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MSc THESIS

Optimising Early Hydration and, CO_2 Sequestration of Ternary Cement Using 2D Materials

Dispersion optimisation of 2D materials, and its impact on hydration kinetics

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MASTER'S THESIS ACEX60

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ABSTRACT

Given the substantial contribution of cement production to global CO_2 emissions, advancing the sustainability of cement materials is imperative. This research addresses the challenge of low early strength in blended cements by exploiting the unique properties of 2D materials to accelerate hydration and improve mechanical performance. This study investigates the enhancement of early hydration kinetics and CO_2 sequestration in ternary cementitious system through the incorporation of two-dimensional (2D) materials, specifically graphene oxide (GO) and graphene nanoplatelets (GNPs). A central aspect of using 2D materials within the cement matrix is its dispersion state, a critical factor in maximizing their benefits. To overcome its agglomeration, physical and chemical dispersion techniques were employed, including the use of polycarboxylate ether (PCE) as a dispersant, ultrasonication, and grinding. Isothermal calorimetry and in-situ X-ray diffraction (XRD) were utilized to analyse hydration kinetics of binder. Results indicate that GO with a PCE/GO mass ratio of 10 achieves superior dispersion in pore solution, with a significant enhancement in hydration kinetics of ternary binder. The incorporation of 0.1 wt. % GO resulted in notable increases in compressive strength of 22%, 24%, and 19% at 1, 3, and 7 days, respectively, compared to the control samples. However, higher GO concentrations, such as 0.4 wt. %, led to reduced strength. XRD analysis further revealed that GO with PCE as dispersant accelerates the precipitation of hydration products. An incorporation of 0.1 wt. % GO also induces an increase in carbonation rate by 83.7%. Despite this effect on kinetics, thermogravimetric analysis (TGA) demonstrated that its effect on CO_2 uptake capacity is negligible. Additionally, although GNPs exhibited a better dispersion sate, but they suppress hydration kinetics. These findings underscore the potential of GO in accelerating early strength development and enhancing carbonation rates in cement systems

Key words: Early Hydration Kinetics; Dispersion Techniques; GO; GNPs; Ternary Cement; CO_2 sequestration.

Contents

Preface

This 60-credit thesis is submitted in partial fulfilment of the requirements for the Master of Science degree in Materials Engineering from the Department of Industrial and Materials Science at Chalmers University of Technology. This research was conducted within the Department of Architecture and Civil Engineering, with a specific focus on the application of 2D materials in cementitious systems to enhance early hydration kinetics and CO_2 sequestration. The study aims to contribute to the broader effort of reducing the environmental impact of cement production, a critical issue given the substantial contribution of this material to global CO_2 emissions.

I would like to express my sincere gratitude to my supervisor, Dr. Liming Huang, for his invaluable guidance, insightful feedback, and unwavering support throughout the research process. His expertise in building materials has been instrumental in shaping the direction and success of this study. I am also deeply appreciative of Associate Professor Arezou Babaahmadi, who served as the examiner for this thesis. Her critical evaluation and constructive feedback have significantly enhanced the quality of this work.

This research was made possible through the financial support of SIO Grafen, whose grant facilitated the exploration of graphene's potential in cement systems. I am thankful for their commitment to advancing sustainable construction technologies and efforts to reduce the climate impact of construction materials by integrating graphene into cement.

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List of Abbreviations

CEM I	Cement 52.5R Type I
GGBS	Ground Granulated Blast Furnace Slag
GNPs	Graphene Nanoplatelets
GO_a	Graphene Oxide
GO_b	Grounded Graphene Oxide
PCE	Polycarboxylate Ether based superplasticizer
DLS	Dynamic Light Scattering
XRD	X-ray Diffraction
CO_2	Carbon dioxide
SCMs	Supplementary cementitious materials

1. Introduction

This chapter will provide a comprehensive overview of using 2D materials in cementitious system, outline the problem statement and articulate the research objectives, establishing the context and relevance of the study. Additionally, it will present the research questions developed in alignment with the objectives and emphasize the significance of the investigation. This approach aims to clarify the study's focus and underscore its contribution to advancing the field of cementitious materials through the integration of advanced nanomaterials.

1.1. Background

Cement is a fundamental material in the construction industry, whose production has surged in response to global urbanization and industrialization. However, its influence extends beyond its structural role, as it also plays a critical part in global CO_2 emissions. The cement industry is responsible for approximately 8% of industrial CO_2 emissions worldwide [3]. The construction sector has a critical role to play in promoting sustainable development by adopting environmental safeguards alongside policies that balance economic growth and societal well-being [4]. A key aspect of sustainability assessments in the built environment is the identification and prioritization of the most relevant parameters for analysis [5]. The cement industry, as a significant source of global CO_2 emissions, faces pressing challenges in reducing its environmental impact. Strategies such as enhancing energy efficiency, implementing waste heat recovery systems, and transitioning to renewable energy sources have been proposed to mitigate emissions [6]. However, to make substantial progress toward sustainability, a reduction in cement consumption is imperative. The utilization of supplementary cementitious materials (SCMs) presents a viable and impactful approach to achieving this GO_a l, as SCMs not only reduce the clinker content in cement but also enhance the performance of concrete, contributing to a lower carbon footprint [7]. Ternary blended cements, which combine Portland cement with two kinds of SCMs, offer potential for reducing environmental impact while enhancing the mechanical properties of concrete and mortar. The use of industrial byproducts in ternary cements is a sustainable approach that can also improve performance. Specifically, the partial replacement of clinker with ground granulated blast-furnace slag (GGBS) and limestone is a promising strategy for developing environmentally friendly ternary cements [9]. However, this method is frequently criticized for its inadequate early strength development, which is largely attributed to the slower pozzolanic reactions and the dilution effect on the cement matrix [8]. As a result, there has been growing interest in the incorporation of 2D nanomaterials into cementitious systems, with the aim of altering the microstructure at the nanoscale to enhance early hydration kinetics and improve overall macroscopic properties [2].

Graphene, a two-dimensional nanomaterial composed of a monolayer of sp^2-bonded carbon atoms, has attracted considerable attention since its discovery in 2004 due to its exceptional mechanical, thermal, and electrical properties. GNPs, consisting of stacked layers of graphene, are known for their chemical inertness and high hydrophobicity. These two-dimensional materials significantly impact the microstructure of cement-based composites, influencing the hydration process and, consequently, the durability, mechanical properties, and fresh mix behavior of concrete [2].

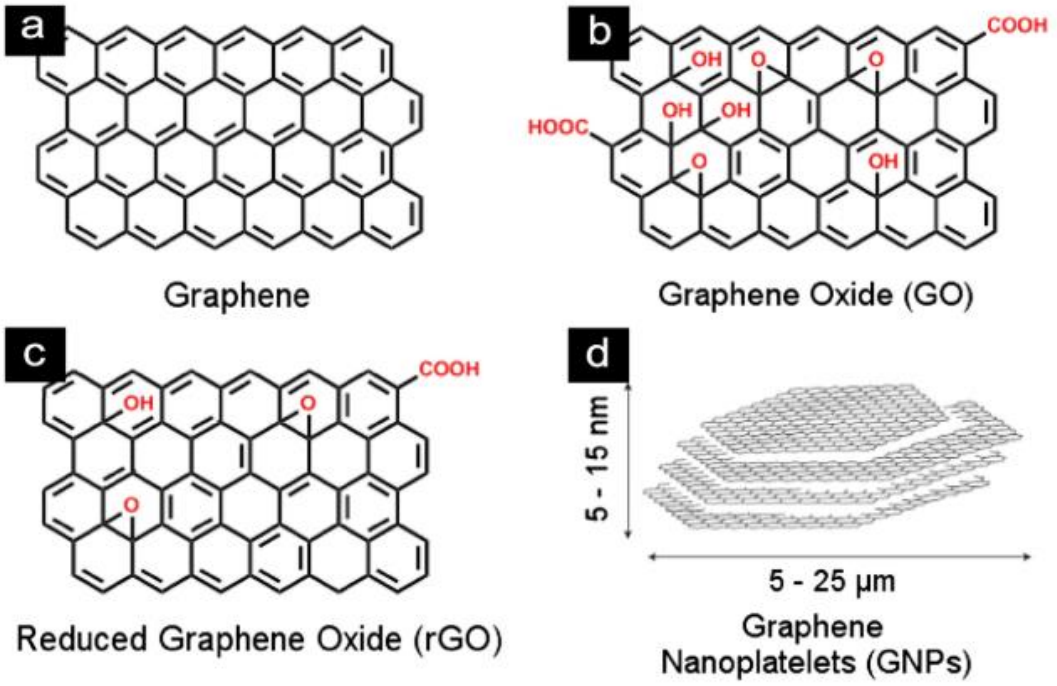

Figure 1: Representation of (a) graphene and its derived substances: (b) graphene oxide (GO), (c) reduced graphene oxide (rGO), and (d) graphene nanoplatelets (GNPs) [20].

The synthesis of GO involves the oxidation of natural graphite flakes. Contrary to earlier assumptions, nano-silica slag activated by alkali does not necessarily lead to improved microstructure or early-age strength gains. Instead, attention should be focused on the formation and development of new hydration products facilitated by graphene-based materials, which are crucial for enhancing the performance of construction materials. Nanomaterials such as GO and its derivatives as shown in Figure 1, which are two-dimensional in nature, are poised to play a pivotal role in next-generation cement technologies. These materials offer superior strength and durability compared to conventional cement, leading to more resilient structures. They also address the issue of inadequate material durability and can be tailored to meet specific building requirements [10].

1.2 Previous Research

Ternary blended cements, which consist of Portland cement combined with two additional supplementary materials, are typically formulated either at the batch plant or during the cement production process. Commonly, these blends include materials such as silica fume, fly ash, slag, along with clinker and limestone. Ternary blends offer significant advantages over binary blends and present even greater enhancements compared to traditional Portland cement. These blends are particularly effective in enhancing the fire-resistant properties of high-performance self-consolidating concrete, while also contributing to a reduction in environmental impact compared to binary mixtures. The use of ternary blended cements not only optimizes fire resistance but also helps mitigate the environmental burdens associated with the use of inferior pozzolans across various damage categories [13].

1.2.1. Common additives: Slag, Limestone, Calcined Clay, Volcanic Ash

Common additives used in ternary blended cement include limestone, slag, volcanic ash, and calcined clay. These supplementary materials offer various benefits by altering the properties of the cementitious matrix, though they also present certain limitations. Limestone fillers, when incorporated into Portland cement, enhance early hydration, leading to higher early strength. However, this can reduce later strength due to dilution effects. Blast furnace slag, on the other hand, contributes to hydration after seven days, significantly improving strength at later ages. This delayed hydration is particularly effective in producing ternary blended cements that achieve compressive strengths comparable to, or even exceeding, those of Portland cement at 28 and 90 days [16]. Calcined brick clays and mixed clays have been shown to enhance the strength and durability of blended cement mortars, although their impact on carbonation resistance and chloride penetration resistance can vary when compared to Portland cement mortar. The introduction of calcined clay and limestone as complex additives leads to a significant reduction in portlandite content, the formation of new hydration products, and a notable increase in compressive strength in blended cement stone. Substituting 30% of Portland cement with calcined clay and silica fume significantly improves the strength and durability of cementitious mortars, while also reducing drying shrinkage and causing less weight and strength loss compared to control mixes [17]. Volcanic ash, a mixture of mineral rock and glass particles from volcanic eruptions, also serves as an effective additive. Incorporating volcanic ash at 10% of the cement weight increases mortar strength and decreases permeability, with the most favourable results observed at 5% and 10% replacement levels [18]. Volcanic ash, when used as a partial cement replacement, offers improved strength and environmental benefits compared to traditional cement, with a 10% replacement level being particularly optimal. When combined with volcanic ash and micro-silica powder in a ternary blend, the strength of self-consolidating green concrete is enhanced, with binder content emerging as a critical factor in determining the overall performance.

1.2.2. Concept and Advantages of Ternary Binders

Ternary blended cements incorporating ground granulated blast furnace slag (GGBS) and limestone powder exhibit significant potential as sustainable cement replacements, offering notable physical and mechanical properties, as well as enhanced resistance to alkali-silica reactions [14]. These ternary blends provide superior performance and synergistic benefits derived from the combination of various supplementary cementitious materials, making them advantageous for environmentally friendly cement production. The inclusion of limestone powder and GGBS in ternary blends contributes to the improvement of late-age strength, leading to increased compressive strength and a reduction in environmental impact. Moreover, ternary blended cements enhance the resistivity of high-performance self-consolidating concrete against elevated temperatures and help to mitigate the environmental burdens associated with the use of inferior pozzolans. The incorporation of slag and limestone powder in ternary blended concrete enhances late-age compressive strength development through pozzolanic reactions and improves resistance to chemical attacks. However, this combination may not lead to significant improvements in early age strength development. Achieving an optimal mixture of cement, slag, and limestone is crucial for the material design of ternary blended concrete. The hydration process considers the mutual interactions among the reactions of cement, slag, and limestone, particularly in terms of calcium hydroxide content and capillary water [15]. The individual reaction degrees of the components within ternary blends are calculated based on hydration kinetics. Additionally, the growth in compressive strength of hydrating ternary blended concrete is determined using the gel-space ratio and Powers' strength theory.

1.2.3 Introduction to Cement Hydration

Cement is widely utilized in the construction industry due to its exceptional compressive strength, primarily attributed to the formation of calcium silicate hydrate (C-S-H) phases within the material [1]. When water is mixed with cement, an exothermic reaction occurs, leading to a significant increase in temperature [12]. This reaction, known as hydration, plays a crucial role in determining the fundamental properties of cement, as it is closely associated with the transformation of the material's hydrological states [2]. The interaction between cementitious materials and water results in a complex suspension of crystalline and amorphous hydrated phases. Additionally, a network of hydration products forms, which is instrumental in the material's hardening and setting behaviour [3]. Hydration begins immediately upon the introduction of water to cement, with the progress and estimated strength of concrete being closely monitored by measuring its temperature. The hydration process is typically divided into five phases: the initial mixing phase, the induction period, strength acceleration, speed reduction, and the final steady development phase, as illustrated in Figure 2. These phases collectively represent the complete hydration process of the material.

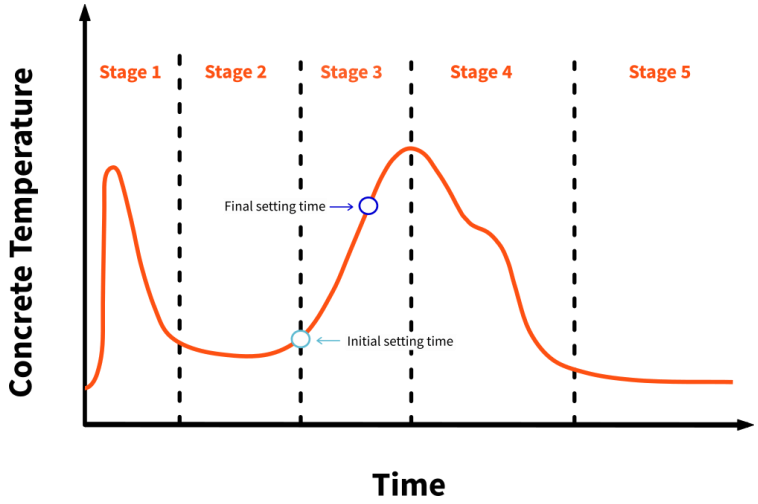

Figure 2: Hydration Process of Cement [6]

1.2.4. Impact of SCMs on Hydration Kinetics and Strength Development

SCMs such as aluminium-containing mineral phases, slag, and limestone powder, play a crucial role in enhancing the fluidity, strength development, and resistance to chloride ion penetration in concrete. These materials are incorporated into concrete mixtures for various purposes, including improving pumpability, increasing durability, reducing permeability, and enhancing finish ability. SCMs also help eliminate alkali reactivity and contribute to the overall hardened properties of concrete through pozzolanic and hydraulic reactions. For instance, the inclusion of micro limestone and C-S-H seeds can accelerate hydration kinetics and promote strength development in cement blends. However, it is important to recognize that the use of ternary blended cements incorporating SCMs, such as slag and limestone powder, may adversely impact hydration kinetics and early strength development due to the nature of the pozzolanic reaction. This reaction relies on the presence of calcium hydroxide to commence, and an insufficient supply of calcium hydroxide can hinder the rate of strength development. Slag, in particular, is known for its slow initial reaction as it depends on the calcium hydroxide generated by the hydration of Portland cement to activate its pozzolanic properties, potentially delaying early strength gains. Limestone powder, while advantageous in improving packing density and providing nucleation sites for hydration products, can also dilute the cement paste,

potentially reducing the availability of calcium hydroxide necessary for the pozzolanic reaction with slag.

Recent advancements in the use of carbon-based nanomaterials, such as graphene and graphene oxide, have shown strong synergies when combined with SCMs. These nanomaterials exhibit high correlations between enhanced hydration kinetics and increased compressive strength. When incorporated into ternary blended cementitious materials, these nanomaterials can significantly accelerate hydration kinetics by nucleating and seeding the formation of various hydration products, including C-S-H gels [19]. This process ultimately enhances the initial strength gains of the cementitious system. Additionally, the potential for carbon sequestration within these nano-reinforced composites presents an important area of study, as it contributes to both environmental sustainability and material performance.

1.2.5 Graphene-Based 2D Materials in Cement

Graphene based 2D nanomaterials possess exceptional potential to enhance the properties of cement while addressing sustainability challenges within the construction industry. The high theoretical strength and conductive nature of graphene render it a promising additive for cement composites [21]. Early research indicates that graphene can significantly improve mechanical properties, such as strength, toughness, and crack resistance, in cement pastes and mortars. Notably, even a minimal addition of graphene, approximately 0.1% by weight of cement, has been shown to increase compressive strength by 19.5% [22].

The proposed mechanisms underlying these enhancements include graphene sheets' ability to impede the growth and propagation of cracks. Additionally, graphene has the potential to reduce porosity within the cement matrix by functioning as a nanoscale filler, provided the particles are adequately dispersed throughout the system. Since cracking in cement can lead to the corrosion of steel reinforcement, the incorporation of graphene could extend the lifespan of cement-based infrastructure [22]. Furthermore, graphene's conductive properties introduce the possibility of developing self-sensing concrete capable of monitoring its own structural health [23].

1.2.6 Overview of Graphene-Based 2D Materials (GO, GNPs)

Graphene, a two-dimensional nanomaterial, consists of a single layer of sp^2 hybridized carbon atoms arranged in a honeycomb lattice [24]. This material has garnered significant attention from researchers due to its exceptional properties, including high tensile strength (130 GPa), superior electrical conductivity (6000 S/m), and remarkable thermal conductivity (5000 W/mK) [25]. However, the production of individual atomically thin graphene sheets presents challenges, and graphene is typically found in the forms of GO and GNPs [26].

GO is typically synthesized through the oxidation of graphite powder, resulting in the presence of epoxy and hydroxyl functional groups on the basal planes and sheet edges of the graphene layers. These oxygen-containing functionalities enable GO to be well dispersed in water and other solvents, yet they also disrupt the graphene lattice structure, diminishing the material's properties compared to pristine graphene [27]. On the other hand, GNPs are produced by exfoliating and breaking down graphite into few-layer stacks, typically five to ten layers thick, through processes such as wet milling or chemical vapor deposition. GNPs retain more of graphene's intrinsic properties, including higher electrical conductivity, but require additional processing to achieve optimal dispersion, unlike GO [28].

Both GO and GNPs are being actively explored as potential additives in cementitious materials. Due to its strong covalent carbon-oxygen bonds and hydrophilic nature, GO can effectively

interact and cross-link with the hydration products of cement. The thin aggregated sheets of GO form a reinforced three-dimensional network within the cement matrix, providing multiple functionalities. While GNPs contribute to mechanical strengthening, optimizing their dispersion in cement remains crucial for maximizing their impact. Some key advantages of incorporating these graphene-based nanomaterials into cement include:

- Mechanical Reinforcement: Even at minimal weight percentages (<1%), the incorporation of GO and GNPs has been shown to significantly enhance the mechanical properties of cement pastes and mortars, with increases of up to 19.5% in compressive, flexural, and tensile strength. This improvement is primarily attributed to the ability of robust graphene sheets to impede crack propagation, thereby reinforcing the material's structural integrity. [22].
- Enhanced durability: GO and GNP additions significantly reduces permeability and increasing the density and tortuosity of pores within the hydrated cement matrix. This results in decreased water absorption and chloride ion penetration [29], thereby improving the material's resistance to aggressive environmental conditions and contributing to an extended service life.
- Environmental benefits: The partial replacement of cement with low-grade SCMs or industrial by-products becomes feasible, as the high aspect ratio of graphene sheets effectively serves as a filler, thereby reducing porosity within the cement matrix [30]. This approach not only contributes to a reduction in CO_2 emissions but also maintains the structural strength of the cementitious material.

Despite their numerous advantages, several challenges remain in the use of graphene-based nanomaterials in cementitious systems. These include optimizing dispersion techniques to ensure homogeneous distribution without agglomeration of hydrophilic GO or hydrophobic GNPs [29]. Additionally, a comprehensive characterization of the interactions between graphene, cement hydration products, and various cement additives is required. The leaching behaviour and long-term effects on material properties post-curing are still under investigation. Overall, graphene-based 2D nanomaterials hold significant promise for advancing the development of sustainable and multifunctional cementitious materials.

1.2.7. Dispersion Challenges due to Agglomeration and Alkaline Environment

Dispersion refers to the process in which particles of one material are distributed within a continuous phase of another material. It can be classified based on the size of the particles being dispersed in the system. In the context of cement composites, achieving optimal properties necessitates effective dispersion of particles. However, the alkaline environment often poses challenges, as particles or materials may agglomerate, leading to clumping [32]. This agglomeration reduces the surface area of the particles and can negatively impact the performance of the materials.

The effects of an alkaline environment and the presence of calcium ions on the re-agglomeration of GO within cementitious materials. Their study demonstrated a decrease in GO dispersion within the cement matrix due to these conditions [33]. They utilized PCE-based superplasticizers to optimize GO dispersion in a saturated solution of $Ca(OH)_2$, simulating the strong alkaline environment of the cement matrix.

Effective dispersion of materials in highly alkaline and calcium-rich cementitious environments is thus highly challenging. To address this, it is crucial to protect GO from detrimental ions by using PCE to control the agglomeration process and maintain stable dispersion in such conditions.

1.2.8. Potential Benefits of 2D Materials in Cement Systems (Enhanced Nucleation, Reduced Porosity

Cement is widely utilized in the construction industry due to its cost-effectiveness. However, the incorporation of SCMs in higher percent often leads to a reduction in early strength development. The addition of 2D materials to cementitious matrices offers significant improvements at the microscopic level, enhancing the material's robustness, durability, and corrosion resistance. Specifically, 2D materials contribute to increased tensile strength, resilience, and reduced porosity of cementitious materials [36].

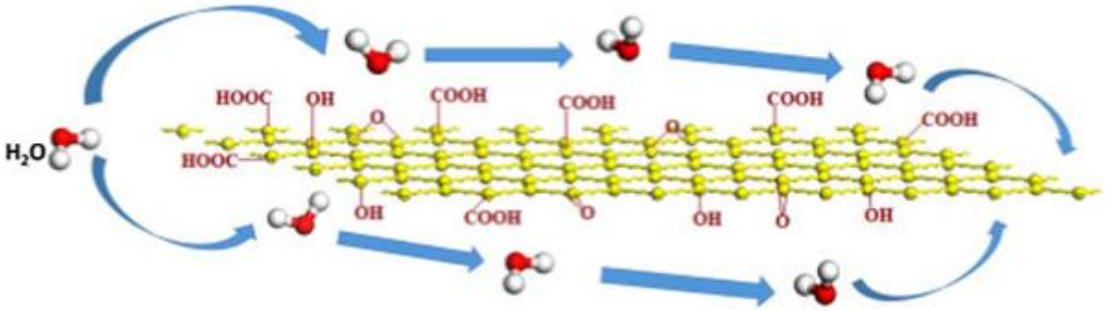

Figure 3: Schematic diagram illustrating the catalytic mechanism of GO in the cement hydration [35]

In the cement industry, both GNPs and GO significantly enhance cement systems [37]. GO plays a pivotal role in accelerating early hydration kinetics in cementitious materials through its nucleation and dilution effects. The functional groups on the GO surface, such as epoxy and hydroxyl groups, exhibit a strong affinity for water molecules and cementitious ions. These groups serve as nucleation sites, thereby expediting the hydration reaction as shown in Figure 3. This interaction facilitates the early formation of hydration products, thereby enhancing the overall hydration process and contributing to improved mechanical properties and durability of the cement matrix [41]. The 2D morphology of graphene, coupled with its hydrophilic nature, enhances its dispersion in water, thereby providing a substantial surface area and high strength for the functionalization of cementitious materials. Porosity is a crucial factor in determining the mechanical strength of cementitious materials, with an inverse relationship observed between mechanical strength and porosity. The development of the microstructure and the mechanical properties of cement are intrinsically linked to porosity. Cracks often initiate within the microstructure under excessive stress. The incorporation of nanostructures and microfibers into cementitious materials can bridge these cracks and refine the pore structure, leading to the formation of denser and more robust microstructures. Consequently, any modifications or additions to the mix, including the incorporation of 2D nanomaterials like GO, must be carefully evaluated to avoid potential adverse effects on the long-term durability and mechanical properties of the cementitious system [43].

1.2.9. Introduction to Carbonation and Carbon Sequestration

Carbonation, a chemical process that predominantly occurs during the later stages of concrete curing, involves the progressive movement of carbon dioxide from the outer to the inner layers as the concrete cures and dries. In contrast, the hydration process moves outward from the inner core. Carbonation is defined as the chemical reaction of carbon dioxide CO_2 with water, producing carbonic acid, carbonates, and bicarbonates. Specifically, in cementitious materials,

carbonation refers to the reaction between calcium hydroxide, hydrated calcium silicate, and CO_2, resulting in the formation of carbonates. This process leads to the permanent sequestration of CO_2 through carbonate development.

Zajac et al. (2020) describe carbonation as a process encompassing the dissolution of hydrates, the transportation of dispersed materials, and the precipitation of reactive products. The initial phases of carbonation, particularly the reaction involving portlandite, are limited by the rate of calcite precipitation and the amount of dispersed CO_2. As portlandite depletes, the kinetics of carbonation are controlled by the diffusion of calcium into solution and the dispersion of other hydrates. The primary products of carbonation include alumina-silica hydrate gel and calcite. The concentration of CO_2 and the properties of the cement paste can significantly influence the rate and extent of carbonation product formation [4].

The increasing concentration of global CO_2 has garnered significant public attention in recent years, prompting scholars worldwide to propose various sequestration methods. However, the application of this process is often limited by its inherently slow reaction rate under normal environmental conditions [8]. Carbonation and carbon sequestration are processes intrinsically linked to CO_2-material interactions, such as those occurring in concrete. Carbonation is a natural chemical reaction where atmospheric CO_2 reacts with calcium hydroxide in concrete to form calcium carbonate. This reaction decreases the alkalinity of the material and may, over time, compromise its structural integrity due to corrosion. However, the formation of calcium carbonate, refines the porosity thereby facilitating the increase in the packing density of the material.

Carbon capture and storage (CCS) involves the long-term storage of CO_2 in various forms, including geological formations, oceans, and mineral carbonates formed through carbonation. By promoting carbonation, atmospheric CO_2 can be sequestered within concrete, thereby contributing to the reduction of greenhouse gas emissions. These mechanisms play a critical role in reducing the overall carbon footprint of construction materials, aligning with broader sustainable environmental protection strategies. Given the environmental challenges posed by CO_2 emissions, innovations in carbon capture, utilization, and storage (CCUS) have been proposed to mitigate carbon emissions. Among these innovations, mineral carbonation encompassing both CO_2 sequestration and storage, has been identified as a promising approach. Magnesium, calcium, and silicate minerals are particularly effective in CO_2 sequestration [8].
The necessity of carbon dioxide sequestration is underscored by the need to mitigate greenhouse gas emissions and the global warming threats posed by the substantial CO_2 emissions from the cement industry. In 2016, global CO_2 emissions from the cement industry alone amounted to 1.45 ± 0.20 Gt CO_2, representing approximately 4% of the total carbon dioxide emissions from fossil fuels. Therefore, it is imperative to develop and further investigate efficient CO_2 treatment technologies specifically tailored for the cement industry [9].

1.2.10 Effect of GO on Carbon Sequestration

Cementitious materials, such as concrete, possess the ability to sequester and store CO_2 through a process known as carbonation. During cement hydration, calcium silicate and calcium aluminate phases react with water to form C-S-H and calcium aluminate hydrates [44]. The primary byproduct of this reaction is calcium hydroxide (CH), which also forms from unreacted free lime present in the original cement. When CO_2 from the atmosphere comes into contact with freshly produced or aging concrete, it reacts with CH in the cement paste through the carbonation reaction. CO_2 dissolves in the pore water within the concrete, forming carbonic

acid. This carbonic acid then reacts with CH to produce calcium carbonate (CaCO3) and water, a process known as mineral carbonation [44].

In systems containing significant amounts of SCMs, the CaCO3 formed occupies less volume than the original CH. This is because the consumption of calcium hydroxide through pozzolanic reactions reduces the amount of CH available for carbonation. As a result, carbonic acid attacks other calcium-bearing compounds, such as C-S-H, leading to the formation of higher-density polymorphs of CaCO3, including vaterite and aragonite. This process increases the porosity within the cement matrix, allowing for further penetration and uptake of CO_2 over time.

By sequestering CO_2 in a solid mineral form, cement-based materials offer a method for passively mitigating global CO_2 emissions through their extensive use in construction. Ongoing research is exploring ways to enhance the capacity and kinetics of carbonation, with 2D materials like GO showing promise for improving carbon uptake from the atmosphere [26]. A study by Mishra et al. (2022) demonstrated that the incorporation of a small amount of GO (0.05 wt.%) in OPC systems increased CO_2 sequestration by 30%. The mechanisms underlying this acceleration, as illustrated in Figure 4, suggest that GO sheets serve as nucleation sites for CaCO3 precipitation, primarily due to their attraction to carbonate ions produced during the carbonation reaction.

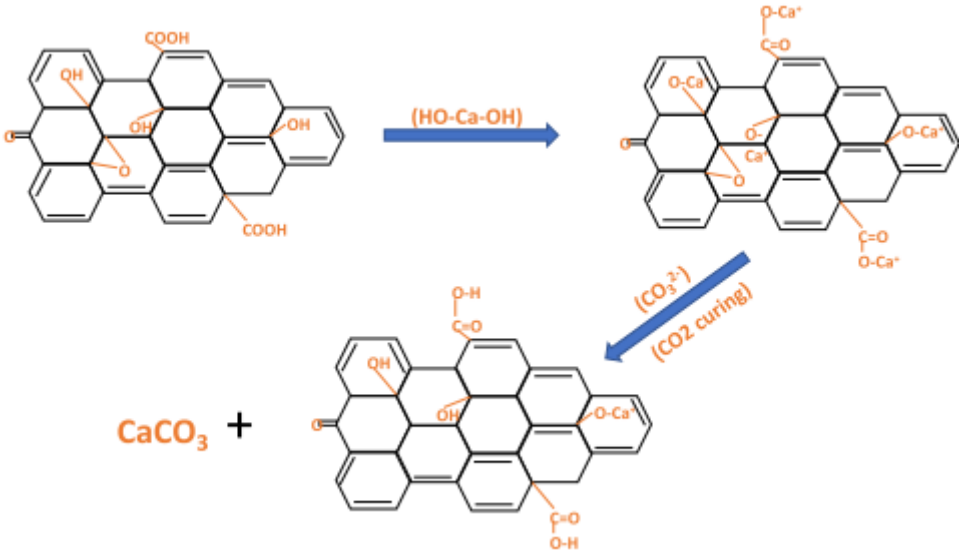

Figure 4: Mechanisms of accelerated carbonation induced by GO [42]

Some of the key strategies currently being researched and developed to enhance CO_2 sequestration in cementitious materials include:

- Admixture optimization: The use of chemical admixtures such as superplasticizers and accelerators are being explored to regulate the cement matrix. This approach aims to accelerate both hydration and carbonation kinetics without compromising the material's properties, thereby enhancing CO_2 uptake [43].
- Alkali activation: The production of geopolymers and alkali-activated binders from industrial byproducts such as fly ash and slag is a promising area of research. These materials sequester CO_2 through different reaction mechanisms compared to conventional hydraulic cements, offering an alternative pathway for carbon capture [45].

- Nanoparticle incorporation: The addition of nanoscale materials, such as GO, increases the specific surface area and provides additional reactive sites for CO_2 sequestration. This enhances the material's capacity to capture and store CO_2.
- Porosity control: Precise engineering of the pore structure through optimized mix design and the incorporation of specific admixtures is critical for achieving the desired permeability, facilitating CO_2 infiltration and carbonation within the cement matrix [45].
- Carbon sink enhancement: The development of blended cements containing high-calcium phases, such as $Ca(OH)_2$-rich layers, as well as composite binders and encapsulated carbonation promoters, is aimed at maximizing the CO_2 sequestration potential of cementitious materials [33].

Continued advancements in these areas hold significant promise for increasing the role of cement-based materials in sustainable carbon management and climate change mitigation.

1.3 Problem Statement

Blended cement systems incorporating SCMs like slag and limestone often exhibit low early strength development, largely due to slower pozzolanic reactions compared to Portland cement hydration [13]. This slow reactivity presents a significant challenge in modern construction, where rapid early strength is increasingly demanded. Improving early hydration kinetics is crucial to enhance the initial curing process and overall performance of these cementitious materials. One primary issue is the variation in particle sizes within the cement mix, which impairs the uniformity of particle distribution, thereby slowing hydration [14].

The incorporation of 2D materials, such as GO and GNPs, into cement matrices offers the potential to address these issues by improving hydration kinetics and mechanical performance. However, these materials face significant challenges, particularly due to their high surface energy and van der Waals forces, which cause them to agglomerate. This aggregation reduces the effective interaction between the cement matrix and water particles, leading to poor particle distribution and diminished functionality [15]. Achieving uniform dispersion of 2D materials is particularly challenging in the highly alkaline pore solutions of cement systems, which can compromise the surface functionalities of GO and GNPs, further exacerbating agglomeration and sedimentation [16].

This inconsistency in dispersion is exacerbated by the heterogeneous nature of cement materials, which promotes coagulation and non-uniform spatial distribution of the 2D materials. Many studies have primarily investigated agglomerated graphene-based materials rather than well-dispersed ones, emphasizing the need for advanced dispersion techniques and a more thorough understanding of the interactions between these materials and the cement matrix. The effectiveness of dispersants, such as PCE, is also critical, with the PCE-to-GO mass ratio playing a key role in influencing hydration kinetics and enhancing carbon sequestration by optimizing dispersion [83].

Moreover, while research has explored the carbon sequestration potential of ternary blended cement systems with graphene-based materials, the impact of these materials on ternary blended cement systems (containing SCMs) has not been thoroughly investigated. Ternary systems show potential for reducing CO_2 emissions through pozzolanic reactions, and the integration of 2D materials could accelerate these carbonation processes by acting as nucleation sites [84]. However, a gap remains in understanding how these materials can be optimized in ternary blends to improve both mechanical properties and environmental performance.
In summary, there is a clear need for research to address several key challenges:

1. Inconsistent dispersion of graphene-based materials: Achieving consistent and stable dispersion of 2D materials in cement matrices remains a major challenge. The varying behaviours of graphene oxide in different environments, particularly in highly alkaline pore solutions, necessitate the development of advanced dispersion techniques [15][16].
2. Optimization of dosage and PCE/GO mass ratios: The precise optimization of the PCE/GO mass ratio is critical to maximize the positive effects of 2D materials on hydration kinetics and carbon sequestration. Existing research has yet to fully explore the optimal conditions for these ratios in cement systems [83].
3. Understanding graphene-based material interactions in ternary blended systems: There is limited research on the interactions between graphene-based materials and SCMs in ternary cement systems, which offer significant potential for reducing CO_2 emissions. More investigation is required to understand the role of these materials in enhancing the properties of ternary blends [36].
4. Carbon sequestration in ternary systems: The role of graphene-based materials in accelerating carbonation processes within ternary systems remains underexplored. Future research should focus on optimizing these materials for enhanced carbon sequestration in blended cement systems [84].

Addressing these gaps will significantly advance the application of graphene-based materials in the development of sustainable, high-performance cementitious systems.

1.4 Objectives

1. Investigate the Role of Graphene-Based 2D Materials in Ternary Blended Cement: This study is centred on elucidating the effects of graphene-based 2D materials on the performance enhancement of ternary blended cement systems. The research aims to explore the behaviour of these advanced materials in relation to supplementary cementitious materials, particularly focusing on their influence on the hydration process. A key objective is to achieve a comprehensive understanding of the dispersion, stability, and integration of graphene derivatives within the cement matrix. Given the potential of these 2D materials to significantly improve early strength, this investigation seeks to provide valuable insights that could lead to the development of superior cement composites incorporating graphene, thereby advancing the field of construction materials.
2. Evaluate Early Hydration Kinetics through Isothermal calorimetry and In-situ XRD, and CO_2 Sequestration Efficiency: The research will employ isothermal calorimetry and in-situ XRD to determine the hydration kinetics of ternary blended cement systems supplemented with graphene-based 2D materials. This approach will enable the identification of both the rate and degree of hydration reactions, as well as the early strength development post-setting [8]. Additionally, the study will forecast the enhanced efficiency of the modified cement in terms of CO_2 sequestration, assessing the impact of optimized cement containing 2D materials on carbonation levels. The ultimate GO_al is to provide a clear and comprehensive evaluation of how these materials can accelerate the hydration process while contributing to the sustainability of construction through improved CO_2 sequestration.
3. Assess Mechanical Properties: A critical objective of this study is the assessment of the mechanical properties of ternary blended cement systems incorporating graphene-based 2D materials. This evaluation will demonstrate whether the enhanced hydration possesses the necessary mechanical properties for application in the construction and infrastructure sectors. By focusing on the mechanical performance, the study seeks to confirm the feasibility of using these advanced materials in real-world construction

scenarios, thereby providing a foundation for the development of durable and sustainable building materials.

1.5 Research Questions

This research seeks to address the following critical questions:

- What are the optimal methods for incorporating graphene-based 2D materials into cementitious matrices to enhance hydration kinetics?
- How do graphene-based 2D materials influence the phase's evolution during the hydration process?
- How do graphene-based 2D materials impact the kinetics and efficiency of carbonation within a ternary cement system?

1.6 Scope of Thesis & Limitations

This thesis focuses on advancing the field of sustainable construction materials by exploring the integration of graphene-based 2D materials, specifically GO and GNPs, into ternary blended cement systems. The motivation behind this research stems from the urgent need to reduce the carbon footprint of cement production while simultaneously improving the mechanical performance and durability of cementitious materials. By investigating the role of GO and GNPs in enhancing hydration kinetics and CO_2 sequestration, this study aims to provide a pathway for developing more efficient, eco-friendly cement composites. A key outcome anticipated from this research is the optimization of 2D material dispersion in highly alkaline cement environments, which is crucial for achieving uniform integration within the cement matrix. The study will also shed light on the impact of these materials on early hydration stages and the development of strength, particularly in the presence of supplementary cementitious materials. Additionally, the research is expected to yield valuable insights into the carbonation kinetics of cement systems modified with GO and GNPs, with the potential to enhance their CO_2 sequestration capabilities. Overall, this work aims to contribute to the development of high-performance, low-carbon cementitious materials that can meet the mechanical and environmental demands of modern construction. The successful incorporation of GO and GNPs into these systems could serve as a foundation for future innovations in sustainable building practices, addressing both durability and climate-related challenges.

This thesis specifically excludes considerations related to energy consumption, waste generation, and life cycle analysis (LCA). The research is focused solely on the material science aspects of ternary blended cement systems incorporating GO and GNPs, with a particular emphasis on their effects on hydration kinetics and carbonation efficiency. By narrowing the scope to these material-specific factors, this study aims to provide a clear and detailed understanding of the direct benefits associated with integrating graphene-based 2D materials into cementitious matrices, without extending into broader environmental impact assessments.

2. Materials and Methods

This chapter will outline the materials and methodologies employed in the study, including the use of Portland cement, two-dimensional materials such as GNPs and GO, simulated pore solution, and various admixtures and supplementary cementitious materials. It details the experimental methods applied to achieve the study's objectives, which include Dynamic Light Scattering (DLS), UV-Visible spectroscopy, and isothermal calorimetry, among others. Each method is described in terms of its purpose and relevance to assessing the performance and characteristics of the 2D materials incorporated ternary blended cement.

2.1 Materials

2.1.1 Cementitious materials

The ternary blended cement investigated in this study comprises Ordinary Portland Cement (CEM I), Ground Granulated Blast Furnace Slag (GGBS), and limestone, with the following weight ratios: 49% CEM I, 35% GGBS, and 16% limestone. The chemical analysis of this blend is detailed in Table 1, including the concentrations of key oxides and Loss on Ignition (LOI). This blend was specifically selected to enhance the mechanical properties and durability of the cement matrix while simultaneously reducing the carbon footprint associated with conventional cement formulations.

Table 1: Chemical Composition and LOI of Each Binder in the Ternary Blend.

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	Cl	LOI
CEM I 52.5 R (wt.%)	62.2	19.6	4.5	3.5	3.5	1.01	0.27	0.07	2.5
Slag (wt.%)	39.11	36.63	13.56	0.49	8.52	0.57	0.46	0.009	-1.07
Limestone (wt.%)	49.5	9	-	0.3	0.3	0.3	0.1	-	40.1

2.1.2 GO and GNPs

The GO slurry utilized in this study was procured from Graphenea SA, presented as a brown suspension with an initial concentration of 20 mg/mL and an estimated bulk density of approximately 1.5 g/cm³. The GO slurry was synthesized through the oxidation of natural graphite flakes using a modified Hummers' method. In the laboratory, the GO slurry was diluted to the desired working concentration and underwent ultrasonication to achieve the final exfoliated graphene product. The GO sheets had an average lateral size of 1-5 microns and a thickness of approximately 1-2 nm. The high oxygen content of the GO, reflected by a carbon-to-oxygen (C/O) ratio of around 1, indicated significant oxidation.

In addition to GO, GNPs were employed in the study. The GNPs were sourced from Talga Advanced Materials GmbH, characterized by an average thickness of 6-8 nm and a lateral size of 5 microns. Prepared through mechanical exfoliation, GNPs are noted for their high electrical conductivity and mechanical strength. Both GO and GNPs were subjected to 60 minutes of ultrasonication before being incorporated into the cement matrix. This procedure was conducted to evaluate the effects of these 2D materials on the mechanical and durability properties of the cement composites.

2.1.3 Simulated Pore Solution

The simulated pore solution was formulated to closely mimic the chemical composition of binder paste. It was prepared by dissolving $Ca(OH)_2$, NaOH, KOH, and $CaSO_4$ in deionized water according to the quantities specified in Table 2. The solution was allowed to stand for 24 hours to ensure complete dissolution and precipitation, after which it was filtered. To maintain purity and prevent carbonation, the solution was siphoned and stored in a sealed container. The alkaline concentration of this solution was deliberately adjusted to replicate the ionic environment typical of cement pore solutions, facilitating the assessment of 2D materials dispersion and their interaction with the cement matrix.

Table 2: Chemical composition of the pore solution and measured pH

$Ca(OH)_2$ (g/l)	NaOH (g/l)	KOH (g/l)	$CaSO_4$ (g/l)	Ca^{2+} (mol/l)	Na^+ (mol/l)	K^+ (mol/l)	$(SO_4)^{2-}$ (mol/l)	pH
Sat.	3.560	10.475	9.938	0.006	0.089	0.159	0.073	13

2.1.4 PCE

The polycarboxylate-based superplasticizer utilized in this study was sourced from the Thomas Concrete Group in Sweden. The PCE exhibited a density of approximately 1.05 g/cm³ and was employed as a dispersing agent due to its comb-like molecular structure, which is particularly effective in suspending nanoparticles within cementitious systems. PCE was incorporated into GO suspensions in varying quantities to enhance their dispersion stability within the simulated pore solution under alkaline pH conditions. The study investigated a range of PCE/GO mass ratios, from 0 to 20, with a focus on identifying the optimal ratio that ensures the long-term stabilization of GO dispersion.

2.2 Sample Preparation

2.2.1 GNPs and GO Suspensions

Cement composites incorporating graphene suspensions, specifically GNPs and GO, were prepared at varying concentrations to investigate their interactions within the cement matrix. Initially, the graphene materials were diluted by adding deionized water to achieve the desired concentration based on the specific graphene dosage. The resulting black suspension mixture was subjected to stirring to ensure uniformity. To further enhance the homogeneity of the GO suspensions, a near-field high-power sonicator operating at 40 KHz was utilized. Initially, the diluted suspensions were placed in an ultrasonic bath and subjected to a 30-minute sonication process. Following this, PCE was incorporated into the GO suspensions at varying concentrations of 0%, 5%, 10%, 15%, and 20% relative to the GO mass, as detailed in Table 3. The final step involved an additional 30 minutes of sonication. The samples underwent a total of 60 minutes of sonication using an ultrasonic water bath, with the water bath being changed every 10 minutes to prevent overheating and ensure the consistency of the sonication process. This study also investigates the effects of mechanical grinding on GO. The grinding process was carried out using a Retsch planetary ball mill (PM100) at a rotational speed of 300 rpm. The total duration of the grinding process was 3 hours, with intermittent breaks of 10 minutes after every 20 minutes of operation, resulting in an effective grinding time of 2 hours. A ball-to-GO mass ratio of 60:1 was employed, utilizing stainless steel balls with a diameter

of 2 mm. For clarity in subsequent discussions, the unground Graphene Oxide will be referred to as GO_a, while the ground Graphene Oxide will be denoted as GO_b.

Table 3: PCE mass ratios and notations

PCE:2D	**0**	**5**	**10**	**15**	**20**
GNPs	GNPs0	GNPs1	GNPs2	GNPs3	GNPs4
GO_a	GO_a0	GO_a1	GO_a2	GO_a3	GO_a4
GO_b	GO_b0	GO_b1	GO_b2	GO_b3	GO_b4

2.2.2 Mortar Preparation

The mortars were prepared using a CEM I/slag/limestone ternary system, with established mass ratios of 49% CEM I, 35% slag, and 16% limestone. A fixed water-to-binder ratio of 0.5 was used to ensure a workable mix. The preparation process involved several key steps:

1. Dry Mixing: The blended cement components and homogenized standard sand were dry mixed in a 1:3 ratio. This process was performed for 1 minute using a laboratory-scale mortar mixer with a speed range of 140 to 285 RPM.
2. GO Suspension Incorporation: Pre-prepared graphene oxide (GO) suspensions were incorporated into the dry mix. This step was followed by an additional 1 minute of mixing with the binder to achieve homogeneity.
3. Final Mixing: The mixtures were then blended for an additional 1 minute at a higher speed to ensure the uniform distribution of the wetted mix. During this step, additional sonicated GO suspensions containing PCE were added to prevent aggregation and ensure better dispersion within the final structure.

Mortars were cast into moulds for subsequent testing. Compressive strength evaluations were conducted on the samples after 1, 3, and 7 days of curing. All samples were cured in a water bath to facilitate hydration, and each experiment was repeated three times to minimize errors and ensure accuracy in the results.

2.3 Experiments

2.3.1 Physical Observations

To evaluate the viability of GNPs and GO agglomeration, a series of experiments were conducted by analysing the appearance of vials containing simulated pore solutions. These vials were prepared with varying mass ratios of PCEs and suspensions of GNPs and GO. The vials were sealed to prevent carbonation and observed at specific time intervals (0 hours, 1 hour, 12 hours, and 24 hours) to monitor changes over time. The effectiveness of dispersion, as a function of the concentration of graphene materials, was assessed by examining the appearance of agglomerates and the clarity of the solution. Images were captured at each designated time interval to systematically evaluate the dispersion state of the substances within the vials.

2.3.2 UV-Vis Spectroscopy

UV-Vis spectroscopy was employed to analyse the optical characteristics and dispersion ability of GO in a simulated pore solution [12]. The measurements were conducted using a spectrophotometer calibrated to cover a wavelength range of 190-500 nm. All GO suspensions were prepared at concentration of 0.02 mg/mL to ensure that absorbance remained below 1. The functional groups of GO were characterized by measuring its UV-Vis spectra, with characteristic absorption peaks observed at approximately 230 nm and 310 nm. Higher absorbance at these wavelengths indicated improved dispersion of GO in the solution. To

eliminate the influence of PCE on the results, batch corrections were performed using pure PCE in the pore solution as a baseline.

2.3.3 Dynamic Light Scattering (DLS)

A Zetasizer, employing DLS technology, was utilized to evaluate the particle size distribution of GNPs and GO in both aqueous solutions and simulated pore solutions. The experimental protocol involved preparing a 1 mg/mL 2D materials suspension, which was subjected to 60 minutes of ultrasonication with varying PCE mass ratios to enhance dispersion. For the dispersion in the pore solution, the 2D materials suspensions were further diluted in the pore solution at a 1:0.01 molar ratio, which had been previously identified as optimal for use with conjugated 2D materials-Tween 80: Chitosan micelles at a 1:1 ratio, yielding a final concentration of 0.5 mg/mL. The DLS measurements were conducted using a particle size analyser equipped with a laser for light emission, enabling the determination of the hydrodynamic diameter of GNPs and GO particles. The extent of agglomeration was assessed by analysing the particle size distribution. Improved dispersion was indicated by a narrower polydispersity index (Pd), smaller median particle size (d50), more consistent particle size distribution (d10/d90 ratios), and lower coefficients of variation (CVs). The resulting particle size distribution data were graphically represented as Gaussian curves, facilitating a comparative analysis of the dispersion behaviour of GNPs and GO in both water and pore solutions with varying PCE ratios.

2.3.4 Isothermal Calorimetry

Calorimetry experiments were conducted using an I-Cal Flex isothermal calorimeter (Calmetrix Scientific Instruments LLC, USA). This instrument measures both heat flow and total heat generated over time, providing insights into the hydration kinetics of cement. For each test, a blended cement binder consisting of 49% CEM I, 35% slag, and 16% limestone was prepared. 1.5 grams of a 2D materials suspension was added to 3 grams of the binder, maintaining a water-to-binder ratio of 0.5. The binder and 2D materials suspension were combined and mixed using a high-speed paste mixer for 1 minute to ensure homogeneity. The resulting mixtures were then transferred to plastic ampoules to prevent moisture ingress and carbonation, which could alter their composition. The ampoules were subsequently placed in the calorimeter, and hydration was monitored at a constant temperature of 20°C. To ensure comparability between samples, the amount of binder mass was used to normalize the data. The total heat was measured one hour after the experiment commenced, accounting for the heat introduced during the initial mixing phase. The total heat was calculated one hour after the experiment commenced.

The effect of varying PCE to 2D materials ratios on the hydration rate was investigated by preparing specimens with different proportions of 2D materials (0.05%, 0.1%, 0.2%, and 0.4% by weight of the binder) and various PCE/2D materials mass ratios (0, 5, 10, 15, 20). Hydration kinetics were assessed by comparing the rate of heat generation over time and the total heat evolved by the samples.

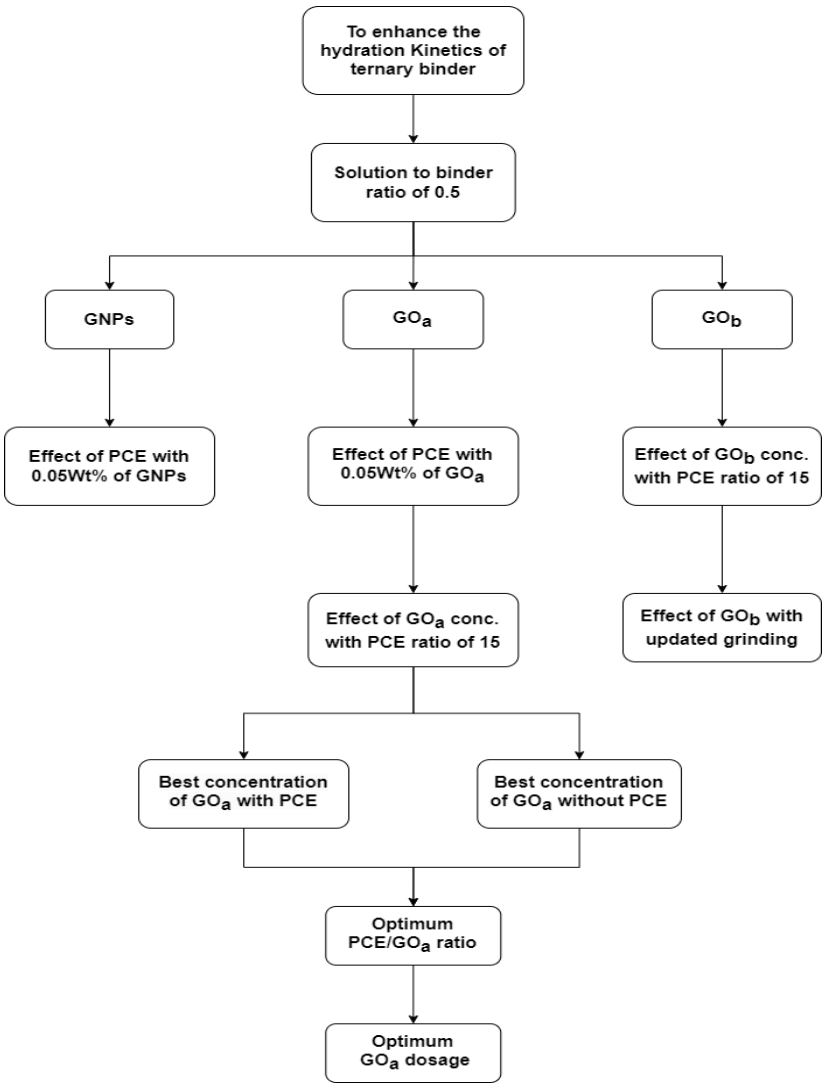

Figure 5: Schematic diagram of isothermal experiments to achieve optimum dosages

This study utilizes the experimental design illustrated in Figure 5 to optimize early hydration kinetics through the systematic adjustment of dosages of 2D materials and PCEs. The methodology begins with the variation of 2D materials dosages to assess their impact on heat evolution and hydration kinetics. Following this, different PCE ratios are evaluated to determine their effect on the dispersion of the 2D materials. The optimal dosages are identified based on metrics such as peak intensity, rates of heat evolution, and improvements in dispersion characteristics. This structured approach facilitates the determination of conditions that maximize early hydration kinetics and overall material performance.

2.3.5 In-situ XRD

To obtain accurate information regarding cement hydration, several key factors must be considered when conducting in-situ X-ray diffraction (XRD) experiments. The experimental setup involves maintaining a constant measurement temperature of approximately 20 ± 0.1°C. The data collection utilizes a Siemens D5000 diffractometer equipped with a SolX detector (Bruker) and operates with CuKα radiation at 40 kV and 30 mA. The procedure begins by preparing a cement paste through the mixing of cement and water, with an additional external impulse applied for one minute to achieve a homogeneous paste. This paste is then put into the XRD sample holder to ensure an even surface for scanning. To prevent water evaporation, the

sample is sealed by applying a 5 μm Kapton polyimide film. Data acquisition is conducted within a 2θ scanning range of 7 to 41 degrees on the diffractometer. The setup parameters for the diffractometer include a step width of 0.024° and a counting time of 0.6 seconds per step. Over a 24-hour period, a total of 96 diffraction patterns are collected, with each pattern taking approximately 15 minutes to acquire.

2.3.6 Compressive Strength

Compressive strength testing was conducted to evaluate the mechanical properties of cement composites after various curing ages. The tests were performed at 1, 3, and 7 days to assess the development of strength in the concrete samples. After an initial setting period of 24 hours, the samples were demoulded and cured in a water bath until testing, providing a thorough analysis of strength development during the early hydration stages.

2.3.7 Carbonation

Samples were subjected to controlled carbonation conditions in a customized carbonation chamber to evaluate their CO_2 capture kinetic and capacity. The chamber environment was meticulously regulated to maintain a CO_2 concentration of 3.0 ± 0.1 %, with the temperature controlled at 20 ± 2°C and relative humidity sustained at 53 ± 5%. These conditions were designed to simulate an accelerated carbonation process.

The carbonation depth of the samples was tested by colorimetric method at weekly intervals over a 28-day period. This procedure involved splitting the samples in half at certain time points, followed by immediate cleaning of the inner surfaces to remove debris and loose particles. A pH indicator, specifically a 1% thymolphthalein solution in ethanol, was then applied to the cleaned surfaces. Thymolphthalein was selected due to its distinct colour change in response to pH variations, enabling precise visualization of the carbonation front.

After a complete carbonation of the paste samples, which took ~42 days, the samples were removed from the carbonation chamber. The carbonation was and verified using the thymolphthalein indicator. Subsequently, the samples were crushed to a fine particle size using a ceramic mortar and pestle and sieved to less than 40 microns The resulting powder samples were stored in airtight containers, and approximately 40 mg of the ground sample was carefully prepared for further experiments.

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TGA/DSC-1 thermal analysis instrument, which measures weight changes in the sample as a function of temperature. all analyses were performed in a nitrogen gas environment over a temperature range of 25–1000°C with a ramp rate of 10°C/min. The key temperature ranges and their significance are as follows:

75–400°C: This range corresponds to the mass loss of chemically bound water from hydrate products such as C-S-H and ettringite.

400–500°C: This range is associated with the dehydroxylation of calcium hydroxide (CH). The CH content can be calculated by multiplying the percentage of weight loss in this temperature range by the molar mass ratio of $Ca(OH)_2$ to H_2O, which is 4.1.

550–900°C: Within this range, the decarbonation of calcium carbonate ($CaCO_3$) occurs. The content of $CaCO_3$ can be determined by multiplying the percentage of weight loss in this temperature range by 2.27, the molar mass ratio of calcium carbonate to carbon dioxide.

The CO_2 uptake is determined using the following equation: (3),

$$CO_2 uptake\ (\%) = \frac{M_{CO_{2carbonated}(Wt.\%)}}{100 - M_{CO_{2carbonated}(Wt.\%)}} \times 100 \quad (3)$$

where $MCO_{2carbonated}$ refers to the ratio of mass loss of the carbonated sample due to $CaCO_3$ decomposition (550–950°C) relative to the dry mass of the sample at 105°C.

3. Results and Discussion

This chapter will present the analysis and evaluation of the principal findings from the experimental investigations. It will include a qualitative analysis of the hydration kinetics and carbonation data, utilizing appropriate mathematical models to interpret the results. Additionally, the chapter will assess microstructural changes and compositional characteristics of the cementitious materials. The discussion will focus on the early hydration processes of the cement, aligning with the study's objectives, and will address other relevant factors impacting the performance of the ternary blended cement.

3.1 Dispersion Assessment

3.1.1 Visual Observations

This thesis presents a detailed investigation into the dispersion and stability of GO and GNPs in simulated pore solutions, particularly in relation to varying PCE mass ratios. The study utilized direct observation techniques to assess the behaviour of these nanomaterials in different conditions. Initially, the dispersion characteristics of GNPs and GO in pore solutions without PCE were examined, as illustrated in Figure 6. The picture of pure pore solution is illustrated in Figure 6 (a) as the reference.

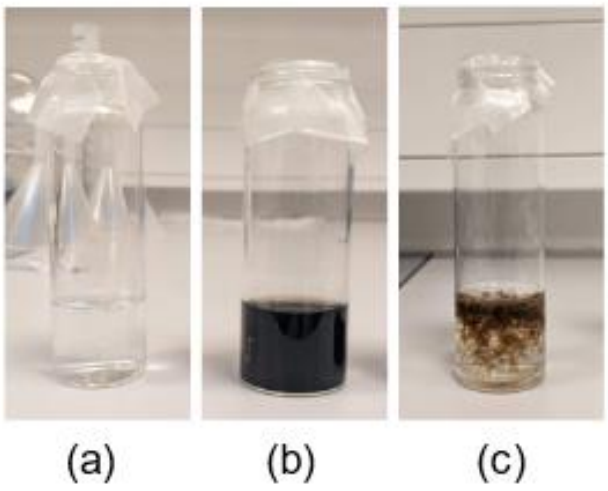

Figure 6: (a)Simulated pore solution, (b) GNPs dispersion, (c) GO_a dispersion

As shown in Figure 6(b), GNPs demonstrated stable dispersion without any signs of agglomeration. In contrast, GO in Figure 6(c) exhibited a rapid right after mixing into the pore solution. Ultrasonication, a widely recognized physical method, is particularly effective in dispersing GO in aqueous solution, as the mechanical forces involved help to break down agglomerates and ensure even distribution of GO. However, these techniques become ineffective in calcium-rich cementitious solutions due to the occurrence of chemical interactions. Specifically, the carboxyl groups on the GO structure react with calcium ions (Ca^{2+}), leading to agglomeration and consequently poor dispersion. This interaction underscores the importance of modifying or 'shielding' the GO surfaces to prevent such occurrences, thereby ensuring stability and homogeneity across different media. In contrast, GNPs do not encounter issues related to platelet aggregation, likely due to the surface chemistry

of GNPs, which does not facilitate interaction with Ca^{2+} ions, thereby allowing GNPs to remain well dispersed without a tendency to form agglomerates.

The GNPs were introduced into pore solutions with varying concentrations of PCE, and their stability was monitored over time, as depicted in Figure 7. During the initial period, the GNPs exhibited consistent behaviour in their interactions, regardless of the PCE concentrations or the presence of pore solution, showing no significant effect on the chemical composition of the solutions, as shown in Figure 7(a). After 24 hours, this dispersion remained stable, as illustrated in Figure 7(b). This stability indicates that GNPs do not undergo chemical reactions with the pore solution. Furthermore, despite the addition of different PCE mass ratios, the dispersion of GNPs was unaffected, suggesting that GNPs are resilient to variations in pH and ionic strength within the medium.

When GO was introduced into pore solutions with varying concentrations of PCE, distinct trends in dispersion and stability began to emerge over time, as shown in Figure 8. When the PCE to GO mass ratio is set at 5, the protective effect of PCE can be described as an "initial protection" phase, wherein PCE likely forms a steric layer around the GO particles, effectively preventing agglomeration at the outset. However, this protection is transient, lasting for no more than one hour. By the two-hour mark, the PCE's effectiveness diminishes, resulting in the reformation and sedimentation of GO particles. This observation suggests that the PCE concentration at this ratio is insufficient to maintain long-term dispersion stability.

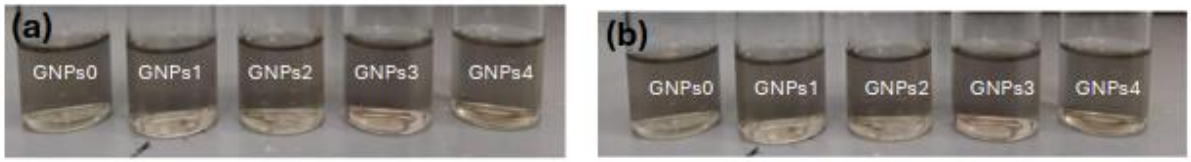

Figure 7: The dispersion of GNPs with different PCE mass ratios at (a) 0h, (b) 24h.

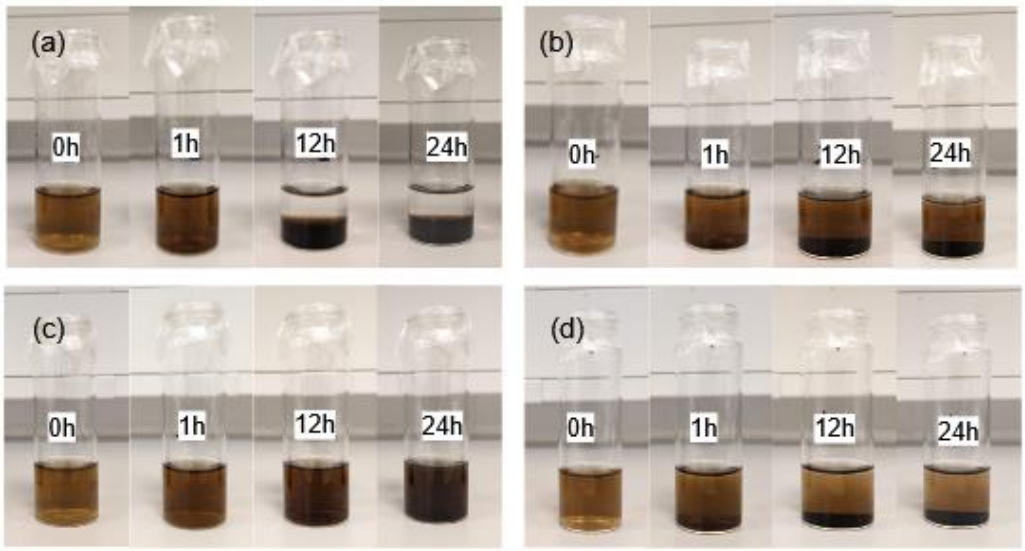

Figure 8: Dispersion of GO_a in pore solution with different PCE/GO ratios, (a) PCE/GO =5, (b) PCE/GO =10, (c) PCE/GO =15 and (d) PCE/GO =20.

At a PCE/GO mass ratio of 10, partial agglomeration and subsequent sedimentation indicate that, although PCE provides slightly better steric hindrance and electrostatic stabilization, it is still not optimal. The concentration at this ratio may not sufficiently encapsulate all GO surfaces, leaving some particles exposed, which leads to bond formation, agglomeration, and eventual sedimentation driven by gravitational forces within 12 hours.

When the PCE/GO mass ratio is increased to 15, there is a notable improvement in stabilization and reducing the likelihood of large-scale agglomeration and sedimentation as shown in Figure 9. However, the increased solution darkness could suggest the potential formation of micro-agglomerates, even at this elevated ratio.

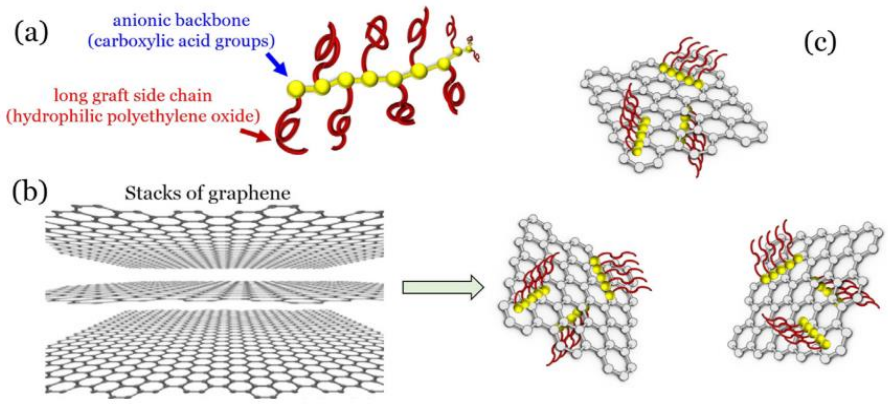

Figure 9: Micro-view of (a) polycarboxylate molecule, (b) flocculation of graphene sheets, and (c) homogeneously dispersed graphene [51].

A PCE/GO ratio of 20 would result in enhanced steric repulsion among the GO particles. While this high level of steric hindrance contributes to preventing agglomeration, it may inadvertently cause the particles to pack more tightly than is desirable due to the size of the PCE chains [53]. Although this higher ratio effectively prevents sedimentation at the beginning, it does not necessarily promote the best stability of dispersion for GO particles.

Based on these findings, a PCE/GO mass ratio of 15 appears to offer the best performance in maintaining dispersion stability over 24 hours within a cementitious system. Although all dispersions appear similar at 0 hours, further analyses, such as UV-Vis and DLS, were conducted to verify these observations.

3.1.2 UV-Vis Spectroscopy

UV-Vis spectroscopy was employed to assess the absorbance characteristics of GO, providing critical insights into the stability and dispersion of these nanomaterials within the cement matrix, particularly during the initial stages of dispersion in the simulated pore solution. This spectroscopic technique is particularly well-suited for evaluating the early dispersion behaviour of GO, as their optical properties are highly sensitive to the degree of aggregation. The numerical analysis of the peak intensity near 230 nm, typically associated with UV-visible absorption characteristics of cementitious materials when additives like GO are involved, can provide insights into the effects of such additives on the dispersion properties.

Figure 10 shows that absorbance measurements in different media revealed distinct peaks for GO and GNPs, reflecting their dispersion quality. In water, GO exhibited a sharp peak at 230 nm, corresponding to the π-π* transitions of the C=C bonds. This peak is characteristic of GO, with its intensity directly proportional to the degree of dispersion. In contrast, GNPs typically display a broader peak at approximately 270 nm, attributed to analogous electronic transitions [58].

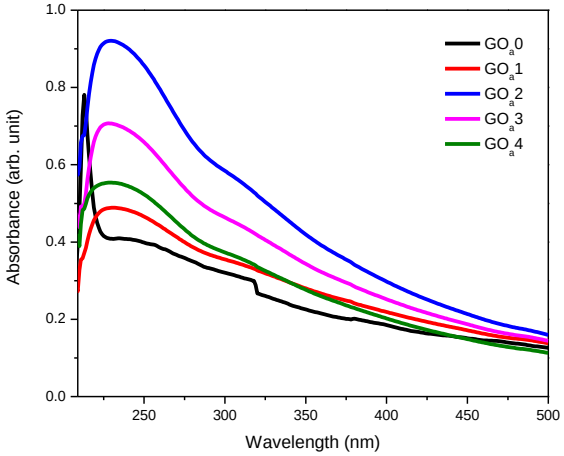

Figure 10: UV-Vis absorbance peak of GO_a in pore solution with different PCE concentrations

The observed peaks, as illustrated in Figure 10, exhibit an acute profile for GO in relation to varying PCE dosages. Specifically, for the GO_a0 sample, no characteristic peak is observed, which suggests a tendency for aggregation in alkaline environments. This aggregation is likely driven by interactions between the surface functional groups of GO and the ions present in the pore solution. The alkaline conditions within cement pore solutions, characterized by high ionic strength, can significantly influence the colloidal stability of GO, promoting aggregation through reduced electrostatic repulsion. When varying doses of PCE were introduced, distinct changes in the absorbance profiles of GO were observed, particularly at 230 nm, reflecting variations in dispersion quality. In the GO_a1 sample, with the lowest PCE dose, the peak intensity was minimal, indicating that the amount of PCE was insufficient to fully stabilize the GO particles [60].

As the PCE dosage increased, the GOa2 sample displayed the highest peak intensity, suggesting improved dispersion due to optimal steric stabilization. The PCE effectively adsorbed onto the GO surfaces, preventing aggregation by counteracting van der Waals forces. However, at higher PCE/GO ratios (15 and 20), a reduction in peak intensity occurred, indicating that excessive PCE may have led to secondary aggregation. This could be due to depletion flocculation, where excess PCE promotes attractive forces between GO particles. Additionally, the high ionic strength in the alkaline pore solution may have reduced electrostatic repulsion, further encouraging aggregation [61].

The broadening of the absorbance peaks with increasing PCE dosages also supports this, indicating the formation of larger aggregates and a reduction in dispersion stability. This trend highlights that the optimal PCE/GO ratio of 10 promotes dispersion, while excessive PCE can destabilize the system, resulting in decreased colloidal stability.

3.1.3 Dynamic Light Scattering (DLS)

Dynamic Light Scattering was utilized to accurately measure the particle size distribution of two-dimensional nanomaterials, specifically GO and GNPs, in aqueous environments. As illustrated in Figure 11, DLS was employed to measure the particle size distributions of GNPs in both water (a & b) and cement pore solutions (c & d). The analysis focused on characterizing the effects of varying concentrations of PCE on the dispersions. Notably, DLS measurements indicated that while changes in scattered light intensity were observed, signifying variations in particle number concentration—the size distribution of GNP particles remained unaffected by different PCE dosages in both water and pore solutions. This finding is particularly significant, as it implies that PCE dosage only slightly influences the concentration of GNP particles in the dispersion, without altering their inherent size distribution due to the inert nature of GNPs.

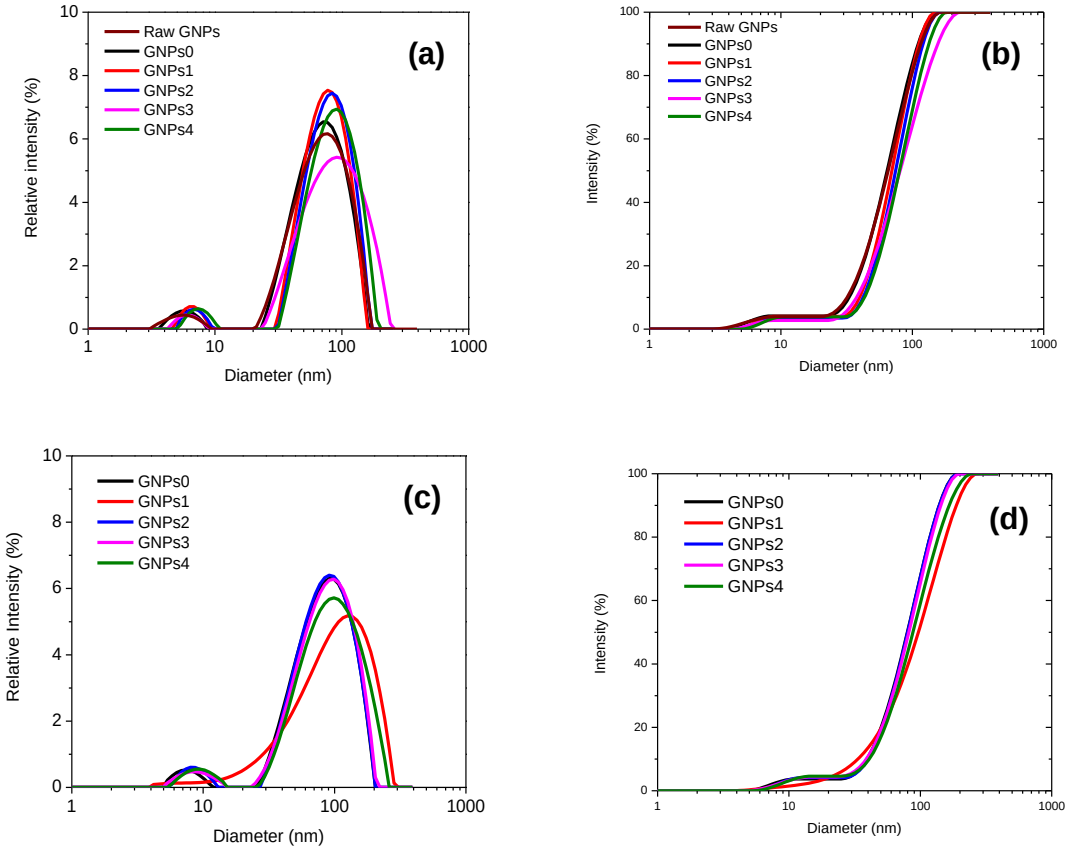

Figure 11: (a & b) DLS curves of GNPs in water and in (c & d) pore solution.

The observed variations in light intensity can be attributed to changes in the concentration of GNPs or the degree of coagulation within the mixture, rather than any alterations in the original particle size. This highlights the role of PCE in modifying the particle interactions within the solution rather than directly affecting the particle dimensions.

Furthermore, as shown in Figures 11 (a) and (c), DLS successfully identified two distinct maxima in the scattering profile, corresponding to different orientations of GNP particles. Specifically, the larger peak is associated with the scattering from the edge plane of the GNP particles, while the smaller peak corresponds to the basal plane. This dual-peak behaviour is a result of the unique scattering characteristics of the edge and basal planes, which differ in terms of surface properties and their interaction with the surrounding medium. The distinct peaks

indicate that the GNPs are well-dispersed, and the presence of these peaks, even in the absence of PCE, strongly supports the study's initial hypothesis that PCE does not alter the size of GNP particles but instead influences their interaction dynamics within the solution.

Figure 12(a & b) shows the effectiveness of sonication in dispersing GO, in the initial particle size distribution curve, the raw GO product displayed larger particle sizes and a broader distribution, indicative of significant agglomeration. This suggests that the GO sheets were clustered together, resulting in non-uniform dispersion. Following sonication, a marked reduction in particle diameter was observed, as evidenced by a shift in the particle size distribution curve toward smaller sizes and a narrower distribution range. This shift reflects the efficacy of sonication in exfoliating the GO sheets into smaller, more uniformly dispersed particles, thereby improving the dispersion quality.

Subsequent to sonication, the introduction of specific ratios of PCE further reduced the particle diameter in a water medium, as illustrated in Figure 12(a & b). The dispersion of GO treated with a higher PCE ratio, referred to as GO_a2, demonstrated a more pronounced decrease in particle size and a more uniform distribution compared to GO treated with lower PCE ratios. This indicates that the GO_a2 sample achieved superior dispersion, attributed to the optimal interaction between GO and PCE. The PCE effectively stabilized the GO particles, preventing them from coalescing, which resulted in a more consistent and finer dispersion. The observed improvements in dispersion and particle size reduction in water medium suggest that in the absence of complex ions, the GO particles maintain a stable dispersion state due to the reduced ionic activity in water, which minimizes the potential for agglomeration.

However, when GO_a0, a sample without adequate PCE stabilization, was introduced into a cement pore solution (as shown in Figure 12(c & d)), no discernible peaks were observed in the particle size distribution. This absence of peaks is indicative of severe agglomeration, where the particles have clumped together extensively, preventing effective dispersion. In a pore solution environment, the presence of various ions can promote agglomeration, leading to a lack of distinguishable particle size peaks in the DLS measurements. In contrast, the introduction of GO_a2 into the pore solution with a PCE mass ratio of 10 significantly improved the dispersion quality. GO_a2 exhibited better dispersion due to its interaction with PCE, which effectively stabilized the GO particles, preventing them from agglomerating despite the complex ionic environment of the pore solution. The DLS measurements of GO_a2 in the pore solution showed a distinct peak, indicating effective dispersion and stabilization within the cementitious matrix. This finding highlights the crucial role of PCE in enhancing the stability and dispersion of GO in environments with high ionic activity.

In figure 12(c), the absence of visible peaks for GO_a0 in the pore solution underscores its inadequate dispersion and instability, whereas the presence of a distinct peak for GO_a2 demonstrates successful dispersion and stabilization. This contrast between GO_a0 and GO_a2 emphasizes the importance of optimizing the interaction between GO and PCE to achieve effective dispersion, particularly in complex solutions such as cement pore solutions, where ionic interactions can significantly influence particle behaviour.

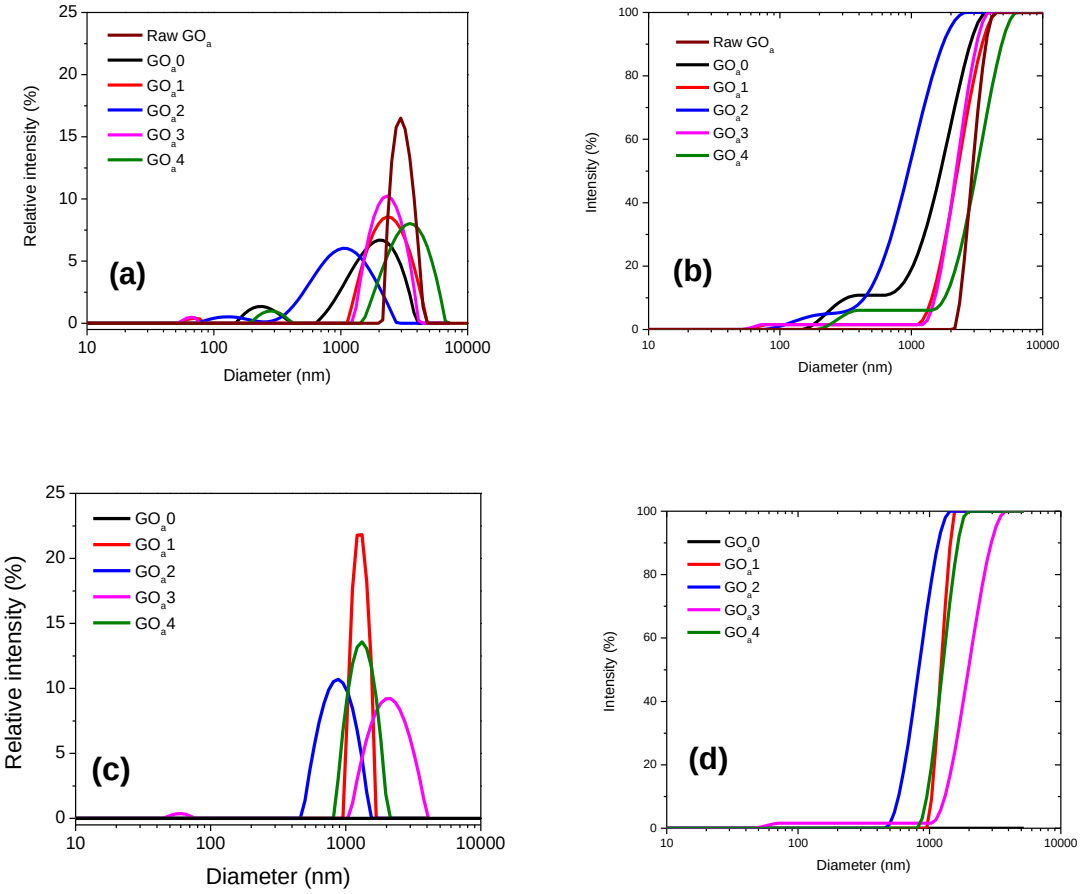

Figure 12: (a & b) DLS curves of GO in water and in (c & d) pore solution.

Figure 13 depicts the Dynamic Light Scattering (DLS) curves for ground Graphene Oxide (GO_b) in both water (a) and simulated pore solution (b). The grinding process was conducted using a Retsch planetary ball mill (PM100) at a rotational speed of 300 rpm for a total duration of 3 hours, with 10-minute breaks after every 20 minutes of operation, yielding an effective grinding time of 2 hours. The grinding process utilized a ball-to-GO ratio of 60:1, with stainless steel balls measuring 2 mm in diameter.

The DLS analysis of GO_b with varying PCE mass ratios in water revealed higher intensity peaks with irregular and non-smooth curves. These irregularities suggest that only a small fraction of the particles fell within the observable size range, while the majority of the particles remained agglomerated, thereby limiting their detection through DLS. This outcome indicates that despite the grinding process, significant agglomeration of GO particles persisted, and the dispersion was not adequately improved by grinding alone. When GO_b was introduced into the simulated pore solution, the DLS measurements revealed no discernible peaks, consistent with prior observations. This absence of peaks suggests that the GO particles underwent substantial agglomeration in the pore solution, further confirming the challenges of achieving effective dispersion in such a complex ionic environment. Even with the addition of PCE, the DLS curves for GO_b1 and GO_b4 exhibited only slight reductions in particle size range. However, the peaks remained irregular and non-smooth, indicating that only a limited number of particles were sufficiently dispersed, while the majority continued to agglomerate.

The primary objective of grinding GO was to reduce the particle size by breaking down the GO sheets, thereby increasing their surface area to enhance interaction with PCE. However,

the results suggest that this objective was not fully achieved. The suboptimal dispersion and persistent agglomeration observed in GO_b may be attributed to the relatively low rotational speed of 300 rpm used during the grinding process, which may have been insufficient to effectively exfoliate the GO sheets and achieve the desired level of dispersion. In response to these findings, the grinding protocol was revised to improve dispersion. Given that a PCE/GO mass ratio of 10 had previously demonstrated improved dispersion of GO in the simulated pore solution, as confirmed by DLS curves, this ratio was incorporated into the GO before grinding. Additionally, the grinding speed was increased to 400 rpm to enhance the mechanical forces acting on the GO particles during the milling process. This combination of a higher rpm and optimized PCE dosage was intended to promote better dispersion of GO particles during the grinding process. The GO prepared under these updated conditions is referred to as GO_c.

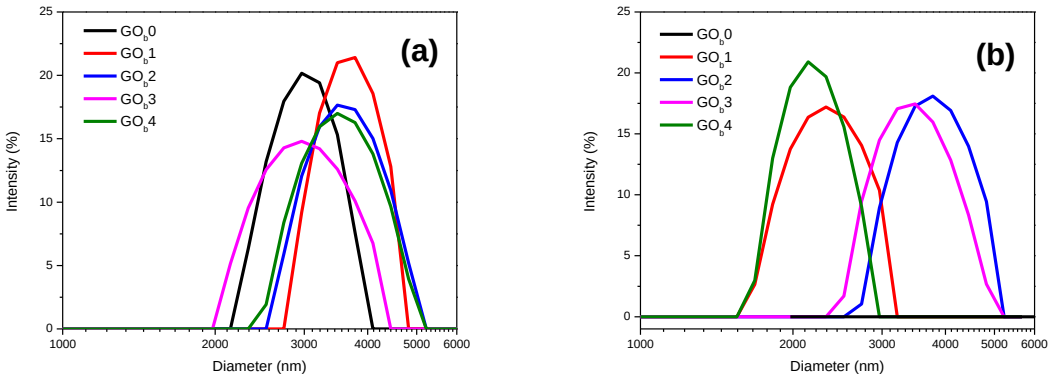

Figure 13: DLS curves of GO_b in water(a) and in pore solution(b)

These modifications to the grinding protocol highlight the critical need for optimizing both mechanical processing parameters and chemical stabilization strategies to achieve effective dispersion of nanomaterials, particularly in challenging environments such as cement pore solutions. The results of the DLS analysis underscore that both sonication duration and appropriate PCE ratios are vital for ensuring the proper dispersion of graphene-based 2D materials in such environments [57]. Achieving this level of dispersion is crucial, as it directly impacts the mechanical and hydration properties of cement systems reinforced with graphene. Enhanced dispersion facilitates better integration of graphene within the cement matrix, leading to improved performance and durability of the resulting composite materials.

3.2 Early Hydration Characterization

3.2.1 Isothermal Calorimetry

Isothermal calorimetry is a pivotal technique for evaluating the heat evolution characteristics of cementitious systems, which is crucial for understanding the impact of additives such as GO and GNPs on cement hydration kinetics. The calorimetric data for the control sample, which did not contain any additives, exhibited the typical hydration trends as shown in Figure 14. The initial peak in heat evolution occurred within the first few hours, driven by the immediate demand for water by the cement and the initial reactions between calcium silicates and water. This initial peak was followed by a relatively dormant period, during which heat evolution significantly decreased. Subsequently, the heat release increased again during the acceleration phase of hydration, which is characterized by the formation of C-S-H and calcium hydroxide.

This acceleration phase is crucial as it marks the development of the microstructure that contributes to the mechanical properties of the cementitious system [28][32].

Figure 14 illustrates the heat evolution curves for a 0.05 wt.% GNPs formulation with PCE. The literature review identified that a 0.05 wt.% addition of GNPs was assessed for its impact on heat evolution in cementitious systems through isothermal calorimetry [43]. Despite the initial effective dispersion of GNPs in the pore solution, their presence was found to adversely affect the early hydration kinetics of cement. This negative influence is primarily attributed to the chemical inertness of GNPs, which increases the induction period of hydration [31]. The inert nature of GNPs leads to their adsorption onto the surfaces of cement particles, effectively creating a physical barrier that impedes the direct reaction of cement with water during the initial stages of hydration [42]. This obstruction results in a deceleration of the hydration process, extending the induction period, which is characterized by minimal heat evolution.

The addition of PCE superplasticizers exacerbates the initial delay in hydration by inhibiting both dissolution and nucleation through surface coverage [46][57]. PCE molecules, known for their dispersing effects, extend the induction period by reducing the availability of water to react with cement particles and hindering the nucleation process. This is reflected in the prolonged low heat evolution phase in the calorimetric analysis as shown in Figure 14(a). The combined presence of GNPs and PCEs further reduces early-stage hydration efficiency, resulting in an extended induction period. Consequently, the total heat evolved in samples containing PCEs is lower than in the control as shown in Figure 14(b), highlighting the inhibiting effects of PCEs on both dissolution and nucleation [57].

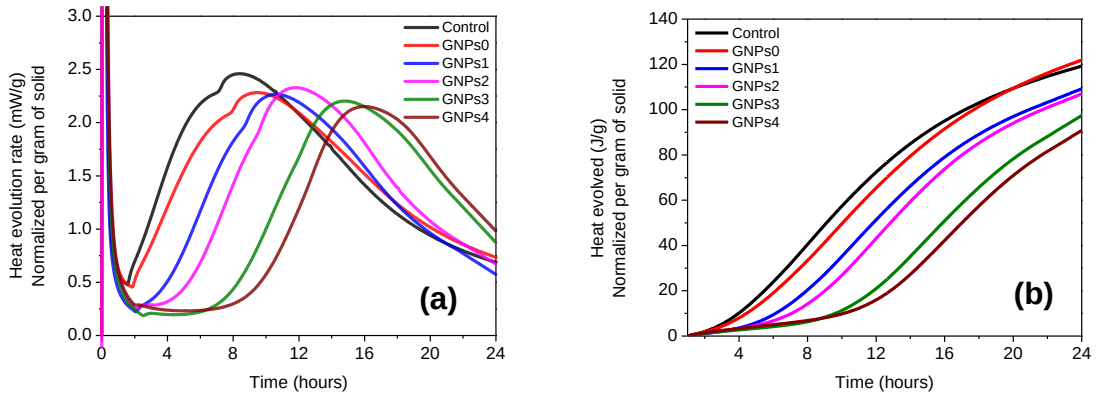

Figure 14(a & b): Heat evolution curves of 0.05wt.% GNPs with PCE effect

Figure 15 (a) demonstrates GO has been shown to significantly enhance the reaction rate, particularly at PCE mass ratios of 10 and 15. GO's effectiveness can be attributed to its unique physicochemical properties, especially its role as a nucleation and seeding agent within the cementitious matrix [62][63].

Initially, the large specific surface area of GO provides nucleation sites for the formation of hydration products. These additional nucleation sites facilitate the early stages of cement hydration by promoting the precipitation of calcium silicate hydrate (C-S-H) and other hydration products. The enhancement of the hydration process by GO is particularly noticeable at PCE ratios, where GO has the best dispersion in mimic pore solution. In this context, GO effectively interacts with the cement particles, reducing the induction period and leading to an earlier onset of the acceleration phase of hydration [35][38].

However, at higher PCE dosages, the influence of PCE becomes more pronounced, and its supressing effect on hydration kinetics can outweigh the beneficial role of GO. Consequently,

the overall reaction rate of binders is reduced, and the acceleration of hydration previously observed with GO is diminished. This complex interaction between GO and PCE underscores the importance of carefully optimizing the ratios of these additives to achieve the desired balance between dispersion and nucleation effects. Too much PCE can screen the effects of GO, leading to a prolonged induction period and slower overall hydration. Therefore, tailoring the PCE dosage is critical for maximizing the performance benefits of GO in cementitious systems, particularly in applications where both early strength development and long-term durability are key considerations [54].

As shown in Figure 15 (c & d), increasing the dosage of GO in cementitious systems necessitates a corresponding increase in the PCE dosage to ensure adequate dispersion. However, this adjustment results in a prolonged induction period during the hydration process. Despite this delay, a significant enhancement in the reaction rate is observed when compared to the PCE-only pastes, underscoring the role of GO in modifying cement hydration kinetics.

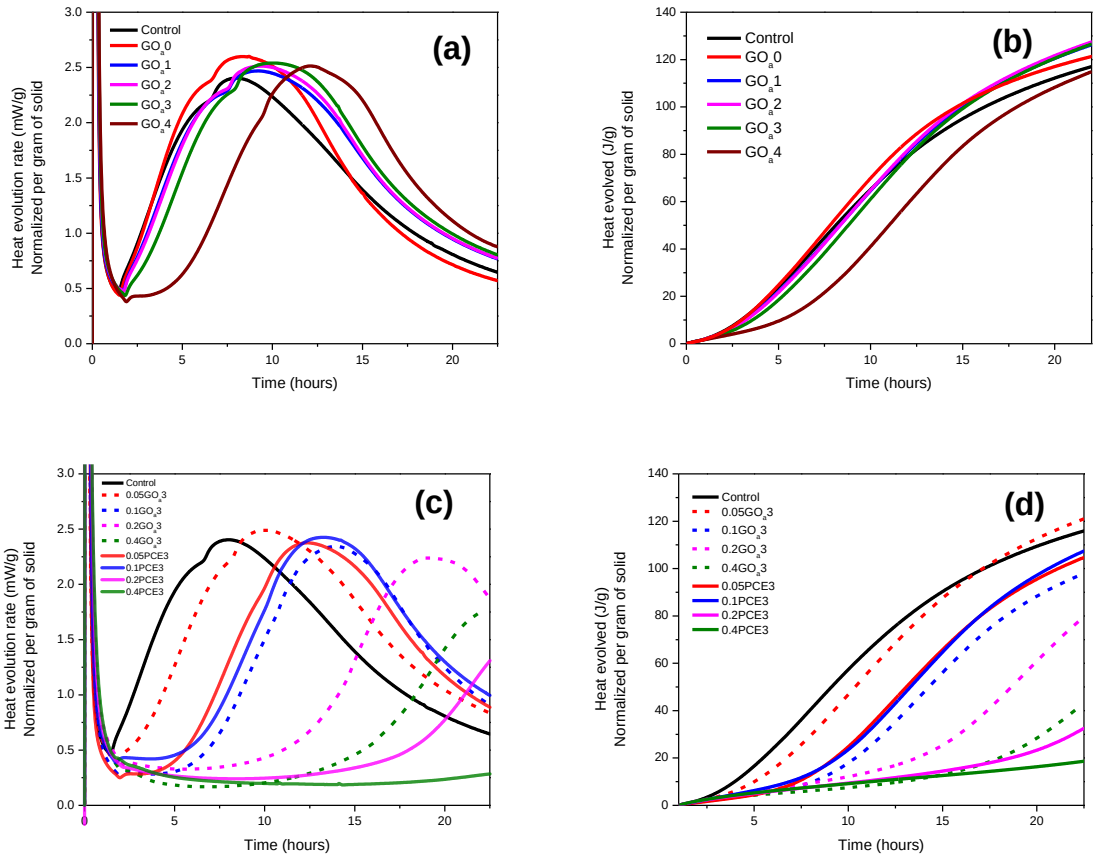

Figure 15: (a & b) The heat evolution curves of 0.05wt.% GO_a with PCE effect and (c & d) PCE 3with GO_a3 with effect

PCE acts as a dispersant by adsorbing onto the surface of GO particles, effectively preventing their agglomeration. This dispersion is crucial for ensuring that GO remains well-distributed within the cement matrix, thereby facilitating its role as a nucleation agent [58][62]. However, as the dosage of PCE increases, its impact becomes more pronounced, potentially impeding the hydration process. The overall hydration process can be hindered, as the formation of hydration products is slowed by the reduced availability of nucleation sites [51]. To address this challenge, the use of ground GO in combination with a PCE dosage of 15 was tested.

Grinding GO increases its surface area and enhances its reactivity, potentially compensating for the reduced nucleation efficiency caused by higher PCE levels as shown in Figure 16.

As a result, the overall hydration kinetics are affected, with the benefits of enhanced dispersion being counterbalanced by the reduced nucleation efficiency. Initially, at lower rotational speeds (RPMs) and shorter grinding durations, the heat evolution rates during the hydration of cementitious systems were observed to be lower than those of the PCE-only reference samples. This reduction in heat evolution can be attributed to the agglomeration of GO particles, which hindered their effective dispersion within the cement matrix. Agglomeration of GO particles, particularly at suboptimal grinding conditions, presents a significant challenge in achieving efficient particle dispersion. When GO particles are not properly dispersed, their ability to act as nucleation sites for the formation of hydration products, such as C-S-H, is compromised [79]. This inefficiency in nucleation and hydration processes directly correlates with lower heat evolution rates, reflecting a slower and less effective hydration reaction.

As shown in Figure 16, even though the updated grinding process resulted in a higher total heat evolution compared to the previous grinding protocol, it remained lower than that of the control sample. The goal was to explore the size effect of GO through enhanced mechanical processing, but it became evident that standard grinding methods were insufficient in significantly improving GO's performance. While increasing the RPM and extending the grinding time did improve GO dispersion to some extent, it did not surpass the effectiveness of the control, indicating that normal grinding does not adequately optimize GO for hydration acceleration.

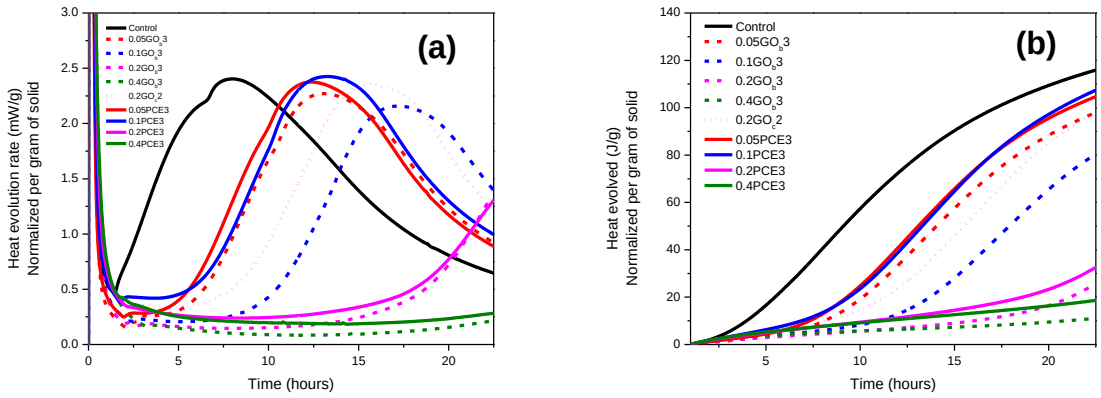

Figure 16: The Heat evolution curves of GO_b3 with dosage effect and Updated GO_b.

Furthermore, the Figure 17 demonstrate the effect of GO dosage on cement hydration. Optimizing GO dosages is essential for achieving the desired enhancement in hydration kinetics.

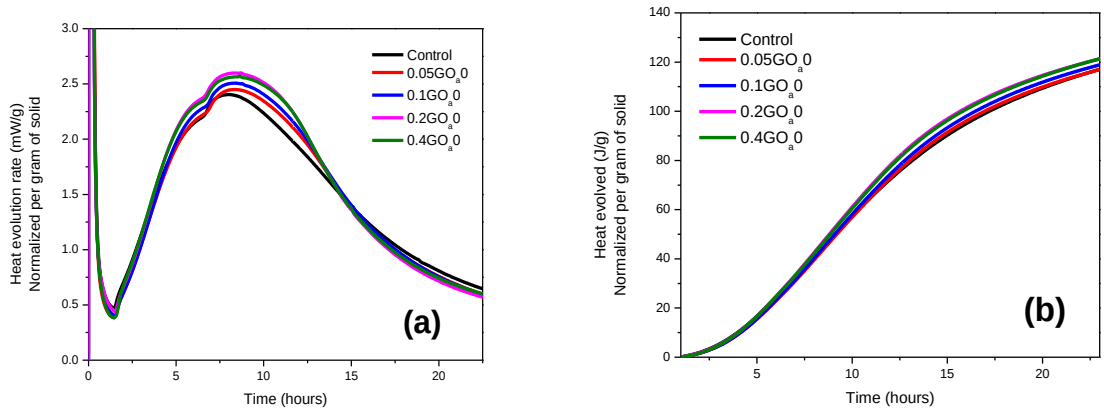

Figure 17(a & b): The hydration heat evolution curves ternary binders with different GO_a dosage

At 0.2 wt.% GO, particles are well-dispersed, minimizing agglomeration and ensuring a uniform distribution in the cement matrix [79]. This promotes better interaction with cement components, enhancing the hydration process compared to other dosages.

At this GO dosage, improved dispersion prevents agglomeration, allowing GO particles to interact efficiently with cement particles, promoting the formation of key hydration products like C-S-H and CH. This enhanced interaction correlates with the higher heat evolution observed at this dosage [80][81]. Additionally, GO acts as a nucleation site, accelerating hydration product formation due to its large specific surface area, further increasing heat release [79][84]. The optimal dispersion at 0.2 wt.% also shortens the induction period, leading to a quicker onset of exothermic hydration reactions and an overall acceleration of the process [83].

As shown in Figure 18, we strategically reduced the PCE dosage by 25% while simultaneously increasing the GO dosage from 0.05 wt.% to 0.2 wt.%. This adjustment was carefully calibrated to align with the PCE concentration levels previously determined to be optimal for GO dispersion assessments. The modified PCE/GO ratio was found to have a profound impact on the early hydration kinetics of the cementitious system, particularly in terms of heat evolution characteristics.

The reduction in PCE, when coupled with the increased GO dosage, led to a significant reduction in the induction period—a critical phase during which hydration reactions are initially slow, and little heat is released. The shortening of this period suggests that the modified formulation facilitated faster initial hydration reactions, which is advantageous for applications requiring early strength development. This improvement is likely due to the more efficient interaction between GO and the cement particles, as the reduced PCE dosage prevented excessive steric hindrance that might otherwise impede the hydration process [85].

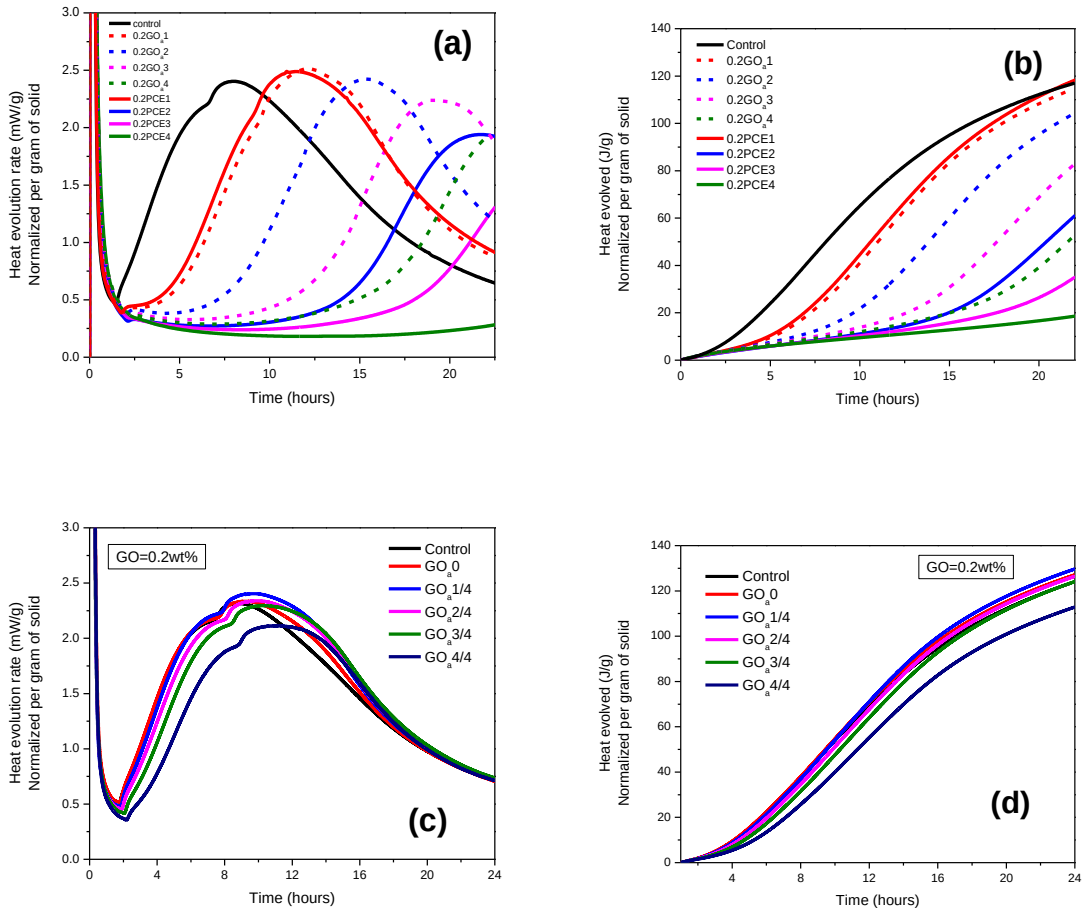

Figure 18: (a & b) Heat evolution curves of 0.2wt. GO_a with PCE effect and (c & d) reduced PCE dosage effect in 0.2wt.%GO_a

The improved concentration, particularly the GO_a1-4 mixture, demonstrated the highest peak intensity in heat evolution as well as the greatest total heat released over the hydration period. These findings indicate that the optimized balance of GO and PCE not only accelerates the early hydration reactions but also enhances the overall hydration process, leading to more extensive formation of hydration products such as C-S-H and CH [83][86]. The increase in peak intensity and cumulative heat release is indicative of improved cement hydration, which is crucial for the development of mechanical strength and durability in cementitious materials. The change of PCE/GO ratio to 0.25 underscores the importance of optimizing both chemical admixtures and nanomaterial dosages to achieve the desired performance in cementitious systems. The reduction in PCE was instrumental in mitigating the potential negative effects of excessive polymer adsorption on the GO surface, which can hinder cement hydration by blocking active sites. As shown in Figure 19 optimization highlights the balance required to maximize the benefits of GO in enhancing cement hydration while minimizing any potential inhibitory effects of dispersants like PCE. The results from the GO_a1-4 formulation suggest that, with the appropriate PCE/GO ratio, it is possible to significantly improve the efficiency of hydration processes, thereby enhancing both the rate and extent of heat evolution [89].

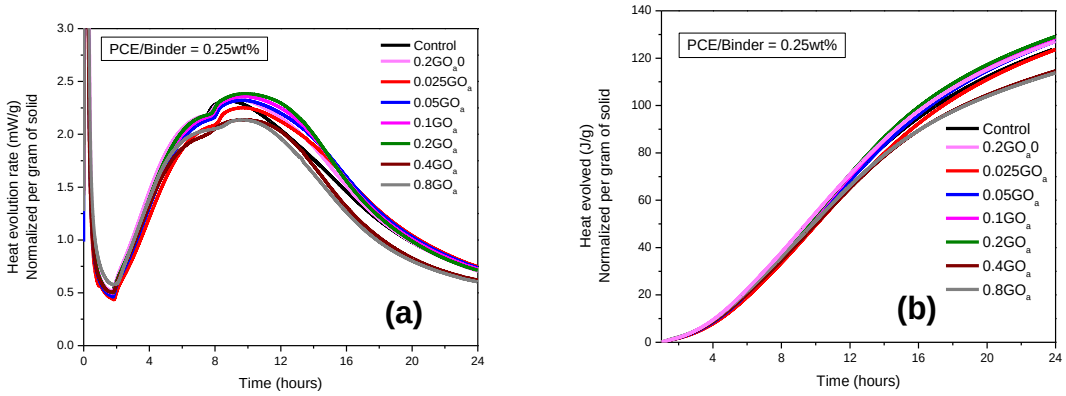

Figure 19(a & b): The heat evolution curves of GO_a dosage effect with optimized PCE dosage

Higher peak intensities observed in the study were selected for further analysis due to their significance in evaluating the material's performance. These intensities, noted in the GO_a1-4 formulation, are indicative of optimal dispersion and interaction of GO within the cement matrix. The observed peak intensities reflect enhanced heat evolution and improved hydration kinetics associated with the incorporation of GO.

Focusing on these peak intensities facilitates a deeper understanding of the relationship between GO dosage, PCE ratios, and their combined effects on material properties. This detailed analysis enables the fine-tuning of formulation parameters, allowing for the optimization of both efficiency and performance in practical applications. By elucidating the influence of GO dosage and PCE ratios on peak intensity, this study aims to provide valuable insights for maximizing the effectiveness of graphene-based materials in cementitious systems.

Figure 20 demonstrates that a PCE-binder ratio of 0.25 achieves the highest peak intensity and a reduced time to reach this peak, indicating optimal dispersion and hydration efficiency [80]. Conversely, the right figure illustrates that peak intensity increases with GO dosage up to 0.1%, but decreases at higher dosages, such as 0.4%. This suggests an optimal GO dosage range where dispersion and hydration benefits are maximized.

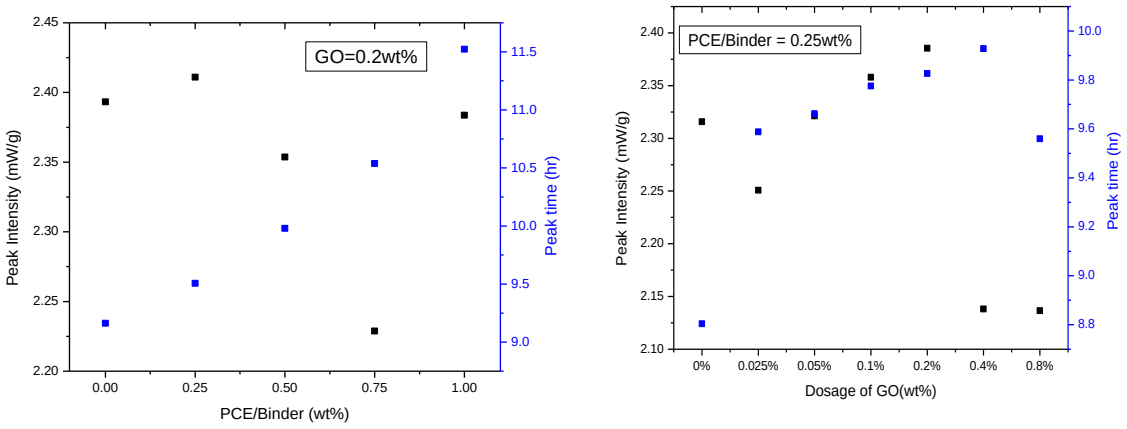

Figure 20: The peak intensity and peak time analysis of optimized PCE and GO_a dosages curve.

The calorimetry results for mixes with GO reveal a marked acceleration in hydration kinetics. The peak hydration temperature for GO-modified cement increased by up to 2°C relative to the control. This temperature rise is advantageous for early strength development but requires careful management to avoid potential thermal cracking in large concrete structures [64].

Overall, the total heat evolution curves for mixes containing GO over a 24-hour period indicate that GO significantly influences the hydration process of cement, enhancing both early and later stages of hydration. The results suggest that GO is effective in modifying hydration kinetics and improving the characteristics of hardened cement paste. Therefore, it is recommended that GO be utilized in applications requiring accelerated early strength development or where precise control of hydration kinetics is essential for achieving the desired performance properties in concrete [62][63][64].

3.2.2 In-situ X-Ray Diffraction

In-situ XRD plays a pivotal role in understanding phase transformations during the hydration of cement, especially when doped with GO. This technique allows for direct observation of the structural transformations of silica and the formation of new hydration products over time, providing crucial insights into the kinetics and mechanisms of cement hydration. In the study, once the control cement mixture was prepared, the XRD patterns were monitored continuously over the first 24 hours of hydration and their peaks illustrated in Figure 21(a). As hydration progressed, specific peaks associated with the crystalline phases of tricalcium silicate (C_3S) at 32.3° 2θ, and dicalcium silicate (C_2S) near 34.4° 2θ and 41.3° 2θ were observed. Over time, these peaks exhibited a noticeable decrease in intensity, signifying the dissolution of C_3S and C_2S during the hydration process. This reduction in peak intensity is a clear indication of the formation of calcium silicate hydrate (C-S-H) and calcium hydroxide as the primary hydration products. These transformations underscore the dynamic changes occurring within the cement matrix as it hydrates and sets.

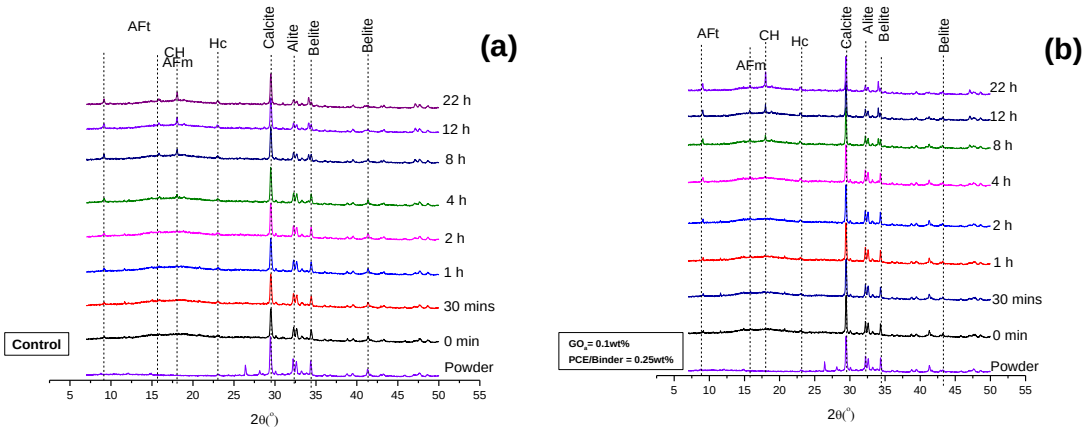

Figure 21: XRD curves at different time of Control(a) and 0.1GO_a(b)

For the control sample, the characteristic peaks of alite (C_3S) and belite (C_2S) gradually diminished over time, indicating the dissolution of these parent compounds as hydration progressed [40]. This reduction in intensity is consistent with the typical hydration process, where the silicate phases break down to form hydration products such as C-S-H and CH.

In contrast, the GO-doped samples exhibited a significant higher CH peak, signalling enhanced formation of hydration products compared to the control [54]. This increase in CH intensity suggests that GO has a positive impact on the hydration kinetics, potentially due to its ability

to facilitate better dispersion and interaction within the cement matrix. The accelerated formation of hydration products in the GO samples can be attributed to GO's influence on the microstructure of the cement, promoting a more efficient hydration process.

Notably, after 12 hours, the peaks in the GO samples were 18% lower in intensity compared to the control, indicating a more rapid consumption of the reactive phases. Furthermore, the characteristic peak of calcite at around 29.4° 2θ appeared earlier and was approximately 22% more intense in the GO samples, reflecting an accelerated rate of C-S-H formation [66]. These findings suggest that GO not only enhances the hydration reactions but also creates nucleation sites that improve the rate of C-S-H formation. Additionally, the dispersion of GO contributed to the formation of ettringite and mono sulphate phases, which are known to retard strength development in cement. The main peak for ettringite in the GO samples was enhanced by 25% in intensity compared to the control after the first six hours of hydration. This suggests that GO promotes the formation of these phases, which could have implications for the early-age strength development of the cement [68].

In conclusion, the in-situ XRD analysis unequivocally demonstrated that the addition of graphene-based materials, such as GO, into cement modifies its phase constitution and accelerates the pore solution-cement reaction. These materials not only promote the early consumption of reactive phases but also enhance the formation of key hydration products. This leads to improvements in the mechanical properties and durability of cementitious composites, although careful consideration of the long-term effects on the microstructure is necessary [69].

3.3 Mechanical Testing

The cube strength test is a critical method for evaluating the mechanical properties of cement-based materials, enabling the assessment of the effects of additives such as GO on cement strength at various curing ages. Strength measurements were conducted at 1, 3, and 7 days to monitor early-age strength development, which is of particular importance for many construction applications [79].

As shown in Figure 22, the incorporation of 0.1 wt.% GO yielded the highest compressive strength at 7 days as shown in Figure 22. The average compressive strength values of the control specimens at 1, 3, and 7 days were 9 MPa, 17 MPa, and 27 MPa, respectively. These figures served as a benchmark to evaluate the influence of GO on the cement matrix. Notably, samples modified with 0.1 wt.% GO demonstrated significant improvements in early-age strength, with compressive strengths of 11 MPa, 21 MPa, and 32 MPa at 1, 3, and 7 days of curing, representing increases of 22%, 24%, and 19%, respectively, compared to the control samples. This enhancement can be attributed to GO ability to accelerate the hydration rate, as confirmed by calorimetric results, which showed faster heat release and quicker formation of strength-generating phases such as C-S-H [79].

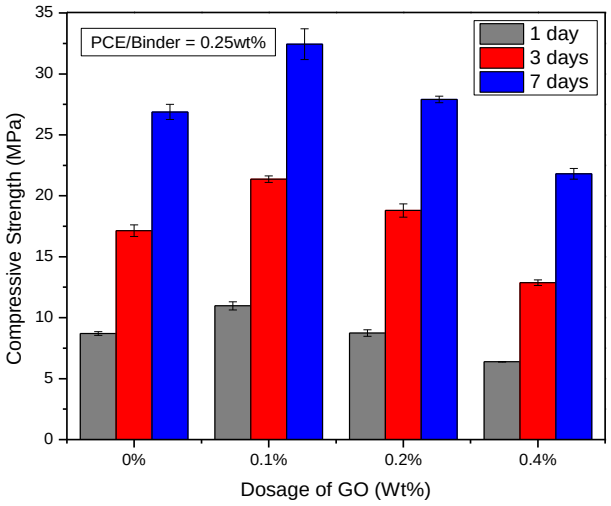

Figure 22: Early age compressive strength of different samples at 1,3 and 7 days.

At a dosage of 0.2 wt.%, the compressive strengths were recorded as 9 MPa, 19 MPa, and 28 MPa at 1, 3, and 7 days of curing, respectively, reflecting increases of 0%, 12%, and 4% compared to the control samples. However, with a further increase in GO content to 0.4 wt.%, compressive strengths decreased to 6 MPa, 13 MPa, and 22 MPa at the same curing ages, corresponding to reductions of 33%, 24%, and 19%, respectively, relative to the control.

The decline in strength with higher GO dosages can be primarily attributed to agglomeration, which is caused by insufficient PCE ratios. The aggregation of GO in the alkaline cement paste adversely affects the material by introducing flaws or weak zones within the cement matrix. The reinforcing mechanisms that contribute to strength enhancement can be summarized as follows: (2) the seeding effects of GO, and (3) GO's capacity to reduce porosity and densify the microstructure [82][43]. The strength peaks observed in the samples with 0.1 wt.% GO can be attributed to the optimal dispersion and interaction of GO within the cement matrix. At this concentration, GO effectively enhances the hydration process and refines the microstructure without significant agglomeration, leading to superior compressive strength. Conversely, as the GO content increases beyond 0.1 wt.%, the risk of agglomeration grows, resulting in less effective reinforcement and reduced overall strength.

3.4 Carbonation Analysis

The accelerated carbonation chamber is a critical instrument for evaluating the specific CO_2 uptake and the carbonation rate of cementitious materials. This apparatus simulates exposure to CO_2 within a controlled environmental chamber, enabling the assessment of carbonation processes under accelerated conditions. The use of this setup is particularly valuable in determining the potential of cement composites, including those incorporating GO, to contribute to CO_2 sequestration and mitigate environmental CO_2 levels. Through this approach, the kinetic and capacity of CO_2 adsorption in cementitious materials in can be systematically studied, providing insights into their environmental impact and sustainability.

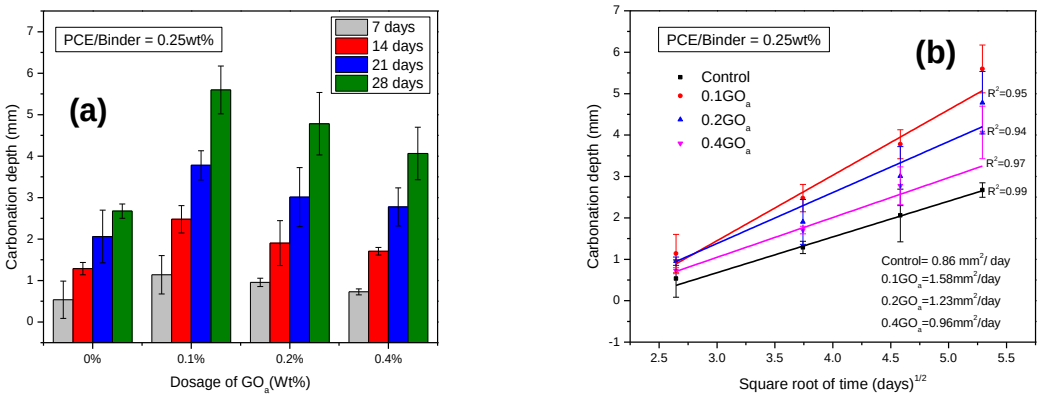

Figure 23: Carbonation depth (a) and carbonation rate(b)

As illustrated in Figure 23(a), the incorporation of 0.1 wt.% GO_a into cementitious materials leads to an increase in carbonation depth until 28 days. However, beyond this concentration, the addition of GO_a lowers the carbonation depth, thereby reducing the overall effectiveness of the carbonation process. The control sample exhibited an average carbonation depth of 2.6 mm after 28 days. In contrast, samples containing 0.1 wt.%, 0.2 wt.%, and 0.4 wt.% GO_a showed significantly increased carbonation depths of 5.6 mm, 4.7 mm, and 4.1 mm, respectively.

As depicted in Figure 23(b), further calculations were performed to determine the rate of carbonation in the cement samples. These rates were quantified by the slopes of the linear regression lines with respective to square root of time, with the 0.1 wt.% GO_a sample exhibiting a slope of 1.58 mm^2/day, compared to 0.86 mm^2/day for the control sample.

TGA is a valuable analytical technique used to quantify CO_2 uptake in cementitious materials by measuring weight loss associated with the decomposition of carbonated phases within the system [74]. This method provides data on the extent of carbonation, enabling a detailed comparison between the degree of carbonation in control cement samples and those modified with additives.

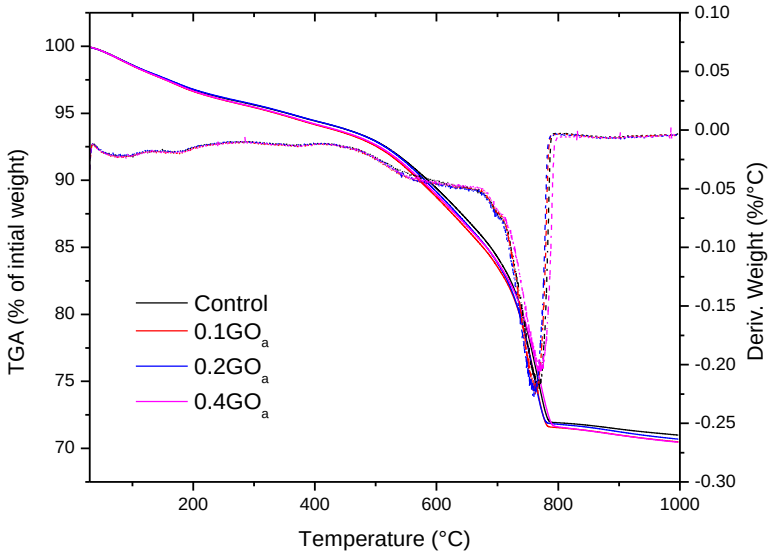

Figure 24. TGA and its derivative curves with respect to GO_a dosage.

Table 4: Calculated percentage of compounds and CO_2 uptake

	BW (%)	CH (%)	$CaCO_3$ (%)	CO_2 uptake (%)
Control	14.4131	6.1795	45.3214	15.2227
0.1GO_a	14.7177	6.5591	45.2065	14.6158
0.2GO_a	14.4657	6.3451	45.5643	15.3531
0.4GO_a	14.7057	6.3771	45.5480	14.9156

TGA was conducted on samples collected from the accelerated carbonation chamber after complete carbonation. The progressive weight loss observed in the tested samples was caused by heating them under a nitrogen flow, which decomposed the carbonated phases. This weight loss between 500-800 ℃ is primarily due to the liberation of CO_2, which is chemisorbed in the calcium carbonate formed during the carbonation of calcium silicate hydrates and calcium hydroxide present in the cement matrix [75].

As Table 4 shown, the control sample recorded a CO_2 uptake of 15.22%, based on $CaCO_3$ decomposition. This reflects the typical CO_2 uptake capacity of ordinary Portland cement before the incorporation of any graphene-based materials. In contrast, the samples modified with 0.1% GO, 0.2% GO, and 0.4% GO exhibited CO_2 uptakes of 14.62%, 15.35%, and 14.92%, respectively. Although there is a slight variation in CO_2 uptake, the overall improvement in CO_2 uptake due to GO incorporation is not substantial when compared to the control. Specifically, the CO_2 uptake in GO-modified samples showed only marginal increases, suggesting that while GO affects the carbonation kinetics, they do not significantly improve the overall CO_2 uptake. A detailed comparison of carbonation profiles obtained from TGA analysis revealed varying extents of CO_2 uptake, along with differences in the forms and stability of carbonated phases [76]. For the control samples, the initial weight loss, starting around 500°C, was primarily due to the decomposition of calcium carbonate. In contrast, GO-modified samples exhibited weight loss at lower temperatures, beginning around 580°C. This shift likely indicates the formation of alternative carbonate structures.

The GO-modified samples displayed a broader range of decomposition temperatures, suggesting the presence of multiple types of carbonation products with varying stability. This variability is likely influenced by the nano-scale interaction between graphene additives and the cement matrix [77].

These variations in CO_2 uptake efficiency suggest that while the incorporation of GO influences the carbonation process, the improvements in CO_2 capture are modest. The enhanced CO_2 uptake observed in some samples indicates a significant improvement in carbonation rate and depth. [71][75][76]. However, the overall efficiency of CO_2 uptake in the modified samples does not show substantial improvement compared to the control.

4. Conclusion and Recommendations

4.1 Conclusion

This study examined the effects of incorporating two-dimensional materials, such as GO and GNPs, into ternary blended cement systems on early hydration and CO_2 sequestration. The research specifically focused on how these nanomaterials influence hydration kinetics and carbonation properties, providing a comprehensive understanding of their potential applications in advancing cement science and technology.

The addition of GO into the cement matrix significantly affects the hydration process. The use of PCE was found to be crucial for achieving optimal dispersion of GO nanoparticles, thereby maximizing their contribution to the hydration process. UV-Vis spectroscopy and dynamic light scattering (DLS) tests indicated that a PCE/GO mass ratio of 10 achieved superior dispersion in the highly alkaline environment of the cementitious system. However, a PCE/GO mass ratio of 15 ensured stable dispersion for up to 24 hours, highlighting the delicate balance required for effective dispersion.

Further findings revealed that an effective PCE/binder mass ratio of 0.25, combined with an optimal PCE/GO mass ratio of 1.25, significantly enhanced hydration kinetics. This underscores the critical role of precise dispersant ratios in optimizing the benefits of GO in cementitious materials. Despite their superior dispersion properties, GNPs were found to impede hydration kinetics. Moreover, the study addressed the adverse effects of grinding on dispersion and hydration kinetics, as grinding processes negatively impacted the dispersion of GO by inducing particle agglomeration, subsequently hindering the hydration process. Even with enhanced grinding and a PCE mass ratio of 10, the negative effects of PCE on particle dispersion persisted.

In situ XRD analysis further elucidated the impact of GO on hydration product formation. The results indicated that the incorporation of GO enhances the precipitation of hydration products during the first day of hydration, with the seeding effect of GO resulting in the formation of additional hydration products compared to control samples.

The compressive strength of the ternary cement blend containing 0.1 wt.% GO showed substantial improvement at 1, 3, and 7 days. However, higher concentrations of GO, such as 0.4 wt.%, led to a decrease in compressive strength due to the agglomeration of GO particles, which impeded the hydration process. In terms of carbonation, accelerated carbonation tests revealed that GO enhances carbonation kinetics, with the carbonation rate for the 0.1 wt.% GO samples being 83.7% higher than that of the control samples. Although agglomeration affected the carbonation rate and depth, leading to a reduction in performance compared to the reference, carbonation rates for 0.2 wt.% and 0.4 wt.% GO samples were still higher than those of the control. However, the addition of GO showed negligible effects on the total CO_2 uptake of ternary pastes under accelerated carbonation curing.

The incorporation of graphene-based materials in cement matrices has demonstrated significant impacts on cement properties. PCE serves as a key dispersant to enhance the performance of these nanomaterials. The effectiveness of PCE in dispersing GO within the cement matrix has been well-documented, showing improved dispersion, reduced agglomeration, and enhanced performance characteristics [83]. Reduced aggregation of GO facilitates better interaction with the cement hydrates, thereby enhancing hydration kinetics. This is evident from isothermal calorimetry data, which indicate that peak hydration temperatures occur earlier in the presence of GO, reflecting a faster reaction rate. Additionally, XRD results reveal that the incorporation

of GO accelerates the consumption of C_3S and C_2S phases while improving the formation of C-S-H and calcium hydroxide, which are crucial for strength development.

Analyses from accelerated carbonation chamber tests offer valuable insights into the environmental impact of incorporating GO into cement. Enhanced carbonation depth and improved CO_2 uptake efficiency suggest that the modified cement can store more carbon, positively affecting efforts to reduce the carbon intensity of the construction industry. GO appears to reform the pore structure of the cementitious systems, increasing the surface area available for carbonation reactions and thus contributing to the overall sustainability of the system [88].

The findings from this study corroborate and extend previous research on the incorporation of nanomaterials into cement. Prior studies have highlighted improvements in mechanical characteristics and hydration processes with the use of nano silica, carbon nanotubes, and other nanomaterials [35]. This research builds on such works by focusing specifically on GO, providing comprehensive experimental evidence of its effects. Enhanced early strength development and accelerated hydration rates are consistent with literature on the nucleation effects of nano-sized particles.

Furthermore, this study introduces new insights into the carbonation processes of nanomodified cements. While previous research has primarily concentrated on mechanical reinforcement and stability, this work offers a detailed discussion on CO_2 sequestration, an area less explored in relation to nanomaterials in cement. The positive results reinforce the potential of GO to improve both performance and environmental sustainability in construction.

In summary, the application of PCE and GO in cement matrices demonstrates several advantages, including enhanced hydration kinetics, improved mechanical properties, and extended CO_2 sequestration capabilities. These benefits are attributed to the effective dispersion of GO achieved through PCE. The study highlights the high efficiency of GO in enhancing cement characteristics and suggests further exploration of graphene-based materials in cement and other sustainable construction practices. The results indicate that with appropriate formulation and processing conditions, significant improvements in both the activity of cementitious materials and their environmental footprint are achievable.

4.2 Future Research Directions

It is crucial to investigate the durability of graphene-modified cement under various environmental conditions to understand its performance in real-world applications. Research should focus on how these materials withstand freeze-thaw cycles, sulphate attacks, and exposure to seawater, as these conditions are particularly relevant for structures in harsh environments or cold climates. Additionally, the environmental impact of manufacturing graphene-enhanced cement has not been thoroughly examined in existing literature. Comprehensive cradle-to-grave assessments are needed to evaluate the environmental implications of incorporating graphene, covering the entire lifecycle from extraction and manufacturing to disposal. This assessment is essential to ensure that the use of graphene in cement provides a net environmental benefit. Further studies should also explore modifying the molecular architecture of PCE, focusing on its main and side branches, to reduce the induction period of cement hydration. Such modifications could optimize the interaction between PCE and graphene, potentially enhancing the overall performance of the cement. Investigating the functionalization of GO with modified PCE is another important research area. Improved dispersion of GO within the cement matrix can lead to more effective reinforcement and enhanced mechanical properties. A detailed rheological study of graphene-enhanced cementitious materials is needed to optimize their flow properties. Understanding how

graphene incorporation affects the workability and consistency of cement mixtures is crucial for ensuring proper application. Lastly, exploring different ternary blends of cement, such as those incorporating calcined clay and limestone (LC^3), in conjunction with graphene additives, can provide valuable insights into the synergistic effects of these materials on cement performance and sustainability.

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