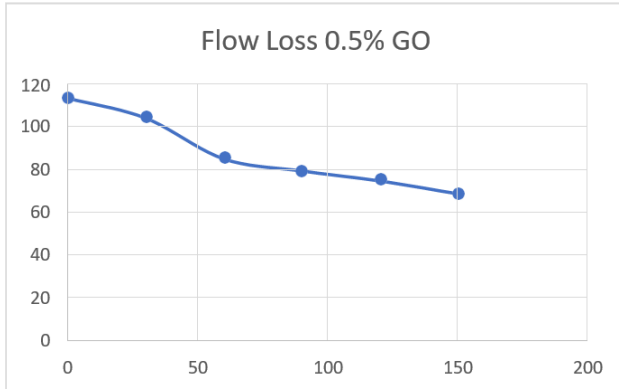


Fig. 10. Flow Loss 0.5% GO

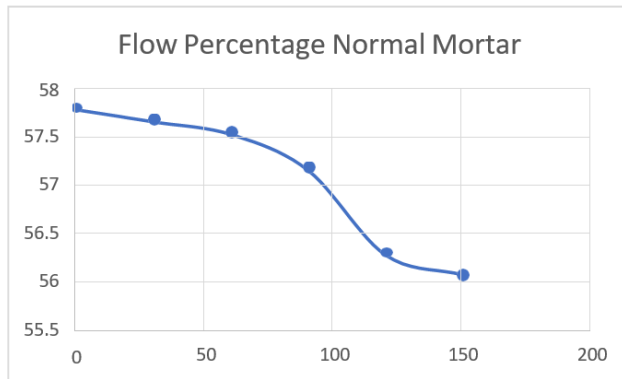


Fig. 11. Flow Percentage Normal Mortar

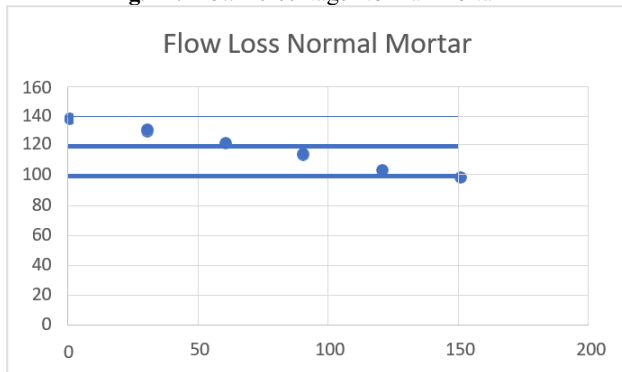


Fig. 12. Flow Loss Normal Mortar

The bar chart below illustrates the flow percentages of mortar with varying concentrations of graphene oxide (GO), measured at 30-minute intervals over two and a half hours. The results are compared to those of normal mortar without graphene

oxide (0% GO). A clear trend of decreasing flow with increasing graphene content is evident, indicating a reduction in workability.

This decrease is ascribed to the hydrophilicity and high specific surface area of graphene oxide, which raise its water absorbency and reduce the amount of free water available in the mortar. Although chemical reactions between super-plasticizers and graphene oxide may introduce side effects on mortar properties, super-plasticizers have been used in previous research to address impaired workability. These interactions are being studied in current research. Similar reductions in mini flow diameter have been reported by other studies, such as those by [15] using fly ash and [13] with 0.03% graphene oxide. These studies emphasize the effect of graphene oxide on rheological properties. Further evidence for these conclusions comes from a study by [12], which links decreased workability to negatively charged graphene oxide particles that entrap free water and cause flocculation, which in turn affects rheological behavior..

4.7 Flowability Loss of Mixtures Containing Different Percentages of Graphene Oxide

The flowability loss for each mixture was determined by calculating the difference between the values obtained before and after 25 blows. Initial readings were taken immediately after the preparation of each mixture, followed by subsequent readings every 30 minutes for each design that is mix. A similar experiment was conducted on a mixture that did not include any graphene oxide, with results compared.

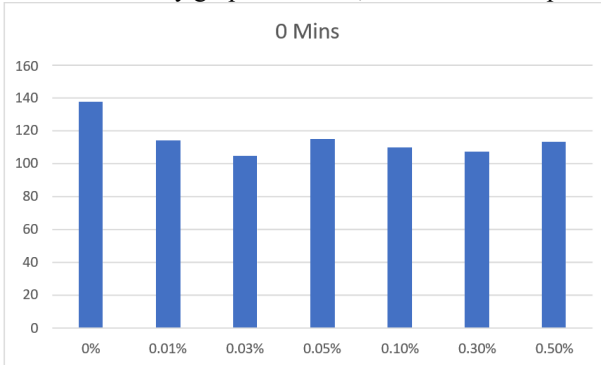


Fig. 13. Flow loss assessment of mortar specimens with varying concentrations of GO at 0 minutes post-preparation.

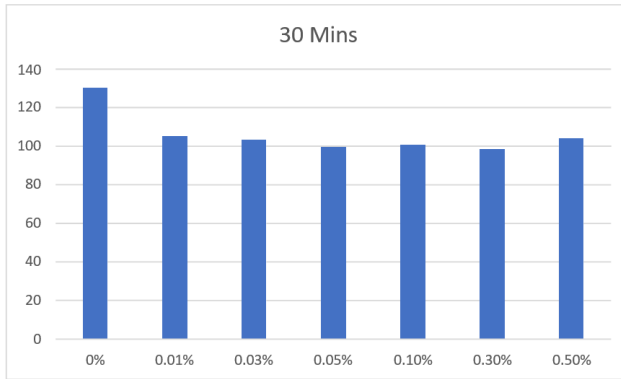


Fig. 14. Flow loss assessment of mortar specimens with varying concentrations of GO at 30 minutes post-preparation.

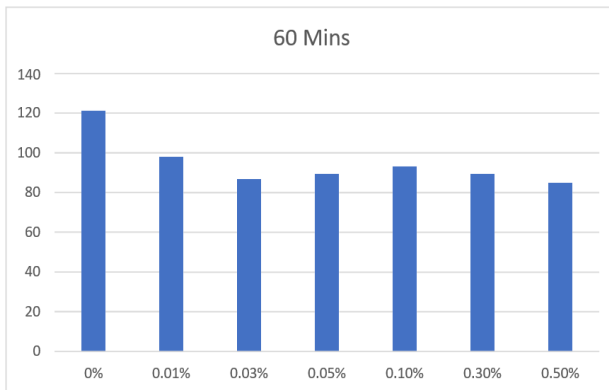


Fig. 15. Flow loss assessment of mortar specimens with varying concentrations of GO at 60 minutes post-preparation.

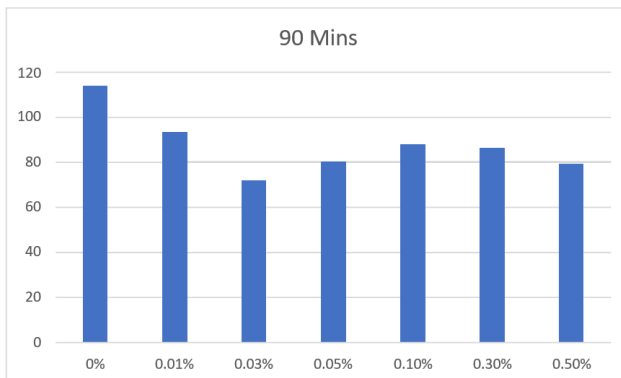


Fig. 16. Flow loss assessment of mortar specimens with varying concentrations of GO at 90 minutes post-preparation.

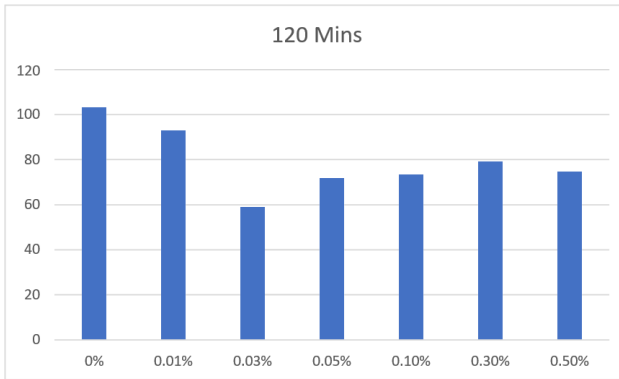


Fig. 17. Flow loss assessment of mortar specimens with varying concentrations of GO at 120 minutes post-preparation.

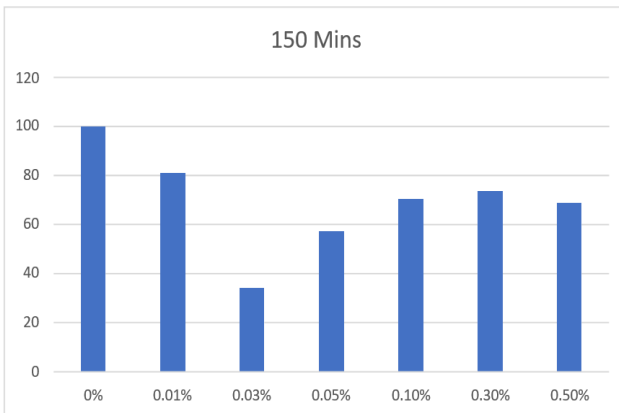


Fig. 18. Flow loss assessment of mortar specimens with varying concentrations of GO at 150 minutes post-preparation.

4.8 Electrical Resistivity

The electrical resistivity results obtained in our research exhibit similar trends to those reported in previous literature. Figure 19 illustrates the electrical resistivity of samples containing different percentages of graphene oxide cured for 7 days. The mixture's electrical resistivity rises until the graphene oxide content reaches 0.05%, from there, it shows a downward trend, reducing until the graphene oxide concentration reaches 0.5%.

The decrease in free water in the mixture is the cause of the increase in electrical resistivity. A cement matrix with capillary pores' electrical resistivity is significantly influenced by its moisture content, as dissolved salts function as electrolytes. When graphene oxide is added, the amount of free water in the matrix decreases, which in turn increases the electrical resistivity.

Conversely, the observed decrease in electrical resistivity in mixtures containing higher concentrations of graphene oxide can be attributed to significant ion diffusion resulting from the breakdown of a dense hydrate barrier. The hydrates that are produced as hydration advances prevent the solution from accessing the unhydrated cement particles. Because of the impact of ion diffusion on electrical resistivity, the mixture containing 0.5% graphene oxide exhibits the lowest resistivity in comparison to other mixtures, which is indicative of its higher graphene oxide content.

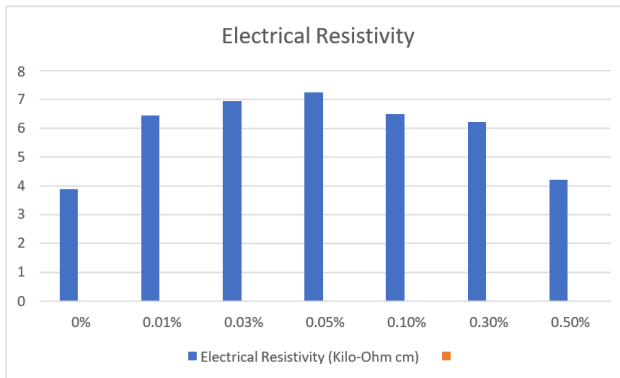


Fig. 19. Electrical Resistivity of Cement Paste Incorporating Graphene Oxide

4.9 Experimental Work

Some pictures are reflected in this section that show the experimental work carried out during the process.



Fig. 20. Graphene Oxide



Fig. 21. Sonicator



Fig. 22. Molds with Different Compositions of Graphene Oxide



Fig. 23. Flexural Testing Machine

4.10 Conclusion

An in-depth exploration of cementitious composites incorporating graphene oxide provided insights into critical characteristics like setting time, workability, and electrical resistivity. Key findings include:

- The addition of 0.05% graphene oxide significantly reduced setting time by 75 minutes, attributed to enhanced nucleation sites. Higher graphene oxide dosages had limited impact on setting time.
- Workability was adversely affected by reduced free water due to the formation of GO agglomerates. The 0.03% graphene oxide mixture exhibited the most substantial reduction in workability.
- Electrical resistivity increased with graphene oxide incorporation, as the reduction in free water resulted in less conductive solutions. The 0.05% graphene oxide mixture exhibited the highest electrical resistivity.

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