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Performance Enhancement of Cementitious Materials by Nano-additives: An Experimental and Numerical Study

(ナノ添加剤によるセメント系材料の性能向上： 実証実験および数値モデル)

by

Mylvaganam Nithurshan

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Approved by the committee in charge,

Yogarajah Elakneswaran, Chair

Naoki Hiroyoshi

Tsutomu Sato

Ryoma Kitagaki

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ABSTRACT

In recent years, nanomaterials like nano-silica and graphene oxide (GO) graphene oxide have been increasingly used to improve cementitious materials' mechanical and durability properties. However, the optimum dosage and achieving the desired mechanical properties of nano-modified cement-based requires significant time, effort, and cost. Furthermore, the precise reinforcing mechanism of these nanomaterials is not yet fully understood. Accurately predicting the dosage and mechanical properties of nano-modified cement-based materials remains challenging. While earlier analytical models failed to account for the complexity of influencing factors accurately, newer Machine Learning (ML) techniques have shown promise but lack transparency. As the microstructure of hydrated cement paste significantly affects concrete strength, recent models have focused on simulating cementitious material hydration to bridge nano and macro properties. However, existing models often rely on assumptions and cannot directly correlate with concrete's macro properties. Therefore, this research aims to explore the reinforcing mechanism of the nanomaterials and to develop a robust model capable of realistically predicting the mechanical properties of nano-modified cementitious materials by incorporating detailed microstructure information, fundamental physics and chemistry, thermodynamic considerations, and particle bonding and packing arrangements.

Nanomaterials such as nano silica and GO were investigated for their impact on the mechanical properties of cementitious materials. Experimental studies, including Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Fourier-transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Silicon and Nuclear Magnetic Resonance (Si & H NMR), and zeta potential analysis, were conducted to understand the effects of these nanomaterials on formation of hydrates and evolution of microstructure. Nano silica enhanced the mechanical properties of cement paste, especially at early ages (< 7 days), through its pozzolanic and

nucleation effects. However, an increase in nano silica content led to agglomeration, diminishing its effectiveness. Moreover, synthesizing calcium-silica-hydrate (C-S-H) with and without GO revealed that GO accelerated C-S-H sheet formation and promoted layer-by-layer C-S-H formation, resulting in very dense C-S-H capable of withstanding higher stress. This layer-by-layer formation also refined the pores. In addition, a robust chemical bond was observed between GO groups, such as carboxyl and Ca, which contain hydration products.

A systematic model was then developed to optimize nano silica use in cement paste and to predict their nonlinear behaviour. The model integrates a hydration model, which calculates the dissolution rate of each clinker mineral, with a thermodynamic model simulating the hydration reaction and interaction between hydrates and nano-silica. The hydration model (HyMEC), which was developed in our laboratory, was modified to account for its reaction degree, dependent on portlandite availability, and to accurately represent the formation of C-S-H with a transition from jennite type to tobermorite C-S-H. The model computed volume fractions of various phases, and a representative volume element (RVE) was formulated for cement pastes with and without nano silica using MATLAB. Finite element analysis with COMSOL Multiphysics was then used to evaluate the RVE, allowing computation of homogenized material properties such as compressive strength and Young's modulus. Predictions aligned well with experimental findings. Additionally, the model was extended to predict mortar mechanical properties, considering fine aggregate content and Interfacial Transition Zone (ITZ) properties, and validated with experimental results.

In summary, this systematic model accurately predicts the nonlinear behaviour of cement pastes with different nano-silica replacement levels and can be extended to predict nano-modified mortar, offering the potential for optimizing cement-based composites in various engineering applications.

概要

近年、セメント系材料の機械強度や耐久性を向上させるために、ナノシリカや酸化グラフェンのようなナノ材料を添加することが検討されている。しかし、これらのナノ改質セメント系材料の強度発現メカニズムは十分には解明されておらず、その機械的特性を正確に予測する手法は確立していない。このため、目的とする強度を発現させるために必要なナノ材料の添加量を決定するためには、実験による試行錯誤を繰り返すしかなく、現状では多大な時間と労力、コストを要している。セメント系材料の強度発現を予測する手法として、近年発達の著しい機械学習モデルは有望視されているが、ナノ材料などの効果を組み込むためには透明性に欠けている。また、従来提案されてきた解析的なモデルも複雑な影響因子を正確に説明することができていない。特に、コンクリートなどのセメント系材料の発現強度に顕著な影響を及ぼすナノレベルの水和セメントペーストの微細構造と機械強度などのマクロレベルの特性とを橋渡しするために妥当性が十分に検証されていない仮定を用いている点に問題がある。本研究では、ナノ改質セメント系材料の力学特性を予測する実用的な手法を確立することを目的として、セメント鉱物の水和過程や強度発現に及ぼすナノ材料の影響を物理化学的な観点から詳しく検討し、粒子や空隙の充填構造に基づく強度予測モデルを提案・開発している。

第1章では、本研究の目的、範囲、独創性について述べている。

第2章では、包括的な文献レビューを行い、セメント系材料におけるナノ材料添加の効果を水和、微細構造の発達、フレッシュ状態の特性、機械的特性に焦点を当てて議論している。

第3章では、既存のセメント系材料の強度予測モデルをレビューし、その利点と限界を評価している。このレビューでは、より頑健で正確なモデルが必要なことを結論している。

第4章では、所定量のナノシリカを添加したセメントペーストを調合し、その鉱物/化学分析（TGA、XRD、SEM 分析）と圧縮強度試験を実施し、クリンカ鉱物の水和とナノ改質セメントペーストの機械的特性に及ぼすナノシリカの影響について検討している。

第 5 章では、クリンカ鉱物の水和と微細構造の変化に対する酸化グラフェンの効果を調べている。また、合成 C-S-H のマイクロ構造の変化に及ぼす酸化グラフェンの影響についても検討し、酸化グラフェンの添加に伴う C-S-H の微細構造変化のメカニズムを議論している。

第 6 章では、第 4 章で得られた結果に基づいて、ナノ改質セメント系材料の強度の発現挙動を予測する新しいモデルを提案している。このモデルは、普通ポルトランドセメント (OPC) の水和に対するナノシリカの効果を組み込んでおり、ナノシリカを添加した際の水和物の体積率や空隙率、収縮率を最初に予測する。次に、予測された水和物や空隙、未反応ナノシリカ粒子の体積分率に基づいて代表体積要素 (RVE) を作成し、これを有限要素法により解析して機械的特性を求める。このモデルの予測結果は実験データとよく一致する。

第 7 章では、第 6 章で提案したモデルを拡張し、細骨材を添加した OPC モルタルの機械的特性を、細骨材周辺の遷移帯 (ITZ) の効果も考慮して計算するモデルを開発している。この拡張モデルを用いたパラメトリック研究も実施しており、骨材の形状、サイズ、ランダム配置などの効果を調べ、モデルの汎用性と頑健性を検証している。

第 8 章では、本研究から得られた主要な知見と今後の研究に対する提言をまとめている。

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CHAPTER 1

INTRODUCTION OF DISSERTATION

1.1 Background of the study

Ordinary Portland Cement (OPC) has been the basis of construction for many years, serving as the primary material in building infrastructure such as buildings, dams, highways, and skyscrapers (Walling and Provis, 2016). Its widespread use is attributed to its reliable performance, ease of use, and cost-effectiveness. However, the rapid increase in population, climate change, and urbanization have led to heightened demands for infrastructures that offer improved mechanical strength and durability (Scrivener et al., 2018). Traditional concrete, although dependable, often falls short of meeting these advanced requirements, leading to the exploration of additional materials to enhance its properties (Ndahirwa et al., 2022).

Various materials have been incorporated into OPC-based mixtures to improve their performance in response to these challenges. Among these, steel, carbon and supplementary cementitious materials (SCMs) have gained significant attention (Lothenbach et al., 2011). Steel fibres enhance concrete's tensile strength and toughness, helping to control cracking and improve post-crack load-bearing capacity. However, they have several drawbacks, including potential corrosion in humid environments or when exposed to de-icing salts, which can compromise structural integrity. Additionally, their distribution within the concrete can be uneven, leading to inconsistent performance, and their addition increases the overall weight of the concrete, which may not be suitable for all applications (Liew and Akbar, 2020). Carbon fibres are valued for their high strength-to-weight ratio and excellent corrosion resistance, making them ideal for applications needing enhanced durability and reduced weight (Muthukumarana et al., 2023). However, their high cost and energy-intensive production process limit their widespread use in

construction. Their low ductility can also lead to brittle failure in concrete composites if not correctly managed.

SCMs like fly ash, slag, and silica fume are used to partially replace OPC in concrete mixtures, enhancing mechanical strength and durability through the pozzolanic reaction (Aydin and Arel, 2017; Liao et al., 2019; Snellings et al., 2022). However, SCMs present challenges such as variability in availability and quality, which can affect concrete consistency. Fly ash's composition varies with the coal source, and slag and silica fumes depend on industrial byproducts. Additionally, SCMs can extend the concrete setting time, potentially delaying construction schedules (Lothenbach et al., 2011). Given these challenges, there is a need for innovative approaches to enhance the properties of OPC-based materials. The ongoing research aims to identify materials and methods that can provide reliable mechanical strength and durability improvements without the drawbacks of current additives.

One promising area of research is the use of nanomaterials, which have the potential to significantly enhance the performance of cementitious materials at relatively low dosages (Sobolev et al., 2008). Nanomaterials, such as nano-silica and graphene oxide (GO), offer unique properties that can address the limitations of traditional additives. Due to their high surface area and reactivity, they can refine concrete microstructure, reduce porosity, and improve mechanical properties. Meanwhile, determining the optimal dosage of these nano additives requires substantial time and expense. Moreover, the evolution of intrinsic properties over time is a critical parameter in material-to-structural mechanical design. Therefore, developing a virtual testing tool—an integrated set of models, algorithms, and procedures for predicting materials' mechanical and durability characteristics—can be a superior alternative. However, scientifically understanding and predicting the mechanical properties of nano-modified concrete is highly complex, as the concrete's microstructure spans from the nanoscale such as calcium-silicate-hydrate (C-S-H) globule to the macro-scale (aggregate). Most previously proposed models predict the progression of microstructure with certain assumptions and simplifications (Bishnoi and Scrivener,

2009; Gao et al., 2019; Tolman, 1999). Therefore, it is necessary to develop more robust models with minimized assumptions and simplifications to predict nano-modified properties reliably.

1.2 Research scope and objectives.

The research aims to experimentally explore the effect of nano additives such as nano silica and GO and develop a novel model capable of identifying the optimal dosage of nano additives and accurately determining the mechanical properties of nano-modified cementitious materials through their evolving microstructure, with fewer assumptions. From a Materials Engineering perspective, considerable effort has been dedicated to understanding microstructural responses, mechanical responses, and durability responses by considering various factors such as different types of cement (clinker composition), water-to-cement ratio (w/c), aggregate content, hydration, and exposure period.

Firstly, cement paste was prepared with varying proportions of nano-silica and GO to identify the optimal dosage and understand their effects on hydration and microstructure development. Based on these insights, the existing hydration model was modified to account for the reactions of clinker minerals and nano additives. Subsequently, a thermodynamic model was developed to simulate the actual hydration process and determine the volume fractions of the hydrates. A Representative Volume Element (RVE) of the cement paste was then created using MATLAB and analysed using finite element techniques in COMSOL Multiphysics to compute the nonlinear behaviour of the nano-modified cement paste. Finally, the model was extended to predict the nonlinear behaviour of mortar. The scope of the research work is summarized in **Figure 1.1**.

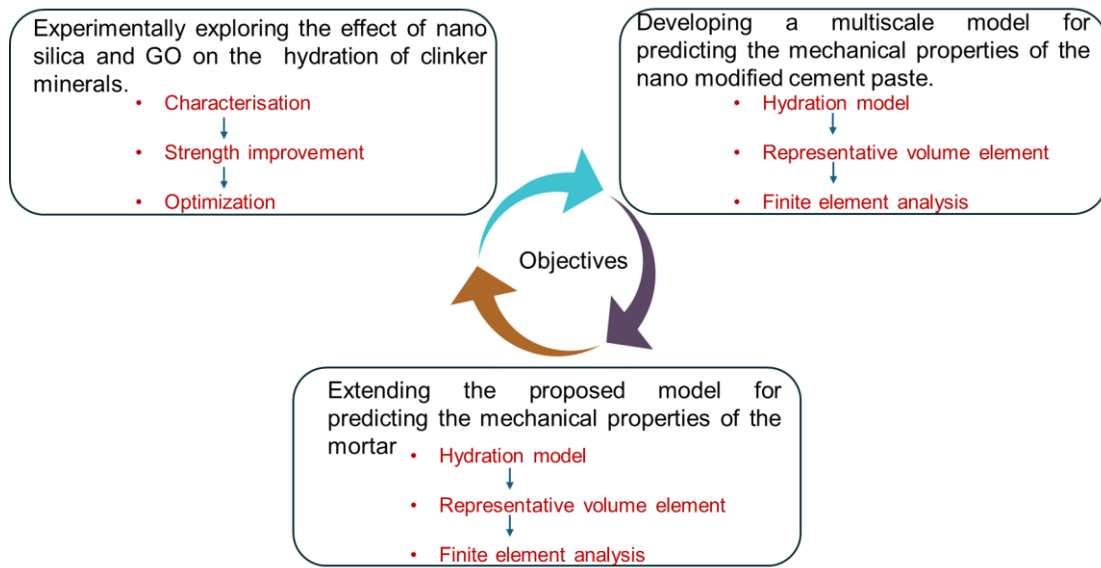


Figure 1.1: Outline of the scope of the research work

1.3 Originality and importance of the study

The construction industry is among the least technologically advanced sectors. Consequently, there is a growing emphasis on predicting the behaviour of cement-based materials. Simultaneously, nanomaterials are being increasingly utilized to enhance these properties due to their versatility and unique characteristics. This research explores the effect of nano additives such as nano-silica and GO in cementitious materials and introduces a novel model for predicting nano-modified cement-based materials' mechanical behaviour. In recent years, machine learning techniques and analytical approaches have been proposed to predict the properties of novel cementitious materials, such as nano-modified concrete. However, these methods do not consider the actual hydration process and microstructural development. Instead, they rely on past available data and attempt to establish relationships between factors such as nano additive dosage, mix proportions, and strength using algorithms. The predicted results may not be realistic, as the prediction mechanism is a black box and solely depends on the input data, the quality of which is questionable.

Furthermore, previous models for cement paste often relied on specific assumptions, including:

- (i) Cement paste is treated as a three-phase material comprising unhydrated clinker, hydration products, and porosity.
- (ii) Disregarding the volume of C–S–H and instead focusing on capillary porosity or gel space ratio to predict mechanical properties.
- (iii) Only C–S–H and portlandite are incorporated in the cement matrix as hydration products.
- (iv) Assuming a single C–S–H matrix with constant gel porosity and overlooking the two C–S–H formation types.

The proposed model aims to overcome these limitations by realistically predicting the mechanical properties of nano-modified cement paste. It achieves this by considering the chemical properties of clinker composition and nano materials, curing condition, water-to-cement ratio, and the detailed microstructure of the hardened matrix, including two types of C–S–H, portlandite, ettringite, monosulfate, hydrotalcite, Fe-siliceous hydro garnet, capillary pores, and chemical shrinkage. Moreover, the proposed model was extended to predict the mechanical properties of the mortar by incorporating the effect of fine aggregates and the ITZ.

1.4 Organization of Dissertation

This dissertation is organized into a total of seven chapters.

Chapter 1 describes the objective, scope and originality of this study.

Chapter 2 presents a comprehensive literature review, examining the effects of nanomaterials in cementitious materials, focusing on hydration, microstructure development, fresh state properties and mechanical properties.

Chapter 3 provides an in-depth review of existing strength prediction models, evaluating their advantages and limitations. The review highlights the need for more robust and accurate models.

Chapter 4 investigates the impact of nano-silica on the hydration of clinker minerals and the mechanical properties of nano-modified cement paste. Cement paste samples were prepared by substituting 0 %, 2 %, and 4 % (by weight) of the cement content with nano-silica. The effects were characterized using compressive strength tests, TGA, XRD, and SEM analyses.

Chapter 5 investigates the effect of the GO on the clinker hydration and microstructure development. In addition, C-S-H was synthesized with and without the incorporation of GO to study the microstructural changes. The changes were characterised using TGA, XRD, XRF, SEM, FTIR, Si NMR, and H NMR. Finally, based on the results, the microstructural changes of C-S-H with GO were proposed.

Chapter 6 outlines the development of a systematic model proposed to predict the optimal dosage and nonlinear behaviour of nano-modified cementitious materials. The model began with modifications to the OPC hydration model to incorporate the effects of nano-silica, as identified in Chapter 4. This model predicted the volume fraction of hydrates, porosity, and shrinkage. A RVE was then constructed based on these volume

fractions using MATLAB and analysed through finite element methods in COMSOL Multiphysics to determine the mechanical properties. The predicted results were validated against experimental data, showing strong agreement with experiment results.

Chapter 7 extends the model proposed in Chapter 6 to predict the mechanical properties of OPC mortar, considering the incorporation of fine aggregates and the ITZ. The extended model was also employed for a parametric study, examining variables such as aggregate shape, size, and random placement to validate the model's versatility and robustness.

Chapter 8 provides a comprehensive overview of the findings and conclusions derived from this study and recommendations for future research endeavours.

CHAPTER 2

LITERATURE REVIEW ON EXPERIMENTAL INVESTIGATIONS AND CHARACTERIZATION OF CEMENTITIOUS MATERIALS WITH NANO ADDITIVES

2.1 Overview of Experimental Studies on Cement and Supplementary Cementitious Materials

2.1.1 Introduction to cement-based materials

The history of cement traces back to ancient civilizations like the Egyptians and Romans, who used early cement forms in their iconic structures. The 19th century saw significant advancements with Joseph Aspdin's invention of Portland cement, named after it resembled Portland stone. Cement plays a vital role in construction as a binding agent in concrete, mortar, stucco, and grout, essential for building infrastructure worldwide. The hydration process is fundamental to cement, wherein it reacts with water to form solid compounds like calcium silicate hydrate and calcium hydroxide, leading to concrete hardening and strength development over time (Nithurshan and Elakneswaran, 2023). Concrete, composed of cement, water, aggregates, and sometimes admixtures, is the cornerstone of modern construction. Its mix design, expressed as ratios of cement, aggregates, and water, determines its properties. Concrete's versatility, durability, and cost-effectiveness have made it the most widely used construction material globally, with an annual production exceeding 10 billion tons. Strength variations in ordinary concrete, typically ranging from 20 MPa to 40 MPa for normal-strength concrete, depending on mix proportions and application requirements, showcasing its adaptability to various construction needs (Gagg, 2014).

2.1.2 Introduction to Supplementary Cementitious Materials

The need for SCMs arises from the desire to improve the performance and sustainability of concrete. SCMs enhance the properties of concrete, such as durability, strength, and workability, and reduce the environmental impact associated with cement production. The production of cement is energy-intensive and a significant source of CO₂ emissions. Incorporating SCMs can help mitigate these environmental concerns. Several factors drive the use of SCMs in concrete: sustainability, by reducing the carbon footprint of concrete through partial replacement of cement with industrial by-products; performance, by improving the mechanical and durability properties of concrete; cost, by lowering the overall cost of concrete production through the use of cheaper materials; and regulatory compliance, by meeting increasingly stringent environmental regulations and standards (Juenger et al., 2019; Lothenbach et al., 2011).

The most commonly used SCMs include fly ash, a by-product of coal combustion in power plants that improves the workability and strength of concrete and enhances its resistance to thermal cracking; slag cement (ground granulated blast-furnace slag, GGBFS), a by-product of iron and steel production that enhances the durability and strength of concrete, especially in harsh environments; silica fume, a by-product of silicon and ferrosilicon alloy production that significantly increases the strength and durability of concrete, making it suitable for high-performance applications; natural pozzolans, such as volcanic ash, which have been used historically and continue to be utilized for their beneficial properties in concrete; and metakaolin, a calcined clay that improves the strength and durability of concrete by enhancing its pozzolanic reactions. In conclusion, the invention and ongoing development of cement and concrete have been pivotal in shaping modern infrastructure. The integration of SCMs into concrete mix designs addresses both performance and environmental concerns, ensuring that this vital material continues to meet the evolving demands of construction sustainably (Danner et al., 2018; Juenger et al., 2019; Lothenbach et al., 2011; Snellings et al., 2023; Suraneni et al., 2019).

2.1.3 Issues with traditional SCMs

Traditional SCMs like fly ash, slag cement, silica fume, natural pozzolans, and metakaolin have been widely used to enhance the properties of concrete and reduce its environmental impact. However, they come with several limitations and challenges. High-quality fly ash is decreasing due to the declining use of coal in power plants, driven by environmental regulations and the shift towards cleaner energy sources (Juenger et al., 2019). The quality of fly ash can be inconsistent, affecting the performance of concrete. Similarly, slag cement production depends on the iron and steel industry, which can fluctuate based on economic conditions, leading to supply issues and inconsistent material properties. Silica fume, although highly effective, is produced in limited quantities and is relatively expensive compared to other SCMs, with its availability constrained by the production levels of silicon and ferrosilicon alloys.

Workability and handling issues also pose challenges. High fly ash content can lead to problems with early-age strength and setting times, while silica fumes require precise handling to avoid increased water demand and reduced slump. Metakaolin can increase the water demand of concrete mixes, necessitating superplasticizers to maintain workability, and it requires careful mixing to ensure uniform dispersion. The performance of natural pozzolans can be highly variable depending on their source and composition, making it challenging to predict and control the properties of the resulting concrete. Additionally, fly ash can contain varying carbon content levels, interfering with air-entrainment admixtures that enhance freeze-thaw resistance (Avet et al., 2018; Aydin and Arel, 2017; Sadique et al., 2013).

Environmental and health concerns further complicate the use of traditional SCMs. Due to its fine particulate nature, handling and exposure to silica fume can pose health risks, necessitating stringent safety measures. Fly ash can contain trace amounts of heavy metals, raising concerns about potential leaching and environmental contamination. These

limitations highlight the need for alternative solutions that provide consistent performance enhancements without the associated drawbacks.

2.2 Overview of experimental studies on nano-modified cement-based materials

2.2.1 Introduction to nanomaterials and nanotechnology

Nanotechnology, which involves manipulating and controlling matter on a nanoscale (typically between 1 and 100 nanometers), has opened new possibilities across various fields due to the unique physical, chemical, and mechanical properties exhibited by materials at this scale. Nanomaterials, encompassing nanoparticles, nanofibers, nanotubes, and nanoplates, are being leveraged to revolutionize industries such as medicine, electronics, energy, and construction. Their significance lies in their ability to enhance performance and functionality, providing superior characteristics compared to bulk materials. In medicine, they enable targeted drug delivery and imaging; in electronics, they contribute to the miniaturization and increased efficiency of devices. The energy sector benefits from improved batteries and solar cells, showcasing the transformative potential of nanomaterials (Rupasinghe et al., 2011).

Despite these advancements, the construction sector has seen a relatively low impact from nanotechnology compared to other industries. This discrepancy is attributed to the industry's traditional conservatism, cost constraints, and the challenges of scaling up nanomaterials for large-scale projects. Additionally, the lack of standardized practices and regulatory frameworks for nanomaterials in construction further hinders their adoption. However, current research focuses on integrating nanomaterials to address specific challenges and enhance construction materials' performance. This research is driven by the need to improve material properties, achieve sustainability goals, develop innovative solutions, and meet regulatory and environmental pressures (Ren and Cheng, 2014; Juan Wang et al., 2020).

The advantages of using nanomaterials in construction are significant. They can enhance materials' strength, durability, and functionality, leading to longer-lasting structures and reduced maintenance costs. Nanomaterials can also improve the workability of construction materials, making them easier to handle and apply, thereby increasing construction efficiency. Their ability to make materials more resistant to environmental factors such as water, chemicals, and temperature fluctuations further extends the longevity of structures. Additionally, specific nanomaterials impart self-healing properties to concrete, allowing minor cracks to be repaired autonomously and enabling smart materials with embedded sensors for real-time structural health monitoring (Metaxa et al., 2021). Several nanomaterials are currently being researched and used in construction. Nano-silica enhances concrete's mechanical properties and durability by refining its microstructure and accelerating the hydration process. Carbon nanotubes (CNTs) improve the mechanical properties and develop conductive materials for smart structures due to their exceptional strength and electrical conductivity. Nano-titanium dioxide (TiO₂) is used for its photocatalytic properties, aiding in self-cleaning surfaces and improving air quality by breaking down pollutants. Nano-alumina enhances hardness and thermal stability, making it useful in coatings and composites. Nano-clay improves fire resistance and mechanical properties by reducing permeability and enhancing barrier properties. Lastly, nano-graphene is noted for its exceptional strength and electrical properties, further enhancing construction materials (Metaxa et al., 2021; Walter et al., 2015).

In conclusion, nanotechnology and nanomaterials are promising to transform the construction industry. While adoption has been slower than in other sectors, ongoing research and development are overcoming current challenges and leveraging nanomaterials' unique properties to create more robust, durable, sustainable construction materials. As the industry continues to evolve, integrating nanotechnology is expected to be crucial in advancing construction practices and building future infrastructure.

2.2.2 Nanomaterials in cementitious materials

The application of nanotechnology in cementitious materials, mainly concrete, presents a significant opportunity to enhance their performance. However, concrete development lags behind other materials in advancements through nanotechnology. Several factors contribute to this lag, including a lack of understanding of concrete's physical and chemical properties at the nanoscale and what nano-modification truly means for concrete. Concrete is a complex liquid-solid composite, and methodologies successful for other materials may not directly translate to improvements in concrete. Despite these challenges, there is substantial potential for improving concrete performance through nanomaterials, necessitating further research.

The field of nanomaterials in concrete is still in its preliminary stages, with many unresolved issues. The nano-modification of concrete involves two primary areas of investigation: nanoscience and nanotechnology. The nanoscience of concrete aims to understand its structure at the nanometer level through measurements and characterization of the nanomaterials present. This includes modelling concrete at the atomistic or molecular level to gain insights into its fundamental properties. On the other hand, the nanotechnology of concrete, or nano-modification, involves manipulating or altering concrete at the nanoscale to enhance its properties, such as strength, ductility, durability, self-cleaning, and self-sensing abilities (Hou et al., 2013; Suo et al., 2022). Concrete is considered a three-phase material comprising a solid phase, liquid phase, and solid-liquid interphase (Krishnya et al., 2021a). Nano-modification can target any of these phases to achieve desired enhancements. This can be accomplished by incorporating suitable nanoparticles or nanotubes into concrete, improving its mechanical, thermal, and durability characteristics. Research shows that incorporating various nanomaterials, such as nano-silica, nano TiO_2 , nano Fe_2O_3 , nano Al_2O_3 , nano-clay, graphene-based materials, and carbon nanotubes (CNTs), in appropriate proportions can significantly enhance concrete performance. Effective mixing methods and suitable dispersion agents are crucial for ensuring these enhancements.

2.2.3 Impact of nanomaterials on cementitious material properties

Nanomaterials possess a much higher surface-area-to-volume ratio than their bulk counterparts, which enhances their reactivity and leads to more effective interactions with the cement matrix. This increased surface area allows nanomaterials like nano-silica to accelerate the hydration process of cement by providing additional nucleation sites, thereby improving early-age strength and reducing setting times. Additionally, nanomaterials can fill micro and nanovoids within the cement matrix, resulting in a denser and more homogeneous microstructure, which reduces permeability and enhances durability. Improved particle packing density due to nanomaterials also boosts the overall mechanical properties of concrete, including compressive and tensile strength (Anwar et al., 2023).

Nanomaterials can modify and strengthen the ITZ between the cement paste and aggregate, often the weakest link in concrete, by reducing its porosity and increasing density, thus improving the bond strength between the aggregates and the cement matrix. Mechanical properties are further enhanced as nanomaterials such as CNTs and graphene-based materials significantly increase concrete's tensile and compressive strength, providing a reinforcing effect at the nanoscale that translates to improved load-bearing capacity and reduced brittleness. Furthermore, nanomaterials improve the ductility of concrete, making it less prone to cracking under stress, which is particularly important for structures subjected to dynamic loads or seismic activity (Lu et al., 2022; Min et al., 2023; Shao et al., 2017). The durability and longevity of concrete are also improved through the incorporation of nanomaterials. By refining the microstructure and reducing pore sizes, nanomaterials decrease the permeability of concrete, making it more resistant to water ingress and aggressive chemicals. This enhanced resistance to environmental factors such as freeze-thaw cycles, sulfate attack, and chloride ion penetration extends the service life of concrete structures. Additionally, nanomaterials like nano-TiO₂ impart photocatalytic properties to concrete, enabling self-cleaning surfaces that break down organic pollutants and reduce maintenance requirements. Nanomaterials with conductive

properties, such as CNTs and graphene, can enable the development of self-sensing or innovative concrete, which monitors its structural health by detecting stress, strain, and damage in real-time (Zhang et al., 2021).

Nanomaterials can also improve concrete's thermal stability and fire resistance, making it suitable for high-temperature applications. For example, nano-alumina enhances the heat resistance of concrete, while some nanomaterials improve thermal conductivity, making concrete more efficient in applications requiring heat transfer or dissipation. Incorporating nanomaterials in concrete, driven by these nanoscale factors, holds the potential to advance concrete technology significantly, resulting in more robustness, durability, and capability to meet the demands of modern construction. However, ongoing research and development are essential to fully realize these benefits and address the challenges of integrating nanomaterials into concrete.

2.2.4 The rationale for focusing on nano-silica and graphene oxide in this study

The selection of nano-silica and GO as focal points in this study is driven by several compelling factors, including their unique properties and advantageous characteristics compared to other nanomaterials. Nano-silica, classified as a pozzolanic material, boasts a remarkable ability to accelerate the hydration process of cement while refining concrete microstructure. Its high reactivity and surface area facilitate a denser cement matrix, improving compressive strength and durability. Moreover, nano-silica's versatility and cost-effectiveness make it an attractive option for enhancing concrete properties. Graphene oxide, renowned for its exceptional mechanical strength, electrical conductivity, and durability, presents another compelling choice for study. GO can be quickly produced with high purity and at a relatively low cost compared to other nanomaterials such as CNTs and nano-TiO₂. Its two-dimensional structure and high surface area allow superior bonding with the cement matrix, enhancing concrete's tensile strength, ductility, and crack resistance.

Focusing on nano-silica and GO in this study, we aim to explore these materials' synergistic effects on concrete properties comprehensively. The combination of nano-silica's pozzolanic reactivity and GO's mechanical reinforcement capabilities holds promise for developing advanced concrete composites with superior strength, durability, and functional characteristics. This research endeavours to harness the versatility, cost-effectiveness, and unique attributes of nano-silica and graphene oxide to address current limitations in concrete technology and pave the way for innovative solutions in construction materials.

2.3 Overview of experimental studies on nano-silica modified cement-based materials.

2.3.1 Properties of nano-silica and its production

Nano-silica, a highly reactive pozzolanic material, is utilized in concrete to enhance its mechanical and durability properties. Chemically, nano-silica primarily consists of silicon dioxide (SiO_2) and typically exists in an amorphous form. Its particle size ranges from 1 to 100 nanometers, significantly smaller than micro-silica, which allows for a greater surface area and reactivity. The micrograph of nano-silica is depicted in **Figure 2.1**. Unlike micro-silica, nano-silica can fill micro and nanovoids within the cement matrix more effectively, leading to a denser and stronger concrete structure. Nano-silica is used in concrete in various forms, including powder and colloidal solutions. The production of nanopowders utilizes several prominent methods, including plasma arcing, chemical vapour deposition, electrodeposition, sol-gel synthesis, ball milling, and the utilization of natural nanoparticles. Among these, the sol-gel process is the primary method for producing nano-silica. This bottom-up approach involves creating a colloidal suspension (sol) and inducing gelation to form a network within a continuous liquid phase (gel). The essential precursors for synthesizing nano-silica are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), often combined with alkoxides such as aluminates, titanates and borates (Wilson et al., 2002).

The sol-gel process comprises several stages (Sobolev et al., 2009; Wilson et al., 2002):

1. Hydrolysis of the precursor: TMOS or TEOS undergo hydrolysis.
2. Condensation and polymerization: Monomers condense and polymerize to form nanoparticles.
3. Particle growth: The particles continue to grow in size.
4. Agglomeration and network formation: Particles agglomerate, forming networks that lead to a gel structure.
5. Drying and thermal treatment (optional): Solvents are removed through drying, and thermal treatment may be applied to remove surface functional groups and achieve the desired crystal structure.

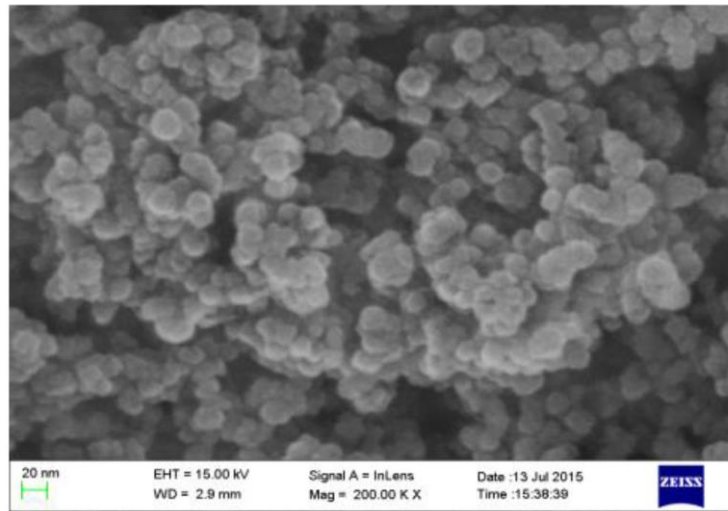
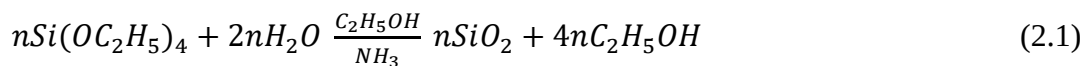


Figure 2.1: Scanning electron microscopic (SEM) patterns of nano-silica (Wang et al., 2016).

The chemical reaction involved in this process is shown in Eq. (2.1) (Sobolev et al., 2009).



Several factors influence the rate of hydrolysis and condensation reactions in the sol-gel process, including pH, temperature, reaction duration, reagent concentrations, the type of catalyst used, the H₂O/Si molar ratio (ranging from 7 to 25), and the ageing temperature and time. When these parameters are meticulously controlled, the process can produce nano-silica particles ranging from 1 to 100 nm in size (Sobolev et al., 2009; Wilson et al., 2002). **Figure 2.2** compares nano-silica's particle size and specific surface area with other concrete constituents.

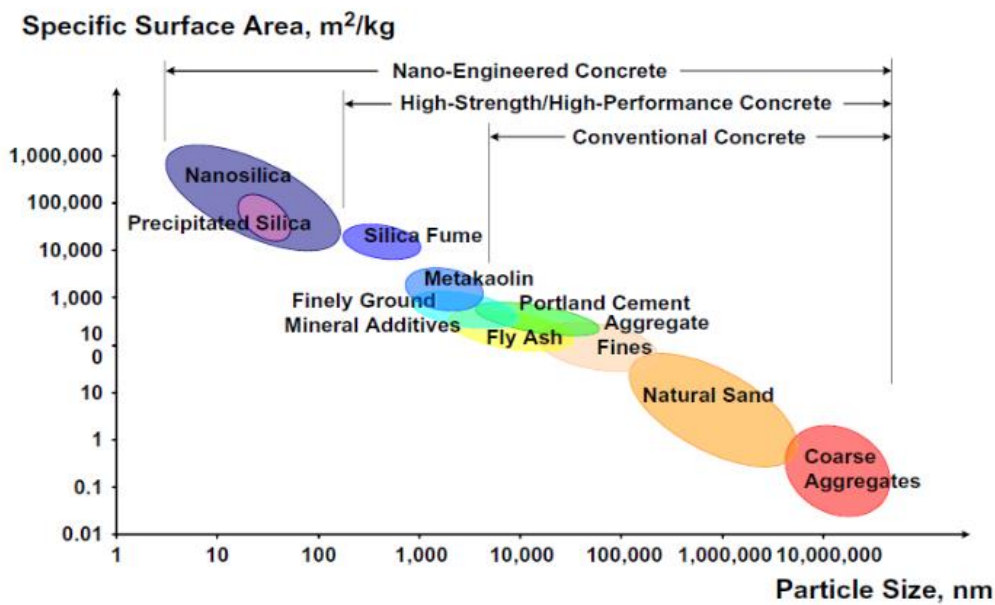


Figure 2.2: Particle size and specific surface area of nano silica compared to other concrete constituents (Rupasinghe et al., 2011).

Another method for producing nano-silica powder involves vaporizing silica at temperatures between 1500 and 2000 °C by reducing quartz (SiO₂) in an electric arc furnace. Additionally, very fine nano-silica particles can be produced by collecting fine particles in a cyclone during the production of silicon and ferrosilicon alloys (Quercia and Brouwers, 2010). Nano-silica can also be synthesized through precipitation, precipitating from a solution within a temperature range of 50 to 100 °C. The precursors used in this method include sodium silicates (Na₂SiO₃), burned rice husk ash (RHA), semi-burned

rice straw ash (SBRSA), and magnesium silicate (Sobolev et al., 2008; Thuadaj and Nuntiya, 2008; Zaky et al., 2008). Colloidal silica is produced by suspending silica particles in a liquid that has been electrostatically stabilized, allowing the particles to remain dispersed within the solution. The silica particles must be smaller than 100 nm; larger particles would settle out of the solution. The production process begins by neutralizing an alkali silicate solution, leading to the formation of silica nuclei. In this process, sodium silicate is typically used as the alkali solution. If the pH of the solution drops below 7 (becoming acidic), the silica particles fuse to form larger, unstable particles.

Conversely, the silica particles remain separated and grow in a basic solution. Once the desired particle size is achieved, the suspension is stabilized by adjusting the pH, preventing further changes and aggregation of the particles. Depending on the required density, the solution is then evaporated. Finally, chemical modifications and optimization procedures are performed to achieve the desired properties (Akzo Nobel, 2014). **Figure 2.3** shows the schematic diagram of the manufacturing process of colloidal nano-silica.

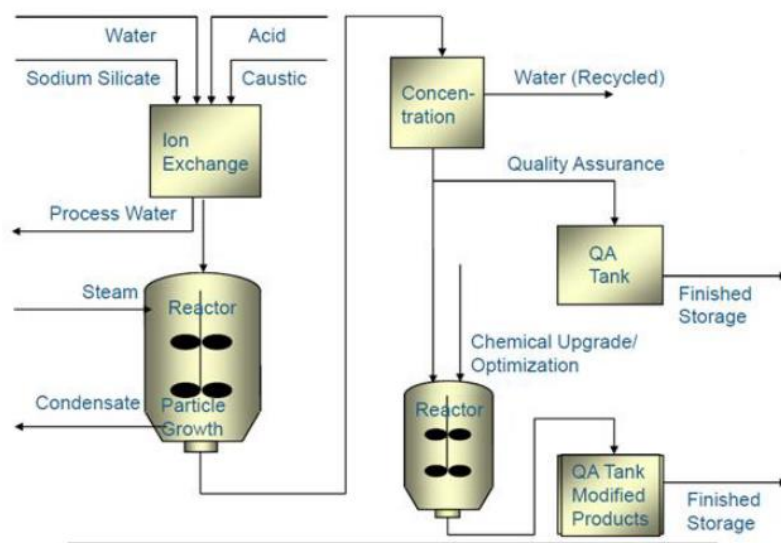


Figure 2.3:. Colloidal silica production process (Akzo Nobel, 2014).

2.3.2 Analysis of chemical and microstructural characteristics

The current experimental studies on the effects of nano-silica in concrete, mortar, and cement paste have focused on analysing the chemical and microstructural characteristics. These investigations have explored various aspects, including heat of hydration, pozzolanic reactivity, backscatter electron (BSE) imaging, and nano-indentation techniques.

2.3.2.1 Heat of hydration

Studies on the impact of replacing cement with nano-silica on hydration characteristics have been conducted using various calorimetric techniques such as isothermal calorimetry (Flores et al., 2017; Liao et al., 2019; Singh et al., 2016b), adiabatic calorimetry (Riding et al., 2012; Said et al., 2012), and semi-adiabatic calorimetry (Hou et al., 2013b; Zabihi and Hulusi Ozkul, 2018). These studies reveal distinct regions in the calorimetric curves, each corresponding to different stages of the cement hydration process. The induction period, characterized by minimal heat release as cement particles react with water to form hydration products, is followed by the acceleration period, during which heat release intensifies rapidly due to increased hydration reactions, particularly the formation of C-S-H gel and calcium hydroxide (CH). Subsequently, the deceleration period witnesses a gradual decline in the heat release rate as hydration reactions slow down, leading to the steady-state or plateau period, indicating that most cement particles have reacted, and hydration is nearing completion.

Calorimetric analyses indicate that nano-silica enhances peak hydration and reaction rates (Flores et al., 2017; Kim et al., 2022; Lavergne et al., 2019; Riding et al., 2012), as shown in **Figure 2.4**. For instance, Yang et al. (2021) found that the reaction rate and hydration heat at early ages are higher with increased nano-silica content. Additionally, Palla et al. (2017) reported a reduction of 4 hours in the dormant period of cement paste with 2 wt% nano-silica compared to neat cement paste (Palla et al., 2017). Furthermore, Asgari et al.

(2016) demonstrated that the cement hydration rate is significantly higher in nano-silica solution than water solution (Asgari et al., 2016). Previous studies (Sobolev et al., 2008; Wu et al., 2016) consistently show that nano-silica behaves as a pozzolan similar to silica fume, fly ash, and rice husk ash, reducing significant amounts of calcium and hydroxyl ions in the pore fluid environment. This reduction leads to the formation of (C-S-H)-seeds on the surface of silica, accelerating the hydration of alite (C_3S) and belite (C_2S). The pozzolanic reaction and "seed effect" of nano-silica synergistically shorten the induction period of the hydration process, resulting in higher hydration degrees than plain cement in the early stages (Heikal et al., 2015; Shih et al., 2006). Another explanation for the shortened induction period is attributed to the high chemical activity of nano-silica due to its smaller particle size and greater surface area, facilitating the consumption of CH and accelerating the hydration process (Wang et al., 2016).

2.3.2.2 Pozzolanic Reactivity of Nano-silica based on X-ray diffraction

Numerous studies have delved into the pozzolanic reactivity of nano-silica employing X-ray diffraction (XRD) analysis (Qing et al., 2007; Singh et al., 2016b, 2016a; Snehal et al., 2020; Wang et al., 2020). Through XRD spectrograms, researchers have elucidated the pozzolanic reactivity of nano-silica, concluding that it diminishes the content of CH in the mix while increasing the content of C-S-H (Singh et al., 2016a; Snehal et al., 2020; Tambara Júnior et al., 2022). In simpler terms, concrete mixes incorporating nano-silica display a reduced intensity of diffraction lines associated with CH and an elevated intensity of diffraction lines linked with C-S-H compared to control mixes. This phenomenon was explicitly noted in the study by Singh et al. (2015), where the intensity of the characteristic peak of unhydrated C_3S decreased as hydration progressed up to 1 h, indicating the dissolution of C_3S over time (Singh et al., 2015). Conversely, in the case of nano-silica-incorporated hydrated C_3S samples, the intensity of this peak (overlapping with the C-S-H peak) increased with time (up to 1 h), signifying the formation of additional C-S-H, which was not observed in the hydrated C_3S samples alone. Hence, a

secondary C-S-H is formed during the early hydration stage in the presence of nano-silica, as evidenced by a new peak.

Similarly, Singh et al. reported a nucleation effect during the early hydration stage (up to 10 h) (Singh et al., 2016b). The intensity of the crystalline CH peak at $2\theta = 18.02$ (Jadhav and Debnath, 2011) increased steadily up to 24 h (**Figure 2.5(a)**), showcasing the natural nucleation effect of hydrated products formed in pure samples. In nano-silica-incorporated C₃S samples, the CH peak's intensity was higher than that of pure C₃S (up to 10 h) (**Figure 2.5 (b)**), indicating a significant increase in the growth of hydrated products. At a later stage (15–24 h), the intensity of this peak was found to be lower than that of the control due to the pozzolanic effect of nano-silica particles (**Figure 2.5(b)**). Furthermore, the peak at $2\theta = 50.7$ was meticulously examined and identified as a characteristic peak of crystalline C-S-H, specifically jennite and tobermorite (Thomas et al., 2009). In the case of pure C₃S samples, this peak manifested at 15 h, with the intensity remaining constant up to 24 h (**Figure 2.6(a)**). However, in the presence of nano-silica particles, this peak emerged at 8 h, and its intensity continuously increased up to 24 h (**Figure 2.6(b)**). This observation suggests that in the presence of SNPs, a well-ordered crystalline C-S-H structure is formed.

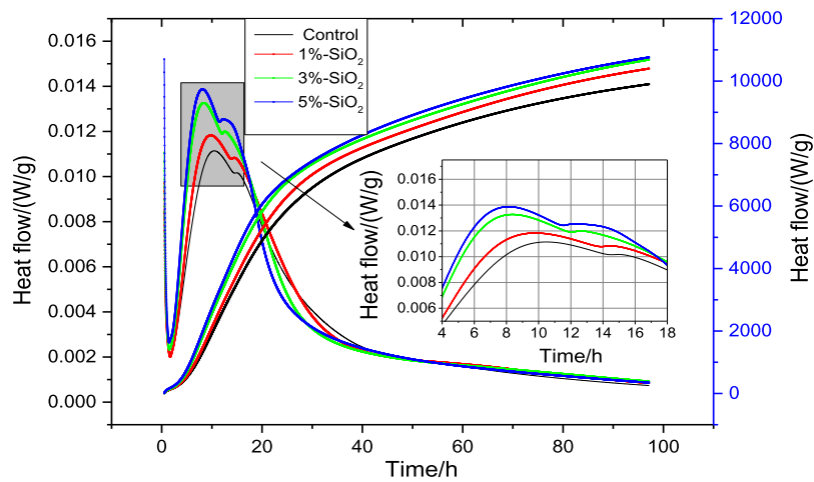


Figure 2.4: The impact of nano-SiO₂ on the exothermic rate and hydration heat of cement hydration (Wang et al., 2016).

Similar XRD patterns were obtained in pure and nano-silica-incorporated hydrated OPC samples. This pozzolanic effect is contingent on particle size, with nano-silica with smaller particles significantly affecting peak intensities due to its higher pozzolanic reactivity resulting from the high surface-to-volume ratio of ultra-fine particles. Consequently, the pozzolanic reactivity of nano-silica at the early stage of hydration is significantly heightened, accelerating strength development at early ages. However, it is imperative to note that comparing peak heights or intensities does not provide precise quantitative analysis. For accurate quantification of different phases, it is preferable to conduct a Rietveld analysis (Lok P. Singh et al., 2012; Tambara et al., 2023).

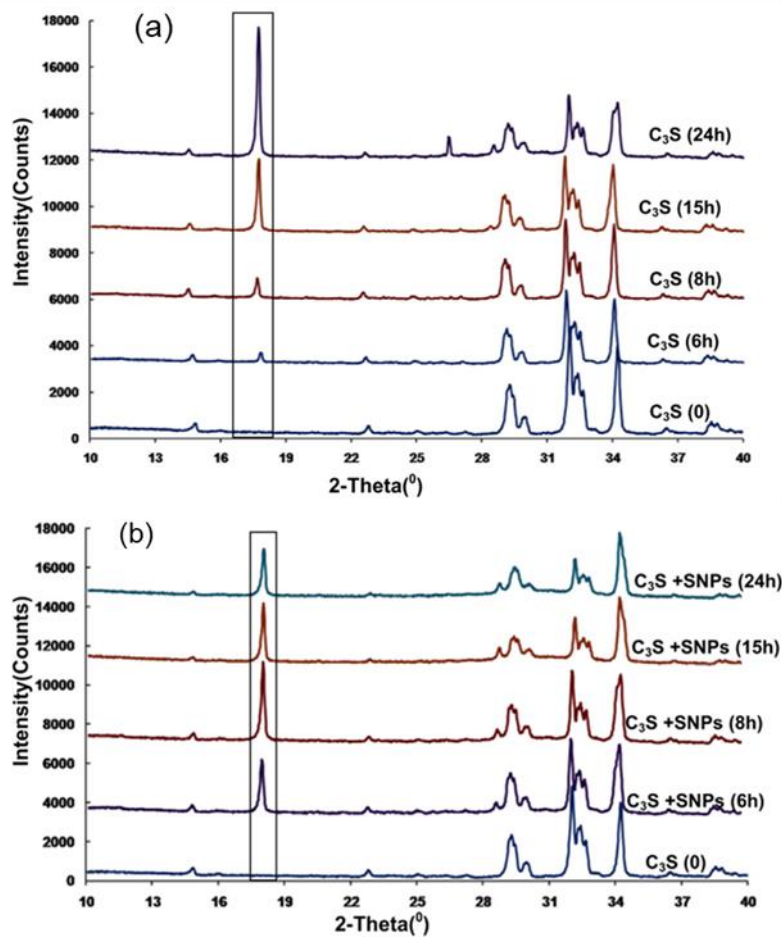


Figure 2.5: Intense peak of CH in plain C₃S (a) and nano silica (SNPs) incorporated C₃S (b) at various times (Singh et al., 2016b).

2.3.2.3 Pozzolanic reactivity of nano-silica based on Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) is a powerful analytical technique used to measure changes in the mass of a material as it is heated over a specified temperature range under an N₂ environment. This technique is beneficial for studying cementitious materials' decomposition and hydration characteristics. When applied to the analysis of nano-silica in cement, TGA helps quantify the pozzolanic reactivity by monitoring the thermal decomposition of CH and C-S-H (Abhilash et al., 2021). A sample is subjected to a controlled temperature program in TGA, and the mass change is recorded continuously, as depicted in **Figure 2.7**. The primary purpose is to identify the temperatures at which various hydrated products decompose, thereby providing insights into the hydration process and the formation of new compounds. For cementitious materials, significant mass losses typically occur due to the decomposition of CH, C-S-H, and other hydration products (Nithurshan et al., 2024).

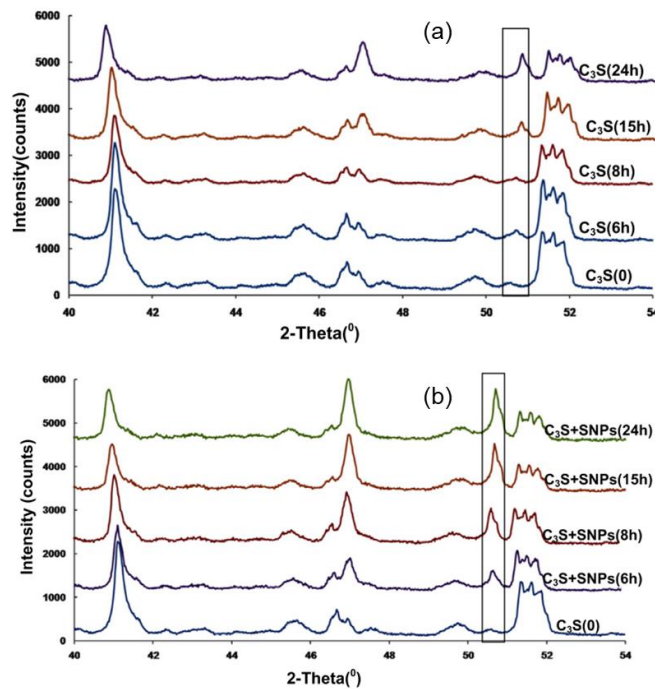


Figure 2.6: Incremental appearance of C-S-H peak in plain C₃S (a) and nano silica (SNPs) incorporated C₃S (b) with time.

Several studies have employed TGA to investigate the pozzolanic reactivity of nano-silica in cement. Nazari and Riahi (2011) performed a thermogravimetric investigation in the range of 110–650 °C, observing the dehydration of hydrated products and increased weight loss in specimens with up to 3% nS particles incorporated into GGBFS self-compacting concrete (SCC) after 90 days of curing (Nazari and Riahi, 2011). Notably, the study by Bastami et al. reported spalling and mass loss in nS-admixed high-strength concrete (HSC) when the specimens were heated above 400 °C, compared to just above 300 °C for HSC without nano-silica. This suggests that nano-silica enhances the thermal stability of the cementitious matrix (Bastami et al., 2014).

Singh et al. also utilized TGA to examine the hydration of cement containing nano-silica. Their results demonstrated a substantial reduction in CH content, with the CH content in cement paste containing nano-silica decreasing to 86 % after the first hydration day and further reducing to 62 % at 28 days (L. P. Singh et al., 2012). Similarly, Wang et al. reported a reduction in CH content from 17.5 % to 15.0 % with the inclusion of 1.2 wt% nS. These reductions indicate the effective pozzolanic reactivity of nano-silica, which reacts with CH to form additional C-S-H, thus lowering the overall CH content in the mix (Jinbang Wang et al., 2020). The lower CH content in nano-silica incorporated cement pastes indicates a higher rate of pozzolanic reaction, where nano-silica reacts with CH to form additional C-S-H, contributing to improved mechanical properties and durability of the concrete. This pozzolanic reaction is quantified by measuring the mass loss associated with the decomposition of CH and C-S-H during the TGA process, as witnessed in **Figure 2.8** and **Figure 2.9**. The greater the mass loss due to CH decomposition, the higher the pozzolanic reactivity, as more CH is consumed in forming C-S-H.

Both TGA and XRD are invaluable chemical analysis techniques for thoroughly examining the pozzolanic reaction of nano-silica in cement pastes. While these methods have been extensively utilized for various materials, their full potential has yet to be realized for nano-silica/cement systems. To comprehensively understand nano-silica's pozzolanic reactivity, it is crucial to quantify the CH content based on different types of

nano-silica (powder or colloidal forms). Additionally, analyzing the behaviour of various nano-silica replacement levels and the effect of the pozzolanic reaction over time will provide a clearer picture of nano-silica's reactivity. This detailed analysis is essential to fully leverage the capabilities of TGA and XRD to improve cementitious materials with nano-silica.

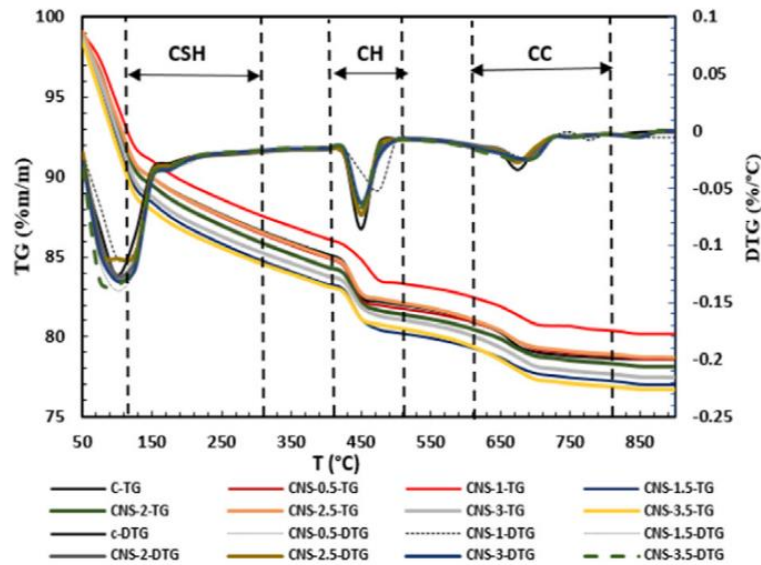


Figure 2.7: Thermogravimetric analysis of cement paste with incorporated varying colloidal nano-silica at 28 days (Snehal et al., 2020).

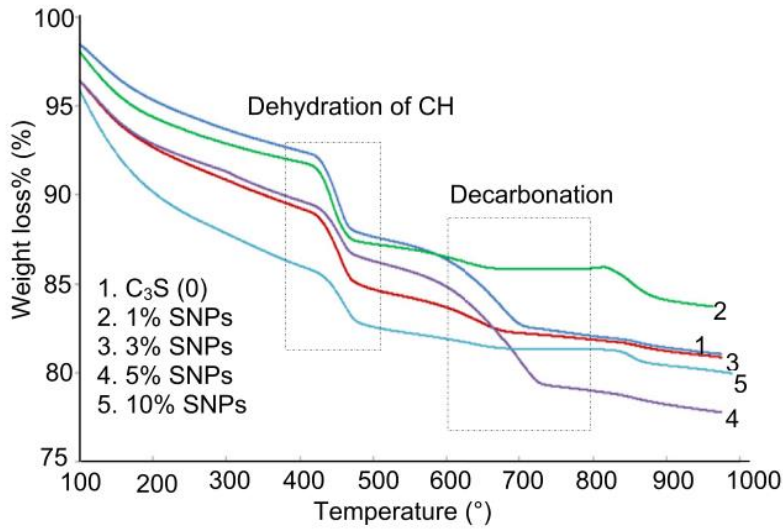


Figure 2.8: TG Curves of C_3S with different nano-silica contents (1-10%) at 1 day of Hydration (Singh et al., 2016a).

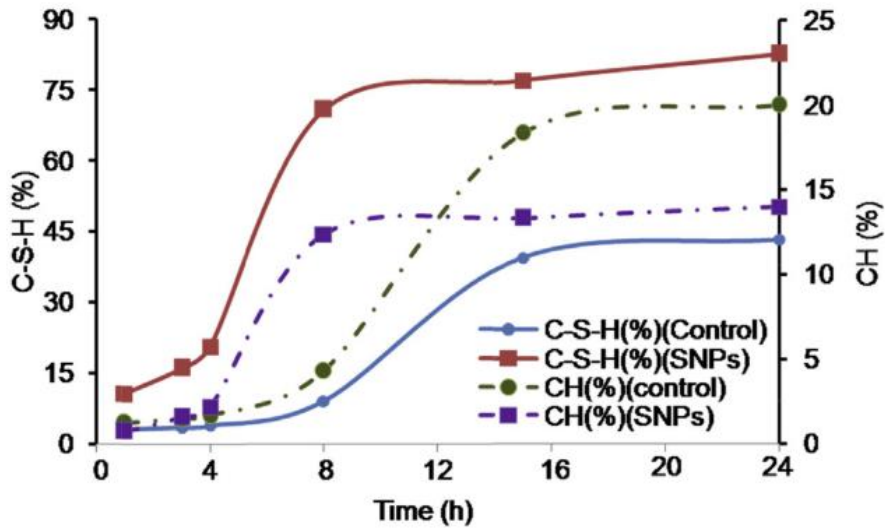


Figure 2.9: Percentage of formation of C-S-H and CH during the hydration of plain C_3S and SNPs-incorporated C_3S (Singh et al., 2017).

2.3.2.4 Microstructural analysis using Scanning Electron Microscopy

Microstructural analysis is a pivotal approach to understanding the enhancements brought by nano-silica in cementitious materials. Examining the material structure at finer scales

can identify necessary modifications to achieve desired properties. Techniques such as SEM, BSE imaging, and Energy Dispersive X-ray Spectroscopy (EDX) play crucial roles in characterizing these materials, especially in observing the pozzolanic reactions and the distribution of hydration products (Li et al., 2004; Singh et al., 2015; Wang et al., 2020; Zapata et al., 2013a). SEM is extensively used to visualize the microstructure of cement paste, mortar, and concrete samples. When combined with EDX, it provides both morphological and compositional analysis. For instance, studies have shown that incorporating nano-silica in C_3S samples accelerates hydration. Singh et al. reported that at 30 minutes of hydration, few hydration products are visible, increasing significantly at 60 and 180 minutes. The nano-silica incorporated samples demonstrated a much faster formation of a thin hydrated layer, which evolved into a dense, foil-like structure within an hour, indicating accelerated hydration and enhanced formation of C-S-H (Singh et al., 2015).

Similarly, Snehal et al. showed that SEM-EDX analysis at 7 and 28 days revealed a lower Ca/Si atomic ratio in samples with nano-silica, indicating a denser matrix. This lower ratio is linked to a more compact and stronger network of C-S-H, as seen in the denser SEM images compared to the control samples (Snehal et al., 2020). Additionally, SEM images have demonstrated a denser microstructure in cement paste with 5% nano-silica compared to plain cement paste. Singh et al. found that the nano-silica samples lacked the characteristic hexagonal CH crystals in the plain samples, showcasing a denser C-S-H gel and indicating effective pozzolanic activity (Lok P. Singh et al., 2012).

BSE imaging provides contrast based on compositional differences, making it helpful in identifying phases and understanding microstructural features. Studies by Darwin et al., Yang and Buenfeld, and others have utilized BSE to identify microcracks (Bernard et al., 2008; Darwin et al., 2006; Yang and Buenfeld, 2001), characterize paste, and analyze pore structures. These studies underscore the capability of BSE to provide detailed visualizations of different phases and structural features within cementitious materials. Yio et al. used BSE to study the reactivity of slag in cementitious materials. Similarly,

BSE imaging has been used to study the interfacial porosity around aggregate particles, providing insights into the material's integrity and durability (Yio et al., 2014). The pozzolanic reaction between nano-silica and CH forms additional C-S-H, which improves the material's strength and durability. This reaction is crucial for enhancing the properties of cementitious materials. SEM and BSE imaging reveal that nano-silica accelerates the hydration process, leading to quicker and more substantial formation of C-S-H. EDX analysis supports this by showing changes in elemental composition, specifically calcium reductions and silicon increases (Snehal et al., 2020).

While qualitative analyses using SEM, BSE, and EDX are prevalent, quantifying the pozzolanic reactivity remains challenging. Rupasinghe attempted to quantify hydration phases and pores using BSE image processing (Rupasinghe, 2015). However, this method might not be fully representative due to the limited area analyzed. Quantifying the pozzolanic reactivity using imaging techniques poses challenges, as the localized analysis may not accurately represent the entire sample. More comprehensive methods, possibly integrating multiple techniques and larger sample areas, are needed to provide a clearer picture of nano-silica's reactivity.

2.3.2.5 Nano-indentation

Nano-indentation, a technique used to characterize the mechanical properties of materials at the micro- and nanoscale, provides valuable insights into the pozzolanic reaction, formation of high-density (HD) C-S-H, and improvement in hardness in cementitious materials containing nano-silica. While applying indentation on specific material phases in a heterogeneous cementitious paste is challenging due to its high heterogeneity, statistical analysis and deconvolution techniques have been employed to overcome this challenge. Singh et al. utilized nano-indentation to perform many indentation grids on the surface of heterogeneous material, followed by statistical analysis and deconvolution to determine the mechanical properties of each material phase (Singh et al., 2017). Results indicated that nano-silica incorporation led to accelerated hydration rates and improved

packing density of C-S-H particles. Furthermore, nano-indentation revealed a reduction in low-density (LD) C-S-H and increased high-density (HD) C-S-H content in samples with nano-silica at 24 hours of hydration, indicating a denser microstructure.

Similarly, using nano-indentation tests, Kong et al. investigated microstructure improvement through nano-silica addition. Modulus contour maps showed an increased volume fraction of HD C-S-H gel in samples with nano-silica, indicating accelerated cement hydration and improved microstructure (Kong et al., 2019). However, samples with nano silica sol (SS) addition exhibited inferior properties compared to LD C-S-H gels formed from cement hydration, suggesting a higher discreteness in strength enhancement. In addition, Xu et al. utilized nano-indentation to analyze the properties of ITZs in concrete samples. Results showed that adding nano-silica improved ITZ's properties, indicated by a reduction in low-modulus areas and no significant impact on ITZ thickness (Xu et al., 2017). Deconvolution analysis of indentation modulus and hardness plots revealed variations in the volume fraction of microstructural constituents, such as Loosely packed (LP) C-S-H, LD C-S-H, HD C-S-H, and CH, as shown in **Figure 2.10**, demonstrating the effectiveness of nano-indentation in characterizing the mechanical properties and microstructure of nano-silica incorporated cementitious materials.

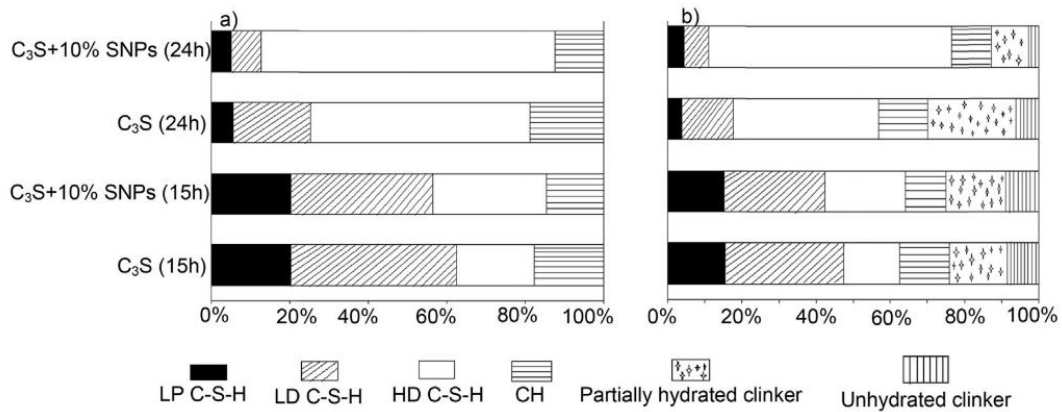


Fig. 11. Phase contents plots for all pastes; a) relative phase content of the hydration phases; b) phase content of the full-range.

Figure 2.10: Phase composition for all pastes: (a) relative phase content of the hydration phase and (b) phase content of the full range (Singh et al., 2017).

2.3.3 Analyzing the Fresh State Properties

Adding nano-silica to cementitious materials significantly impacts their fresh properties, including consistency, setting time, workability, and rheological behaviour. Several studies have documented the effects of nano-silica addition on the fresh properties of cementitious materials and proposed strategies to mitigate any adverse effects while enhancing desirable properties. Singh et al. observed that incorporating nano-silica into cement paste and mortar increases water demand, reduces flow spread, and enhances cohesion and yield stress. To maintain workability, the delayed addition of water was suggested, along with increased plastic viscosity and compressive strength increment (Singh et al., 2013). Similarly, Senff et al. noted that nano-silica decreases lubricating water in mortar mixes, leading to increased yield stress and reduced spread diameter on the flow table. Additionally, the setting time is anticipated, and the dormant period is reduced with nano-silica incorporation (Senff et al., 2009).

Zapata et al. reported nonlinear behaviour in grouts with micro and nano-silica particles, affecting saturation dosage, flow time, and loss of fluidity. While nano-silica improved rheological behaviour at low water-to-binder ratios and replacement levels, higher replacement levels exhibited better fluidity at high water-to-binder ratios (Zapata et al., 2013b). Khan et al. highlighted that incorporating nano-silica into cementitious materials accelerates initial and final setting times but reduces workability. As the percentage of nano-silica increases, the slump of fresh mix decreases due to higher water demand and inadequate water availability. However, a more uniform distribution of nano-silica can improve workability (Khan et al., 2022). Abhilash et al. also observed a decrease in workability with nano-silica incorporation, attributed to increased water demand and decreased slump values. They found that well-dispersed nano-silica can enhance concrete workability by facilitating rolling effects between particles (Abhilash et al., 2021).

In summary, while nano-silica addition offers benefits such as accelerated setting times and improved compressive strength, carefully considering water demand, polymer

interactions, and dispersion methods is essential to maintain workability and optimize fresh properties in cementitious materials.

2.3.4 Mechanical properties of nano-silica reinforced Cement-based materials

2.3.4.1 Compressive strength

Integrating nano-silica into cementitious materials significantly enhances their compressive strength, a crucial mechanical property determining the material's load-bearing capacity (Abhilash et al., 2021). Research has extensively explored the impact of nano-silica on compressive strength, identifying optimal dosages, potential problems with overdosage, and the mechanisms through which nano-silica enhances strength. The primary mechanism through which nano-silica enhances compressive strength is its pozzolanic reaction with CH in the cement matrix, forming an additional C-S-H gel. C-S-H is the product responsible for the strength and durability of cementitious materials. Due to its high surface area and reactivity, nano-silica significantly accelerates this reaction, especially early, leading to a denser and more homogeneous microstructure (Abhilash et al., 2021; Du et al., 2014). Nano-silica also acts as a nano-filler, filling the micro-pores and refining the pore structure of the cement matrix. This filling effect reduces porosity and increases the density of the material, contributing further to the compressive strength improvement (Du et al., 2014). The smaller the particle size of nano-silica, the more effective it is in filling these micro-pores and contributing to strength enhancement.

The optimal dosage of nano-silica is critical for achieving the maximum enhancement in compressive strength. Studies have shown that the ideal range for nano-silica incorporation lies between 1 % to 3 % by weight of cement. For instance, Chithra et al. reported a 43 % increase in 1-day compressive strength and a 27 % increase in 28-day strength with 2 wt% nano-silica (Chithra et al., 2016a). Similarly, Khan et al. observed an improvement in compressive strength by 16-25 % after 7 days and 12-17 % after 28

days with 1.5 % nano-silica (Khan et al., 2022). However, exceeding the optimal dosage can lead to agglomeration of nano-silica particles, adversely affecting compressive strength (Khan et al., 2022). Excessive nano-silica tends to cluster, forming weak zones within the cement matrix. These agglomerates disrupt the homogeneity of the matrix, creating points of weakness that can reduce overall strength. Chithra et al. and other studies have noted this reduction in strength at higher dosages due to the formation of these weak links. Similarly, Li et al. reported that higher dosages of nano-silica led to poor workability and microcracks, further compromising strength (H. Li et al., 2006).

The size and dispersion of nano-silica particles play a crucial role in their effectiveness. Smaller particles, such as those with an average size of 15 nm, are more effective in early age strength improvement than larger particles of 80 nm (Naji Givi et al., 2010). This is due to their higher reactivity and better filling ability. However, larger particles may contribute more to compressive strength over long curing periods due to reduced agglomeration risks and better dispersion within the matrix. Comparing results across different studies is challenging due to the diversity in experimental conditions and methodologies. Factors such as the type of nano-silica, its production method, the type of cement used, water-to-binder ratio, admixtures, and the specific cementitious system (paste, mortar, or concrete) vary significantly between studies (Nithurshan et al., 2024). For example, some studies use colloidal nano-silica, while others use powdered forms. These differences lead to variations in how nano-silica interacts within the cement matrix and affects compressive strength. Furthermore, the methods of nano-silica dispersion, such as ultrasonic dispersion or mechanical stirring, also influence the outcomes. Poor dispersion can lead to agglomeration, reducing the effectiveness of nano-silica in enhancing strength (Kim et al., 2022; Kooshafar and Madani, 2020). Additionally, the curing conditions and duration impact the hydration process and compressive strength development over time.

In conclusion, nano-silica is a powerful additive for enhancing the compressive strength of cementitious materials. Its optimal incorporation improves the microstructure through

pozzolanic reactions and nano-filling effects, particularly at early ages. However, careful control of dosage and dispersion is essential to avoid the adverse effects of agglomeration and ensure maximum strength enhancement. Due to the variability in experimental conditions and nano-silica characteristics, results across different studies are not directly comparable, highlighting the need for standardized testing methods to understand better and utilize nano-silica in cementitious materials.

2.3.4.2 Flexural and Tensile Strength

Incorporating nano-silica into cementitious materials such as cement paste, mortar, and concrete has enhanced their flexural and tensile strengths. Although research on these mechanical properties is less extensive than compressive strength, existing studies consistently demonstrate that nano-silica can significantly improve flexural and tensile strengths, provided the dosage is optimized. Nano-silica's contribution to flexural and tensile strengths is primarily due to its pozzolanic activity and its ability to refine the microstructure of the cement matrix. Flexural strength, which measures a material's ability to resist deformation under load, shows considerable improvement with incorporating nano-silica. For instance, Ye et al. reported that replacing 5% of cement with nano-silica increased the flexural strength of cement pastes by 43% and 88% at 7 and 28 days, respectively, compared to control samples (Qing et al., 2007). This enhancement in flexural strength is attributed to the denser and more compact microstructure formed due to the pozzolanic reaction of nano-silica, as observed in SEM micrographs by (Li et al., 2004). These micrographs showed that nano-silica-modified cement pastes have a more interconnected C-S-H network and reduced porosity than those without nano-silica.

Similarly, adding nano-silica benefits from tensile strength, particularly splitting tensile strength. Liu et al. found that at dosages of 1.5 %, 2.5 %, and 2.5 %, the splitting tensile strength of concrete at 3, 7, and 28 days was 1.5 MPa, 2.6 MPa, and 3.8 MPa, respectively (C. Liu et al., 2021). These values represented increases of 7.1 %, 23.8 %, and 15.15 %

over control specimens. This improvement is significant even when the cement content is reduced by 20 %, highlighting the efficiency of nano-silica in enhancing tensile strength through improved particle packing and matrix densification. However, the effectiveness of nano-silica is highly dependent on its dosage. Yu et al. noted that the optimum replacement content for enhancing strength characteristics is around 4 % (Yu et al., 2014). Beyond this optimal dosage, the tendency of nano-silica particles to agglomerate can negatively impact strength. Bahadori and Hosseini observed a decrease in tensile strength with higher nano-silica content, attributing this reduction to the formation of weak agglomerates within the cement matrix, similar to the effects seen with compressive strength at high dosages (Bahadori and Hosseini, 2012). The studies conducted by Sobolev et al. and Said et al. support the trend that both flexural and tensile strengths increase with nano-silica content up to an optimal point (Said et al., 2012; Sobolev et al., 2009). The effectiveness of nano-silica in these applications is primarily due to its nano-filling effect and its ability to produce a denser and more homogeneous matrix. This refined microstructure translates into improved mechanical properties, making nano-silica a valuable additive for enhancing the performance of cementitious materials.

In conclusion, incorporating nano-silica into cementitious materials enhances flexural and tensile strengths by refining the microstructure and increasing the amount of C-S-H gel. While the optimal dosage typically ranges between 1 % and 4 %, exceeding this range can lead to agglomeration, negatively impacting mechanical properties. Despite the challenges in standardizing comparisons across different studies due to varying experimental conditions, the positive impact of nano-silica on flexural and tensile strengths is well-documented and promising for future applications in construction materials.

2.4 Overview of experimental studies on GO-modified cement-based materials

2.4.1 Introduction to GO

GO is a derivative of graphene, characterized by the presence of oxygen-containing functional groups such as hydroxyl, epoxide, carboxyl, and carbonyl groups distributed across its basal plane and edges. A simplified molecular structure of GO is depicted in **Figure 2.11**. Carbon, oxygen, and hydrogen chemical composition grants GO its unique properties, harnessed in various industries. Structurally, GO retains a hexagonal honeycomb lattice similar to graphene but is heavily functionalized with oxygen groups. These functional groups introduce significant defects in graphene's otherwise perfect sp^2 hybridized carbon network, leading to a mixed sp^2/sp^3 hybridization. This altered hybridization endows GO with a two-dimensional, highly wrinkled structure that significantly influences its properties (Compton and Nguyen, 2010).

The size of GO sheets can vary widely, typically ranging from a few nanometers to several micrometres, depending on the production method. The thickness of a single layer of GO is approximately 1 nm. GO's crystal structure is characterized by a layered arrangement, where intercalated oxygen groups separate each layer. This layered structure, combined with its high surface area, makes GO attractive for various applications. GO is commercially available in several forms, including aqueous dispersions, dried powders, and thin films. These forms facilitate easy integration into various matrices, allowing for broad application in different fields (S. Yang et al., 2021).

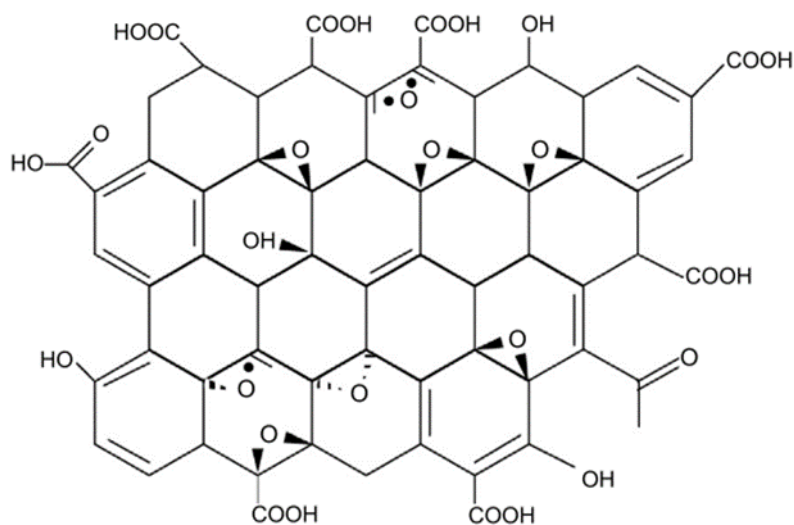


Figure 2.11: A simplified molecular structure of GO (Qureshi and Panesar, 2019).

GO has garnered interest across numerous industries due to its versatile properties. In electronics and sensors, GO is used to develop flexible electronic devices and sensitive sensors, leveraging its electrical conductivity and large surface area. In energy storage, GO is incorporated into batteries and supercapacitors to enhance energy storage capacities and improve charge-discharge cycles. Its biocompatibility and ability to functionalize with various biomolecules make GO valuable in biomedical applications such as drug delivery systems, biosensors, and tissue engineering. Additionally, GO's high adsorption capacity makes water purification and environmental remediation practical, removing heavy metals and organic contaminants.

Several advantageous properties drive GO's incorporation into cementitious materials. It improves the mechanical properties of cementitious composites by acting as a nano-reinforcement, enhancing tensile, compressive, and flexural strengths. GO promotes the formation of C-S-H gel, which is crucial for the strength and durability of concrete, leading to a denser and more homogeneous cement matrix. GO also enhances the durability of cementitious materials by reducing porosity and impeding the propagation of microcracks, resulting in better resistance to environmental factors such as freeze-thaw cycles and chemical attacks.

Compared to nano-silica, GO offers distinct advantages in cementitious materials. Its abundant functional groups improve dispersion within the cement matrix, ensuring better integration and uniformity. Studies have shown that GO can provide superior enhancements in tensile and flexural strengths due to its high aspect ratio and two-dimensional structure. GO's flexibility and large surface area enable it to effectively bridge microcracks, reducing crack width and propagation more efficiently than nS. While both materials enhance compressive strength, GO typically offers better tensile and flexural strength performance due to its unique structure and mechanical properties. The hydrophilic nature of GO, attributed to its oxygen groups, allows for better dispersion in aqueous cement mixtures, reducing the likelihood of agglomeration, which is often a challenge with nS. GO's ability to refine the microstructure of cementitious materials contributes to improved long-term durability, reducing permeability and enhancing resistance to aggressive environments.

In conclusion, graphene oxide represents a promising nanomaterial for improving the performance of cementitious materials. Its unique chemical composition, versatile forms, and significant enhancements to mechanical properties make it a superior additive to traditional nano-silica. Integrating GO into cement-based composites makes achieving stronger, more durable, and crack-resistant construction materials possible, paving the way for more sustainable and resilient infrastructure. As research continues, the full potential of GO in cementitious applications is likely to be further realized, offering innovative solutions to the construction industry.

2.4.2 Production of GO

The production of GO involves several methods, each influencing the material's properties by affecting the number and type of oxygen-containing groups formed (Jiríčková et al., 2022). Unlike graphene, GO is hydrophilic, making preparing suspensions in water or organic solvents relatively easy. Industrial-scale production of GO generally involves the chemical oxidation and exfoliation of natural graphite (Gr)

into single-layered GO, typically using various oxidizing agents. This process introduces oxygen functionalities—such as hydroxyl and epoxy groups on the basal planes and carboxyl groups at the edges—leading to changes in the material's properties (Anwar et al., 2023; Ikram et al., 2020; Yu et al., 2016). During the oxidation process, the graphite oxide (GrO) layers lose their conjugation, causing the hybridization of carbon atoms to shift from planar sp^2 to tetrahedral sp^3 . This alteration increases the interlayer spacing from approximately 0.335 nm in graphite to more than 0.625 nm in GO, significantly reducing its electrical conductivity and enhancing its hydrophilic nature (He et al., 1998; Hontaria-Lucas et al., 1995; Uhl and Wilkie, 2004). The result is the exfoliation and dispersion of GO in aqueous solutions, forming colloidal dispersions of thin GO sheets. Further reduction of GO, achieved through various techniques such as chemical, thermal, or electrochemical methods, results in reduced graphene oxide (rGO) (Pei and Cheng, 2012). This process removes oxygen-containing functional groups, restoring oxidation defects and improving electrical conductivity (Nurunnabi and McCarthy, 2019).

Historically, the production of GO dates back to Brodie's method in 1859, which involved treating a slurry of graphite and fuming nitric acid with potassium chlorate (May et al., 2012). This method was risky due to the potential for explosions. Staudenmaier later improved the method using a mixture of sulfuric and nitric acids, though the process still posed explosion risks and was time-consuming (Staudenmaier, 1898). The Hummers method, developed in 1958, became the most popular technique for GO production, as illustrated in **Figure 2.12**. It involves treating graphite with a mixture of sulfuric acid and potassium permanganate, resulting in efficient oxidation at lower temperatures, thereby reducing explosion risks (Hummers and Offeman, 1958). Despite its efficiency, the Hummers method has flaws, such as the generation of toxic gases (i.e. NO_2 and N_2O_4) and residual ions (i.e. Na^+ and NO_3^-) in the wastewater (Ren and Cheng, 2014; Ye et al., 2019).

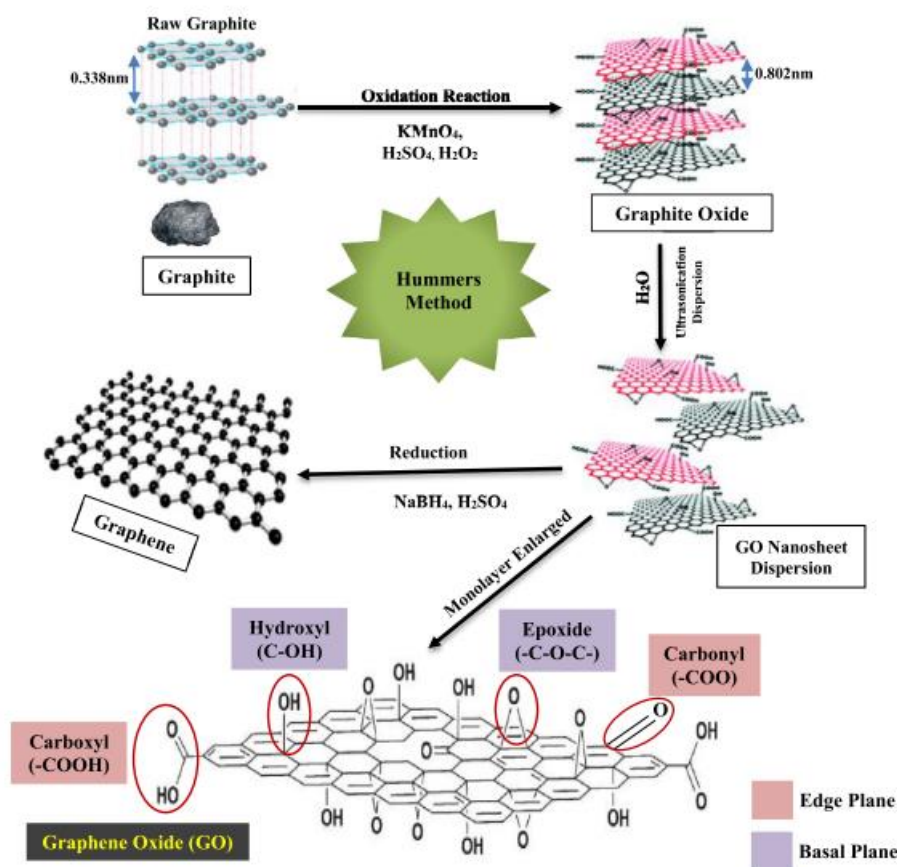


Fig. 10. Schematic presentation of GO fabrication [37,60,61].

Figure 2.12: Manufacturing of GO using the Hummers method (Anwar et al., 2023).

Several modifications to the Hummers method have been proposed to enhance efficiency and safety. The Tour's method, for instance, increased the concentration of potassium permanganate and replaced sodium nitrate with phosphoric acid, improving yield and reducing toxic gas emissions. Improved versions of the Hummers method further eliminate sodium nitrate and optimize the oxidation process using different catalysts (Dimiev et al., 2014).

This study synthesised GO using an improved version of Hummer's method by Ceylon Graphene Technologies Pvt Ltd, Sri Lanka. The first step involves intercalating graphene (63–90 μm) with H_2SO_4 . The concentrated (98 %) acid is cooled to 10 $^{\circ}\text{C}$, and raw graphite powder is added and continuously stirred while maintaining the temperature

below 20 °C. In the second step, the intercalated graphene is oxidized using KMnO_4 as the oxidizing agent. KMnO_4 is gradually added to the graphite-acid mixture, with the reaction temperature maintained at 50 °C for 3 h. A mixture of ice and chilled distilled water is added, and the suspension is stirred for an additional hour at 60 °C. The dropwise addition of H_2O_2 follows the process to quench the reaction and terminate further oxidation. The final suspension is centrifuged, and the supernatant is decanted. The residue is washed multiple times with HCl and deionized water to remove residual salts and un-exfoliated GO. Finally, GO is obtained as a slurry with a moisture content of 84 %. This slurry is then mixed with water to create a 10 g/L aqueous solution of GO. The mixture undergoes shear mixing for 15 min. at 3000 rpm, followed by ultrasonication for 10 cycles (1 min. of ultrasonication at 30 Hz followed by 1 min. of rest) (Liu et al., 2023).

In addition to chemical routes, electrochemical synthesis presents an eco-friendly alternative for GO production. This method reuses electrolytes and minimizes washing, reducing environmental impact. Electrochemical GO (EGO) production allows better control over oxidation levels and defect densities without oxidizing agents, resulting in higher purity GO (Jankovský et al., 2016). Biological systems using bacteria like *Acidithiobacillus ferrooxidans* or *Pseudomonas* offer another environmentally friendly approach to GO synthesis (Jankovský et al., 2017), although achieving homogeneous oxidation remains challenging. Overall, the production of GO is a complex process with multiple methods, each offering distinct advantages and limitations. The choice of method impacts the properties of the resulting GO, influencing its suitability for various applications, including those in electronics, composites, and cementitious materials.

2.4.3 Analysis of chemical and microstructural properties

2.4.3.1 Heat of hydration

GO significantly impacts the hydration heat and hydration process of cementitious materials. The effect of GO on cement hydration has been widely studied, revealing that

it can influence both the rate and extent of hydration reactions. According to Basquiroto de Souza et al., GO promotes higher dissolution of cement grains and facilitates the seeding of more hydration products. These products fill the pores within the cement matrix, enhancing the overall microstructure, although the detailed mechanisms behind this process remain somewhat unclear (Basquiroto de Souza et al., 2022). Zhao et al. observed that adding 0.02 wt% GO to cement paste decreased the cumulative hydration heat and the heat release rate by over 50 % compared to plain paste. This reduction in heat evolution can be attributed to the changes in the dissolution dynamics of cement particles. The dissolution rate is highly dependent on the degree of undersaturation of the solution concerning the dissolving phase, where rapid dissolution occurs at high undersaturation levels. After the initial induction period, cement hydration accelerates with rapid nucleation and growth of hydration products, primarily influenced by the number of nucleation sites available. GO has been found to slightly alter cement paste's typical heat evolution curve, accelerating the hydration process by increasing the peak heat flow and shortening the induction period. However, these effects are less pronounced when GO is used in aggregated forms (Zhao et al., 2018).

Meng et al. demonstrated that cement pastes containing GO (CGO) showed a more extended induction period than pastes without GO (PC). The peak heat flow for GO-containing pastes was higher, indicating that GO enhances the exothermic rate of cement hydration. The total accumulated heat of hydration also increased with the inclusion of GO, particularly evident within the first 24 hours. This acceleration in hydration is attributed to the increased number of nucleation sites provided by GO, which facilitates the growth of hydration products (Meng et al., 2021). Vallurupalli et al. reported that including 0.04 % GO increased the peak heat flow by 18 % compared to plain cement paste, primarily due to the nucleation of hydration products onto the GO. The increase in heat flow peaks and the reduction of the induction period suggest that GO acts as a catalyst in the hydration process, enhancing the rate at which hydration products form. However, higher dosages of GO, particularly when combined with high superplasticizer (SP)

content, can offset these benefits due to the increased activation energy required for nucleation and growth of hydrates (Vallurupalli et al., 2020).

Li et al. explored the effects of varying GO dosages (0.02 % to 0.06 %) on cement paste hydration. GO was found to reduce the dormant period and shift the heat flow peaks to earlier times, indicating accelerated hydration of C_3S due to increased nucleation sites. The increased heat flow peaks at higher GO dosages demonstrate that GO significantly enhances early-age hydration reactions, leading to greater heat release within 14 hours. This accelerated hydration correlates with improved early-age mechanical strength of concrete (W. Li et al., 2017b).

In summary, GO accelerates cement hydration by providing additional nucleation sites, which enhances the formation and growth of hydration products. This acceleration leads to higher early-age heat release and improves the microstructural properties of the cement matrix. Compared to traditional additives like nano-silica, GO offers unique advantages due to its large surface area and active functional groups. However, the overall impact of GO is dose-dependent, with higher dosages potentially leading to agglomeration and diminished benefits. Thus, careful optimization of GO content is crucial to maximizing its positive effects on cement hydration.

2.4.3.2 Reactivity of GO based on X-ray diffraction

XRD is an essential technique for identifying crystalline phases and examining structural properties in materials. In cement hydration studies, XRD helps to understand the impact of GO on the formation of hydration products by analysing the presence and intensity of specific diffraction peaks. Ganesh et al. used XRD to analyse cement mortars with and without 0.03 % GO. The patterns revealed distinct peaks corresponding to various hydration products: SiO_2 at 20.67° , 26.71° , and 49.96° ; $Ca(OH)_2$ at 18.10° , 34.07° , 47.09° , and 50.80° ; CASH at 12.14° , 23.03° , and 30.96° ; C-S-H at 29.45° , 32.26° , and 55.05° ; calcite at 23.03° and 35.63° ; and ettringite at 8.69° and 23.03° . GO-modified mortar showed increased d-spacing for $Ca(OH)_2$ (0.49715 nm compared to 0.4901 nm in control)

and C-S-H (0.2795 nm compared to 0.2778 nm in control) (Ganesh et al., 2023). Indukuri et al. observed that GO influenced the morphology of hydration products such as ettringite (AFt), monosulfate (AFm), and CH. XRD patterns showed that GO facilitated the formation of flower-like and polyhedron-like crystals, enhancing the mechanical properties of cement composites (Indukuri et al., 2020). Besides, Mokhtar et al. reported that XRD patterns of cement composites with GO nanoparticles (GONPs) showed an increase in calcium carboaluminate hydrate due to GO's functional groups reacting with the C₃A phase, contributing to improved composite durability (Mokhtar et al., 2017).

Qureshi and Panesar found that GO increased the intensity of CH and other crystalline phases like C-S-H gel at different hydration stages. Rietveld analysis confirmed higher CH and C-S-H content with GO, with optimal increments at 0.06 % and 0.02 % GO, respectively (Qureshi and Panesar, 2019). Yang et al. demonstrated that GO accelerated the hydration process without altering the basic structure of C-S-H. XRD measurements showed increased Ca(OH)₂ crystalline phases with higher GO content, and changes in GO's interlayer distance indicated higher hydration and oxidation levels (Yang et al., 2017b). Chintalapudi and Pannem studied cement composites subjected to sulfuric acid attack and found that GO enhanced durability. XRD patterns revealed the formation of gypsum and ettringite due to the reaction of Ca(OH)₂ with sulfate ions, consistent with improved durability (Chintalapudi and Pannem, 2022). Moreover, they conducted XRD analysis on specimens with 0.02 % and 0.03 % GO after 28 days of curing. The results showed that GO increased the crystallinity of the cement matrix, with higher peak intensities for C-S-H and other phases, indicating accelerated hydration and enhanced mechanical strength (Chintalapudi and Pannem, 2019).

Overall, XRD analysis consistently shows that GO significantly impacts the hydration process and the formation of crystalline phases in cement composites. GO enhances the formation of crucial hydration products such as C-S-H, CH, and CASH, improving mechanical properties and durability. The detailed crystallographic data from XRD, including peak positions, intensities, and d-spacing measurements, provide valuable

insights into how GO modifies cementitious materials' hydration kinetics and microstructure.

2.4.3.3 Reactivity of GO based on thermal gravimetric analysis

TGA is a critical technique to investigate materials' thermal stability and composition by monitoring mass change as a function of temperature. In the study of cement hydration, TGA provides insights into the decomposition of hydration products and the presence of various phases, such as CH, C-S-H, and calcium carbonate (CaCO_3). The addition of GO has been shown to influence these hydration products, and TGA can quantify these effects by identifying and comparing the thermal degradation patterns of plain and GO-modified cement composites.

Mokhtar et al. used TGA to analyse the contents of CH in OPC and GO nanoparticle (GONPs)-inforced cement pastes after 28 days of curing. The TGA results, alongside derivative thermogravimetric (DTG) curves, identified various phases based on specific decomposition temperatures. Peaks at about 140 °C corresponded to nearly amorphous C-S-H, while a peak at 190 °C indicated micro-crystalline C-S-H. Peaks at 640 °C and 690 °C were due to the decomposition of amorphous and crystalline CaCO_3 , respectively, and CH was detected between 415–475°C. Adding GONPs resulted in sharper CH peaks, indicating better CH phase crystallisation than the plain paste. There was a slight decrease in the C-S-H peak and an increase in CaCO_3 peaks, suggesting that GONPs may promote the formation of calcium carboaluminate hydrates due to the reaction of the $-\text{COOH}$ groups with CH (Mokhtar et al., 2017). This is corroborated by the observed increase in carbonation peaks in DTA curves with increasing GONP content, which aligns with XRD findings. Yang et al. also utilized TGA and DTG to quantify hydration degrees and their correlation with mechanical strength. The analysis outlined specific temperature ranges for phase changes: loss of evaporable water and part of the bound water (30–105 °C), decomposition of bound water from C-S-H (110–300 °C), dehydroxylation of CH (450–550 °C), and decarbonisation of calcium carbonate (650–800 °C). The study found that

CH content increased with curing time, except at one day, when GO's large surface area absorbed water, reducing available free water for complete hydration. This initial reduction in CH was mitigated over time as hydrated phases nucleated, facilitating the formation of strong interfacial bonds between GO and hydrated cement phases (Yang et al., 2017b).

Overall, TGA analysis reveals that GO significantly affects cement composites' hydration process and thermal stability. The detailed mass loss profiles and phase decomposition temperatures provide valuable insights into the interaction between GO and cement hydration products. GO enhances the crystallization and formation of crucial hydration phases, such as CH and C-S-H, improving cementitious materials' mechanical properties and durability. The comprehensive data from TGA, including weight loss percentages and DTG inflections, offer a robust understanding of GO-modified cement composites' thermal and chemical stability.

2.4.3.4 Backscatter Electron Imaging

SEM is a powerful tool for investigating the microstructural characteristics of materials at high magnification. In cement composites, SEM is employed to observe the morphology and distribution of hydration products, which is crucial in understanding the effects of additives like GO on cement hydration and mechanical properties. The following discussion synthesizes findings from several studies to elucidate the effects of GO on cement composites as observed through SEM analysis.

Ganesh et al. observed that GO acts as a nucleation site, significantly influencing the morphology of the hydration products. In their study, SEM images revealed that the control cement mortar displayed a higher intensity of ettringite, characterized by thin rod-like crystal projections on C-S-H. However, with the addition of 0.02 % GO, the mortar exhibited fewer rod-like crystals and an increased presence of C-S-H. At 0.03 % GO, no thin rod crystals were visible; instead, tobermorite-type C-S-H crystals were prominent. At a higher GO content of 0.04 %, a disrupted matrix with fibrous C-S-H was observed,

indicating that the optimal GO concentration for enhancing strength is around 0.03 %, where pure C-S-H gel was more crystalline compared to the ettringite-dominated structures in lower GO concentrations and fibrous C-S-H at higher concentrations (Ganesh et al., 2023). Lv et al. explored the effects of smaller GO nanosheets (average thickness 3.1 nm and average size 72 nm) on cement paste. Their SEM images indicated that at a 0.01 % dosage, many rod-like and flower-like crystals were present, suggesting that GO at low dosages effectively regulates the shape and distribution of hydration crystals. As the GO dosage increased to 0.02 %, these rod-like crystals aggregated into flower-like structures. At higher dosages (0.03 % to 0.06 %), dense clusters of rod-like crystals and tightly packed polyhedral crystals were observed. This suggests that highly dispersed, smaller GO nanosheets can promote the formation of tightly packed hydration crystals, which contribute to the toughening of the cement paste. The GO nanosheets act as templates, promoting the assembly of regular flower-like and polyhedral crystals from rod-like or needle-shaped crystals (Lv et al., 2014a).

Cui et al. (2017) highlighted the occurrence of carbonation during SEM sample preparation. Their SEM images displayed flower-like crystals on the surface of the cement samples, identified as calcium carbonate (CaCO_3), through EDS and XRD analyses. This carbonation likely occurred during oven drying, a standard step in SEM sample preparation, suggesting that care must be taken to distinguish between hydration products and carbonation artefacts. The study underlines the necessity for careful sample handling to avoid misleading interpretations of SEM results (Cui et al., 2017a). Indukuri et al. discussed the 'template effect' of GO, where GO controls the growth patterns of hydration products. SEM images showed that GO facilitated the formation of thick, column-like and flower-like hydration crystals, which dispersed into the pores and cracks of the cement paste, acting as fillers and crack arresters. This structural modification effectively enhanced the toughness and reduced the brittleness of the cement composites. The study concluded that GO incorporation significantly improves the mechanical properties of cement composites by modifying the hydration crystals (Indukuri et al., 2020).

In summary, GO acts as a nucleation site, influencing the type and distribution of hydration products, with optimal concentrations (around 0.03 %) promoting the formation of tobermorite-type C-S-H, enhancing the strength of the cement matrix. GO nanosheets, significantly smaller and highly dispersed, serve as templates for forming regular and tightly packed hydration crystals, contributing to improved mechanical properties. SEM sample preparation can induce carbonation, necessitating careful interpretation of observed microstructures to distinguish between actual hydration products and artefacts. Overall, incorporating GO leads to forming hydration crystals that fill voids and cracks, significantly enhancing the toughness and reducing the brittleness of cement composites. SEM analysis thus provides critical insights into the microstructural changes induced by GO in cement composites, highlighting its value as an additive for improving the performance of cement-based materials.

2.4.3.5 Nano-indentation of GO-modified cement system

Nanoindentation is a powerful technique used to investigate the micromechanical properties of cementitious materials at the microscale. It provides insights into the hardness, indentation modulus, and creep compliance of materials and helps in understanding the macroscopic mechanical behaviours of concrete (Fu et al., 2018). By applying nanoindentation, researchers can characterize clinker and C-S-H of different density levels, offering a detailed view of the microstructural modifications brought about by the inclusion of GO (Chuah et al., 2014; Long et al., 2018a; Yang et al., 2017a). Zeng et al. utilized nanoindentation to study the effects of GO on cementitious materials. Their findings demonstrated that nanoindentation can quantitatively assess the ITZ modifications due to GO inclusion. At a curing age of 28 days, modulus mapping indicated that GO reduced the thickness of the ITZ, increased its toughness, and strengthened the interface (Nguyen et al., 2021; Zeng et al., 2023). Similar results were reported by Meng et al., who found that GO significantly improved the indentation modulus of ITZ and paste specimens (Meng et al., 2022). Imaging techniques combined with nanoindentation further provided insights into the local mechanical properties,

confirming the existence and strengthening of the ITZ between aggregate and bulk paste. Despite the utility of imaging tests and simulations, nanoindentation remains preferred for its quantitative results, which are crucial for validating molecular simulations (Cho et al., 2020; Constantinides and Ulm, 2004; Hu and Li, 2014). However, challenges remain, including the isotropy of hydrated calcium silicate and the roughness of concrete surfaces, which can complicate nanoindentation analysis (Abdolhosseini Qomi et al., 2014; Gautham and Sasmal, 2019).

Long et al. conducted extensive nanoindentation tests and statistical analyses to understand the effect of GO on cementitious materials. Their study showed that GO increased the volume fraction of HD C-S-H and reduced the volume fraction of LD C-S-H and medium-density products (MP) (Long et al., 2018a). This alteration in the proportions of hydrated products contributed to the improved macro-scaled properties of the cement-based composites. The nanoindentation results revealed that GO promotes the formation of densely packed hydration products, reducing capillary pores and enhancing the overall mechanical properties (Tong et al., 2016). Nanoindentation combined with BSE imaging in SEM provided further insights. The BSE results identified four phases in the OPC system: porosity, C-S-H, CH, and unreacted/brittle regions. The study found that GO incorporation notably increased the CH phase and reduced the pore phase, indicating enhanced cement hydration. The combined use of nanoindentation and SEM-BSE allowed for comprehensive identification and quantification of GO-incorporated cement-based materials' microstructure and micromechanical properties (Long et al., 2018a).

In conclusion, nanoindentation is a crucial technique for characterizing the micromechanical properties of cementitious materials, particularly in the presence of GO. It provides quantitative data on the hardness and modulus of different phases, highlighting the role of GO in enhancing the density and mechanical properties of C-S-H gels. Despite the challenges associated with sample preparation and material heterogeneity, nanoindentation, especially when combined with imaging techniques, offers valuable

insights into the microstructural modifications and mechanical enhancements induced by GO in cement-based composites.

2.4.3.6 Analysing the fresh state properties

GO in cementitious materials significantly influences their fresh properties, particularly in fluidity, viscosity, and setting time. According to Indukuri et al., adding GO decreases the fluidity and increases the cement paste's viscosity and setting time. This effect is especially pronounced at a 0.03 % GO concentration, where a marked change in workability is observed. GO's large surface area and numerous functional groups enhance the hydration process and lead to the aggregation of cement particles, thus shortening the setting time and reducing fluidity (Indukuri et al., 2020). Further studies by Bhojaraju et al. reinforce these findings, showing that higher dosages of GO significantly reduce the mini-slump flow, indicating a decrease in fluidity. For example, a 0.06 % addition of GO can reduce mini-slump values by up to 75%. The study also reveals that adding ground-granulated blast-furnace slag (GGBS) can counteract some of the fluidity loss caused by GO. At 45 % GGBS content, the flow diameters of GO-modified cementitious materials can even surpass those of control samples, suggesting that GGBS mitigates the flocculation and increases flow (Bhojaraju et al., 2021).

Gong et al. found that adding 0.03 % GO to cement paste reduced the mini-slump diameter by approximately 34.6 %, confirming that GO additives reduce workability. The large specific surface area of GO absorbs free water, increasing viscosity and yield stress, as also observed by Shang et al. (Shang et al., 2015). Shang et al. noted that GO's hydrophilic nature and large surface area lead to water absorption, reducing free water content and fluidity while increasing viscosity. Electrostatic interactions between negatively charged GO and cement particles result in aggregate formation, reducing fluidity and increasing viscosity (Gong et al., 2015a). Newell and Garcia-Taengua conducted Marsh cone tests to measure the flow times of cement pastes with GO. Increasing GO content leads to higher t700 values, indicating less flowable mixes. Their

regression analysis showed that GO at 0.03 % increased the flow time by 70.3 %, emphasizing GO's impact on reducing workability. This reduction in flowability was more pronounced in the presence of nano-silica, which has a finer particle size and a more significant impact on workability (Newell and Garcia-Taengua, 2019).

Overall, incorporating GO in cementitious materials results in decreased fluidity, increased viscosity, and shorter setting times due to its large specific surface area and functional groups that enhance hydration and particle aggregation. However, the addition of materials like GGBS can improve these properties by increasing the flowability and counteracting the effects of GO. The complex interactions between GO, cement particles, and other additives highlight the need for careful optimization of nanomaterials in cementitious composites.

2.4.3.7 Mechanical properties of GO-modified cement-based materials

(a) Compressive strength

GO in cementitious materials has significantly enhanced their compressive strength. Various studies have investigated the impact of different GO dosages on the mechanical properties of cement composites. Indukuri et al. observed that increasing the GO dosage from 0.01 wt% to 0.04 wt% led to a marked improvement in flexural and compressive strengths. Specifically, at a GO dosage of 0.04 wt%, the compressive strength increased by 46.6 % after 28 days compared to control samples without GO. This enhancement is attributed to the high oxygen content (28.95 %) of the GO used, which likely promotes better interaction with the cement matrix (Indukuri et al., 2020). Liu et al. studied the compressive strength of 3D-printed mortar specimens with varying GO contents and found that GO enhanced the compressive strength to different extents depending on the concentration. Notably, a 0.015 % GO addition improved compressive strength by at least 10%, while a 0.03 % GO addition resulted in a 5 % increase. The anisotropy in compressive strength was also analysed, and it was influenced by pore shape and

orientation during the printing process. The study highlighted that higher GO content could lead to printing quality issues, such as under-filling, which increases porosity and affects strength (Liu et al., 2023).

Yang et al. reported that GO additions significantly improved the early-age compressive strength of cement samples. For instance, the compressive strengths of samples with 0.15 % and 0.20 % GO increased by 30.7 % and 42.3 % after 3 days, respectively. The maximum improvement in compressive strength was observed at early curing stages, suggesting that GO's nucleation seed effect plays a crucial role. However, the strength improvement decreased over time, showing a more minor increase at 28 days (Yang et al., 2017b). Wang et al. presented normalized data from various studies, demonstrating that GO significantly improves compressive strength. The most substantial increase reported was a 177.3 % relative strength rate at 1 % GO. Other studies showed compressive strength improvements of over 150 % with lower GO dosages, highlighting GO's effectiveness in enhancing mechanical properties. However, the benefits of GO in ultra-high strength concrete (UHSC) were less pronounced, with improvements ranging from 104.59 % to 107.82 % (Juan Wang et al., 2020). Kedir et al. summarized the general trends in GO's impact on compressive strength, noting that even small amounts of GO (0.02 %-0.06 %) can significantly enhance the mechanical properties of cement composites. The study emphasized the importance of optimal GO dispersion and curing conditions for achieving the best results. It also noted that GO improves early-age strength more substantially than long-term strength (Kedir et al., 2023).

These studies demonstrate that adding GO to cementitious materials can substantially improve their compressive strength, particularly at early curing stages. The optimal GO content varies, but generally, dosages between 0.02 % and 0.08 % yield significant improvements without adverse effects. The enhancement mechanisms include improved cement hydration, reduced porosity, and the barrier effect against microcrack propagation.

(b) Flexural and tensile tests

According to numerous studies, incorporating GO into cementitious materials has shown promising enhancements in flexural and tensile strength. These improvements are particularly significant in increasing the toughness and durability of these materials. Research by Wang et al. indicates that the addition of GO significantly enhances the flexural strength of cementitious materials (Juan Wang et al., 2020). Their data reveals that a 0.02 % GO addition can increase flexural strength by 85.11 %, demonstrating the best effect among the various dosages studied. Generally, GO-modified cementitious materials exhibit a flexural strength improvement of over 30%, a notable enhancement in the material's toughness. In contrast, the effect of graphene powder (GP) on flexural strength is less pronounced and can even reduce strength under certain conditions. For example, Tragazikis et al. found a significant reduction in the flexural strength of GP-modified mortar (Tragazikis et al., 2019).

The flexural strength improvement with GO is dose-dependent. Wang et al. reported that the flexural strength increases with GO dosage up to a certain point (0.02-0.04 %), after which it begins to decrease (Juan Wang et al., 2020). This suggests an optimal range for GO concentration that maximizes strength without causing adverse effects due to agglomeration or other factors. Studies by Long et al. further support these findings, showing that GO-modified recycled fine aggregate mortar exhibits significant improvements in strength. For example, GO additions of 0.02-0.04 % can lead to substantial enhancements in flexural strength, highlighting GO's effectiveness in improving the mechanical properties of cementitious materials (Long et al., 2018b, 2018c, 2017). Ganesh et al. reported similar trends, noting that the optimum GO percentage for flexural strength enhancement in mortar with GO paste and powder is around 0.03 %. The maximum increase in flexural strength was around 44% for mortar with GO paste and 80 % for mortar with GO powder. The higher performance of GO powder is attributed to differences in water-to-cement ratios and the presence of a polycarboxylate ether (PCE)

superplasticizer, which further improves dispersion and performance (Ganesh et al., 2023).

The tensile strength of GO-modified cementitious materials also shows significant improvements, though fewer studies have been conducted in this area compared to flexural strength. Lv et al. observed that a 0.03 % GO addition can increase the tensile strength by 78.6 %. This enhancement is substantial, indicating that GO can significantly boost the tensile properties of cementitious composites (Lv et al., 2013). Ganesh et al. also noted improvements in splitting tensile strength with GO additions. The maximum increase observed was 84 % for mortar with GO paste at a 0.03 % concentration, while the increase was 62 % for mortar with GO powder. Despite the differences in enhancement levels, the trend remains consistent: GO improves tensile strength up to an optimal concentration, after which further increases in GO content may lead to diminished returns or even reductions in strength due to potential agglomeration issues. Comparing the effects of GO on flexural and tensile strength, it is clear that GO has a substantial impact on both properties, though the degree of improvement can vary. The maximum reported improvements in tensile and flexural strength are 178.6 % and 178.3 %, respectively, indicating that GO can significantly enhance the mechanical performance of cementitious materials across different strength parameters (Kireitseu et al., 2008; X. Li et al., 2017).

In summary, incorporating GO into cementitious materials greatly enhances their flexural and tensile strengths, with optimal improvements typically observed at GO dosages of 0.02 % to 0.05 %. These enhancements are attributed to GO's ability to improve the microstructure and mechanical properties of the cement matrix, thereby increasing the material's overall toughness and durability.

2.5 Conclusion: Identification of the research gaps in experimental investigations

2.5.1 Nano-silica-modified cement-based systems

Experimental investigations of nano-silica cement systems have been pivotal in advancing our understanding of cementitious materials at the nanoscale. However, notable research gaps warrant attention and exploration amidst the progress made. One such gap lies in identifying and characterising the properties of C-S-H phases or the Ca/Si ratio in nano-silica cement systems. The importance of studying the properties of C-S-H phases or the Ca/Si ratio cannot be overstated. These parameters are crucial in dictating cementitious materials' mechanical, physical, and chemical properties. Understanding the nano-scale structure and composition of C-S-H phases is essential to elucidate the mechanisms underlying the hydration process and develop material properties. Moreover, variations in the Ca/Si ratio can significantly influence the microstructure and performance of cementitious systems, making it imperative to investigate their effects in nano-silica cement systems comprehensively.

Another critical research gap pertains to the reaction rate of nano-silica in cement systems. Despite the widespread use of nano-silica as a supplementary cementitious material, there remains ambiguity regarding its reaction kinetics and mechanisms. Investigating the rate of nano-silica reaction is crucial for determining its optimal dosage, ensuring proper incorporation into cement matrices, and predicting the long-term performance of nano-silica cement systems. Furthermore, there is a need to verify the actual effects of nano-silica in cementitious materials through systematic experimental investigations. While numerous studies have reported enhancements in mechanical properties and durability attributes with the addition of nano-silica, there exists a lack of consensus due to contradictory findings across different research works. Addressing this gap requires rigorous experimentation under controlled conditions to accurately assess the impact of nano-silica on various properties of cement systems. Moreover, validating proposed

models that predict the behaviour of nano-silica cement systems is essential for advancing predictive capabilities and enhancing the understanding of structure-property relationships. Many existing models rely on assumptions about the chemical composition, curing conditions, and other factors, which may not always align with experimental observations. By validating these models through experimental data, researchers can refine and improve predictive tools, thereby facilitating the design and optimization of nano-silica cement systems for specific applications.

In conclusion, the identification of research gaps in experimental investigations of nano-silica cement systems underscores the need for comprehensive studies aimed at elucidating the properties of C-S-H phases, understanding nano-silica reaction kinetics, verifying actual effects, resolving contradictory findings, and validating predictive models. Addressing these gaps will deepen our understanding of nano-silica cement systems and contribute to developing more efficient and sustainable construction materials.

2.5.2 GO-modified cement-based systems.

Experimental investigations of GO cement systems have garnered significant attention due to GO nanosheets' potential mechanical properties and durability enhancements. However, several research gaps persist in this burgeoning field, requiring further exploration and clarification. One critical aspect that warrants attention is characterising C-S-H properties or the Ca/Si ratio in GO cement systems. Understanding the properties of C-S-H phases or the Ca/Si ratio is paramount in elucidating the fundamental mechanisms underlying the performance of cementitious materials modified with GO. These parameters profoundly influence the microstructure, hydration kinetics, and mechanical strength of cement composites. Investigating the nano-scale structure and composition of C-S-H phases in GO-modified cement systems can provide insights into the interaction mechanisms between GO nanosheets and cementitious matrices, thereby

facilitating the optimization of GO dosage and dispersion for enhanced material properties.

Moreover, there is a pressing need to verify the actual reinforcing effect of GO in cementitious materials through systematic experimental investigations. While numerous studies have reported improvements in mechanical properties such as compressive strength, tensile strength, and flexural strength with the incorporation of GO, discrepancies and contradictory findings exist across different research works. Addressing this gap requires comprehensive experimental studies under standardized conditions to accurately assess the impact of GO on the mechanical performance of cement systems. Furthermore, validating proposed models that predict the behaviour of GO cement systems is essential for advancing predictive capabilities and optimizing material design. Many existing models rely on assumptions regarding the chemical composition, curing conditions, dispersion quality, and interaction mechanisms between GO and cement phases. Validating these models through experimental data can enhance their reliability and applicability, enabling more accurate predictions of GO-modified cementitious materials' mechanical and durability properties.

In conclusion, the identification of research gaps in experimental investigations of GO cement systems underscores the need for focused studies aimed at characterizing C-S-H properties, verifying the reinforcing effect of GO, resolving discrepancies in research findings, and validating predictive models. Addressing these gaps will advance our understanding of the interaction mechanisms between GO nanosheets and cement matrices and facilitate the development of high-performance cement-based composites with tailored mechanical and durability properties.

CHAPTER 3

LITERATURE REVIEW ON MODELING APPROACHES FOR PREDICTING THE PERFORMANCE OF CEMENT- BASED MATERIALS

3.1 Introduction

Understanding the performance of nano-modified concrete is crucial both academically and practically. Academically, the complexity of cement hydration and microstructural development poses challenges in isolating individual mechanisms and parameters. Relating these characteristics to concrete performance requires extensive experimental analysis and advanced theoretical modelling techniques. From an academic perspective, studying concrete performance, including nano-modified concrete, involves examining hydration chemistry and microstructural development. These factors impact concrete's mechanical properties and durability. Numerical modelling plays a vital role in deciphering these relationships by simulating hydration and microstructure development. This enables researchers to predict how variations in composition, such as the inclusion of nanomaterials, affect concrete performance.

From a practical perspective, despite the potential benefits, nano-modified concrete has not yet seen widespread adoption in the construction industry. One of the barriers to its broader use is the lack of a robust methodology for predicting the strength characteristics of nano-modified concrete. Developing a reliable modelling framework is crucial for designing more sustainable, high-performance concrete materials with complex mix designs. Accurate predictive models can guide the proportioning of mixtures to optimize both the mechanical properties and durability of the final product, thereby fostering confidence in using nanomaterials in construction.

Numerical modelling of concrete performance is inherently complex due to the multiscale nature of its components, which range from the nano to macro scales. The exact behavioural characteristics and the relationships between chemical and microstructural features and mechanical performance are not yet fully established, even for ordinary concrete. Therefore, a comprehensive understanding of existing theories and models is essential before significantly advancing in this area. The current review of literature and research focuses on three main areas. First, it examines studies that model the performance of cement systems, which provide a foundational understanding of how cementitious materials behave under various conditions. Second, it discusses the modelling of cement hydration, including the various models available to simulate this crucial process. Third, it analyzes studies on modelling the mechanical properties of nano-silica and GO-modified concrete. Numerous factors, including chemical composition, microstructural development, and environmental conditions, influence the performance of ordinary and nano-modified cement systems. Numerical models help predict how these factors interact and affect the material's performance. These models can simulate the hydration process, the development of the microstructure, and the resulting mechanical properties, providing valuable insights into the optimization of cementitious materials.

In conclusion, the importance of numerical modelling in the study of ordinary and nano-modified concrete cannot be overstated. These models provide a framework for understanding the complex interactions between chemical, microstructural, and mechanical properties. They enable researchers to predict the performance of concrete under various conditions, thereby facilitating the development of more sustainable and high-performance construction materials.

3.2 Modelling techniques for predicting the performance of concrete

3.2.1 Analytical methods

Compressive strength models have been proposed based on the conceptual postulation of how the hydrated cement interacts with other particles (i.e., aggregates) and hardens (Chidiac et al., 2013). The literature demonstrates that Feret was the first to develop a relationship between compressive strength and the ratio of cement to paste and air, as shown by expression 1 in **Table 3.1**, in 1892, by postulating that the strength mainly depends on the volume fraction of cement, water and air in concrete (Feret, 1892). However, Popovics reported a poor agreement with experimental data and this ratio, and the proportionality coefficients had to be determined for each trial mix. These features of this model limited its usage (Popovics, 1985). In 1919, Abrams proposed a model by considering the ratio of water to cement in replacement for the ratio of cement to paste and air in the Feret model, as shown by expression 2 in **Table 3.1**, because the expression was more straightforward and showed consistency with experimental strength data for non-air entrained concrete (Abrams, 1919). However, the model could not be widely accepted as the coefficients (A and B) varied with cement type and strength, curing and testing conditions, and concrete age (Karni, 1974; Moutassem and Chidiac, 2016). Coefficients A and B were estimated to be 96 MPa, and 7 or the concrete was made with a water-cement ratio between 0.3 and 1.2 (Abrams, 1919).

Similarly, in 1926, Slater (Slater, 1926) demonstrated that the strength of concrete linearly changes with the w/c ratio, as given in expression 3 in **Table 3.1**, and later his concept was adopted in ACI 2000 I (ACI 2000-I, 2000). Importantly, Slater's model can only be used to predict the strength of concrete without a superplasticizer in its mixture. Powers and Brownyard (Powers and Brownyard, 1946) slightly modified Feret's model with another factor, gel-to-space ratio (X), by considering how the porosity of the cement paste influenced the concrete strength in 1946. The gel-to-space ratio was defined as the volume of hydration products (gel) divided by the sum of the volumes of gel and capillary pores.

In addition, they have introduced the degree of hydration (α) in their strength model. Hence, his model can be used to calculate the strength of concrete made with a particular water-cement ratio and no air voids at a certain degree of hydration, as given in expression 4 in **Table 3.1**. However, the model did not account for different cement strengths (i.e., CEM I 32.5 or 42.5) (Karni, 1974), and a degree of hydration has to be found. Thus, Tango (Tango, 2000) attempted to simplify Powers and Brownnyard's model by substituting the degree of hydration with the function of transformed time, which accounts for initial hydration and its derivative, as given in expression 5 in **Table 3.1**. Although the model becomes more straightforward with easily found concrete properties such as water-cement ratio and concrete age, two more (D and E) calibration coefficients were included, which restricted the application of the model. Karni (Karni, 1974) has reviewed Powers and Brownnyard's model and suggested that the volume of the gel should be related to the overall volume of the paste deducts anhydrate cement because anhydrate cement is embedded particles and does not affect the concrete strength. This deduction was recommended to avoid the fraction of capillary pores, which depend on the degree of hydration and the water-cement ratio (Karni, 1974). Hence, Karni postulated that the deduction of dry (anhydrate) cement from gel does not affect the availability of "space", whereas the additional air (bubble) leads to increasing the space (Karni, 1974). Thus, following Bolomey's formula (Bolomey, 1935), as given in expression 6 in **Table 3.1**, Karni concluded that this effect shows linear proportionality with compressive strength, as shown by expression 7 in **Table 3.1**.

In 1985, Popovics studied Bolomey's linear model, which depends on the water-cement ratio, and then incorporated the empirical effect of air content shown by expression 8 in **Table 3.1** (Popovics, 1985). Thirteen years later, Popovics (Popovics, 1998) modified Abrams' model by incorporating a cement model, which accounts for the hardening of cement (C_3S and C_2S) using a mathematical approach that considers the hardening of cement as the sum of the first-order reaction of two hardening processes, as given in expression 9 in **Table 3.1**. In addition, the air content was empirically accounted for in the model, but aggregate properties and gradation were not considered. In 2008, the same

researcher realized that the given water-cement ratio could have different strengths with its cement content. In other words, the one with higher cement content yielded a lower strength (Popovics and Ujhelyi, 2008). Thus, Popovics and Ujhelyi (Popovics and Ujhelyi, 2008) suggested a modification to Abram's model by incorporating the cement content and air content empirically, as shown by expression 10 in **Table 3.1**. However, a few concrete samples were used to calibrate these factors, and the revised model was insignificant compared to the original model (De Brito et al., 2018).

De Larrard (De Larrard, 1999) noted that when a compressive force is applied to a dry-packed mixture of particles, the coarse particles experience the maximum stress accordingly by pouring cement paste into that mixture, the paste confined by coarse particles will also experience the same stresses. He then proposed a formula, as given in expression 11 in **Table 3.1**, to calculate the distance between the aggregates, defined as Maximum Paste Thickness (MPT) (De Larrard, 1999). Based on this theory, he amended Feret's model by considering the effect of the aggregate maximum size, packing density, and concrete age, as shown by expression 12 in **Table 3.1**. It should be noted that De Larrard was the first to incorporate aggregate properties into strength models. Further, he developed his model to account for the type of aggregates using coefficients m_1 and m_2 , as given in expressions 13 and 14 in **Table 3.1**. In addition, a formula for cement paste strength, f'_{cm} , was further modified empirically to accommodate the effect of pozzolanic admixtures and limestone fillers (De Larrard, 1999). Besides, De Larrard's model, which contributed significantly to current strength models, did not account for cement's chemical and physical properties and degree of hydration, and experimental data used to validate the formula was insignificant (De Brito et al., 2018). Mechling et al. (Mechling et al. 2009) revisited de Larrard's model and incorporated the effect of the chemical composition of cement, such as C_3S content, as given in expression 15 in **Table 3.1**.

In 2013, Chidiac et al. (Chidiac et al., 2013) formulated a new compressive strength model to predict the strength of concrete based on the excess paste theory, which says the excess amount of cement paste (needed to fill up the voids between the coarse particles)

lubricates the particles and disperses in the concrete mix (Mechling et al., 2009; Powers and Brownyard, 1946). Accordingly, they have mathematically developed the Average Paste Thickness (APT) theory to account for aggregate gradation and mixture proportions. In addition, they have incorporated the following models: the cement hydration model (Schindler and Folliard, 2005) to account for the chemical properties of cement and degree of hydration, the bond strength model developed by de Larrard to account for the cement paste to aggregate bond strength, cement strength model developed by de Larrard to account for the cement strength class and Popovic's model (Popovics, 1985) to calculate capillary pores and air pores. The Chidiac model's final form is expressed in expression 16 in **Table 3.1**. The cement hydration model proposed by Schindler and Folliard (Schindler and Folliard, 2005), as shown by expression 17 in **Table 3.1**, has been adopted in the Chidiac et al. model. One of the significances of the model is that Chidiac et al. incorporated the actual strength developing pattern in which strength is zero until a degree of hydration reaches a critical value, and then it develops strength linearly proportional to the degree of hydration. The expression 18 (in **Table 3.1**) was proposed by Rasmussen et al. (Rasmussen et al., 2002) to calculate the critical degree of hydration, in which the constant “k” is 0.43 for OPC.

The Chidiac et al. model is a complete analytical strength model compared to previous models, as it accounts for the most critical factors affecting concrete strength. The model can be used to design concrete mixtures for specific strength requirements, determine the strength in less than three days to check whether the concrete achieved the required strength before removing the formwork, and optimize the aggregate content in the mixture using average paste thickness (Chidiac et al., 2013). However, the Chidiac model was validated using only 28 concrete samples with a water-cement ratio between 0.4 and 0.7, with water content ranging from 175 to 228 kg/m³. Therefore, this model may not be applicable, especially for high-strength concrete, to predict the general compressive strength of the water-cement ratio less than 0.3 (Asselani et al., 1989).

Moreover, there have been many purely empirical models (Adewole et al., 2014; Caquot, 1937; Fuller and CE, 1907; Hicks, 2009; Pann et al., 2003; Yeh, 2006) which generally postulate refinement to Feret's model or Abram's model. For instance, Cheng (Yeh, 2006) worked on the Abrams model and then empirically incorporated the effect of concrete age on strength. Similarly, Pann et al. (Pann et al., 2003) modified the Abrams model empirically to include the capillary porosity of cement paste and claimed his revised model was superior to Abram's model. In addition, several statistical (Hwang et al., 2001; Namyong et al., 2004; Nipatsat and Tangtermsirikul, 2000) or mathematical (Hamid et al., 2006; Kabir et al., 2012; Zain and Abd, 2009) models have been developed through the years mainly based on the mixture proportions or early strength of concrete, whereas those models did not account for the cement properties, gradation of aggregate and the age of concrete.

Table 3.1: Summary of analytical models for predicting concrete strength

No	Mathematical expressions	Notations	Reference
1	$f'_c = A \left(\frac{V_c}{V_c + V_w + V_a} \right)^B$	V_c, V_w, V_a : volume fractions of cement, water and air, respectively	(Feret, 1892)
2	$f'_c = \frac{A}{B^{w/c}}$		(Abrams, 1919)
3	$f_{cm} = 0.007(2700 \times \frac{c}{w} - 760)$	c/w : cement to water ratio	(Slater, 1926)
4	$f'_c = A(X)^B = A \left(\frac{0.66 \alpha}{\frac{w + V_a}{c} + 0.32 \alpha} \right)^B$	X : gel-to-space ratio α : degree of hydration V_a : volume fraction of air	(Powers and Brownyard, 1946)
5	$f'_c = \frac{A}{B^{(\frac{w}{c})} E^{(\frac{w}{c})} t^{-0.5} D^{t^{-0.5}}}$	w/c : water to cement ratio t : concrete age	(Tango, 2000)
6	$f_{cm} = A1 \left(\frac{1}{w/c} - 0.5 \right) \quad \text{if } w/c > 0.4$ $f_{cm} = A2 \left(\frac{1}{w/c} + 0.5 \right) \quad \text{if } w/c \leq 0.4$		(Bolomey, 1935)

7	$f'_c = A \left[\frac{\alpha \times 100}{1.53 \left(\frac{w + V_a}{c} \right) + \frac{\alpha}{2.066}} - B \right]$	X : gel-to-space ratio α : degree of hydration V_a : volume fraction of air (Karni, 1974)
8	$f'_c = A \frac{c}{w} + B \times 10^{-0.038V_a}$	V_a : volume fraction of air (Popovics, 1985)
9	$f'_c = \frac{A}{B^{w/c}} \sqrt{\frac{S_s}{S_o}} \cdot \frac{100 - C_3 S e^{-b_1 t} - (100 - C_3 S) e^{-b_2 t}}{100 - C_3 S e^{-90 b_1} - (100 - C_3 S) e^{-90 b_2}} \times 10^{c.V_a}$	$C_3 S$: weight ratio t : concrete age S_s, S_o : the specific surface of the cement and that of a typical ASTM type 1 cement (Popovics, 1998)
10	$f'_c = \frac{A}{B[(W/c)+mc]} \times 10^{-0.038V_a}$	V_a : volume fraction of air (Popovics and Ujhelyi, 2008)
11	$MPT = D_{max} \left(\sqrt[3]{\frac{\phi^*}{\phi}} - 1 \right)$	ϕ^* or ϕ_{max} : maximum packing density of aggregates ϕ, ϕ_s, ϕ_{ca} : volume fraction of aggregates, fine and coarse aggregates (De Larrard, 1999)
12	$f'_c = K R_{c28} \left[A \log(t/28) + \left(\frac{V_c}{V_c + V_w + V_a} \right)^B \right] MPT^m$	D_{max} : maximum diameter of the total particles gradation R_{c28} : standard cement strength at 28 days

$$13 \quad f'_c = \frac{m_1 f'_{cm}}{m_2 f'_{cm} + 1}$$

$$14 \quad f'_{cm} = 13.4 R_{c28} \left[A \log(t/28) + \left(\frac{V_c}{V_c + V_w + V_a} \right)^B \right] MPT^m$$

$$15 \quad f'_c = K R_{c28} (0.2 [C_3 S] - 1.65) \times \left[A \log(t/28) + \left(\frac{V_c}{V_c + V_w + V_a} \right)^B \right] MPT^m$$

$$16 \quad f'_c(t) = \begin{cases} 0 & \alpha(t) \leq \alpha_{cr} \\ K R_{c28} \left(\frac{APT}{D} \right)^A B^{\frac{w+V_a}{c}} (\alpha(t) - \alpha_{cr}) & \alpha(t) > \alpha_{cr} \end{cases}$$

K : paste to aggregate bond strength constant

t : concrete age

f'_{cm} : compressive strength of the matrix

$C_3 S$: weight ratio

APT : average paste thickness of aggregates

D : mean diameters of the total particles gradation

α, α_{cr} : degree of cement hydration, critical degree of cement hydration (Mechling et al., 2009)

D, D_s, D_{ca} : mean diameters of the total particles gradation, fine aggregate gradation, and coarse aggregate gradation

Where,

$$\begin{aligned} APT & \approx -\frac{1}{2} \left(D_s + \frac{\phi_{ca} D_s^2}{\phi_s D_{ca}} + \frac{\phi D_s^2 (1 - \phi_{max})}{\phi_s \phi_{max} D} \right) \\ & + \frac{1}{2} \sqrt{\left(D_s + \frac{\phi_{ca} D_s^2}{\phi_s D_{ca}} + \frac{\phi D_s^2 (1 - \phi_{max})}{\phi_s \phi_{max} D} \right)^2 + \frac{4 (\phi_{max} - \phi) D_s^2}{\phi_{max} \phi_s}} \end{aligned}$$

(Chidiac et al., 2013)

17	$\alpha = \alpha_u \exp \left(- \left[\frac{\tau}{t_e} \right]^\beta \right)$ Where, $\tau = 66.78 \cdot p_{C3A}^{-0.154} p_{C3S}^{-0.401} \cdot Blaine^{-0.804} p_{SO3}^{-0.758} \cdot \exp(2.187 \cdot p_{SLAG} + 9.5 \cdot p_{FA} \cdot p_{FA-CaO})$ $\beta = 181.4 \cdot p_{C3A}^{0.146} \cdot p_{C3S}^{0.227} \cdot Blaine^{-0.535} \cdot p_{SO3}^{0.558} \cdot \exp(-0.647 \cdot p_{SLAG})$ $\alpha_u = \frac{1.031 \cdot w/c}{0.194 + w/c} + 0.50 \cdot p_{FA} + 0.30 \cdot p_{SLAG} \leq 1.0$	α_u : ultimate degree of cement hydration τ, β : hydration time parameter and hydration shape parameter t_e : equivalent age $p_{C3A}, p_{C3S}, p_{SO3}$: weight ratios in terms of total cement content $p_{FA}, p_{SLAG}, p_{FA-CaO}$: weight ratios of mineral admixtures proportions in terms of total cement content	(Schindler and Folliard, 2005)
18	$\alpha_{cr} = k \times w/c$	α_{cr} : critical degree of cement hydration k : Constant	(Rasmussen et al., 2002)

$A, A1, A2, B, b1, b2, D, E, m, m1, m2$: Calibration coefficients, w/c : water to cement ratio

The predictive precise of the analytical models of Chidiac et al. (Chidiac et al., 2013), Mechling et al. (Mechling et al., 2009), de Larrard (De Larrard, 1999), Tango (Tango, 2000), Pann (Pann et al., 2003), Popovics (Popovics, 1998), Karni (Karni, 1974), Popovics (Popovics and Ujhelyi, 2008), Powers and Brownyard (Powers and Brownyard, 1946), Popovics (Popovics, 1985) and Feret (Feret, 1892) were assessed using over 250 experimental concrete strength results from different concrete mixtures, by Moutassem et al. (Moutassem and Chidiac, 2016). The compressive strength at different ages (i.e., 3, 7, 28 and 191 days) and mixture proportions of regular concrete were collected from seven works of literature (Chidiac et al., 2013; Gardner, 1990; Kim et al., 1998; Namyong et al., 2004; Popovics et al., 2005; Walker and Bloem, 1960; Zain and Abd, 2009). The constant parameters in each model were calibrated according to the experimental data as a different aggregate type was used for different works of literature. The 28th-day compressive strength of all mixes and models was computed using the calibrated parameters and theoretical variables. The authors have determined the correlation coefficient (R^2) to measure the goodness of the results from each model and experimental data. The assessment results revealed that among the other models, the Chidiac model, which mathematically accounts for the effect of APT, provided very close values to the experimental data. Also, the R^2 computed for the Chidiac model was the highest value equal to 0.89.

The comprehensive literature review reveals that compressive strength models have been developed in various forms over the years but are mostly limited to conventional concrete or normal concrete. Therefore, further research should be carried out to formulate a model which realistically predicts the strength of concrete based on the microstructure of the hardened cement paste along with other strength influencing factors for full-spectrum (short and long term), as the structure of the hardened cement paste has been identified as the main controlling factor on concrete strength in the recent years (Bentz, 1999).

3.2.2 Machine learning

It is well known that concrete constituents such as cement paste, aggregates and additives possess great chemical and physical complexity. Thus, developing a strength prediction model that simultaneously accounts for the effect of essential influence factors such as chemical and physical properties of cement, aggregate bond strength, aggregate properties, cement hydration, etc., is a great challenge using an analytical or mathematical approach. Therefore, in recent years, researchers have started using machine learning (ML) techniques to estimate concrete strength as ML has already proven its extraordinary complex problem-solving ability in the construction field, including quality management, optimizations in design, fracture mechanics, structural health monitoring and risk control (Cheng et al., 2014; Shahin, 2016; Taffese and Sistonen, 2017). Machine learning, a subset of Artificial Intelligence (AI), works on algorithms that allow computers to learn from a given data set without being programmed explicitly (Marsland, 2011). It should be noted that many studies have been carried out to predict the compressive strength using ML techniques for particular types of concrete, such as ultra-high-performance concrete, recycled aggregate concrete, self-consolidating concrete, fibre-reinforced concrete, etc., as novel concrete requires complex mixture design due to the large number of mixture components, which led to complex non-linear relationships (Abuodeh et al., 2020; Cascardi et al., 2017; Deng et al., 2018; Ke and Duan, 2021). On the other hand, ML is not popular for predicting the compressive strength of conventional concrete because the correlation between concrete strength and mixture contents could be modelled simply by applying traditional statistical procedures such as linear and non-linear regression analyses, and those models have shown prediction accuracy satisfactorily (Chou and Pham, 2013; Ni and Wang, 2000; Unanwa and Mahan, 2014).

The machine learning model is established by dividing the input data for training, validation, and testing. In the training step, the model learns the underlying patterns in the data. The validation step helps to assert the results predicted during training, and eventually, at the testing step, testing on new data that was not included in the training

step is used to evaluate the performance of the prediction of the developed model (Marsland, 2011). Critical importance should be given to selecting appropriate hyper-parameters that are user-defined when configuring ML models to gain the best predictive accuracy of ML models. For instance, the hyper-parameter is the number of hidden layers in artificial neural networks (ANN), the regularization parameter for support vector machine (SVM) and the number of trees in tree-based ensembles (Tsirikoglou et al., 2017). Since hyper-parameters are specific to the model and data set, an appropriate selection of hyper-parameters is crucial to avoid overestimation (Tsirikoglou et al., 2017). Thus, model configuration and tuning its hyper-parameters are essential steps to better realize the performance of the applied algorithm for a specific problem (Chopra et al., 2015). To predict the compressive strength of concrete, various ML algorithms such as ANN, SVM, Genetic algorithms, tree-based ensembles and hybrid procedures have been studied in the literature (Gupta, 2006; Topcu and Saridemir, 2008; Xu et al., 2019). In predicting the compressive strength of conventional and non-conventional types of concrete mixtures ANN technique, which functions similarly to human neural systems (Prieto et al., 2016), is widely used (Ni and Wang, 2000). Generally, the ANN model has three layers: the input layer, hidden layer, and output layer, as shown in **Figure 3.1**. The first layer is the input layer, where a weight is assigned to each input parameter, while the last is the output layer. In each of the layers in ANN, there are nodes called neurons that process the data in the network by a sum and transfer function (Agatonovic and Beresford, 2000). Finally, the output is calculated through the activation function. The prediction accuracy of ANN models mainly depends on the number of neurons in the hidden layer, one of the hyperparameters in ANN, as high numbers of neurons have been reported to enhance the closeness of model output (Chopra et al., 2015).

Several researchers have considered different factors that influence concrete strength as input variables. Xu et al. (Xu et al., 2019) have identified key variables such as water-cement ratio, maximum aggregate size, and aggregate-to-cement ratio for their study to estimate the mechanical properties of concrete that incorporated recycled concrete aggregates in its mix using ANN. Similarly, the studies using ANN to predict the

compressive strength of rice husk ash concrete, Ultra-High-Performance Concrete and fibre-reinforced high-strength self-compacting concrete concluded that ANN outperformed other ML models and measured the highest overall coefficient of determination (R^2). Therefore, the ANN approach is highly recommended to predict the compressive strength of concrete, especially for novel concretes, due to its versatility and simplicity without being written for heavy programming (Cascardi et al., 2017; Khademi et al., 2016; Xu et al., 2019). In addition, ANN has several merits, such as being able to predict accurately even with poor or corrupted data sets, being a self-adapting model to different environmental conditions, having parallel processing capabilities, and having highly non-linear mapping properties. In comparison, the lack of clarity in their predicting process (black box system) limits its wide application (Nunez et al., 2021).

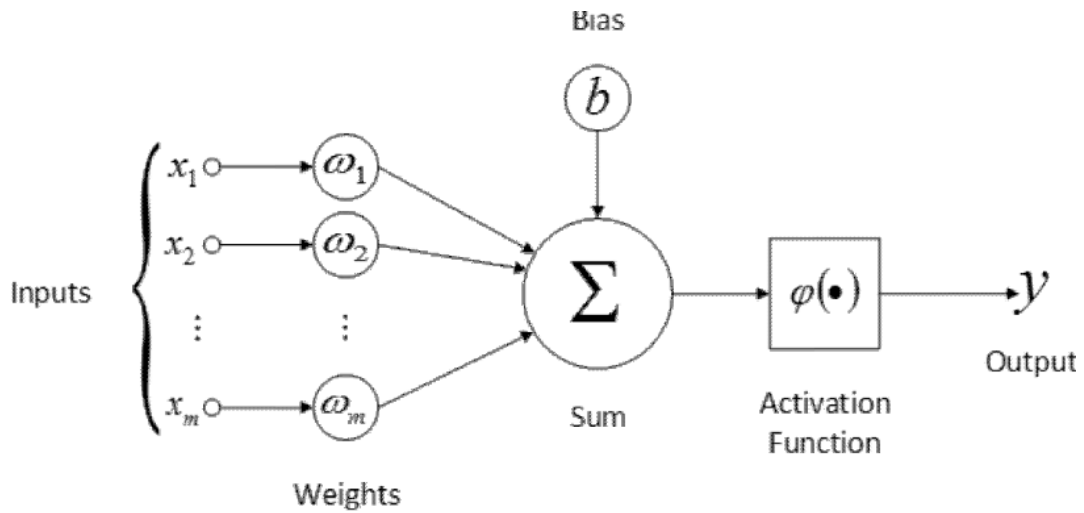


Figure 3.1: Schematic representative of Artificial Neural Network (Sampaio et al., 2021).

An SVM, commonly used for classification and regression analysis, is also employed to predict the compressive strength of high-performance concrete [64,84]. It should be noted that SVMs help find the global minimum, whereas other models, including ANN, find undesirable local minima (Lin et al., 2006). However, the prediction accuracy of SVM models depends on optimising hyperparameters such as the regularization parameters and

kernel functions (Yu et al., 2018). Yu et al. (Yu et al., 2018) used a support vector machine to predict the compressive strength of HPC. They also adopted an enhanced cat swarm optimization (ECSO) algorithm to improve the predictive ability of the model and found the optimal hyperparameters, including the penalty function, kernel function parameter and the intensive loss factor, which is consistent with similar studies (Cheng et al., 2014; Mustapha and Mohamed, 2017). Moreover, even though SVM models work well with smaller sample sizes and computation time, the prediction accuracy highly depends on the selected weighting function, and SVM models show comparatively less predictive accuracy than ANN models.

The genetic algorithm has become popular among ML models to predict the compressive strength of concrete in recent years, and it has been addressed to the “black box” operation of many ML models such as ANN (Nunez et al., 2021). It is developed through the inspiration of Darwin’s theory of evolution (survival of the fittest), as shown in **Figure 3.2**. Gene expression programming (GEP), genetic programming (GP), and genetic algorithm (GA) are commonly used genetic models reported in the literature to model the compressive strength of special types of concrete (Castelli et al., 2013; Cheng et al., 2014; Mousavi et al., 2012). Besides, in most studies, it has been recorded that genetic models could not predict with higher accuracy than ANN. However, the predictive accuracy of genetic models can be improved when combined with other algorithms. For example, Chen and Wang [89] carried out the research by combining grammatical evolution (GE) with a genetic algorithm (GEGA) to predict the compressive strength of high-performance concrete. They compared the results with multiple regression analysis and ANN with a back propagation network (BPN). They found that improved GEGA showed better accurate results than BPN, accounting for 4 %.

The hyper-parameters that have been generally used in genetic models are a population of chromosomes, crossover and mutation (Mitchell, 1999), and the reported values are 100 or 200, 0.1–0.8 and 0.044–0.3, respectively (Nunez et al., 2021). Mousavi et al. (Mousavi et al., 2012) proved that genetic models are effective techniques compared to

other regression models for estimating the compressive strength of high-performance concrete. Their study considered water, cement, blast furnace, slag, fly ash, superplasticizer, coarse aggregate, fine aggregate, and age of specimens.

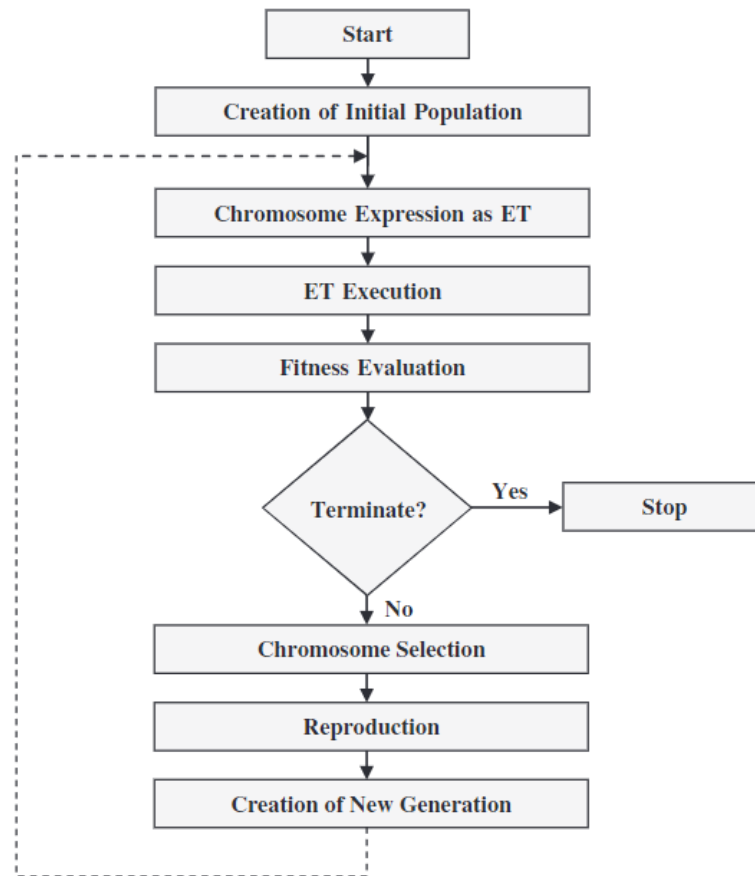


Figure 3.2: A simple representation of the GEP algorithm (Mousavi et al., 2012).

Tree-based ensembles, including random forest, extra trees, and gradient boosting, have been successfully used to estimate the compressive strength of different types of concrete, such as high-performance and ultra-high-performance concrete. Such ensembles are recommended due to their enhanced performance with reduced variables and over-fittings. Kaloop et al. (Kaloop et al., 2020) deployed a gradient tree boosting model to evaluate the compressive strength of high-performance concrete using 1030 data sets along with nine variables. They noticed that ensembles could estimate the concrete strength with

superior accuracy where the correlation coefficient and mean absolute error (MAE) were 0.965 and 0.037 MPa, respectively. However, tree-based ensembles deliver significantly less accurate results than ANN and SVM models.

Furthermore, to address the demerits of each ML model discussed above, hybrid procedures have been introduced to improve the functionality of the ML models, where two different algorithms or ML models are coupled. Coupling is executed in either way: 1) an optimization algorithm is deployed to tune the hyperparameters of the base ML model, or 2) tuned ML models are coupled with an optimization algorithm to get the optimum mix design of concrete incorporating several optimization considerations, including cost, workability, and environmental impact (Ke and Duan, 2021; Vakhshouri and Nejadi, 2018). Hybrid models were studied using a different combination of optimum algorithms and ML models in the literature, which is proven effective (Erdal, 2013).

Overall, ML techniques have successfully predicted the compressive strength of different types of novel concretes. Since ML algorithms are most efficient in data analysis, they can be utilized to conduct a parametric study of mixture proportions for different types of concretes without extensive experimental programs. In addition, such a study by ML models reduces the significant cost associated with laborious trial mixes, the need for human resources and material wastage. However, the performance of the ML models highly relies on the sample data set and hyper-parameters, not based on the hydration process and concrete microstructure. There is no definite rule yet for selecting appropriate hyper-parameters and the size of data sets for model training and validation (Raudys and Jain, 1991). Thus, assessing the performance of ML modes adopted in similar studies is difficult.

3.2.3 Cement hydration model

In recent years, efforts have been carried out to simulate the hydration of complex cementitious materials realistically and their fresh and hardened multi-phase microstructure using high-performance computers as a virtual experimental tool (Bentz,

1999; Jennings et al., 2008) as conventional analytical models such as the nucleation growth model could not accurately predict the strength development, porosity and heterogeneity of multiple cement phases (Thomas et al., 2011). Computer modelling of hydration was initiated with the development of ‘computational material science’, which defined the ability of the computer to predict the microstructure of the cementitious materials at the appropriate length scale using algorithms that compute accurate mechanical properties (Bentz, 2001). Wittmann et al. (Wittmann et al. 1985) were the first to simulate the structure of concrete in two-dimensional (2D) space numerically, where aggregates dispersed in a cement paste matrix representing concrete microstructure were generated and mapped onto a finite element grid. Thus, the properties such as thermal conductivity and elastic moduli were computed. Then, in 1986, Jennings and Johnson (Jennings and Johnson, 1986) developed a three-dimensional (3D) model, independently simulating the hydration processes of C_3S . Their pioneering work contributed to considering the microstructure prediction on a micrometre scale, which means it is at the cement particle level (Bullard et al., 2004). A range of cement particle sizes, representing the actual particle distribution of cement, were modelled as continuum spherical particles that were dispersed randomly in a defined 3-D space where conditions were applied to spherical particles to dissolve and hydration products (especially C-S-H) to grow outward of the spherical surface concentrically (Liang, 1997). The model was further developed, incorporating the particle size distribution and chemical composition of the cement, water-cement ratio and the actual reaction temperature, and finally released with the name “HYMOSTRUC” in 1994 (Breugel, 1995).

HYMOSTRUC, a three-dimensional numerical model, could simulate the hydration and development of the microstructure of cement paste, as shown in **Figure 3.3**, by considering the complexity of the hydration and the process involved in microstructural development. Thus, the model mainly emphasized the formation of interparticle contacts between swelling cement particles on a serological aspect and other factors like chemical composition, particle size distribution, water-to-cement ratio, and temperature regime. The detailed model development can be found in (Breugel, 1995). Even though the

microstructure mentioned above model was not capable of directly predicting the mechanical properties (compressive strength and elastic moduli) of concrete, Breugel (Breugel, 1992) proposed a composite model named the ‘bar model’, which says that mechanical properties develop with the evolution of connectivity between solid phases during hydration, to be used at the concrete scale. However, the proposed bar model overestimates the elastic moduli for a lower degree of hydration, especially for less than 0.2 (Stefan et al., 2010), and further research is recommended to include the chemical aspects even though the HYMOSTRUC model showed comparable results with experimental data.

Further, researchers (Bentz, 1999) from the National Institute of Standards and Technology (NIST) idealized a simple microstructure model while trying to apply a random walk algorithm to Jennings’s continuum model. The simple model was then developed using the ideas of the random walk algorithm and digital images. Subsequently, the model, named “CEMHYD3D”, predicts the digital image of the three-dimensional microstructure of cement paste and thus computes the chemical shrinkage and physical properties such as elastic moduli (Liang, 1997).

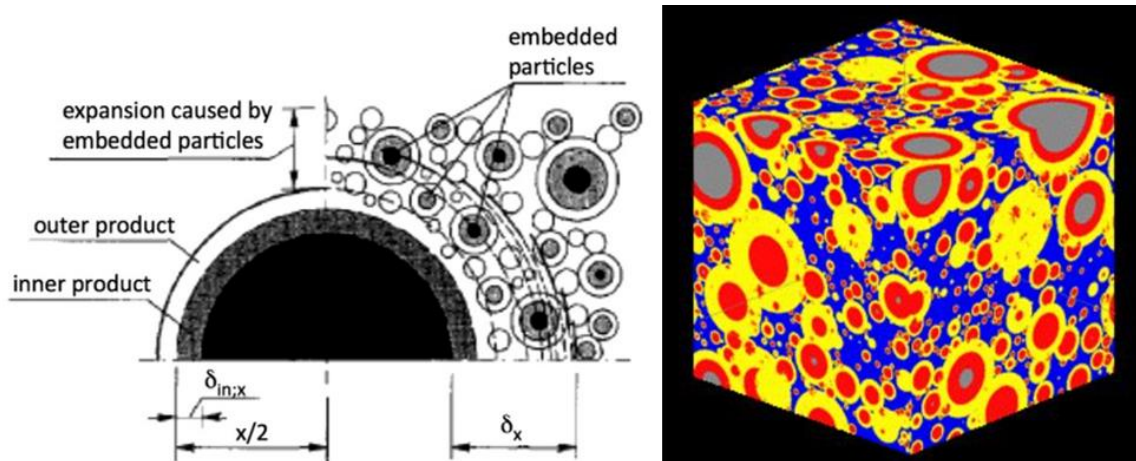


Figure 3.3: Representation of concentric growth of sphere particles (left) (Thomas et al., 2011) and the microstructure of cement paste after hydration (right) (Cement, 2012) using the continuous approach in the *HYMOSTRUC* model.

The CEMHYD3D model predicts cement paste's hydration and microstructure development, as shown in **Figure 3.4**, based on the minimum input data such as measured particle size distribution and detailed SEM/X-ray image of cement powder (Bullard et al., 2004). The correlations files were developed to convert the properties, such as volume fractions and surface fractions measured in 2D to 3D. Then, the four major clinker phases (C_3S , C_2S , C_3A , and C_4AF) are randomly distributed in a computational volume that consists of a uniform grid of cubic volume pixels called “voxels”, and the microstructure is then fed into the hydration model where curing conditions (sealed, saturated, isothermal, semi-adiabatic and temperature) can be defined by the user. The evolution of the microstructure of cement paste is simulated using cellular automata (CA), where random-walk voxels are assigned to diffusion particles to perform collisions and reactions (Bishnoi and Scrivener, 2009). The detailed modelling program is available in (Liang, 1997). As hydration progresses, properties like chemical shrinkage, heat release, setting, capillary porosity, percolation, pH, concentrations of pore solution, and strength development can be output as a function of hydration time.

Moreover, significant refinements such as incorporating the effect of limestone fillers, the reaction of slag and the measurement of pH and pore solution concentrations during hydration were made for the broad application of the model. However, even the voxel approach used in the CEMHYD3D model has the main advantage of representing the special distribution of different phases and shapes. Particle sizes which are less than the size of mesh (voxels) cannot be modelled (Bishnoi and Scrivener, 2009), and the number of voxels is limited to one to ten million in general simulations so that particles in the size of $0.1\text{ }\mu\text{m}$ or less cannot be modelled (Garboczi and Bentz, 2001). In addition, the kinetics of structural development used in the model were simulated using semi-empirical parameters that must be verified against experimental results for each mix design (Jennings et al., 2008). Notably, the CEMHYD3D model could not be used to predict the compressive strength of concrete straightly, but the output from the model can be used to estimate compressive strength using Power's model, which states concrete strength is proportional to the gel-space ratio (Bishnoi et al., 2018).

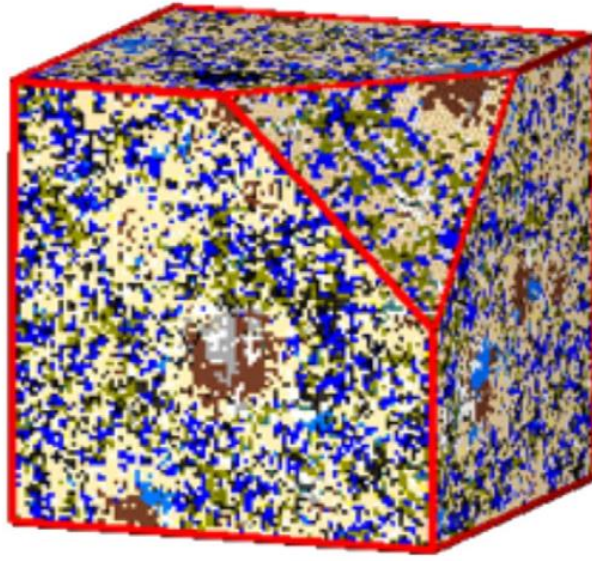


Figure 3.4: Microstructure of (14-day aged) hydrated OPC paste simulated using CEMHYD3D (Bullard, 2002).

Similarly, in recent years, several advanced microstructural models including HydratiCA (Bullard, 2007), μic (Bishnoi and Scrivener, 2009), Integrated Particle Kinetics Model (IPKM) (Pignat et al., 2005), etc. have been developed based on the well-studied principles of the CEMHYD3D model and HYMOSTRUC model to overcome the problems such as resolution inadequacy in CEMHYD3D and non-accountability of real solution phase chemistry in HYMOSTRUC. The μic (pronounced “mike”) model is a recently released microstructural modelling platform developed based on the original vector approach by Jennings and Johnson, as discussed above. **Figure 3.5** illustrates the system's microstructure with a wide range of particle sizes, such as cement with fine fillers. Since it is well known that concrete is a multi-phase material, the output from these models has been correlated with the compressive strength of concrete using various techniques, including homogenization and multi-scale model techniques (Chen et al., 2016; Haile et al., 2019; Hlobil et al., 2016; Ulm et al., 2004), perhaps due to the inability of incorporating the fracture mechanics into such microstructural models (Bishnoi et al., 2018). Homogenization and multi-scale model techniques state that the estimated

heterogeneity properties of the nanoscale systems can be up-scaled to the macroscopic scales since the nanoscale system (i.e., C-S-H globule) has many parallel similarities with cementitious materials (Jennings et al., 2008).

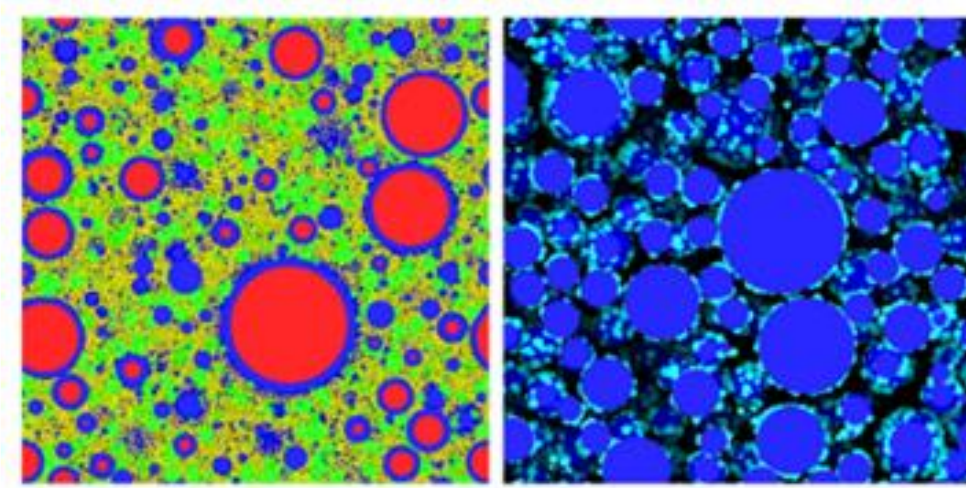


Figure 3.5: Simulated microstructure with fine fillers and a large number of particles (left) and after hydration (right) using μic platform (Thomas et al., 2011).

Furthermore, Maekawa et al. (Chaube et al., 1999) attempted to develop a multi-scale model to predict the performance and durability of structural concrete in 1999 and later, in 2009, the model was released under the name DuCOM (Durability CONcrete Model) with advanced features including structural, mechanical analysis in the range of 10^{-3} to 10^{-1} meter scale volume that includes micro-cracks (Chaube et al., 1999; Maekawa et al., 2008). Chemo-physics was systematically integrated to predict the macroscopic material properties from the microstructure of cementitious materials. Prime consideration was given to the nano-micro-pores (ranges from 10^{-9} to 10^{-3} m) where thermo-dynamic reactions and hydrology physics control the formation of mutual linkage of micropore structure of cementitious materials. Even though the DuCOM model was developed by considering the hydration and nanostructure of cementitious materials, the model is presented in explicit mathematical formulae (not pixel-based). Nearly 250 non-linear governing equations were developed to incorporate the events such as cement hydration,

pore structure formation, water transport in micropores, etc., in the range of a 10^{-9} to 10^0 -meter scale, as shown in **Figure 3.6**, to simulate the microstructure of the cementitious materials and to quantitatively predict the macroscopic properties such as strength and stiffness by upscaling (Maekawa et al., 2008). In addition, in the model, the strength prediction of concrete accounted for factors like water-to-binder ratio, mineral composition of cement, curing temperature, internal porosity and admixtures (silica fume). Even though the strength predictability of the DuCOM model was verified with available literature with 2.95 N/mm² of standard deviation, the model did not account for the fundamental factors that affect the concrete strength, such as aggregate properties (strength), ITZ, air content, etc. (Chaube et al., 1999; Ishida and Maekawa, 2013). However, the DuCOM model, among the several strength prediction models, directly correlates the strength of cement paste to the strength of concrete, whose features extend its wide applications.

Notably, the fundamental issues in the existing models must be addressed to extend the predictive capacity of new cementitious materials (Garboczi and Bentz, 2001; Jennings et al., 2008; van Breugel, 1995). Therefore, there is a need for a more robust model that can realistically predict the properties of concrete. However, it seems possible only with collaborative efforts from different disciplines. For example, the predictive model will become more powerful once the experimental result of the nanostructure of cement paste is available. In addition, the new model should follow fundamental chemical and physical principles, including the nanostructure of C-S-H and thermodynamic consideration to be applied to the system containing mineral admixtures.

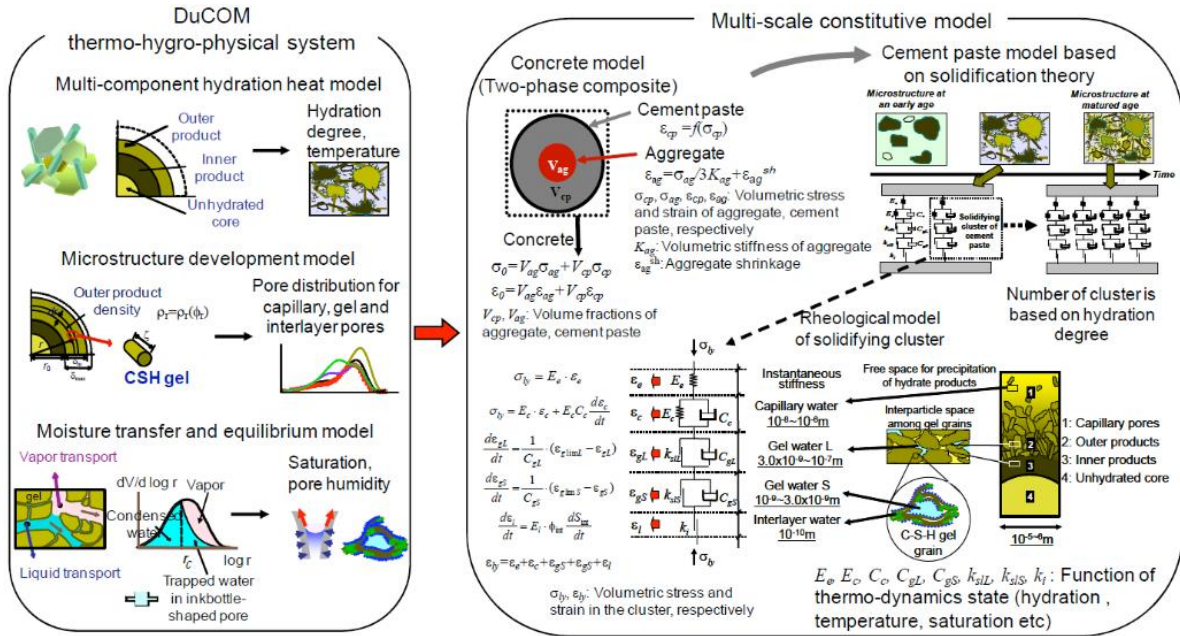


Figure 3.6: A schematic representation of the multi-scale approach in the *DuCOM* model (Ishida and Maekawa, 2013).

3.3 Current approaches for predicting the performance of nano silica-modified cement composites

3.3.1 Homogenization Model by Kim et al. (2010)

Kim et al. proposed a homogenization model to investigate the effects of nano-silica on the strength and stiffness of concrete. This study utilized a composite homogenization method to model nano-silica reinforced cement paste, considering a four-phase system: hydrated cement paste, unhydrated cement paste, capillary pores, and unreacted nano-silica (J. J. Kim et al., 2010a). The volume fractions of these four phases within the representative volume elements (RVEs) were determined using cement hydration models. Nano-silica was integrated into the model by treating it as micro-silica with an equivalent surface area. Existing models for micro-silica hydration were applied to predict the

pozzolanic behaviour of nano-silica. Constitutive models for the four phases were derived from literature data. The cement paste was modelled as randomly distributed spherical particles of these four phases, and RVEs were developed accordingly. Suitable boundary conditions were applied to obtain the nano-modified cement pastes' compressive strengths and elastic properties. The modelling results indicated that increasing the nano-silica content (up to 10 % of the cement content) enhanced the strength and stiffness of the cement paste, as illustrated in **Figure 3.7**.

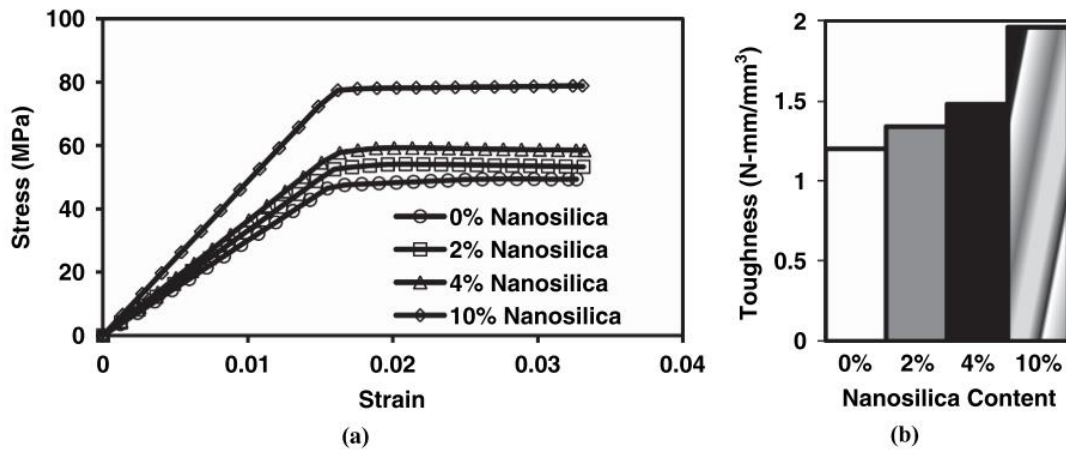


Figure 3.7: Effect of nano silica on the behaviour of cement paste: (a) stress-strain relationship and (b) toughness calculated as the area under the stress-strain curve.

While the proposed model is a valuable method for evaluating the characteristics of nano-silica-modified cement paste, it has several drawbacks. One significant issue is the incorporation of nano-silica reactivity. The authors used pozzolanic reaction models available for micro-silica to predict nano-silica performance, which is problematic because nano-silica and micro-silica do not behave identically during the hydration process (Mondal et al., 2010). Using pozzolanic reaction models designed for micro-silica may not accurately simulate the characteristics of nano-silica within the paste, potentially leading to errors in the final results.

Moreover, the authors did not validate the model for volume fraction calculation using experimental techniques, which would have strengthened their findings. Additionally, the model's predictions for compressive strength were not validated against experimental results or values from the literature. The study only modelled the cement paste without considering the mortar and concrete stages. Although the behaviour of nano-silica within cement paste can be indicative of its behaviour in concrete with similar nano-silica/cement proportions, it would have been beneficial for the authors to suggest a modelling approach for predicting the properties of nano-silica reinforced mortar and concrete or to conduct experimental analyses to relate the performance of cement paste to mortar and concrete.

3.3.2 Machine learning-based compressive strength estimation of nano silica-modified concrete.

Several researchers have employed ML models to predict the properties of nano-silica (NS)-modified concrete. The primary goal of this study is to enhance the accuracy of predicting compressive strength (CS) in NS-modified concrete, aiming to improve design efficiency and reduce costs. Traditional methods for determining concrete strength are labour-intensive, time-consuming, and costly. By providing quick and accurate predictions, ML techniques reduce the need for extensive physical testing, saving labour, time, and costs. Incorporating NS in concrete enhances its strength and durability, contributing to sustainable construction practices. The application of ML in analyzing concrete has garnered growing attention. However, a significant research gap exists in applying ML approaches in NS-modified concrete. Zaman et al. proposed ML models to predict the CS of cement paste, excluding the effects of fine and coarse aggregates (Zaman et al., 2023).

On the other hand, Garg et al. conducted ML analysis on NS-modified concrete using a relatively limited dataset of 100 samples (Garg et al., 2022). It is well-known that larger datasets typically yield more reliable results for ML models (Wang et al., 2020; Zhou,

2022). In this study, seven ML techniques are developed and evaluated using a larger dataset of 1143 samples, providing a comprehensive understanding of the interactions among various parameters in NS-modified concrete. The results and corresponding graphs are presented to exhibit their performance. The ML workflow in this study includes six stages: problem definition, data collection, data pre-processing, model development, model evaluation, and model deployment. The dataset comprises 1143 data points from 39 peer-reviewed research papers focusing on the CS of concrete containing NS. Key parameters influencing CS, such as cement content, water content, fly ash (FA), ground granulated blast-furnace slag (GGBS), silica fume (SF), NS, coarse aggregate (C-Agg), fine aggregate (F-Agg), superplasticizer (SP), water to binder ratio (W/B), age, and specific surface area (SSA) of NS, are included in the analysis. For consistency, CS values of different sample sizes were normalized to 150x150x150 mm cubes.

While the study makes significant strides in using ML to predict CS in NS-modified concrete, it has limitations. The models' capabilities are constrained by the dataset derived from existing literature, limiting their generalizability. The study's reliance on available data means that the ML models are only as robust as the dataset used for training. The study focuses primarily on CS without addressing other critical properties, such as durability and mechanical characteristics beyond compressive strength. This narrow focus may limit the practical applicability of the findings in real-world scenarios where a comprehensive understanding of concrete performance is necessary.

A notable drawback of this study lies in the method used to quantify the hydration characteristics of nano-silica concrete. Nano-silica's direct interaction with the cement paste in the reaction highlights the limited prominence of its effects on aggregate particles. For a more accurate modelling of nano-silica performance in concrete, separating the aggregate particles and focusing solely on analyzing the cement paste would have been advantageous. Subsequently, introducing the aggregate particles in a secondary step could have yielded more promising and reliable results than the proposed method.

Future research endeavours should prioritize the expansion of datasets to enhance the robustness and reliability of ML models. Researchers can improve the models' predictive power and generalizability by collecting more extensive and diverse datasets. Additionally, future studies should incorporate analyses of other essential concrete properties, such as durability and mechanical characteristics, using ML modelling techniques. This broader scope of analysis would enable the development of more comprehensive models for predicting the performance of NS-modified concrete in various applications. Furthermore, empirical validation of ML model predictions through extensive experimental testing is crucial to strengthen the credibility and applicability of the findings.

3.3.3 Multiscale approach to predict the compressive strength of nano-silica incorporated cement systems

The study by Rupasinghe et al. is significant as it addresses the need for a deeper understanding of the chemical characteristics of nano-silica integrated concrete and how these characteristics influence the material's mechanical properties (Rupasinghe et al., 2017a). By integrating experimental analysis with numerical modelling, the research aims to predict the performance of nano-silica-modified cementitious materials more accurately. Due to its high reactivity and small particle size, Nano-silica has the potential to enhance concrete's mechanical properties and durability significantly. Understanding these enhancements at multiple scales (cement paste, mortar, and concrete) is crucial for optimizing concrete formulations for various structural applications.

The methodology employs a multiscale modelling approach combined with experimental investigations to predict the compressive strength characteristics of nano-silica-modified concrete. Cement paste samples with varying levels of nano-silica replacement were observed using SEM under BSE mode. The BSE images were analyzed to quantify the unhydrated cement and capillary pore phases using image processing software and energy-dispersive X-ray spectroscopy (EDS) data. The volume fractions of different

phases (unhydrated cement, capillary pores, unreacted nano-silica, and hydrated phase) were quantified. This quantification was used to compute the hydrated phase volume directly related to the material's strength. RVEs were developed for cement paste (micro-scale), mortar (meso-scale), and concrete (macro-scale). The finite element method was used to analyze these RVEs, with properties determined from microstructural investigations feeding into models at higher scales. Compressive strength tests were conducted at 7 and 28 days for cement paste, mortar, and concrete samples. The experimental results were compared with the model predictions to validate the multiscale model.

Significant findings include the observation that increasing the nano-silica content up to 8 % enhances the fraction of the hydrated phase and reduces porosity. The hydrated phase is the main strength-carrying component, and its increase results in higher compressive strength. The study identified that 8% nano-silica content is optimal for maximum strength enhancement. Beyond this percentage, the dilution effect of replacing too much cement with nano-silica reduces the production of strength-carrying C-S-H, leading to no further strength gains. The compressive strength of samples with 8% nano-silica content increased by approximately 20 % at 7 and 28 days compared to control samples. This increase is attributed to the pozzolanic reactivity of nano-silica, which produces additional C-S-H. The proposed multiscale model accurately predicted the compressive strength of cement paste, mortar, and concrete, with predictions closely matching the experimental results. However, the study has some drawbacks. The quantification of phases from microstructural analysis and image processing may not be entirely realistic, leading to potential errors in the volume fraction calculations. The study did not consider the ITZ, a crucial factor influencing the strength of mortar and concrete. Nano-silica is known to improve the ITZ characteristics, and omitting it from the model could lead to an incomplete understanding of the material's performance. While the study found that 2D and 3D models show similar stress-strain responses, using 2D models for mortar and concrete might still overlook some three-dimensional effects in real-world applications.

Future studies should employ advanced phase quantification techniques to improve volume fraction calculation accuracy. Combining multiple analytical methods could provide a more comprehensive understanding of microstructural changes. The ITZ should be explicitly included in future models to capture its impact on the overall mechanical properties of nano-silica integrated concrete. This inclusion would provide a more detailed and accurate prediction of material performance. In addition to compressive strength, future research should focus on the long-term durability of nano-silica-modified concrete, including resistance to environmental factors such as freeze-thaw cycles, chemical attack, and abrasion. Conducting experiments at larger scales and under different environmental conditions would help validate the multiscale model further and ensure its applicability to real-world scenarios. While 8 % was found to be optimal in this study, the optimum content might vary with different types of cement and nano-silica. More studies are needed to determine the best composition for different applications.

In conclusion, this study provides valuable insights into the effects of nano-silica on cementitious materials through a comprehensive multiscale modelling approach. By addressing the identified drawbacks and following the recommendations, future research can build on these findings to enhance the performance and applicability of nano-silica-integrated concrete.

3.4 Current approaches for predicting the performance of GO-modified cement composites

3.4.1 Analytical modelling of mechanical properties of graphene-oxide cement composites

GO has emerged as a promising additive for enhancing the mechanical properties of cementitious composites due to its excellent dispersion properties and high surface area. Enhancing mechanical properties such as the elastic modulus is crucial for developing more durable and resilient construction materials. Despite extensive experimental

research into the mechanical properties of GO-cement composites, there is currently a lack of predictive models that accurately estimate these properties, posing a challenge for the proper analysis and design of GO-cement-based materials.

A study by Duan et al. (Duan et al., 2018) aimed to address this gap by developing a novel multi-scale analytical model for predicting the elastic modulus of GO-cement composites. By considering the effects of the GO/cement ratio, porosity, and mechanical properties of different phases, the model provides a comprehensive tool for predicting the mechanical performance of these advanced materials. The outcomes of this research could significantly accelerate the application of GO in civil engineering, leading to more robust and more durable infrastructure. The methodology employed in this study combines experimental and analytical approaches to investigate the mechanical properties of GO-cement composites and develop a predictive model for their elastic modulus. The multi-scale analytical model utilizes Eshelby tensor and Mori-Tanaka solutions to upscale the elastic properties of GO-cement through different length scales, from micro to macro. RVEs are introduced to ensure homogeneity at each scale. Experimental verification includes in-situ micro-bending tests to observe the behaviour of GO-cement composites under stress and validate the model, SEM analysis to examine fracture mechanisms and crack propagation, and mercury intrusion porosimetry (MIP) tests to assess the effects of GO addition on the porosity of the cement. Bulk and shear moduli of GO and C–S–H are selected as crucial parameters influencing the macroscale Young's modulus. The volume fractions and mechanical properties of different phases at various length scales are incorporated into the model.

This study's significant findings reveal that adding GO significantly improves the mechanical properties of the cement. Experimental results indicate an increase in Young's modulus with the incorporation of GO, demonstrating enhancements of 8.6 % and 11.7 % for 0.02 wt% GO inclusion by weight. The predicted Young's modulus values from the developed model show good agreement with the experimental results, validating the model's accuracy in estimating the elastic properties of GO-cement composites.

Furthermore, the relationship between the increase in GO dosage and the enhancement of Young's modulus is non-linear, with the enhancement rate of Young's modulus being higher than that of GO addition. Additionally, the addition of GO alters the morphology of the cement, contributing to improved mechanical properties. However, the study has several drawbacks. The model assumes GO particles are spherical rather than their actual disk-like shape, which may lead to inaccuracies since single-layer GO dispersion, critical for maximizing efficiency, was not considered. The analytical model does not account for the stress state of particles in three dimensions, potentially compromising the reliability of the results. Additionally, the model assumes perfect bonding between GO and cement, which may not always be the case in practical scenarios, leading to overestimating the elastic modulus.

Future studies should consider the actual disk-like shape of GO particles and investigate the impact of single-layer GO dispersion on the mechanical properties of cementitious composites. Developing models that account for the stress state of particles in three dimensions would enhance the accuracy and reliability of predictions. Introducing realistic interfacial bonding conditions between GO and cement in the model could provide more accurate estimates of the mechanical properties. Conducting a broader range of experimental tests, including different types of mechanical loading and environmental conditions, would further validate and refine the predictive model. Additionally, investigating GO-cement composites' long-term durability and performance under various environmental conditions would benefit practical applications in civil engineering. By addressing these recommendations, future research can build on the findings of this study to develop more accurate and reliable predictive models for the mechanical properties of GO-cement composites, thereby enhancing their application in the construction industry.

3.4.2 A machine learning approach for assessing the compressive strength of cementitious composites reinforced by graphene derivatives

The existing predictive models for evaluating the impact of graphene derivatives (GDs) on cementitious composites (CC) compressive strength are mainly based on machine learning. The study by (Montazerian et al., 2023) addressed a substantial gap in the application of ML models to predict the compressive strength of graphene derivative-reinforced cementitious composites (GDRCCs). Traditional experimental methods are labour-intensive, time-consuming, and costly. By developing tailored ML models, this research offered a reliable and efficient alternative capable of investigating the combined influence of various factors on the compressive strength of CCs. This approach enhances the current understanding of the reinforcing effects of GDs and paves the way for more cost-effective and time-efficient future studies in this field.

The research began with a comprehensive literature survey to compile a unique dataset that includes continuous and discontinuous factors affecting the compressive strength of GDRCCs. The dataset was designed to capture the typical mixture design properties of CCs and the properties and fabrication details of GDs. Machine learning models were employed, including ANN, SVR, decision trees (DT), and linear regression (LR). The dataset featured nine continuous and four discontinuous parameters, such as GD type, size, thickness, cement strength grades, and curing methods. The backward elimination technique refined the dataset by identifying and removing redundant properties. The predictive performance of the ML models was assessed using the coefficient of determination (R^2), root mean square error (RMSE), and normalized root mean square error (NRMSE). A sensitivity analysis was conducted to identify the most influential factors affecting the compressive strength of GDRCCs.

The study found that GDs significantly enhance the compressive strength of CCs, with their efficiency depending on a combination of factors, including GD properties, mixture design properties, and fabrication conditions. The ANN model showed superior

prediction performance with an RMSE of 3.66 MPa, R^2 of 0.91, and an NRMSE of 0.08. The sensitivity analysis revealed that the lateral size of GDs had the highest impact on compressive strength, with smaller GDs providing greater enhancement. Among the fabrication conditions, the dispersion technique was the most influential factor. Overall, the water-to-cement ratio was identified as the most critical parameter, significantly affecting GD dispersion and, consequently, the compressive strength enhancement.

One drawback of the study is the inherent complexity of accurately modelling the diverse properties of GDs and their interactions within the cement matrix. The assumption that the ML models could generalize across different experimental setups and conditions may not hold true in all cases. Additionally, the study did not account for certain GD properties, such as functional groups and specific surface area, which could further influence the compressive strength of GDRCCs. Furthermore, the ML models did not consider the actual hydration and microstructure development, relying instead on correlations within the input dataset. This approach can be seen as a "black box" procedure, potentially overlooking crucial mechanistic insights.

Future research should incorporate a broader range of influential factors, including the specific functional groups and surface areas of GDs and detailed manufacturing parameters like sonication energy, mixing time, and speed. Integrating ML models with experimental design could help validate and refine the predictions. Moreover, expanding the dataset to include more variations in GD properties and fabrication conditions would enhance the models' robustness and accuracy. This study lays the foundation for future research, encouraging exploring the intricate relationships between GD properties, manufacturing details, and the compressive strength of GDRCCs.

3.5 Concluding remarks on predicting the performance of cement-based materials

Numerous studies have investigated the hydration characteristics of ordinary cement paste, mortar, and concrete and numerically modelled their mechanical performance. However, adding nano-silica and GO to cement-based materials is a relatively new area of research, with limited analytical work on modelling their performance. The models available for predicting the performance characteristics of nano-silica and GO were discussed in **Sections 3.3** and **3.4** of this chapter, along with their strengths and weaknesses. A clear research gap exists in quantifying the pozzolanic reactivity of nano-silica and the actual effect of GO and integrating these into numerical models to predict performance.

An analysis of models for simulating cement hydration kinetics makes a modelling approach based on cement hydration more suitable for the present study. Among the techniques discussed, cement hydration models are the only methods that can predict the mechanical properties of the system. This research aims to evaluate the behaviour of nano-silica and GO in cement-based materials and determine their effects on mechanical properties, using cement hydration models as the foundation appropriate. This approach allows for the precise integration of the pozzolanic reaction effects of nano-silica, unlike other modelling methods. Similarly, the impact of GO on cement hydration needs to be determined and incorporated into the cement hydration model. Different methodologies for predicting the mechanical properties of cement systems (cement paste, mortar, concrete) were discussed in Sections 3.3 and 3.4. It was concluded that a multiscale-based approach is the most effective way to model the characteristics of cement systems. Concrete is a composite material with components ranging from the nanometre to the macroscale. A multiscale-based technique is more suitable than modelling performance solely at the macroscale, as it addresses characteristics at each length scale in detail, making model predictions more accurate and reflective of realistic behaviour.

The literature review on modelling the performance of nano-modified cement systems concluded that a cement hydration model will be used as the base to model the mechanical properties of nano-silica and GO-reinforced cement systems in the present research. The pozzolanic reactivity of nano-silica and the reactivity of GO will be integrated into the cement hydration model. A multiscale-based approach will then be employed to predict the mechanical properties of nano-modified cement-based materials.

CHAPTER 4

EXPERIMENTAL INVESTIGATION OF NANO-SILICA EFFECTS ON CEMENT PASTE PROPERTIES

4.1 Introduction

The growing demand for durable and sustainable construction of buildings and infrastructure has spurred a focus on high-performance cement-based materials (Makul, 2020). SCMs such as nano-silica are gaining popularity in the construction industry because they enhance durability, strength, and sustainability (Lothenbach et al., 2011). The high reactivity and small particle size make nano-silica attractive for applications requiring rapid strength development (Akhnoukh and Elia, 2019). Nano-silica in cement-based materials acts as a nucleation site, which promotes the hydration of clinker minerals and pozzolanic materials; during this process, calcium hydroxide reacts with nano-silica to form C-S-H gel (Khan et al., 2022). Consequently, the microstructure becomes denser, possessing a higher strength than that without incorporating nano-silica (Snehal et al., 2020).

Nano-silica has been effectively combined with various additives and SCMs, such as fly ash (Praveen Kumar and Dey, 2023; Singh et al., 2019), slag (Chithra et al., 2016b; X. Liu et al., 2021), glass powder (Cai et al., 2019), metakaolin clay (Raheem et al., 2021), and calcined clay (Lin et al., 2022), in construction industries to enhance the performance of cement-based materials. For instance, Hou et al. (Hou et al., 2013a) demonstrated that the pozzolanic reaction of colloidal nano-silica and its nucleation occurred rapidly in fly ash mortar, particularly at a very early age, compared with the addition of the same quantity of silica fume. The addition of 5 % colloidal nano-silica increased the compressive strength of the fly ash mortar by 45 and 12 % on days 7 and 28, respectively. However, at later ages, the acceleration effect of nano-silica diminished. Therefore, the

effectiveness of nano-silica in cement-based materials varies depending on its properties, such as particle size and morphology, specific dosage, and incorporation method. For instance, Meng et al. (Meng et al., 2020) examined the microstructural transformation of cement pastes with different nano-silica particle sizes (15 and 50 nm) using XRD, SEM and TGA. The results revealed that larger nano-silica particles demonstrated superior compressive strength compared to smaller nano-silica particles. In addition, nano-silica with a smaller particle size resulted in a denser microstructure with a reduced average pore size. Moreover, nano-silica morphology affects the characteristics of cement mixtures. Colloidal nano-silica considerably lowered the workability of cement mixtures compared to silica gel and silica fume, owing to the high absorption of free water and agglomeration of nano-silica particles in the cement composite (Kooshafar and Madani, 2020).

Appropriate quantities of nano-silica are required to achieve excellent outcomes and compatibility with the other cementitious materials used in cement composites (Khan et al., 2022). According to literature, nano-silica has been utilised as an additive or replacement in cementitious materials at various dosages, ranging from 0.5 % to 7 % in cement pastes (Qing et al., 2007; Senff et al., 2009; Stefanidou and Papayianni, 2012), 1 % to 12 % in mortar (Haruehansapong et al., 2014; Hou et al., 2013a; Senff et al., 2009), and 0.5 % to 10 % in concrete (Abhilash et al., 2021; Khan et al., 2022). However, determining the ideal replacement level and properties of nano-silica combined with different SCMs is laborious and time-consuming. This study uses several experimental techniques to study nano silica's effect on hydration and cement paste's mechanical performance.

4.2 Experimental procedures

4.2.1 Materials and sample preparation

OPC, which conforms to the Japan Industrial Standard JIS R 5201:2015, was acquired from the Japan Cement Association. Nano-silica, with an average particle size of 18.5 nm and 99.9 % purity, was purchased from Kanto Chemical. Co., Inc. The XRD pattern in **Figure 4.1** confirms the amorphous phase of the nano-silica. The chemical and physical properties of the cement and nano-silica are listed in **Table 4.1**.

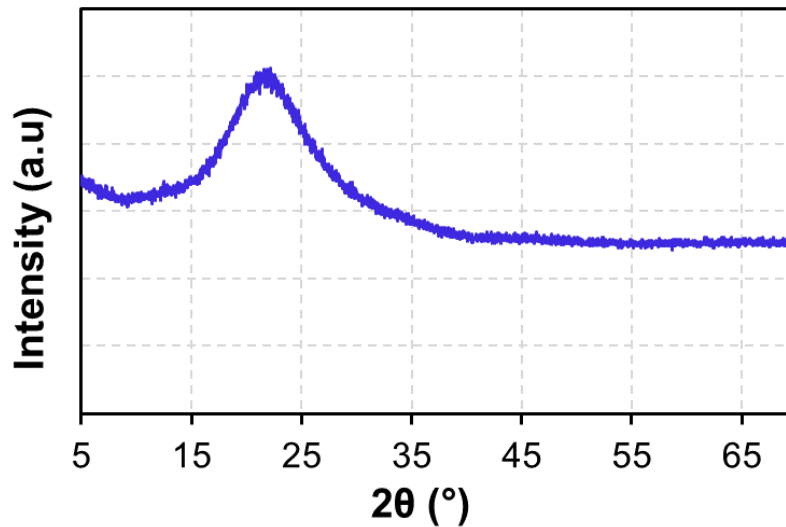


Figure 4.1: XRD pattern verifying the amorphous phase of nano-silica.

Nano-silica was incorporated into cement pastes at replacement levels of 0, 2, and 4 % by weight while maintaining a consistent water-binder ratio of 0.40 across all mixtures. The workability of each mixture was evaluated by measuring the flow diameter at intervals of 0, 20, 60, and 120 min, as outlined in JASS15M-103. **Figure 4.2** illustrates a substantial decrease in slump compared to the control sample, with flow reductions of 33.9 and 38.1 % observed for the 2 and 4 % replacement levels, respectively, at the initial stage (zero minutes). This decrease in workability associated with nano-silica incorporation was attributed to its high water retention capacity (Quercia et al., 2012),

stemming from its high surface area and reactivity. This characteristic reduces the amount of free water necessary for fluidity in the mixture, thereby increasing viscosity and decreasing workability. Previous research has revealed similar findings with nanoparticles possessing high surface areas (Elkady et al., 2013; X. Liu et al., 2021). The water demand associated with the incorporation of nano-silica in cement pastes can be effectively managed by introducing appropriate quantities of superplasticisers to achieve the desired workability (Wang et al., 2016). Notably, this study did not use superplasticisers, as it falls beyond the scope of the present investigation. The compositions of the mixtures are listed in **Table 4.2**.

Table 4.1: Chemical composition and physical characteristics of utilised cement and nano-silica (wt. %)

Properties	Cement	Nano-Silica
SiO₂	21.42	>99.5
Al₂O₃	5.52	-
Fe₂O₃	2.81	-
CaO	64.23	-
MgO	1.42	-
SO₃	2.17	-
Na₂O	0.25	-
K₂O	0.58	-
TiO₂	0.27	-
P₂O₅	0.42	-
MnO	0.04	-
Cl	0.015	-
Density (kg/m³)	3160	2200
Specific surface area (m²/kg)	339	33700

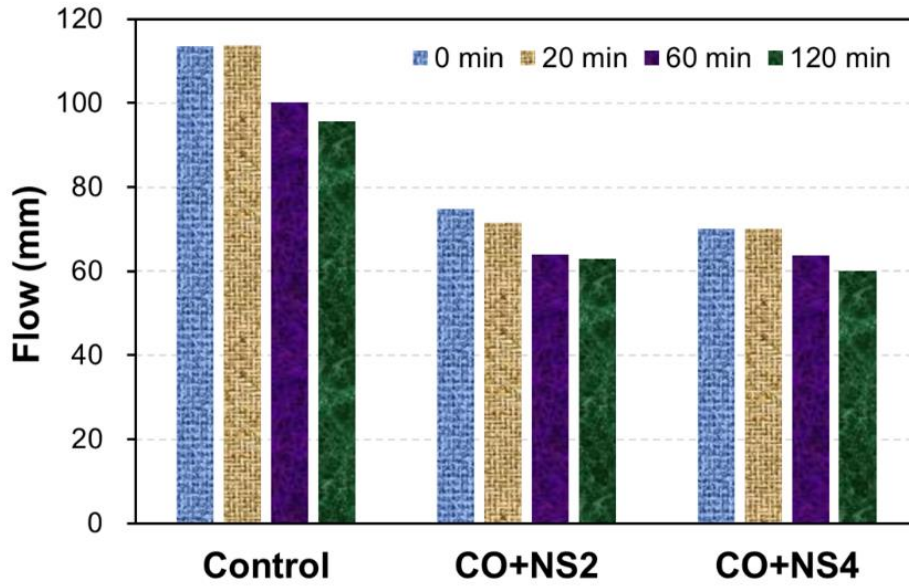


Figure 4.2: Changes of flow with time for all the pastes

Table 4.2: Composition of the paste mixtures

Sample ID	Cement (g)	Nano-silica (g)	Water (g)
CO	100	0	40
CO+NS2	98	2	40
CO+NS4	96	4	40

Owing to the ultrafine nature of nano-silica particles and their strong van der Waals forces (Xu et al., 2021), which can result in particle agglomeration, a specified quantity of deionised water and nano-silica was combined in a beaker. The resulting mixture was ultrasonically dispersed for 10 min. The dispersed solution was subsequently introduced into a cement blend using a Hobart N50 5-quart mixer. The mixing process involved an initial one-minute period at low speed and another 1 minute at high speed. After pausing the mixing, the bowl's surface was cleared using a spatula, following which a two-minute high-speed mixing was implemented to ensure the pastes' uniformity. The prepared pastes

were poured into lightweight cylindrical moulds measuring a diameter and height of 50 and 100 mm, respectively, in a two-layer arrangement. Each layer was subjected to 20 s of vibration to eliminate larger pores, which may have arisen due to reduced workability. Once moulded, the specimens were hermetically sealed and placed in a curing environment at a constant temperature of 20 ± 2 °C. After a curing period of 24 h, the specimens were carefully removed from the moulds, covered in polyester film, and stored under controlled conditions at 20 ± 2 °C. The specimens of designated ages (1, 3, 7, 28, and 56 d) were finely crushed into pieces measuring 20 mm or less using a hammer (Maruyama and Igarashi, 2014). Subsequently, they were immersed in acetone for three days to halt the hydration process. The specimen pieces were separated using suction filtration and placed in a temperature chamber at 40 °C for two days to eliminate residual acetone. Once thoroughly dried, the samples were carefully ground using a mortar and pestle to avoid excessive heating. The resulting powder was sifted through a 75 µm sieve for subsequent measurements.

4.2.2 Experimental Characterisation

The effectiveness of nano-silica in enhancing the strength was evaluated using an automatic compressive strength testing machine (Hi-ACTIS-2000), following the ISO 679 standard. A constant load rate of 0.6 N/mm²·s was maintained, with three replicate specimens per hydration age (1, 3, 7, 28, and 56 days) to ensure reliable compressive strength measurements. Cement hydration with and without nano-silica was quantified by TGA under a nitrogen atmosphere using a HITACHI TG/DTA 7220 instrument. The heating rate was 10 °C/min within a 20–950 °C temperature range. Furthermore, a Rigaku X-ray diffractometer, utilising CuK α radiation and adhering to the following conditions, was employed to determine the hydrate contents: a tube voltage of 40 kV, tube current of 40 mA, scanning range (2θ) of ~ 5 – 70° , step width of 0.02° , and scanning speed of $6.5^\circ/\text{min}$. A BGMN Rietveld refinement program (Profex) was used for phase quantification. The morphologies of the hydrates and their elemental compositions were studied by SEM and energy-dispersive X-ray spectroscopy (EDS). The powdered samples

were coated with a thin gold layer before examination using an SEM (JSM-IT200 microscope (JEOL, Japan)), operated at 15 kV and a working distance of 10 mm.

4.3 Results and discussions

4.3.1 Analysis of hydration products

4.3.1.1 Thermogravimetric analysis

TGA was performed on all the cement pastes (CO, NS2, and NS4) at different hydration ages (1, 3, 7, 28, and 56 days). DTG and mass losses are plotted in **Figure 4.3**. These DTG profiles consistently exhibited two distinct peaks at all hydration ages, indicative of the release of unbound and bound water from the phases encompassing C-S-H, ettringite, and monosulfate within the temperature range of 80–200 °C (Rupasinghe et al., 2017b), and of CH decomposition around 450 °C (Hou et al., 2013a). Subsequently, the CH content was quantified using Eq. (3.1).

$$CH = (WL)_{CH} \cdot \frac{74}{18} \quad (3.1)$$

where $(WL)_{CH}$ is the weight loss due to the decomposition of portlandite in the TG curve, and the fraction (74/18) is the ratio of CH and water (H₂O) molar masses.

Figure 4.3 shows how introducing nano-silica increased CH content during the initial stages, specifically on days 1 and 3. This enhancement can be attributed to the nucleation effect of nano-silica, which accelerates cement hydration and consequently boosts CH production (Singh et al., 2016b). This effect was most pronounced at a 2 % replacement level. However, after three days, the CH content declined owing to the pozzolanic effect, where CH was consumed, leading to reduced free CH content within the cement matrix (Snehal et al., 2020). Furthermore, the CH contents across all formulations were normalised to the nano-silica substitution level to account for the dilution effect resulting from the decreased cement content in the mixture due to nano-silica incorporation. These

normalised values were plotted against the hydration age, as shown in **Figure 4.4**. **Figure 4.4** distinctly illustrates the CO+NS4 sample, exhibiting a reduced CH content at all ages. This can be attributed to the dominant influence of the pozzolanic effect on the nucleation effect at higher replacement levels (Abhilash et al., 2021; Khan et al., 2022).

Additionally, the aggregation effect of nano-silica, owing to its substantial surface area, may hinder the hydration process, thereby highlighting this reduction. This observation is further supported by **Figure 4.3d**, which shows significant decomposition of C-S-H. The tendency for aggregation could potentially limit the reactivity and hinder the diffusion of clinker minerals, consequently affecting the overall CH production during hydration (Singh et al., 2016a). Certain studies (Rupasinghe et al., 2017b; Singh et al., 2017) have presented conflicting findings, indicating a reduction in CH content upon introducing nano-silica during the initial stages of hydration. However, these investigations did not distinctly explain the effects of the nucleation sites and pozzolanic reactions (Rupasinghe et al., 2017b, 2017a).

In contrast, the results of the present study clarify the actual influence of nano-silica on cement paste hydration (Flores et al., 2017). These observations suggest an optimal level of cement replacement with nano-silica. Below this optimal threshold, free CH remains in the mixture, and the quantity of nano-silica within the paste is insufficient to react with CH fully. Conversely, surpassing the optimal nano-silica content results in a lack of available CH for interaction with nano-silica, causing the nanoparticles to primarily function as inert fillers without actively participating in the pozzolanic reactions. Considering the specific experimental parameters and type of nano-silica employed, the analysis conducted in this study advocates a 2 % replacement level of nano-silica as the optimal configuration to achieve maximum benefits through nucleation and pozzolanic reactivity.

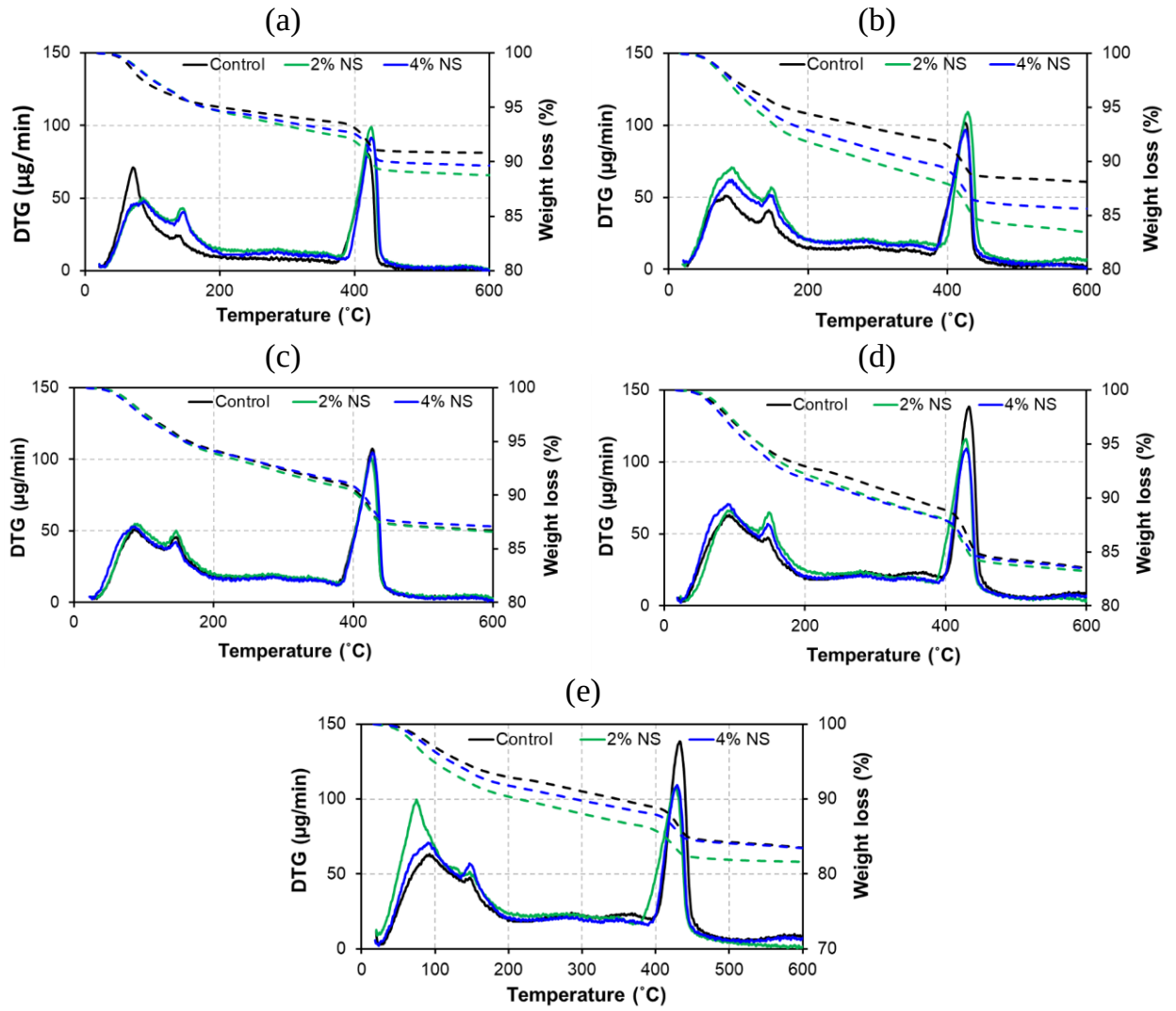


Figure 4.3: TGA and DTA curves of the cement pastes at (a) one, (b) three, (c) seven, (d) 28, and (e) 56 days.

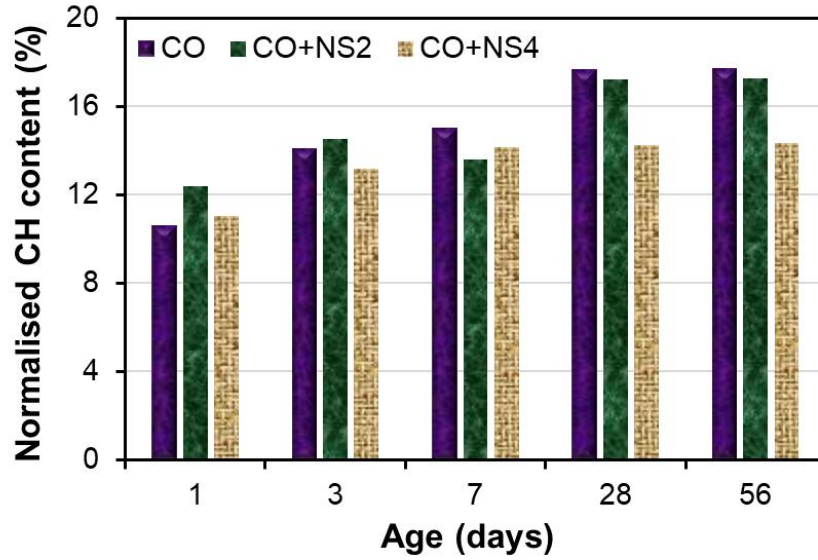


Figure 4.4: Normalised CH content of the cement pastes at different ages.

4.3.1.2 Analysis of the XRD diffraction patterns of cement pastes

Figure 4.5 depicts the X-ray diffraction patterns for all the paste samples (CO, CO + NS2, and CO + NS4) at different hydration ages (1, 3, 7, 28, and 56 days). As shown in **Figure 4.5**, portlandite, ettringite, monosulfate, alite, and belite are the principal crystalline phases at all hydration ages. Notably, the peak intensities associated with these phases exhibited distinct variations upon nano-silica substitution. **Figure 4.5** (a) highlights that the presence of nano-silica leads to increased intensity corresponding to ettringite ($2\theta = 9.1$) and monosulfate ($2\theta = 9.9$). This increase confirms the acceleration of cement hydration induced by nano-silica. Conversely, the peak intensity attributed to portlandite ($2\theta = 34.1$) diminished upon introducing nano-silica. This reduction is aligned with the increased pozzolanic activity of nano-silica, which engages in the substantial consumption of portlandite, thereby fostering the generation of supplementary C-S-H (Rupasinghe et al., 2017b). Compared to the earlier stages, this trend was particularly noticeable on days 7, 28, and 56, supporting the findings discussed in Section 4.1.1. These observations collectively enabled a qualitative analysis of the influence of nano-silica on cement clinker through variations in the peak intensity. **Figure 4.6** provides a graphical

representation of the hydration reactions within individual clinker minerals (C_3S , C_2S , C_3A , and C_4AF) and the overall degree of cement hydration, as determined by the XRD/Rietveld analysis. Although the hydration degree of C_3A remained unchanged, the presence of nano-silica significantly affected the hydration degrees of C_3S , C_2S , and C_4AF . This effect can be attributed to the apparent pozzolanic reactivity and nucleation effect caused by nano-silica. However, these alterations in the degree of hydration did not affect the overall degree of cement hydration (**Figure 4.6 (e)**).

4.3.2 Analysis of microstructure

SEM utilising backscattered electron (SEM-BSE) imaging was employed to analyse the cement paste with (2 % by weight) and without nano-silica at three and seven-day ageing intervals. This investigation aims to determine the influence of nano-silica on the microstructures of cement pastes. The SEM micrographs of the pastes are shown in **Figure 4.7**. The increase in nucleation sites facilitated by nano-silica substitution is prominent in the initial stages, as indicated by the degradation of the portlandite (CH) surface in **Figure 4.7(b)**. Moreover, replacing nano-silica yielded a more compact microstructure within the cement paste. This microstructural change is due to the pozzolanic effect of nano-silica (Sargam and Wang, 2021a), which triggers a secondary hydration reaction. Consequently, this secondary reaction leads to the formation of supplementary C-S-H through the consumption of portlandite (**Figure 4.7(d)**). The increased microstructure density can also be attributed to the filling effect of nano-silica. Considering ultrafine particles, nano-silica effectively occupied the pores within the cement paste, contributing to the overall densification.

The impact of substituting nano-silica on the chemical composition of the resulting hydrates was investigated using elemental composition analysis (SEM-EDS). EDS analysis points were chosen by visual distinctions in the grey scale intensities within the BSE images and significant elevations in the intensities of the major elements (Ca, Si, and Al) in the EDS maps. Approximately 50 specific points were targeted during EDS

point analysis to capture the atomic ratios of Ca, Si, and Al. **Figure 4.8** depicts the distribution of the Al/Ca and Si/Ca ratios within the C-S-H phase of the control sample and sample with 2 % nano-silica after seven days. A particular trend emerged, with points exhibiting an upward shift upon nano-silica substitution. This trend, resulting in an increased silicon-to-calcium (Si/Ca) ratio as the Si content in the paste increased, was attributed to the presence of Si originating from nano-silica. The Al/Ca and Si/Ca ratios within the primary C-S-H phase, encompassing inner and outer regions, span broad ranges of 0.03–0.25 and 0.21–0.52, respectively.

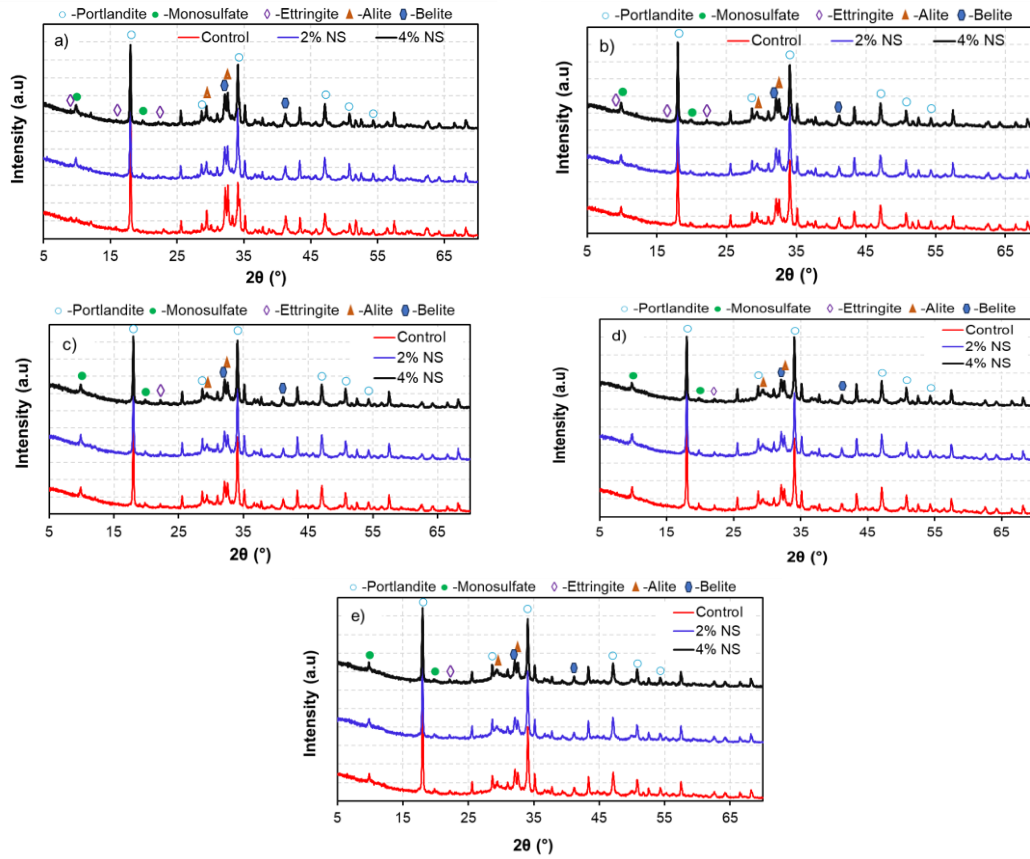


Figure 4.5: X-ray diffraction curves of the cement pastes at (a) one, (b) three, (c) seven, (d) 28, and (e) 56 days.

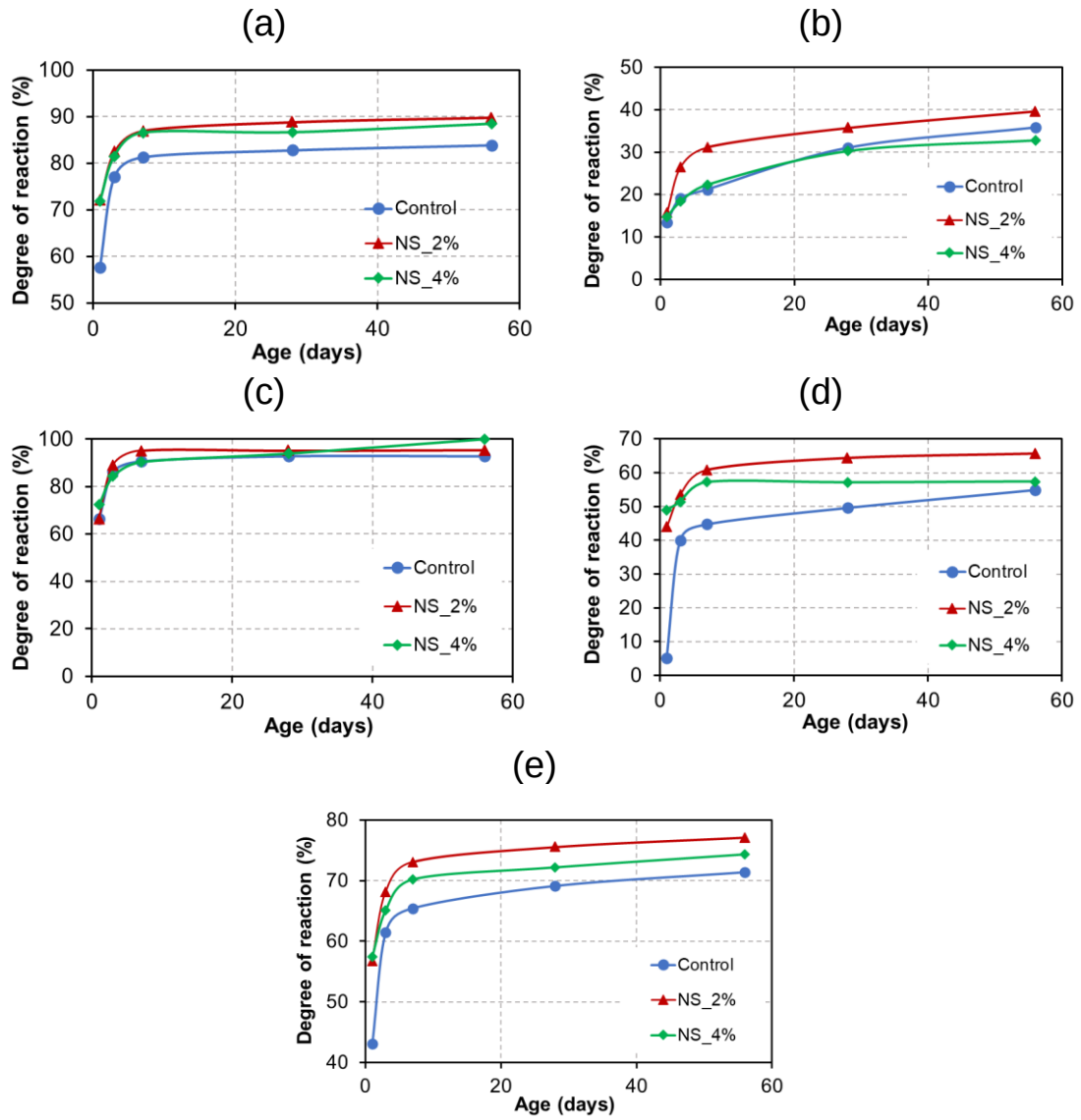


Figure 4.6: Reaction degree of clinker minerals in the cement pastes: (a) C_3S , (b) C_2S , (c) C_3A , and (d) C_4AF . (e) Overall hydration degree of cement pastes.

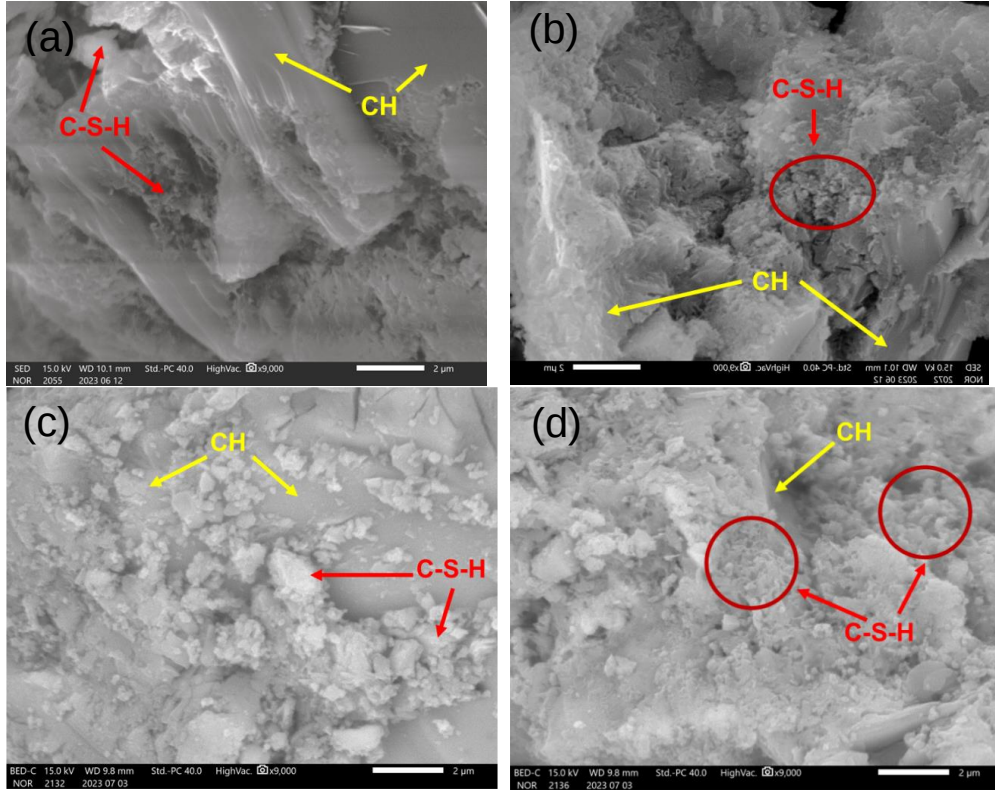


Figure 4.7: SEM-BSE micrographs of (a and b) control paste, at days one and seven, respectively, and (c and d) 2% nano-silica substituted paste at days one and seven.

Furthermore, an increase in the Al/Ca ratio, which was noted within additional secondary C-S-H formations, was attributed to the pozzolanic reaction of nano-silica. In this scenario, the C-S-H structure absorbs Al in place of Si. This finding aligns with the prior literature (Lothenbach et al., 2011; Richardson, 2004; Sargam and Wang, 2021b), demonstrating the emergence of C-S-H structures at elevated Si/Ca ratios reminiscent of tobermorite-like structures. Therefore, the Si/Ca ratios of the nano-silica substituted samples were considered to be 0.67, slightly higher than that of the control sample (0.58). Furthermore, partially reacted nano-silica was characterised by elevated Si/Ca and reduced Al/Ca ratios (**Figure 4.8**) (Sargam and Wang, 2021b).

In contrast, fully reacted nano-silica created an additional secondary C-S-H phase through pozzolanic reactions. This variant of secondary C-S-H demonstrated a tendency to absorb

or incorporate a greater quantity of alkali, which was attributed to the negative surface charge of C-S-H. Collectively, the results obtained through TGA, XRD, and SEM assays validate the favourable influence of nano-silica substitution on the characteristics of cement paste. This advantageous impact can be attributed to the synergistic effects of the nucleation and pozzolanic reactions induced by nano-silica. This phenomenon was carefully incorporated into the coupled hydration and thermodynamic model, as explained in Section 3.1, to comprehensively capture and simulate this phenomenon and ensure a realistic representation of the intricate influence exerted by nano-silica.

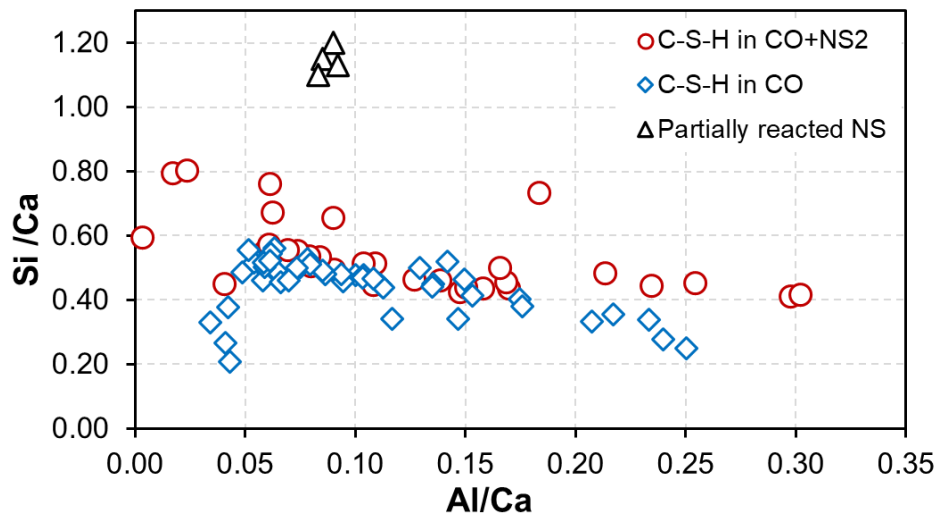


Figure 4.8: Variation of Al/Ca and Si/Ca ratios of C-S-H structure found in control paste and 2% nano-silica containing paste at 7 days.

4.3.3 Mechanical properties

All tested cylinders failed by exhibiting columnar vertical cracking extending through both ends. No well-formed cones were observed. Since the mix lacks aggregates, the likelihood of shear crack formation or conical failure is minimal. Consequently, columnar vertical cracking was consistently observed in all cylindrical samples, as shown in **Figure 4.9**.

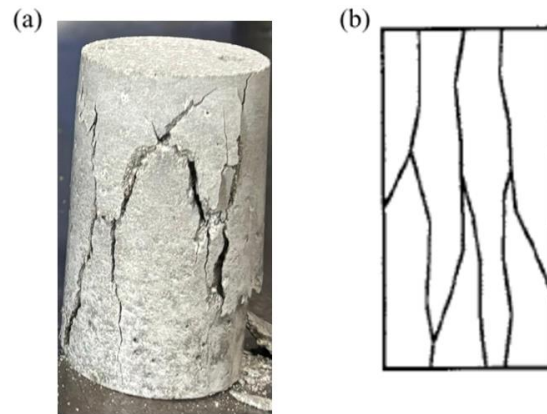


Figure 4.9: (a) Columnar vertical cracks were observed in all the cylindrical samples. (b) Columnar vertical cracks were similar to those described in ASTM C39/39M-10 (2011).

The effect of nano-silica replacement on the compressive strength of cement pastes, specifically at 2 % and 4 % substitution levels, is depicted in **Figure 4.10**, which presents the compressive strengths of all cement pastes at various ages. A notable improvement in strength compared to the control paste was observed with increasing concentrations of nano-silica substitution, particularly during the early stages of hydration. This enhancement is attributed to nano-silica's nucleation and pozzolanic effects, as confirmed by TGA and XRD analyses. These effects lead to a significant presence of hydrated phases, primarily C-S-H, which are crucial for strength development in cement pastes. However, it was observed that a 4% substitution of nano-silica resulted in a lower compressive strength than the 2% substitution. This decrease can be attributed to the agglomeration of nano-silica particles, as discussed in Section 4.3. Agglomeration impedes the such as C-S-H formation.

Experimental results demonstrate that substituting 2 % nano-silica increases the compressive strength by 35.2 %, 21.2 %, and 17.2 % at one, three, and seven days, respectively. In contrast, a 4% nano-silica substitution increases compressive strength by 17.8 %, 7.6 %, and 15.9 % at the same respective ages. These findings suggest that while

nano-silica significantly enhances compressive strength at an optimal substitution level, excessive amounts can lead to diminished returns due to particle agglomeration hindering adequate hydration.

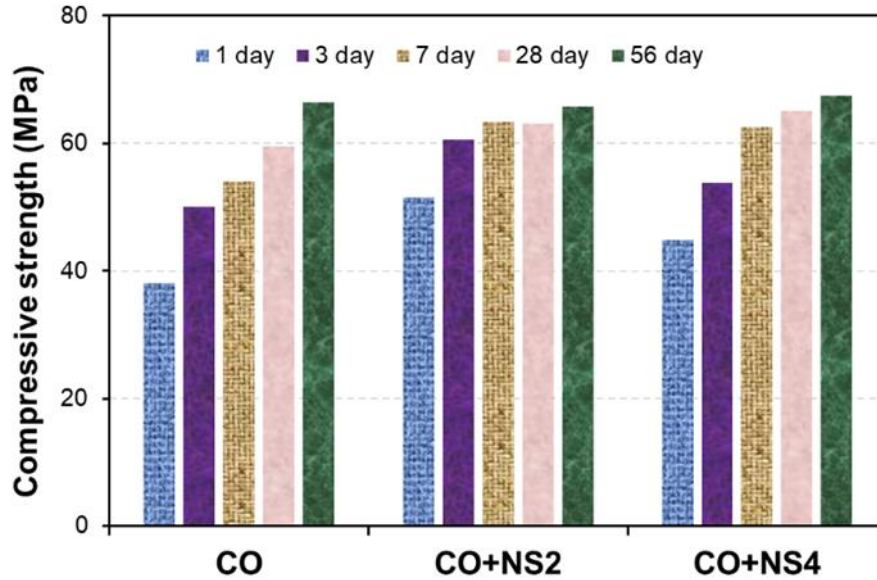


Figure 4.10: Compressive strength variation over time for different nano-silica replacement levels.

4.4 Summary

The incorporation of nano-silica in cementitious materials has a significant impact on hydration and mechanical properties. Due to its nucleation effect, nano-silica initially increases CH content, especially within the first three days. This enhancement is most effective at a 2 % replacement level. Beyond three days, the CH content decreases due to the pozzolanic reaction, which consumes CH and reduces its free content in the cement matrix. Our study identifies 2 % as the optimal nano-silica substitution level, balancing nucleation and pozzolanic effects for maximum strength improvement. At higher dosages, nano-silica leads to particle agglomeration, impeding hydration and diminishing returns on strength gains. XRD and SEM analyses confirm that nano-silica accelerates cement

hydration and promotes the formation of additional C-S-H, resulting in a more compact microstructure. The optimal 2 % substitution increases compressive strength by 35.2 %, 21.2 %, and 17.2 % at one, three, and seven days, respectively, while a 4 % substitution shows lower gains. Additionally, XRD results revealed that replacing nano-silica did not affect the reaction rates of clinker minerals such as C_3S , C_2S , C_3A , and C_4AF .

In summary, a 2 % nano-silica replacement optimally enhances flow and compressive strength without altering the reaction rates of key clinker minerals. Future research should focus on nano-silica's pore refinement effects to further improve cement-based materials' performance and durability.

CHAPTER 5

EXPERIMENTAL INVESTIGATION OF GO-MODIFIED PROPERTIES OF CEMENT PASTE

5.1 Effect of Graphene Oxide on cement paste

5.1.1 Introduction

The demand for enhanced mechanical properties and durability in cement-based materials has grown significantly, driven by the increasing necessity for sustainable and resilient infrastructure (Zhang et al., 2017). Traditional cement-based materials frequently face challenges related to strength, durability, and environmental impact, prompting the exploration of advanced materials (Afroughsabet et al., 2016; Aïtcin, 2003). Various methods have been employed to address these limitations, including chemical additives, fibre reinforcements, and mineral admixtures (Nithurshan and Elakneswaran, 2023). While these approaches have demonstrated some efficacy, they often have drawbacks, such as limited effectiveness, high cost, and adverse environmental impacts (Ferraris et al., 2001; Karapati et al., 2014; Shao et al., 2017). In recent years, integrating nanomaterials into cementitious composites has emerged as a promising strategy to enhance their mechanical properties and durability (Li et al., 2004; Z. Li et al., 2006; Manzur and Yazdani, 2016; Nithurshan et al., 2024). Nanomaterials, owing to their nano size and high surface area, offer unique properties that can significantly improve the performance of cement-based materials (Kedir et al., 2023; Khan et al., 2022; Zhang et al., 2021). However, incorporating nanomaterials into cement-based materials presents several challenges, including dispersion, agglomeration, and compatibility with the cement matrix (Afroughsabet et al., 2016; Shao et al., 2017).

GO distinguishes itself among other nanomaterials due to its distinctive features and compatibility with cement-based materials (Suo et al., 2022; Yang et al., 2017a; Zhao et al., 2020). GO can be uniformly dispersed in mixing water because of oxygen-containing functional groups on its basal and edge planes (Gong et al., 2015b; Lerf et al., 1998; Walter et al., 2015). Besides, its high surface area and two-dimensional structure provide numerous sites for interaction with cement hydrates (Bandaru et al., 2017; Basquiroto de Souza et al., 2022; W. Li et al., 2017a). Furthermore, GO's exceptional mechanical properties, including high tensile strength and Young's modulus, make it ideal for reinforcing cement-based materials (X. Li et al., 2017; Zhang et al., 2021). Moreover, GO's chemical properties facilitate improved interfacial bonding with the cement matrix, enhancing mechanical properties and durability (Basquiroto de Souza et al., 2022; W. Li et al., 2017a). Literature reported that the addition of a minimal amount of GO (0.01-0.05 wt.%) can significantly enhance the mechanical properties, particularly the compressive strength and flexural strength, of cement paste, mortar, and concrete, with varying degrees of improvement (Anwar et al., 2023; Kadir et al., 2023; Suo et al., 2022; Juan Wang et al., 2020). This variation is attributed to factors such as the dosage of GO, dispersion techniques employed, and the purity of the purchased or synthesised GO (Li et al., 2018; Lv et al., 2022).

Furthermore, there have been contrasting proposed mechanisms regarding the role of GO in cementitious materials. For example, Lv et al. (2014) suggested that GO adsorbs clinker particles onto its surface, promoting the nucleation of C-S-H, which then grows outward in a flower-like structure due to spatial constraints (Lv et al., 2014b). However, Cui et al. (2017) have proposed that these flower-like structures were the result of calcite polymers formed during prolonged exposure to the environment during scanning electron microscope (SEM) sample preparation (Cui et al., 2017b). Similarly, while some studies have indicated that GO significantly influences the hydration of clinker minerals (W. Li et al., 2017b; Vallurupalli et al., 2020; Yang et al., 2017c), others have reported no significant change in the degree of hydration but highlight a refinement in the microstructure (Metaxa et al., 2021; Juan Wang et al., 2020). Moreover, while a few

studies have suggested that GO improves the strength of mortar by enhancing hydration without altering the C-S-H structure (Kang et al., 2019; Yang et al., 2017c), many others have reported that the incorporation of GO significantly affects the morphology of C-S-H (Djenaoucine et al., 2024). These conflicting results highlight the complexity of the interactions between GO and cementitious materials and underscore the need for further research to elucidate the actual reinforcing mechanisms. Consequently, the primary objective of this study is to establish a correlation between the enhancements in cement paste properties and GO's diverse characteristics.

5.1.2 Materials and methods

5.1.2.1 Materials and Characterisation

The graphene oxide used in this study was obtained from Ceylon Graphene Technologies (Pvt) Ltd in Sri Lanka, and its characterisation was conducted using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). OPC, which adhered to the Japan Industrial Standard JIS R 5201:2015, was sourced from the Japan Cement Association. The GO was obtained as a 10 g/L dispersion in water. **Figure 5.1(a)** depicts graphene oxide's molecular structure and characterisation results. XRD analysis employed a Rigaku X-ray diffractometer with Cu-K α radiation, covering a 2θ range of 5–70°, a step size of 0.02°, and a rotating speed of 6.5°/min. The measurements at 2 s per scan revealed a significant diffraction peak at $2\theta \sim 11.2^\circ$ for GO, as depicted in **Figure 5.1(b)**. Comparable XRD patterns for GO have been documented previously (Mohammed et al., 2018). The spacing between graphene layers in GO, as calculated through Bragg's equation, was identified to be 0.79 nm.

FTIR spectroscopy, performed using a Jasco 6200HFV instrument from Japan, covered a wave number range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . The vibrational stretching modes of various molecular bonds in GO were investigated, as shown in the FTIR graph in **Figure 5.1(c)**. The spectrum indicated bond stretching peaks for hydroxyl

(-O-H at $\sim 3300\text{ cm}^{-1}$), carbonyl (C=O at 1650 cm^{-1}), aromatic (C=C at 1550 cm^{-1}), carboxyl (C-O at 1190 cm^{-1}), epoxy (C-O-C at 1100 cm^{-1}), and C-OH (at 1050 cm^{-1}). These infrared patterns align with those reported in prior studies (Mohammed et al., 2018).

5.1.2.2 Sample preparation for Zeta potential test

The Zeta potential analyser (ELSZ-1000, Japan) was utilised to measure the zeta potential, a gauge of particle charge at the shear plane, for GO suspended in a liquid. The liquid phase of early cement paste primarily consists of Na^+ , K^+ , SO_4^{2-} , and Ca^{2+} ions, with Ca^{2+} playing a crucial role in the kinetic, morphological, and structural characteristics of C-S-H. Consequently, $\text{Ca}(\text{OH})_2$ solutions were prepared at varying concentrations (0.6, 0.8, 2, 4, 6, 8, 10 mmol/l). GO was introduced at a concentration of 0.05 g/L, and the suspension was allowed to settle for 24 hours. Before measurement, the residual suspension solution underwent ultrasonication for 1 minute. The average zeta value was determined for each suspension through three repeated measurements involving the zeta potential analysis conducted 10 times.

5.1.2.3 Cement Paste Preparation

Two sets of cement paste were meticulously formulated, one with graphene oxide (GO) and the other without. GO was added at a weight percentage of 0.06 % of the cement content, a proportion determined as optimal in preliminary experiments. To facilitate effective dispersion and homogeneous mixing of GO in the cement pastes, a water-to-cement ratio (w/c) of 0.40 was selected (Li et al., 2018). In the initial step, GO was dispersed in water before blending with cement. This dispersion process unfolded in two stages: i) GO (10 g/L) was homogenised with deionised water using a homogeniser at 10000 rpm for 5 minutes, and ii) the resulting solution underwent ultrasonication using a 400 W sonicate for 10 minutes.

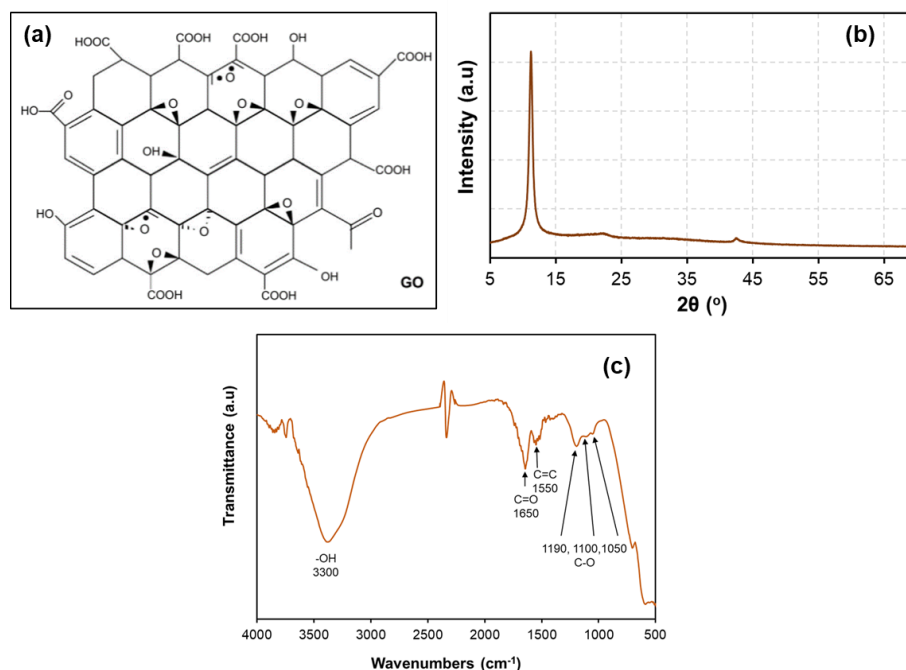


Figure 5.1: Characterisation of GO; (a) a simplified molecular structure of GO, (b) XRD patterns of GO, and (c) FTIR spectra of GO

The cement pastes were prepared using a planetary-type mixer (Hobart N50 5-quart mixer). Initially, water or the GO solution was introduced into the cement within the mixer at low speed for 1 min, which was succeeded by an additional 1-min duration at high speed. After a momentary pause in mixing, the surface of the mixture was cleared using a spatula. Subsequently, a 2-min high-speed mixing phase ensued to ensure the uniformity of the pastes. The resulting pastes were poured into cylindrical moulds measuring 50 mm in diameter and 100 mm in height, adopting a two-layer configuration. Each layer underwent 20 s of vibration to eliminate larger pores that could arise from reduced workability. Once moulded, the specimens were hermetically sealed and positioned in a curing environment at a constant temperature of $20 \pm 2^\circ\text{C}$. Following a curing period of 24 h, the specimens were carefully extracted from the moulds, enveloped in polyester film, and stored under controlled conditions at $20 \pm 2^\circ\text{C}$.

Additionally, to prepare samples for ^1H NMR analysis, another set of cement paste with and without GO was prepared using the same method as before, but with white cement. White cement was chosen because it is free of iron ions, which can interfere with NMR signals. After one day of curing, samples for ^1H NMR were cored using a core driller with a 7 mm diameter (as shown in **Figure 5.2**), and the cored samples were approximately 20 mm in height. The samples were then immediately transferred to NMR sample tubes with a 10 mm diameter (**Figure 5.3**). The tubes were sealed with plastic caps and secured with parafilm to prevent moisture transfer.



Figure 5.2: Sample extraction using core drilling

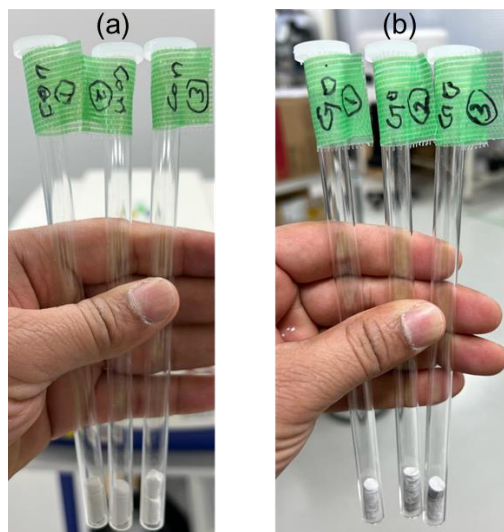


Figure 5.3: The core drilled sample is placed into an NMR tube and sealed: (a) Control paste and (b) GO paste

5.1.2.4 Analysis of Hydration and Microstructure

The hydration and microstructure evaluation of the cement pastes involved TGA, XRD, and SEM. Cylinders were crushed into pieces measuring 20 mm or more minor using a hammer at 7, 14, and 28 days to obtain samples for analysis. These pieces were then immersed in acetone for 2 days to arrest the hydration process. After separation through suction filtration, the specimen pieces underwent a 2-day drying period in a temperature chamber set at 40 °C to eliminate residual acetone. After thorough drying, the samples were carefully ground using mortar and pestles, with precautions to avoid excessive heat. The resulting powder was sifted through a 75 μm sieve, and only the fraction that passed through was employed for subsequent analysis.

Quantification of cement hydration, specifically Portlandite ($\text{Ca}(\text{OH})_2$) content, both with and without GO, was achieved through TGA under nitrogen conditions using a HITACHI TG/DTA 7220. The heating rate was set at 10 °C /min within the 20-950 °C temperature range. XRD analysis was conducted using a Rigaku X-ray diffractometer with $\text{CuK}\alpha$

radiation, employing specific parameters such as a tube voltage of 40 kV, tube current of 40 mA, scanning range of $2\theta = 5\sim 70^\circ$, step width of 0.02° , and a scanning speed of $6.5^\circ/\text{min}$. After scanning, the unprocessed diffraction data were compared with the Crystallography Open Database (COD) using Profex software for peak identification. Subsequently, phase quantification was conducted through Rietveld analysis. SEM imaging of specimens obtained at the 7-day was carried out using a JSM-IT200 microscope manufactured by JEOL in Japan. The instrument operated at 15 kV, and the working distance was 10 mm. Before examination, powder samples were coated with a thin layer of gold for enhanced imaging quality.

A Bruker minispec mq20 NMR analyser, equipped with a digital filter, was used for the NMR relaxometry measurements. The instrument operated at a resonance frequency of 20 MHz (0.47 T) for protons, with a $\pi/2$ pulse length of $2.4\ \mu\text{s}$ and a relaxation delay of 1 s (Kojima et al., 2023). For all samples, a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence with 256 scans was employed to acquire the distribution of T_2 relaxation times quantitatively. The resulting CPMG data were processed using CONTIN, which utilizes an inverse Laplace transform (ILT) algorithm, to obtain quasi-continuous T_2 distributions (Kojima et al., 2023).

5.1.3 Results and discussion

5.1.3.1 Zeta Potential Analysis

The initial pH of the $\text{Ca}(\text{OH})_2$ solutions ranged from 10.5 to 12.7, and the addition of GO did not significantly affect the pH. **Figure 5.4** illustrates the zeta potential variation of GO with varying Ca^{2+} concentrations, showing a pattern similar to fillers such as limestone powder, quartz sand, and C-S-H particles (Meng et al., 2021). At a Ca^{2+} concentration of 0.6 mmol/L, the zeta potential of GO is -15.34 mV, likely due to the dissociation of carboxylate groups on the surface. The isoelectric point (IEP), where the zeta potential is 0, occurs at a Ca^{2+} concentration of approximately 3 mmol/L, similar to

quartz sand and C–S–H particles (Ouyang et al., 2017). The zeta potential increases from 3 to 10 mmol/L, reaching a maximum value of 21.55 mV at a Ca^{2+} concentration of 10 mmol/L. This increase is attributed to the dominance of surface calcium ion hydrolysis at low Ca^{2+} concentrations (< 3 mmol/l). In comparison, at high Ca^{2+} concentrations (> 3 mmol/l), the adsorption of external Ca^{2+} ions, rather than surface ion hydrolysis, dominates the surface charge, resulting in a ‘reversal’ of the zeta potential. These observations suggest a more enormous affinity of the GO particle surface for Ca^{2+} .

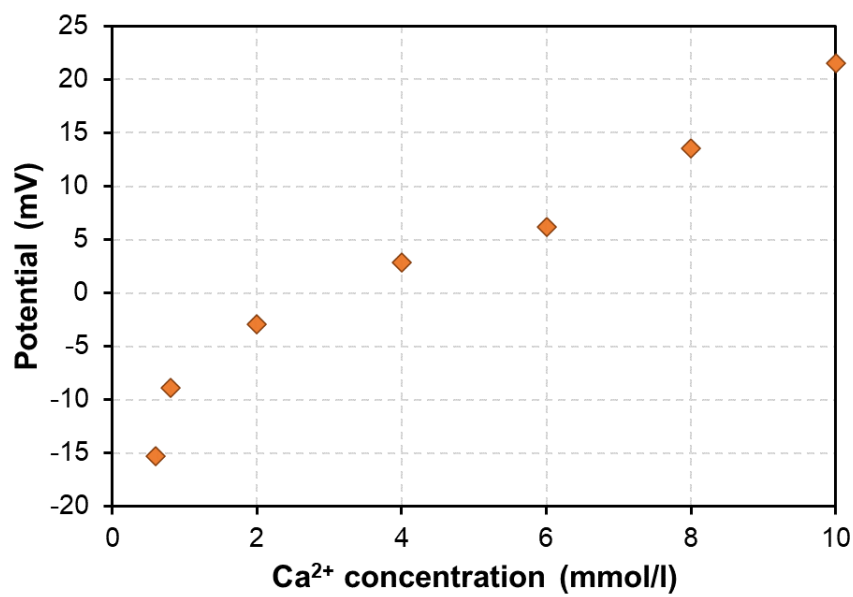


Figure 5.4: Variation of zeta potential of GO with Ca^{2+} concentration in $\text{Ca}(\text{OH})_2$ solution

5.1.3.2 Thermogravimetric analysis

Calcium hydroxide (CH) concentration in the pastes was determined through TGA-DTG graphs and presented at specific time intervals (7, 14, and 28 days). Notably, the GO paste displays a more significant mass loss for portlandite than the control (

Figure 5.5). The increased mass loss and variability in portlandite content between the GO paste and the control indicate a rise at 7 and 28 days. The higher CH content at 28

days suggests that the GO paste undergoes more extensive hydration than the control samples.

In the initial 24 hours of hydration, GO expedites the cement paste's hydration process, fostering nucleation and yielding increased portlandite content in the pastes at 1 and 7 days. Moreover, GO's hydrophilic nature allows it to absorb extra water molecules on its surface and within the interlayer (Qureshi and Panesar, 2019; Yang et al., 2017c). This absorption, gradually occurring after 7 days, may release the essential free water content for continued hydration. As a result, this additional hydration contributes to a heightened portlandite content at 28 days.

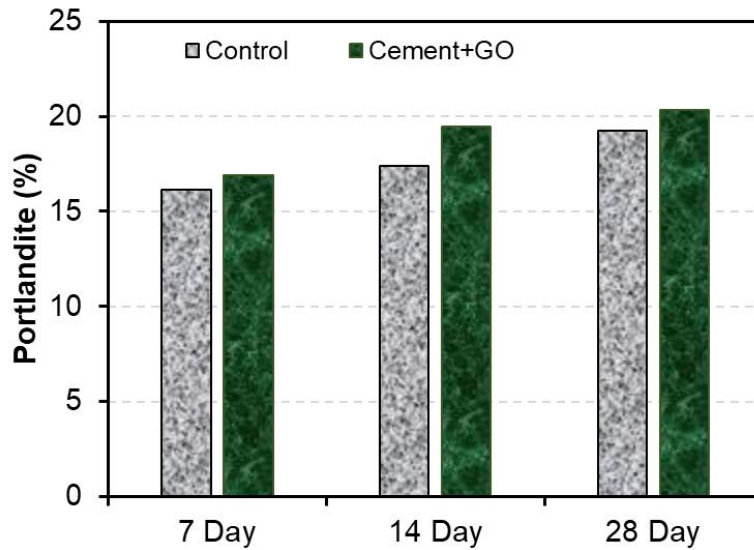


Figure 5.5: TGA quantified Portland content at 7, 14, and 28 days.

5.1.3.3 X-ray diffraction analysis

Figure 5.6a–c depicts the cement paste's XRD patterns at 7, 14, and 28 days. The identified cement hydration products include monosulphate, portlandite, C_3S , and C_2S at all ages. The XRD analysis aligns with the hydration phases revealed by thermogravimetric analysis. The intensity of portlandite phases exhibits an increase with the inclusion of GO in the cement paste and with the progression of time. Simultaneously,

the crystalline phases also increased with the presence of GO. Since XRD cannot directly distinguish amorphous phases, a quantitative analysis using Rietveld software (Profex) was applied to the hydrated pastes to quantify the content of amorphous C-S-H gel and other hydration products.

Rietveld quantification findings illustrate that GO promotes the development of portlandite and amorphous C-S-H gel phases (**Figure 5.6d**). In comparison to the control paste, the rise in portlandite content is approximately 2.9 %, 4.1 %, and 5.4 %, while the C-S-H content registers at about 4.6 %, 5.0 %, and 7.3 % at 7 days, 14 days, and 28 days, respectively. The thermogravimetric analysis further verifies the increased portlandite quantity in the presence of GO, which is attributed to GO functional groups' effective dispersion and active involvement.

5.1.3.4 Microstructural analysis

The SEM images in **Figure 5.7** demonstrate the characteristic pore-sealing properties of GO in the paste at 7 days. The analysis indicates that the micropores within the cement paste are randomly filled with GO, effectively sealing smaller pores with amorphous C-S-H and crystalline materials, as evidenced in **Figure 5.7(a and b)**. The high dispersibility of GO in water and its small plane size ($1.2 \pm 0.8 \mu\text{m}$) contribute to this effective pore-filling performance. Additionally, the microstructure of GO paste displays a higher density than the control.

Furthermore, SEM investigations reveal that GO is highly compatible with cement hydration products, enhancing the microstructure of the cement paste. GO accelerates cement hydration by promoting nucleation on its surface. The functional groups on the GO surface, including hydroxyl, epoxy, carbonyl, and carboxylic acid, adsorb clinker particles and water molecules and promote nucleation on its surface. As a result, hydration products such as C-S-H are formed in a constrained space, resulting in a flower-like shape, as shown in **Figure 5.7(b)**.

Moreover, due to GO's affinity for calcium ions, as discussed in **Section 5.1.3.1**, the adsorption of calcium ions onto the GO surface is enhanced, reducing the mobility of these adsorbed Ca^{2+} ions. This leads to the facilitation of the formation of stable nuclei, which subsequently grow to form macroscopic particles. Consequently, many C-S-H nuclei are generated on the GO surfaces, as supported by the microscopic observations of the morphology and distribution of hydration products on the GO surfaces, as shown in **Figure 5.7**.

In addition, oxygen-containing functional groups in GO enable it to form covalent bonds with the silicate structures in C-S-H. Conversely, GO may involve the adsorption of Ca^{2+} ions in portlandite onto its surface. Moreover, the positive charge of these ions can interact with the negatively charged functional groups on GO, leading to the formation of covalent bonds, as illustrated in **Figure 5.8** and contributing to the densification of the microstructure.

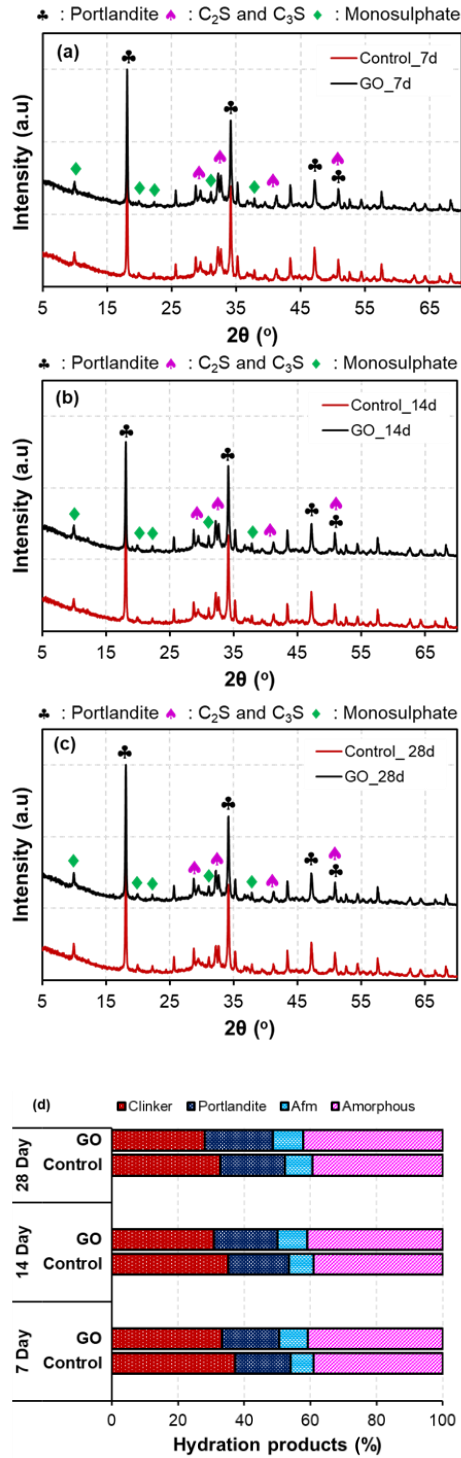


Figure 5.6: XRD patterns of control and GO pastes at 7 days (a), 14 days (b) and 28 days (c), and Phase quantification by Rietveld analysis (d).

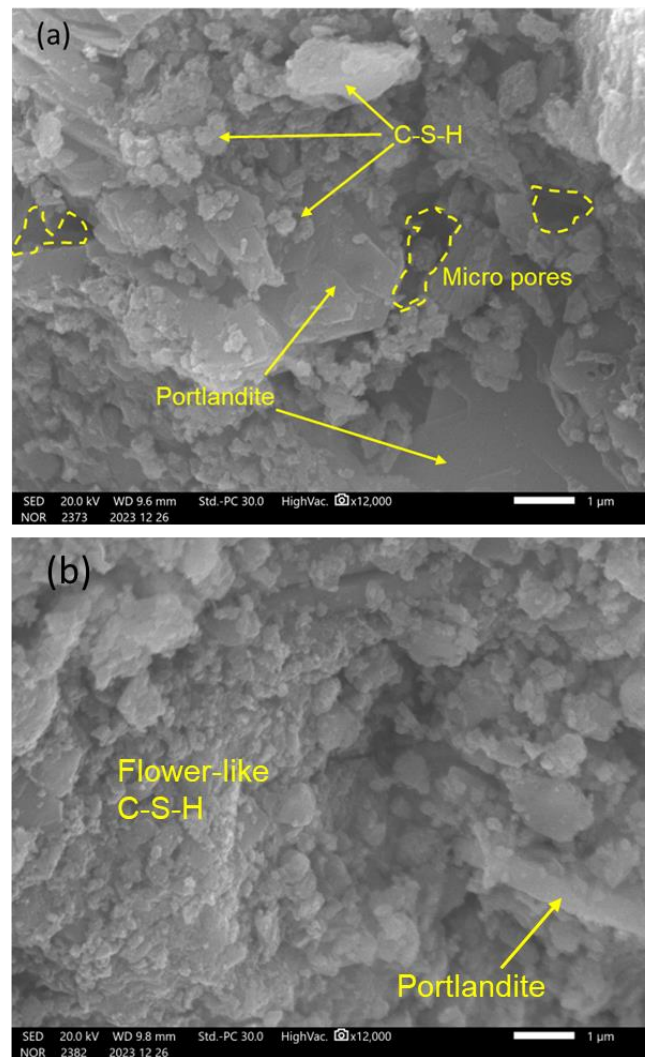


Figure 5.7: SEM images; (a) control paste, and (b) GO paste

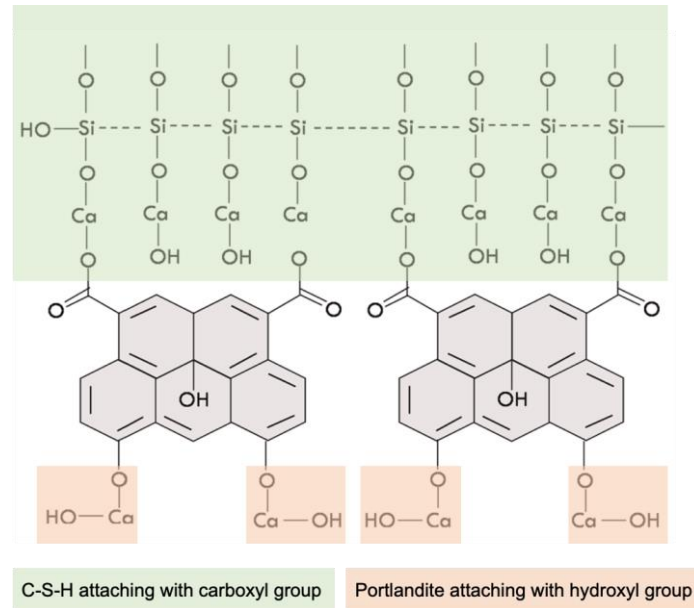


Figure 5.8: Chemical interaction between functional groups (Carboxylic acid/hydroxyl) in GO and the hydration products (portlandite and C-S-H)

5.1.3.5 ^1H NMR Analysis

Figure 5.9 illustrates the T_2 distribution map for the cored sample at curing ages 1, 3, 7, and 28 days. On one day (**Figure 5.9a**), the control sample exhibits a combined curve representing intrerhydrate water (free water) and interlayer water, whereas the GO paste displays two distinct peaks corresponding to intrerhydrate water and gel water. This effect can be attributed to GO adsorbing water molecules on its surface, temporarily forming a water reservoir between C-S-H layers, thereby increasing the gel pore water detected in the paste. It should be noted that capillary water was not detected in any of the samples at any age, likely because it evaporated during core drilling due to exposure to the environment, even at room temperature. By 3 days of hydration (**Figure 5.9b**), the control sample shows a broad peak centred at 0.67 ms, representing intralayer, gel, and interhydrate pores as a single unit. In contrast, the GO paste exhibits a resultant curve with a comparatively larger amount of interlayer water and pore water, suggesting that

the adsorbed water by GO promotes C-S-H formation. Additionally, interhydrate water was detected in both pastes, indicating that hydration was still in the early stages.

At 7 days (**Figure 5.9c**), interhydrate water had disappeared entirely, confirming the absence of free water in both pastes. The control sample displays a broad peak centred at 0.56 ms, indicative of gel pores, while the GO paste shows a broad peak centred at 0.48 ms, corresponding to interlayer water. This suggests that the GO paste promotes hydration and increases C-S-H layers faster than the control paste. At 28 days (**Figure 5.9d**), the control sample exhibits a combined curve of gel pores and interlayer water, while the GO paste shows two distinct interlayer peaks at 0.17 and 0.47 ms. This indicates that GO converts gel water into interlayer water much faster than the control paste. As explained by Muller et al., “In the absence of remaining capillary water, hydration continues to take place (creating C-S-H layers) using gel water” (Albert MULLER, 2014). Thus, inserting new C-S-H layers into a gel pore reflects a decrease in gel water fraction, known as “gel densification,” resulting in a more ordered C-S-H structure.

Based on these results, it can be concluded that the incorporation of GO decreases gel pores and increases interlayer water, evidencing the formation of high-density C-S-H with a more ordered structure.

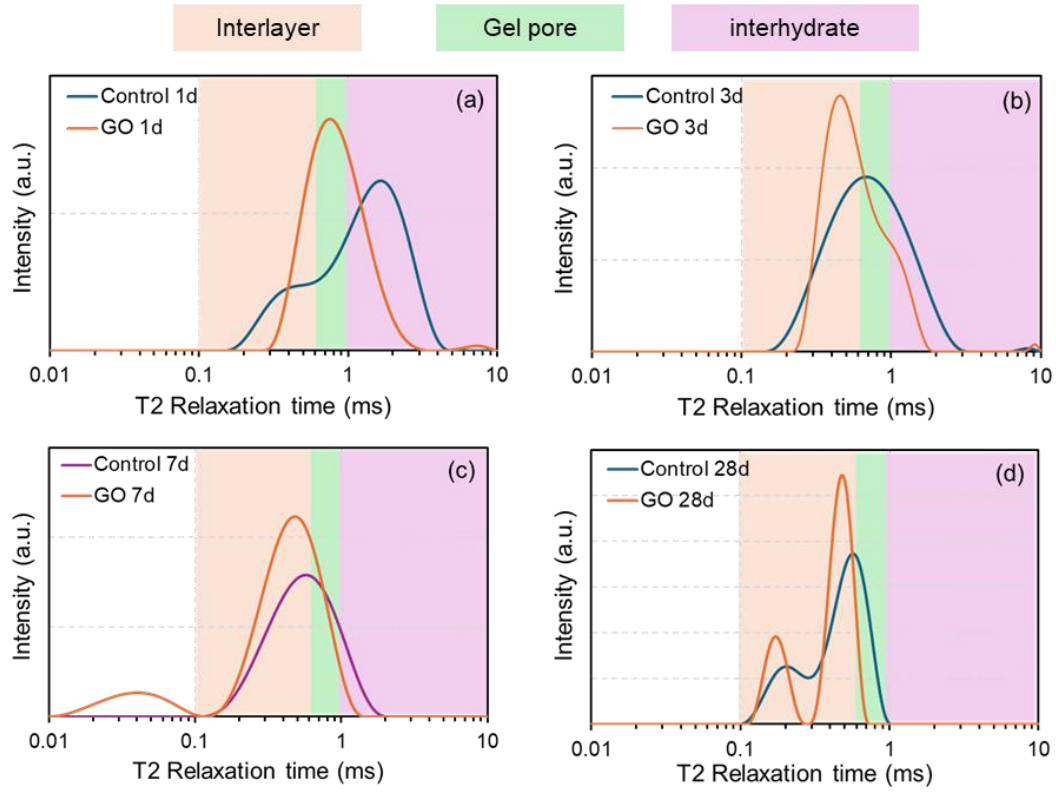


Figure 5.9: T₂ distribution of control paste and GO paste at 1 day (a), 3 days (b), 7 days (c), and 28 days(d)

5.1.4 Conclusions

The impact of GO on cement pastes was systematically explored by assessing both hydration processes and microstructural changes. The characterisation analysis effectively verified the presence of functional groups within the GO. TGA further clarified the influence of GO on clinker hydration, demonstrating an accelerated process that resulted in higher production of portlandite compared to the control. TGA further clarified the influence of GO on clinker hydration, demonstrating an accelerated process that resulted in higher production of portlandite compared to the control. This finding was confirmed by a Rietveld analysis of X-ray diffraction patterns, revealing distinct variations in the intensities of hydration products upon adding GO. The X-ray diffraction patterns displayed typical hydration products, with differing intensities indicating the

modifying effect of GO. Microstructural investigations aligned with the XRD and zeta potential results, illustrating that micro-pores were filled with portlandite and C-S-H due to the formation of covalent bonds between hydration products and the surface of GO. Moreover, H NMR results corroborated these findings by evidencing a reduction in gel pores and an increase in interlayer water, indicating a denser and more ordered C-S-H structure formation. This comprehensive analysis provides valuable insights into the intricate interplay between GO, clinker hydration, and microstructural development in cement composites.

5.2 Exploring the reinforcing mechanism of Graphene Oxide in cementitious materials through microstructural analysis of synthesised C-S-H

5.2.1 Introduction

C-S-H, the primary hydration product of Portland cement, plays a crucial role in determining the mechanical performance and durability of cement-based materials (Allen et al., 2007; Kunther et al., 2017; Miao et al., 2023; Zhao et al., 2018). C-S-H gel occupies approximately 70% of the volume and is responsible for the hydrates' initial strength and long-term durability (Tu et al., 2022). The formation of C-S-H gel involves polymerising silicate ions to form long chains of silicon-oxygen tetrahedra, which are coordinated with intralayer calcium sheets and sandwiched by interlayer water and calcium ions (Chiang and Chang, 2021). The dissolution of C_3S and C_2S provides the calcium ions. The C-S-H gel can exist in both amorphous and crystalline forms, with its structure highly variable depending on the calcium-to-silicon (Ca/Si) molar ratio. The Ca/Si ratio typically ranges from 1.2 to 2.3 in regular hydration, with a mean value of 1.7 (Allen et al., 2007; Richardson, 1999). A lower Ca/Si ratio results in a more ordered structure with interlayer and intralayer calcium, while higher Ca/Si ratios lead to a more

disordered structure (Wang et al., 2019a; Zhu et al., 2016). Theoretically, C–S–H nanoparticles can nucleate the hydration of cement within 24 hours, quickly leading to large-sized C–S–H gels during the early stage (Brykov et al., 2013). Therefore, any modifications to the microstructure of C-S-H, such as those induced by incorporating GO, can significantly impact cement-based materials' mechanical properties and durability. Understanding the interactions between GO and C-S-H at the nanoscale is crucial for optimising the performance of cement-based materials. Hence, this study aims to investigate the effect of GO on the microstructural properties of C-S-H and its subsequent impact on the mechanical strength of cementitious materials, aiming to provide valuable insights into the reinforcing mechanisms of GO in cement-based materials and aid in the development of more sustainable and resilient infrastructure materials.

5.2.2 Methods and materials

5.2.2.1 Synthesis of C-S-H with/without incorporating GO

Typically, the hydration of Ordinary Portland Cement (OPC) results in the formation of C-S-H with a Ca/Si ratio ranging from 0.8 to 2.3, and most studies on C-S-H focus on structures with Ca/Si ratios of 1.0 and 1.5 (Richardson, 2004, 1999). Therefore, in this study, C-S-H with Ca/Si ratios of 1.0 and 1.5 was synthesized using the co-precipitation method (Yoshida et al., 2021) to investigate its microstructural properties. Under controlled conditions, a special grade of $\text{Ca}(\text{OH})_2$ supplied by Kanto Chemical Co., Inc, Japan, and high-purity SiO_2 from Nippon Aerosil Co., Ltd, were mixed in deionized water with molar ratios of 1:1 and 1.5:1, maintaining a water-to-powder ratio of 20 mL/g in a PET bottle. N_2 gas was purged into the solution to remove entrapped air, and the bottle was tightly sealed. The sealed bottle was placed in a temperature-controlled chamber at 50 °C for 10 days, with the mixture being shaken for 2 minutes every day. After the curing process, the resulting slurry was filtered using a suction filter. The solid particles were washed three times with deionized water to remove any adsorbed ions from the C-S-H surface. The moisture in the solid particles was then removed by freeze-drying

for two days (Kopitha et al., 2023). Finally, the C-S-H fine powder samples were stored in a desiccator to prevent carbonation before analysis.

To study the effect of the GO on the microstructural properties of the C-S-H, the GO was added with two different weight percentages (0.5 and 1.0) of the total weight of $\text{Ca}(\text{OH})_2$ and SiO_2 . It should be mentioned that when the GO is added to the solution, a few drops of diluted NaOH solution are added to maintain the alkali environment (H. Li et al., 2017). **Table 5.1** summarises the mixing proportions to prepare pure C-S-H (denoted by CSH) and GO-incorporated C-S-H (denoted by CSH-GO).

Table 5.1: Mix proportions for C-S-H with and without incorporating GO.

Sample ID	Ca/Si ratio	$W_{\text{Ca}(\text{OH})_2}$ (g)	W_{SiO_2} (g)	W_{GO^*} (mL)	W_{water} (g)
CSH 1.0	1.0	18.50	15	-	670.00
CSH 1.5	1.5	27.75	15	-	855.00
CSH-GO 0.5	1.0	18.50	15	16.75	653.25
CSH-GO 1.0	1.0	18.50	15	33.50	636.50

*GO concentration was 10g/l

5.2.3 Characterisation methods

The prepared GO and synthesised C-S-H, with and without graphene oxide incorporation, were characterised using a combination of analytical techniques, including XRD, FTIR, XRF, TGA, SEM, silicon nuclear magnetic resonance spectroscopy (^{29}Si NMR), and hydrogen nuclear magnetic resonance spectroscopy (^1H NMR). To measure the crystalline phases in the samples, XRD analysis employed a Rigaku X-ray diffractometer equipped with $\text{CuK}\alpha$ radiation, adhering to the following conditions: a tube voltage of 40 kV, tube current of 40 mA, scanning range of $2\theta = 5\sim 70^\circ$, step width of 0.02° , and a scanning speed of $6.5^\circ/\text{min}$. FTIR spectroscopy (6200HFV, Jasco, Japan.) was used to detect the chemical bonding of samples between 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . XRF (SEA 1200VX, Hitachi, Japan) was used with an excitation voltage of 40 kV

and tube current of 1 mA to determine the elemental composition quantitatively. TGA was performed using a HITACHI TG/DTA 7220 on powdered samples under a nitrogen atmosphere with a 110 mL/min flow rate to examine their thermal behaviour. The samples were heated from 20 °C to 950 °C at 10 °C/min. In addition, the morphologies were observed by SEM (JSM-IT200, JEOL, Japan). Powder samples were prepared by coating them with a thin layer of gold (Nithurshan et al., 2024).

The CSH and CSH-GO samples were prepared for ¹H NMR by filling a 10 mm diameter NMR sample cell up to 15 mm. The cell was sealed with a plastic cap and wrapped with parafilm to ensure a tight seal, then stored at a temperature of 20 ± 1 °C. A Bruker minispec mq20 NMR analyser, equipped with a digital filter, was used for the NMR relaxometry measurements under the conditions explained in **Section 5.1.2.4**. The samples were prepared for silicon solid-state magic angle spinning (MAS) NMR (²⁹Si NMR) by filling a 3.2 mm probe. They were analysed using a Bruker 500 MHz spectrometer operating at a resonance frequency of 99.4 MHz (11.74 T) for silicon nuclei, with a pulse width of 1.5 µs. The Si NMR spectra for each sample were obtained by performing 2800 scans with a recycle delay of 20 seconds. The ²⁹Si nuclei were referenced to hexamethylcyclotrisiloxane (C₆H₁₈O₃Si₃) at a one mol/L concentration.

5.2.4 Results and Discussions

5.2.4.1 Characterisation of pure GO and C-S-H

The XRD diffraction pattern of GO revealed a prominent peak at approximately 11.2 degrees, as shown in **Figure 5.10(a)**, and the interlayer spacing of GO sheets was determined to be 0.79 nm using Bragg's equation (Eq. (4.1)), which is consistent with previous studies (Ganesh et al., 2023; Qureshi and Panesar, 2019).

$$\lambda = 2 \cdot d \cdot \sin(\theta) \quad (4.1)$$

Where λ represents the wavelength of the X-ray beam (0.154 nm), d is the distance between adjacent GO layers, and θ is the diffraction angle.

FTIR spectroscopy of GO is depicted in **Figure 5.10(b)**, revealing vibrational stretching modes characteristic of various oxygen-containing molecular bonds. These spectral features confirm GO's purity and provide insights into its active functional groups. The spectrum exhibits distinct peaks corresponding to hydroxyl (-O-H at $\sim 3300\text{ cm}^{-1}$), carbonyl (C=O at 1650 cm^{-1}), aromatic (C=C at 1550 cm^{-1}), carboxyl (C-O at 1190 cm^{-1}), epoxy (C-O-C at 1100 cm^{-1}), and C-OH (at 1050 cm^{-1}) groups. These transmittance peaks closely align with those reported in previous studies (Ganesh et al., 2023; Mohammed et al., 2018), further confirming the purity and chemical composition of the GO sample.

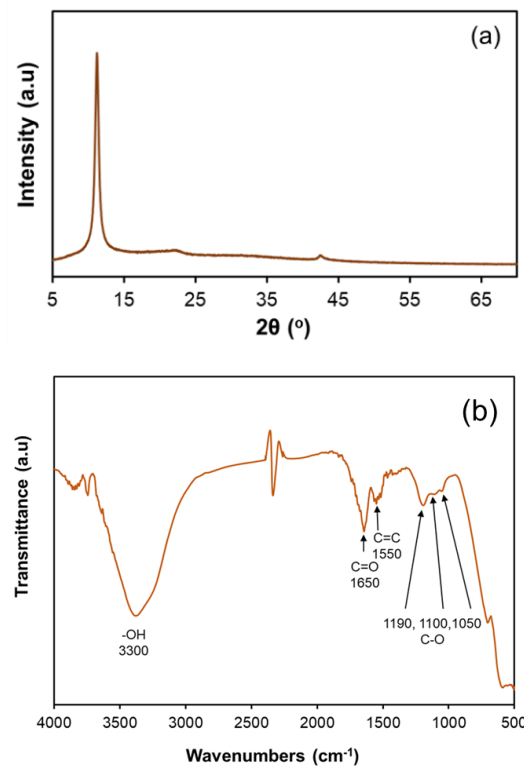


Figure 5.10: XRD (a) and FTIR (b) analysis of GO.

The XRF analysis of the synthesised pure C-S-H, targeting Ca/Si ratios of 1.0 and 1.5, revealed CaO percentages of 51.8% and 56.5 % and SiO₂ percentages of 47.35 % and 42.6 %, respectively. The remaining oxides were found to be less than 1%. Based on the oxide percentages of CaO and SiO₂, the actual molar ratios of Ca/Si in CSH 1.0 and CSH 1.5 were determined to be 1.17 and 1.42, respectively, closely matching the targeted Ca/Si ratios.

5.2.4.2 Microstructural changes of C-S-H with GO incorporation

(a) TGA analysis

The TG and DTG curves of pure C-S-H and C-S-H with GO obtained by TGA analysis are presented in **Figure 5.11**. The TG weight loss in the temperature range of 50–105 °C is attributed to the evaporation of adsorbed water, while the weight loss between 110 °C and 250 °C is caused by the dehydration of the C-S-H phase (K. Li et al., 2024). Further weight loss observed in the temperature ranges of 600–850 °C is due to the decomposition of Calcite. Contrary to findings reported in many studies, no portlandite (Ca(OH)₂) formation was observed in any of the samples as dehydration of portlandite in the 400–600 °C range. This absence may be attributed to this study's improved C-S-H synthesis method. When the Ca/Si ratio in C-S-H increases from 1 to 1.5, the mass loss increases, as depicted in **Figure 5.11(b)**. This increase is attributed to the greater abundance of calcium ions with a higher Ca/Si ratio, leading to more water molecules bound within the C-S-H structure. Moreover, the observed weight loss falls within the range of 17 %-20 %, as reported in the literature (Baltakys et al., 2007).

Moreover, incorporating GO into C-S-H increased the TG mass loss of C-S-H. This effect was more pronounced with increasing amounts of GO, from 0.5% to 1.0 % by weight. In addition, the shift of the DTG peak curve towards the lower temperatures (below 105 °C) with increasing GO content was observed in **Figure 5.11(b)**. This shift is attributed to the increased adsorption of water molecules in the CSH-GO composite due to GO's active

functional groups, such as hydroxyl, carboxyl, and epoxy(Miao et al., 2023). Moreover, above 170 °C, the dehydration of CSH in the CSH-GO composite occurred more rapidly (steep-slope) compared to samples with lower GO content or pure C-S-H. This observation confirms that the polymerisation degree of C-S-H is increased with GO incorporation. This increased polymerisation of C-S-H can be attributed to the adsorption of Ca^{2+} ions on the surface of GO, facilitated by its active functional groups, which promote nucleation (Basquiroto de Souza et al., 2022).

Furthermore, the formation of calcite was observed upon the incorporation of GO. This phenomenon cannot be attributed to sample preparation procedures; instead, it is attributed to the decomposition of oxygen functional groups on the surface of GO in alkaline media (Yaseen et al., 2018). This decomposition releases CO, CO₂, and water, vital in forming Calcite. However, the amount of Calcite formed was small, accounting for less than 1 % of the total mass.

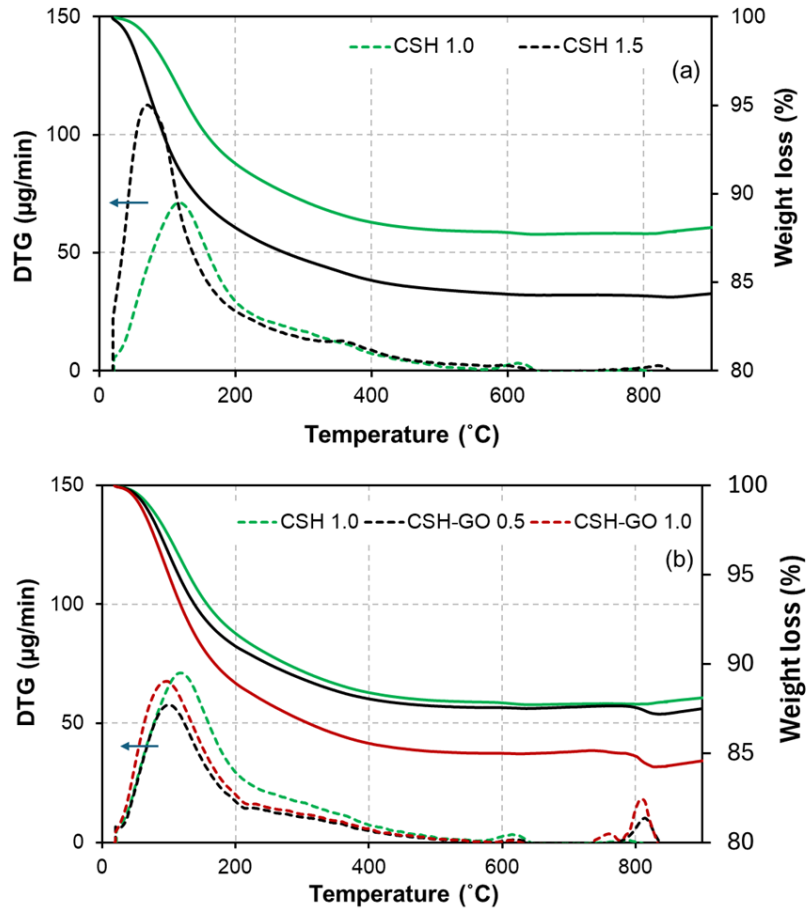


Figure 5.11: DTG-TG curves of pure C-S-H (a) and C-S-H with GO (b).

(b) XRD analysis

The XRD diffraction patterns of C-S-H synthesised at different Ca/Si ratios and GO wt% are depicted in **Figure 5.12**, where the single peak at around 29° is attributed to the existence of C-S-H (F. Kim et al., 2010). Moreover, the peak corresponding to calcite was not detected because of its highly amorphous state. XRD confirms no portlandite ($2\theta = 18$ and 34) is formed (Yaseen et al., 2018). A peak at 7.5° was observed, which indicates the basal (001) reflection of the tobermorite-like structure ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$) (Grangeon et al., 2013). This peak increased with increasing Ca/Si ratio and GO wt%, confirming the enhancement of highly ordered crystalline C-S-H formation. To access the

crystallinity of the C-S-H influenced by GO, Full Width at Half Maximum (FWHM) was measured using ORIGIN software for the major peaks observed at 28° (Peak 1), 32° (Peak 2), 50° (Peak 3) and 55° (Peak 4) degrees and tabulated in **Table 5.2**. Increasing the Ca/Si ratio from 1.0 to 1.5 leads to a decrease in the full width at half maximum (FWHM) of C-S-H for all peaks, indicating the presence of larger and more ordered crystallites (Grangeon et al., 2013). In C-S-H, silicon exists as SiO_4 tetrahedra organised in chains, which carry negative charges, facilitating cation retention in the silicate interlayer. Therefore, an increase in the Ca/Si ratio or the concentration of Ca^{2+} ions can provide charge balance, enabling them to bind to the negatively charged surface of C-S-H. This neutralises the silanol group, improving silicon conversion (Tomita et al., 2021).

Moreover, the incorporation of GO indicated a decrease in FWHM values for all peaks compared to CSH 1.0. This is attributed to GO's ability to adsorb Ca^{2+} ions due to its high surface area and the presence of carboxylic and hydroxyl groups. This increases the availability of Ca^{2+} concentration, promoting the conversion of Si into solid C-S-H (Basquiroto de Souza et al., 2021). The XRD findings suggest that the incorporation of GO enhances the formation of larger and more ordered C-S-H crystallites. This improvement in crystallite size and order can enhance the strength and durability of cement-based materials by facilitating better load transfer and interlocking of crystals (Baskoro et al., 2018; Ganesh et al., 2023; P. Li et al., 2024; Li et al., 2018).

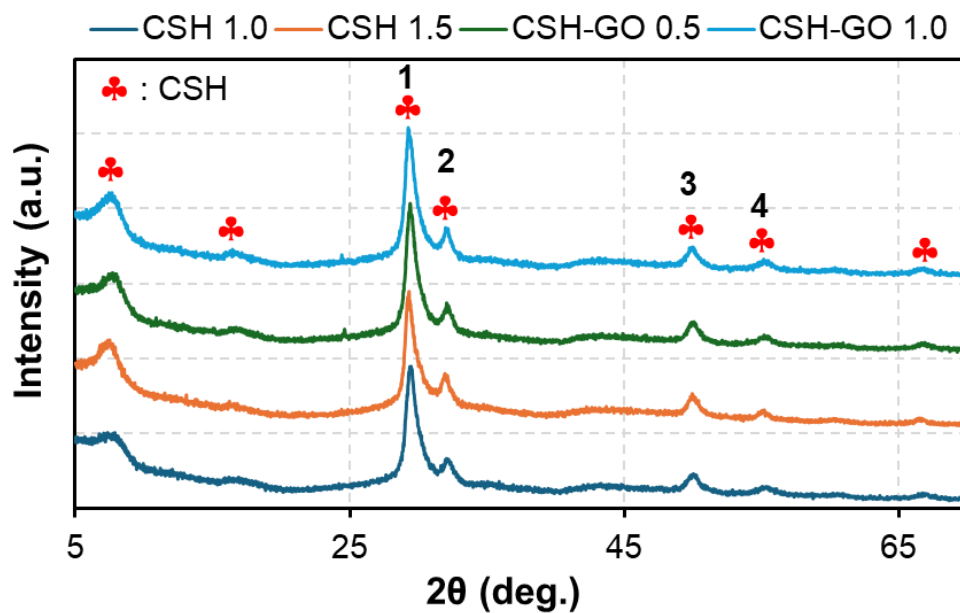


Figure 5.12: XRD diffraction patterns of various C-S-H samples.

Table 5.2: FWHM values of significant peaks of pure C-S-H and GO incorporated C-S-H.

Sample ID	Peak 1	Peak 2	Peak 3	Peak 4
CSH 1.0	1.067	1.560	1.363	2.274
CSH 1.5	0.976	1.374	1.210	1.286
CSH-GO 0.5	0.980	1.332	1.404	2.007
CSH-GO 1.0	0.985	1.260	1.371	1.564

(c) FTIR

FTIR analyses were conducted on all types of C-S-H; the results are presented in **Figure 5.13**. The infrared spectra of C-S-H exhibited a characteristic set of bands within the 400–1200 cm^{-1} range. The most significant bands observed in the infrared spectra include

broadband centered at 1101 cm^{-1} (4 in **Figure 5.13**), attributed to the asymmetric stretching of Si–O–Si bonds. A band centered at 796 cm^{-1} (3 in **Figure 5.13**) was also observed, attributed to the symmetric stretching of Si–O–Si bonds originating from the Q^2 tetrahedron. This band is part of a complex group related to Si–O symmetric and asymmetric stretching vibrations. Furthermore, a band near 665 cm^{-1} (2 in **Figure 5.13**) was linked to Si–O–Si bending vibrations. Finally, a band at 467 cm^{-1} (1 in **Figure 5.13**) was observed, which is attributed to the bending of O–Si–O bonds due to internal deformations of the SiO_4 tetrahedron (Baltakys et al., 2007; Miao et al., 2023).

The intensities of the Si–O–Si bands indicate the overall degree of polymerisation of the silica network (Basquiroto de Souza et al., 2021). Generally, a lower intensity corresponds to a lower degree of polymerisation (Baltakys et al., 2007). Therefore, it can be speculated that the degree of polymerisation of C–S–H increased with increasing Ca/Si ratio and GO wt%. This is supported by the observation that the bands corresponding to CSH 1.5, CSH-GO 0.5, and CSH-GO 1.0 become sharper and more intense. These FTIR results are consistent with the findings from XRD and SEM analyses.

Furthermore, the band at 1510 cm^{-1} (5 in **Figure 5.13**) is due to CO_3^{2-} stretching of calcite formed in the GO incorporated C–S–H, found in the TGA findings. Broadband, present in each spectrum around 1650 cm^{-1} (6 in **Figure 5.13**), is associated with deformation vibrations of –OH and together with stretching vibrations of –OH at 3740 cm^{-1} (K. Li et al., 2024), the presence of water molecules in the samples proved by DSC-TG measurement. Furthermore, it should be noted that the bands corresponding to GO were not detected in **Figure 5.13**. This may be because the amount of GO used in the C–S–H synthesis process was insufficient to be detected within the sensitivity range of the FT-IR instrument (Yang et al., 2017b).

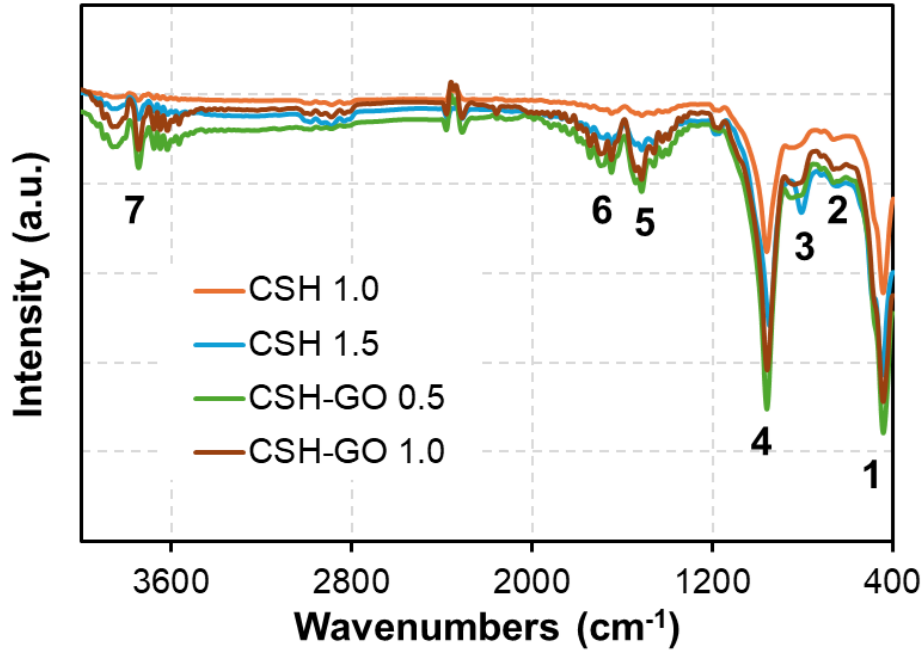


Figure 5.13: FTIR analysis of pure C-S-H and C-S-H with GO incorporation.

(d) SEM

Pure C-S-H with a Ca/Si ratio of 1.0 exhibited a nanostructure characterised by thin foils arranged in a random configuration (Basquiroto de Souza et al., 2022), as depicted in **Figure 5.14(a)**. This structure includes out-of-plane defectives. Consequently, their assembly appears disordered, leading to the commonly observed loose, crumpled mesoscale packing of C-S-H (Basquiroto de Souza et al., 2022), with pores ranging from nano-to micron-sized. In contrast, in C-S-H with a Ca/Si ratio of 1.5, a plate-like or laminar structure was formed due to the higher amount of calcium ions readily binding with water and hydroxide ions to form sheets or layers (Kang et al., 2019). This plate-like structure results in a more dispersed and less interconnected C-S-H, leading to finer pores, as shown in **Figure 5.14(b)**. The excess calcium available for hydration also forms these finer pores.

Furthermore, in CSH-GO 0.5 (**Figure 5.14(c)**), the C-S-H gels grew larger, and finer nano-foils with folding structures were observed, attributable to the maximised nucleation

effect of GO (Miao et al., 2023). These foils exhibited a 2D geometry and were aligned with the GO nanosheet (Basquiroto de Souza et al., 2022). Notably, deformations, wrinkles, or sudden changes in direction, commonly seen in foil-like pure C-S-H products, were absent. In addition, the C-S-H products covered the surface of the GO, forming a dense 2D layer with only tiny gel pores. This is because Ca^{2+} ions, which neutralise the high negative charge density of C-S-H, are attracted to and chemically react with the negatively charged GO surface via the ring-opening of epoxide/alkoxy groups (Basquiroto de Souza et al., 2021). This finding suggests that GO acted as a structure-directing platform, facilitating more efficient stacking of foils and the formation of dense C-S-H microplates. At higher GO mass ratios (**Figure 5.14(d)**), the C-S-H foils began to grow outwardly from the surface of the C-S-H microplate, appearing as folded foils.

Consequently, they exhibited a flat rather than spherical geometry, indicating that the growth of C-S-H proceeded in the plane directions of GO. Therefore, the microstructure of C-S-H is well-regulated, exhibiting relatively higher crystal growth, and is more compact and denser with the addition of GO. A network of closely packed C-S-H microplates is anticipated to absorb and distribute mechanical stresses throughout the matrix effectively.

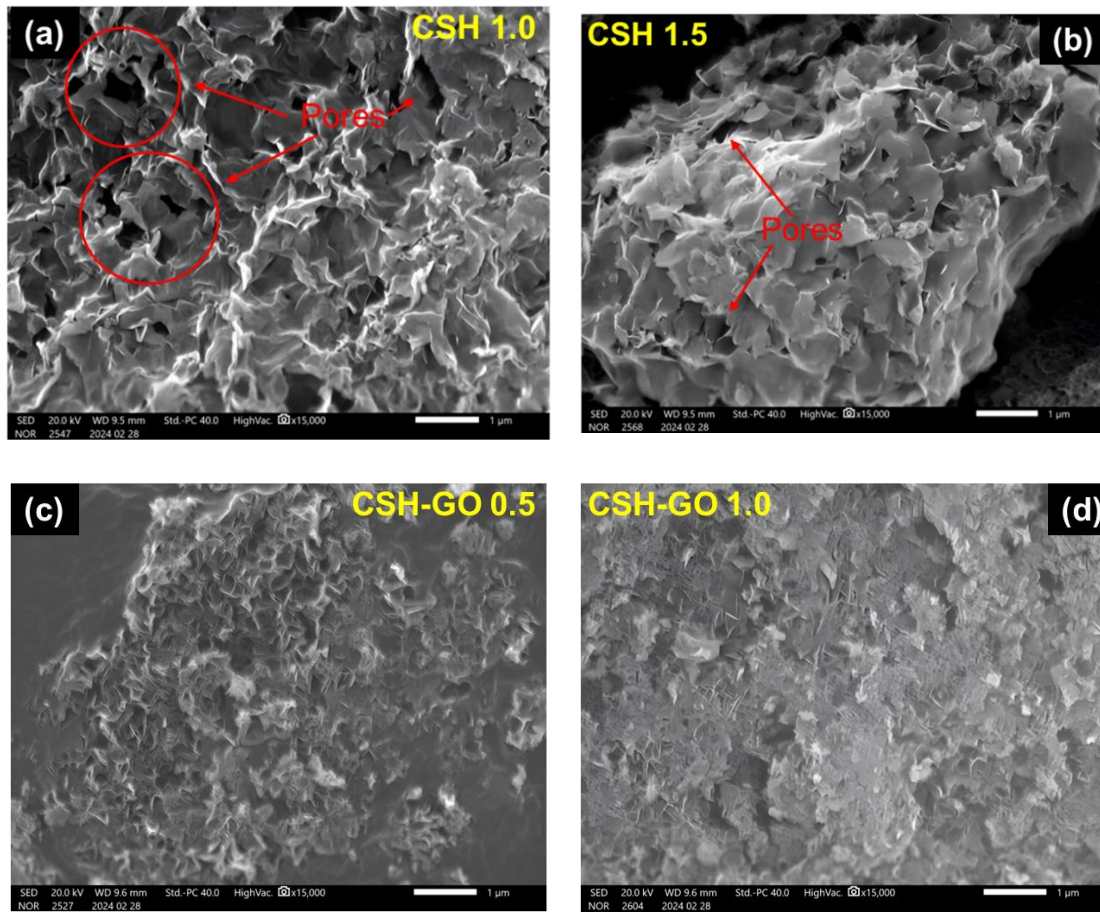


Figure 5.14: SEM images of pure C-S-H with different Ca/Si ratios (a and b) and C-S-H incorporating GO at different weight percentages (c and d).

(e) Si NMR

^{29}Si MAS NMR is a highly effective method for analysing the silicate structure of solid materials, particularly for characterising the amorphous C-S-H gel formed in hydrated cement (Kang et al., 2019; Wang et al., 2019b). Variations in chemical shifts and peak intensities observed in ^{29}Si NMR spectra provide valuable insights into the structural changes occurring in C-S-H gels. Silicate tetrahedra with n shared oxygen atoms are denoted as Q^n , where n represents the number of bridging oxygen atoms linked to other SiO_4 units. Specifically, Q^0 corresponds to discrete SiO_4 tetrahedra, Q^1 relates to dimers

and end-chain SiO₄ tetrahedra, Q² represents middle-chain SiO₄ tetrahedra, Q³ illustrates branch-chain SiO₄ tetrahedra, and Q⁴ symbolises SiO₄ tetrahedra in three-dimensional networks (Lippmaa et al., 1980). The corresponding chemical shifts of Qⁿ can be found in (Gartner et al., 2017). The mean chain length (MCL) is the number of silicates bound together in a chain, which can be described as the polymerisation degree of SiO₄ tetrahedra in C-S-H gels (Kim et al., 2013). The MCL of C-S-H gels was calculated using the Eq. (4.2) (Zhao et al., 2018);

$$MCL = \frac{2(IQ^1 + IQ^2)}{IQ^1} \quad (4.2)$$

where IQ¹ and IQ² represent the integral intensities of the signals of Q¹ and Q², respectively.

NMR spectra of each type of C-S-H are depicted in **Figure 5.15**, and statistical deconvolution analysis was conducted on the NMR results and presented in **Table 5.3**. For the deconvolution analyses of NMR spectra, each peak was measured within the following ranges: Q⁰: -66 to -78 ppm, Q¹: -78 ppm, Q^{2b}: -82 ppm to -84 ppm, and Q^{2p}: -85 ppm to -87 ppm, as reported in the literature (Kim et al., 2013; Kojima et al., 2023). Some studies have reported that the incorporation of GO increases the MCL of C-S-H. However, our study observed that the MCL of C-S-H slightly decreases with the incorporation of GO compared to pure C-S-H, consistent with (Chiang and Chang, 2021). In addition, the chain lengths observed (~6) are similar to those reported for tobermorite 11⁰ (Chiang and Chang, 2021; Shaw et al., 2000).

Statistical deconvolution analysis revealed a significant effect on Qⁿ by adding GO at different weight percentages. Specifically, when GO is added at 0.5%, there is a significant increase in the Q^{2b} state (from 26.69% to 47.43%) and a decrease in the Q^{2p} state (32.88% to 6.60%). This can be attributed to the presence of GO providing additional nucleation sites for forming C-S-H, where the water molecules react with interlayer calcium to form ionic bonds, forming more cross-linked silicate chains (Q^{2b} state).

Additionally, the hydroxyl groups (-OH) on GO can interact with the silicate chain length of C-S-H, leading to fewer partially polymerised silicate chains and a decrease in the Q^{2p} silicon state, thereby decreasing the MCL from 6.44 to 6.09 (Chiang and Chang, 2021).

Moreover, as the mass of graphene oxide (GO) increases from 0.5 wt% to 1.0 wt%, there is a significant decrease in the Q^{2b} state and an increase in the Q^0 and Q^{2p} states. This can be attributed to the higher concentration of nucleation sites for the formation of C-S-H with an increase in the mass of GO. The study can explain this (Chiang and Chang, 2021). The excessive pairing of tetrahedral vacancies could accommodate more silanol groups in silicate chains. Additionally, the hydroxyl groups on GO protonate non-bridging oxygen sites at the end of silicate chains, promoting the formation of partially polymerised silicate chains (Q^{2p} state) in C-S-H (Thomas et al., 2003). Therefore, the Q^0 and Q^{2p} silicon states increase with the addition of GO. These observed changes in the silicon states (Q^0 , Q^1 , Q^{2b} , and Q^{2p}) with increasing GO mass from 0.5 wt% to 1.0 wt% are consistent with SEM observations, which demonstrate the formation of a denser microstructure with short-layered C-S-H sheets.

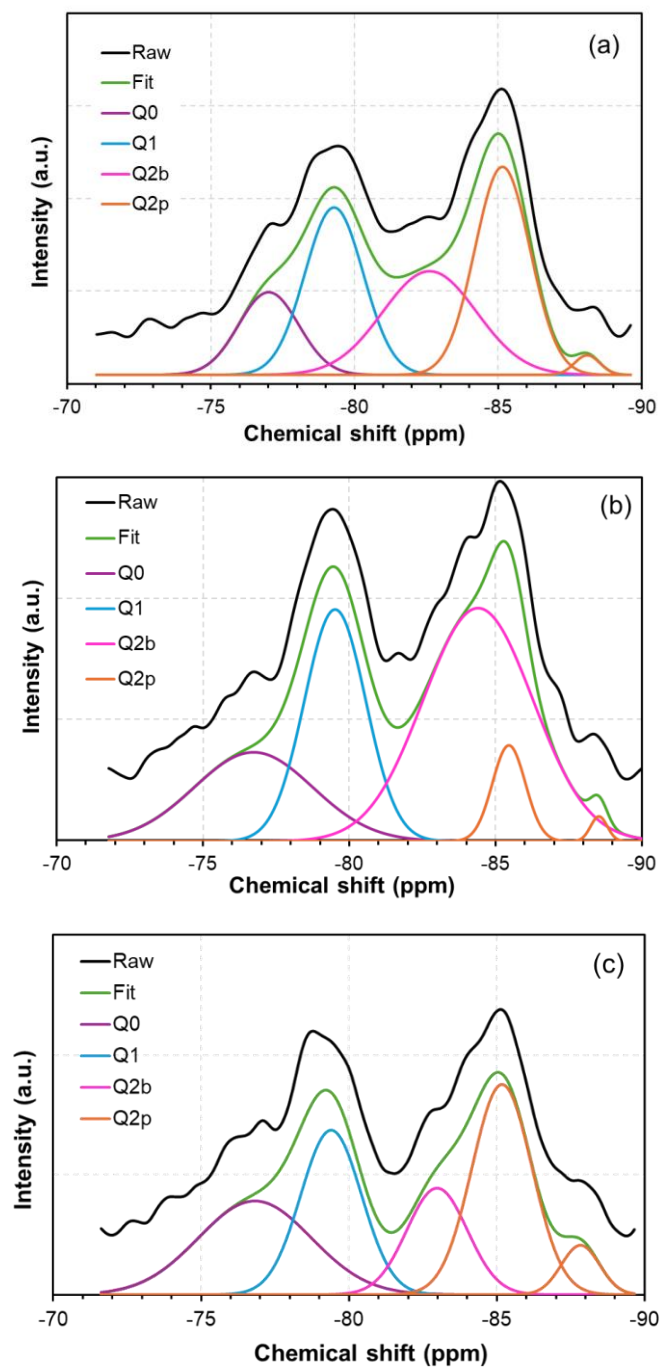


Figure 5.15: Deconvolution of ^{29}Si MAS NMR spectra for C-S-H 1.0 (a), C-S-H-GO 0.5 (b), and C-S-H-GO 1.0 (c).

Table 5.3: Silicate Chemical Shift percentages and MCL from ^{29}Si MAS NMR deconvolution analysis

Sample	Integral intensity of Q^n (%)				Q^2/Q^1	MCL
	Q^0	Q^1	Q^{2b}	Q^{2p}		
CSH 1.0	13.61	26.82	26.69	32.88	2.22	6.44
CSH-GO 0.5	19.57	26.40	47.43	6.60	2.05	6.09
CSH-GO 1.0	25.55	24.08	15.51	34.86	2.09	6.18

(f) ^1H NMR

The ^1H -NMR relaxometry is the best technique to study the C-S-H structural change and analyse the pore structure of among the existing other experimental techniques such as mercury intrusion porosimetry (MIP) and nitrogen sorption isotherms as it requires pre-treatment of drying, which causes the inevitable microstructure changes due to colloidal nature of C-S-H. (Kiran et al., 2020; Arnaud C.A. Muller et al., 2013). **Figure 5.16** illustrates three principal peaks corresponding to interlayer water (from 0.1 to 0.5 ms), gel water (up to 1.0 ms), and inter hydrate water (up to 10 ms), arranged from shortest to longer T_2 relaxation time (Gajewicz et al., 2016; Kojima et al., 2023; A. C.A. Muller et al., 2013). It should be noted that with the addition of GO, the peaks below 1 ms (**Figure 5.16(b)**) became broader. This is because the interlayer and gel voids appear to be a single unit, and the centre of the peak moves leftward with the increasing GO wt%, suggesting that the interlayer becomes narrower (Kojima et al., 2023).

The amount of each state of water detected in the C-S-H samples was calculated based on the individual peak intensity relative to the total intensity. In C-S-H with a Ca/Si ratio of 1.0, approximately 93.2 % gel water and 6.8 % interhydrate water were detected. However, with an increase in the Ca/Si ratio (CSH 1.5), inter-hydrate water disappeared, and the percentage of gel water increased from 93.2 % to 96.1 %. In addition, 3.9 % of

interlayer water was detected in C-S-H 1.5. This change is attributed to the higher concentration of calcium ions present in C-S-H with higher Ca/Si ratios, which promotes the polymerisation of C-S-H, resulting in higher proportions of interlayer and gel water compared to C-S-H with lower Ca/Si ratios (Arnaud C.A. Muller et al., 2013). Furthermore, when GO was incorporated at 0.5 wt%, the gel water content of CSH 1.0 was converted to interlayer water with reduced intensity (from 93.2 % to 90.3 %), while interhydrate water content increased from 6.8% to 9.7%. This suggests that GO adsorb more Ca^{2+} ions and replaces the water molecules, making the C-S-H sheets closer (Maruyama et al., 2019), enhancing the more ordered formation of C-S-H on the GO surface, as illustrated in **Figure 5.17**(a and b). In addition, lower GO masses that contained fewer oxide groups were available to prevent the deformation of the C-S-H sheets, resulting in a slight increase in inter-hydrate water.

However, with a further increase in GO mass to 1.0 wt%, only a broadened peak cantered at 0.2 ms was observed as 100% interlayer water (Kojima et al., 2023). This observation highlights the significance of GO-CSH interlayer bonding. When the GO mass increases, the attraction between GO and C-S-H sheets increases, and the spacing between the C-S-H becomes smaller, as illustrated in **Figure 5.17** (c). Hence, the polymerisation of C-S-H is enhanced, and C-S-H is formed layer by layer on the GO sheets, as evident in the SEM images. This results in the densification of the C-S-H microstructure due to the strong interaction between GO and C-S-H. These ^1H NMR results are consistent with previous studies, which have reported that adding GO refines the pore structure and reduces the porosity of the hydrates (Kang et al., 2019; Zhao et al., 2018).

Water within tiny pores can be categorised as either surface water, located near the pore surface, or bulk water, located within the core of the pore (Kurihara and Maruyama, 2022). Based on the rapid exchange between the surface and bulk layers, the fast exchange model correlates with the T_2 relaxation rate, as shown in Eq. (4.3).

$$\frac{1}{T_2} = \frac{\varepsilon \cdot S}{V} \cdot \frac{1}{T_{2,surface}} \quad (4.3)$$

where, S and V represent the surface area and volume of the pore, respectively. The ratio S/V indicates the surface-to-volume ratio of the pore. T_2 is the experimentally observed T_2 relaxation time while $T_{2,surface}$ represents the relaxation time of water adsorbed on the surface. The parameter ε denotes the thickness of the surface-adsorbed layer, which can vary in different studies. In this study, a value of 0.28 nm for the thickness of the water monolayer, as reported in the literature, has been used (D'Orazio et al., 1990; Gajewicz et al., 2016; Halperin et al., 1991).

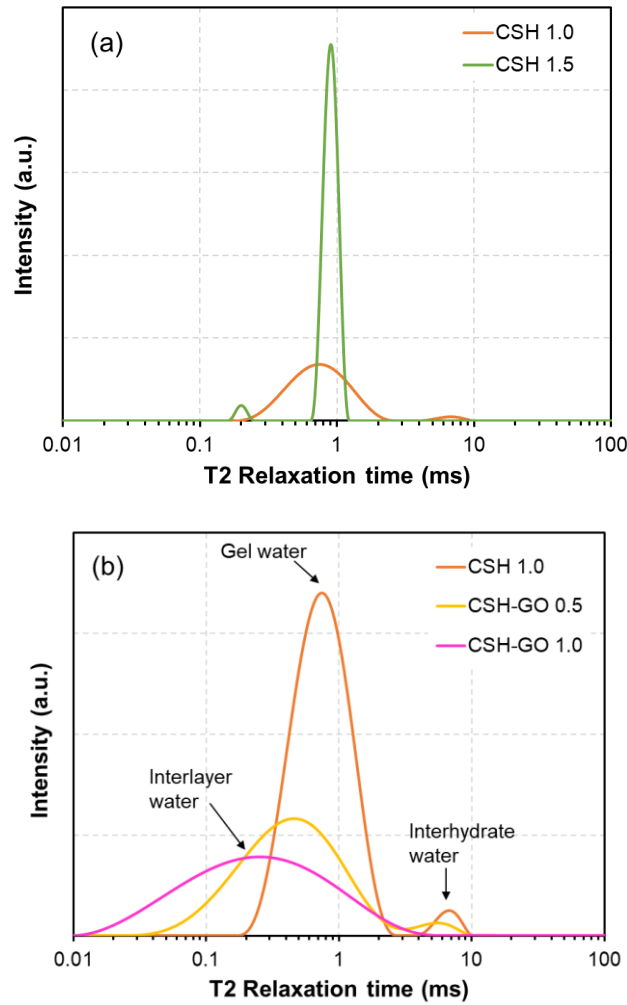


Figure 5.16: T_2 distributions of C-S-H obtained by CPMG echo signal decays.

Eq. (4.3) can be modified as shown in Eq. (4.4), considering the pore geometry as planar, where S/V equals $2/d$ (where d is the pore width). It is important to note that the surface relaxivity ($\varepsilon/T_{2,surface}$) arise with the hydration products of cement (Dalas et al., 2014) and are sensitive to temperature and the magnet setup used (Gajewicz, 2014; Halperin et al., 1991; “Water Resources Research,” 1969). However, in this study, the surface relaxivity was assumed to be 3.73×10^{-3} nm/ μ s, as used in previous studies on C-S-H (Arnaud C.A. Muller et al., 2013).

$$\frac{1}{T_2} = \frac{2}{d} \cdot \frac{\varepsilon}{T_{2,surface}} \quad (4.4)$$

It is observed that the incorporation of GO indicated a significant transition of gel pore size of 5.52 nm in CSH 1.0 to interlayer size of 3.40 nm for CSH-GO 0.5. This may be attributed to the formation of more ordered C-S-H sheets, which results in a transition from the formation of “less dense” to “denser” C-S-H structures (**Figure 5.17(b)**). Additionally, with the increase in GO content in C-S-H, the interlayer spacing was further reduced to 1.87 nm, confirming that C-S-H sheets become closer due to GO-CSH attraction, as illustrated in **Figure 5.17(c)**. This is also confirmed by ^{29}Si MAS NMR in which pairing SiO_4 tetrahedrons increased. Besides, the calculated interlayer spacing in CSH-GO 0.5 is slightly higher than the reported value. This discrepancy may be attributed to the frequency-dependent nature of surface relaxivity and variations in mineral polymorphs of C-S-H, such as tobermorite 14^0 (Pelisser et al., 2012). These findings suggest that the dense microstructure of C-S-H contributes to improved mechanical properties and durability in several ways. The reduced interlayer spacing indicates a denser microstructure, which enhances the overall strength and toughness of the composite material. This denser arrangement restricts the movement of sheets relative to each other, thereby increasing resistance to deformation and fracture under mechanical stress. Specifically, the closer spacing between C-S-H sheets leads to a more compact and cohesive structure, enhancing the material's ability to withstand mechanical loads and reducing overall porosity. A denser microstructure with smaller interlayer spacing

reduces the overall porosity of the material, leading to fewer weak points where cracks can initiate and propagate.

In terms of durability, the dense microstructure restricts the penetration of chemically vulnerable ions, such as chloride and sulfate ions, by reducing the size and connectivity of pores. This minimizes the risk of chemical degradation processes like corrosion and sulfate attack. Additionally, higher density in the material makes it less permeable to aggressive agents from the environment, prolonging its service life. The enhanced interaction between GO and C-S-H contributes to mechanical reinforcement and improves the composite's chemical stability (Baskoro et al., 2018). This is supported by evidence of a lower decalcification rate, indicating that the material is less susceptible to chemical breakdown (Arnaud C.A. Muller et al., 2013).

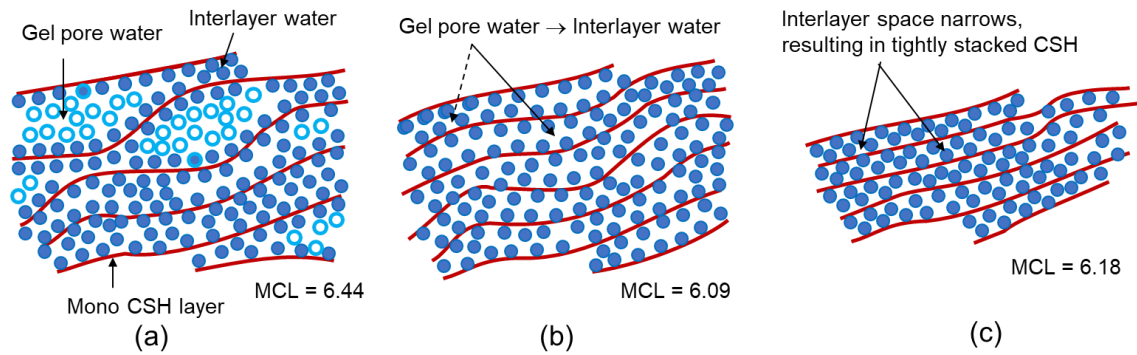


Figure 5.17: Illustration for the microstructural changes of C-S-H: (a) gel pore water entrapped by mono C-S-H layers, (b) gel pore water becomes interlayer water by the C-S-H layers attraction, and (c) tightly stacked mono C-S-H layers with interlayer water

5.2.5 Conclusion

This study employed a co-precipitation method to synthesize C-S-H with and without GO to investigate the microstructural changes induced by GO incorporation. TGA revealed a higher water loss in GO-incorporated C-S-H, indicating increased polymerization of C-S-H due to the active functional groups of GO acting as nucleation sites. XRD analysis,

particularly the FWHM measurements, confirmed that the crystallinity of C-S-H significantly improved with GO incorporation. This enhancement is attributed to the adsorption of Ca^{2+} by GO, which promotes the incorporation of Si into solid C-S-H. FTIR spectroscopy supported the XRD findings, showing enhanced formation of more ordered and crystalline C-S-H, evidenced by sharper and more intense Si–O–Si bands with GO incorporation. SEM images revealed that pure C-S-H exhibits defective sheets with micro-sized pores.

In contrast, with 0.5 wt.% GO incorporation, C-S-H gels formed larger, finer nano-foils with many folding structures due to the maximized nucleation effect of GO. At 1 wt.% GO, the C-S-H sheets were observed to stack and fill folding structures with highly dense C-S-H, resulting in a significant reduction in pores compared to pure C-S-H. Furthermore, Si NMR results indicated that GO provides additional nucleation sites for C-S-H formation, with water molecules reacting with interlayer calcium to form ionic bonds. This reaction leads to more cross-linked silicate chains, consistent with the SEM observations. H NMR results demonstrated the rearrangement of the C-S-H structure due to GO-CSH interactions, resulting in more ordered C-S-H monolayers with smaller interlayer spacing (1.87 nm) compared to pure C-S-H. Overall, incorporating GO improves the crystallite size and creates a more ordered C-S-H structure, which is expected to enhance the strength and durability of cement-based materials by facilitating better load transfer and interlocking of crystals.

CHAPTER 6

DEVELOPMENT OF A MULTISCALE MODEL FOR PREDICTING THE MECHANICAL PROPERTIES OF NANO SILICA-REINFORCED CEMENT PASTE

6.1 Introduction

Cement paste, the binding component in concrete, is crucial for the material's overall strength and durability. Understanding the characteristics and behaviour of cement paste is essential for predicting and enhancing the performance of concrete. Since concrete is a multi-scale material, studying cement paste is fundamental in examining nano-modified concrete. Aggregates in concrete function as inert fillers, leaving cement paste as the sole chemically reactive component. Consequently, any modifications to the cement paste, such as integrating nano-silica, directly impact the concrete's properties. Nano-silica influences the hydration process, leading to changes in the microstructure and, ultimately, the mechanical and durability characteristics of the concrete.

In this research, the focus on cement paste allows for a detailed analysis of how nano-silica affects the hydration and evolution of the cementitious matrix. By isolating the cement paste, researchers can better understand the mechanisms at play without the confounding effects of aggregates. This approach facilitates the development of an integrated hydration model for cement/nano-silica systems, providing a clearer picture of how nano-silica enhances or alters the performance of cement paste. This foundational understanding is pivotal because the behaviour observed in the cement paste phase will directly influence the overall performance of nano-modified concrete. Therefore, the study of nano-silica in cement paste is not just an isolated investigation but a critical step

towards advancing concrete technology, ensuring that future models and applications can accurately predict and optimize the benefits of nano-modification in concrete.

6.2 Quantification of the degree of hydration of plain cement paste and pozzolanic reactivity of nano-silica

Thermodynamic models have become valuable tools for understanding the intricate chemical reactions during cement hydration (Elakneswaran et al., 2016a; Lothenbach and Zajac, 2019). By employing thermodynamic principles, these models facilitate the prediction of phase assemblages, hydration products, and properties of cementitious systems (Elakneswaran et al., 2016b). This study conducted chemical thermodynamic calculations of the phases formed during hydration using the open-source geochemical software PHREEQC (Parkhurst and Appelo, 1999). The phases considered in this study were consistent with those employed in (Elakneswaran et al., 2016b), ensuring continuity and comparability. However, additional consideration was given to the equilibrium of various C-S-H phases as end members in the chemical thermodynamic calculations (Lothenbach et al., 2019). This consideration is crucial because of the influence of nano-silica in altering the formation of C-S-H phases by modifying the Ca/Si ratio (Scrivener et al., 2019; Singh et al., 2017, 2016b). The phase equilibrium module, which relies on the mass-action equation (Parkhurst and Appelo, 1999), was utilised to predict the stable solid phases and pore solution composition in the hydrated cement matrix concerning hydration time, based on thermodynamic principles (Elakneswaran et al., 2016a). Essential parameters, such as equilibrium constants ($\log K_p$) and standard heats of reaction ($\Delta_r H_0$), were obtained from Cemdata18 (Lothenbach et al., 2019) and the default database within the PHREEQC software. The phase equilibrium module utilised in this study requires specific input parameters, including a designated saturation index (set at zero for equilibrium) and the quantity of each phase. To quantify the amounts of the significant clinker phases, such as C_3S , C_2S , C_3A , and C_4AF , at each time step, a cement hydration model developed by Parrot and Killoh (Parrot and Killoh, 1984) was employed. The Parrot–Killoh model has been extensively employed and validated through

experimental findings from prior studies (Elakneswaran et al., 2016a; Krishnaya et al., 2021b). Their approach encompasses three main controlling mechanisms for a realistic consideration of the reaction degree of each clinker phase: nucleation and growth of products (Eq. (6.1)), diffusion of ions through the layers of previously formed products (Eq. (6.2)), and formation of hydrate shells around the unreacted material (Eq. (6.3)). Eqs describe these mechanisms. (1–3). Among these three reaction rates ($R_{t,1}^m$, $R_{t,2}^m$, and $R_{t,3}^m$), the minimum value is chosen as the actual controlling rate for calculating the hydration degree α_t^m at time t using Eq. (6.4).

Nucleation and growth rate ($R_{t,1}^m$):

$$R_{t,1}^m = \frac{K_1}{N_1} (1 - \alpha_t^m) (-\ln(1 - \alpha_t^m))^{(1-N_1)} \quad (6.1)$$

Diffusion rate ($R_{t,2}^m$):

$$R_{t,2}^m = \frac{K_2(1-\alpha_t^m)^{\frac{2}{3}}}{1-(1-\alpha_t^m)^{\frac{1}{3}}} \quad (6.2)$$

Hydrates shell formation ($R_{t,3}^m$):

$$R_{t,3}^m = K_3(1 - \alpha_t^m)^{N_3} \quad (6.3)$$

The hydration degree of a clinker mineral (α_t^m):

$$\alpha_t^m = \alpha_{t-1}^m + \Delta t \cdot \min(R_{t,1}^m, R_{t,2}^m, R_{t,3}^m) \cdot \beta_{w/c} \cdot \lambda_{RH} \cdot \frac{A}{A_0} \cdot \exp\left(\frac{E_a^m}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad (6.4)$$

Here,

$$\beta_{w/c} = (1 + 3.333 \cdot (H^m \cdot \frac{w}{c} - \alpha_{t-1}^m))^4 \quad \text{for } \alpha_{t-1}^m > H^m \cdot \frac{w}{c} \quad (6.5)$$

$$\beta_{w/c} = 1 \quad \text{for } \alpha_{t-1}^m \leq H^m \cdot \frac{w}{c} \quad (6.6)$$

$$\lambda_{RH} = \left(\frac{RH-0.55}{0.45} \right)^4 \quad (6.7)$$

In the above equations, T represents the actual curing temperature in K, T_0 corresponds to a reference temperature (293.15 K), Δt denotes the time interval, $\frac{w}{c}$ stands for the water-to-cement ratio, RH signifies the relative humidity, A represents the Blaine surface area of the cement (m^2/kg), A_0 is the reference surface area of cement ($385 \text{ m}^2/\text{kg}$), E_a^m is the apparent activation energy of the clinker mineral, and K_1 , N_1 , K_2 , K_3 , N_3 , and H are equation constants associated with the type of clinker mineral. The specific values used for OPC are listed in **Table 6.1**.

Table 6.1: Coefficients for computing the hydration degree of the clinker phases
(Lothenbach et al., 2008; Lothenbach and Winnefeld, 2006)

	C₃S	C₂S	C₃A	C₄AF
K_1	1.5	0.5	1	0.37
N_1	0.7	1	0.85	0.7
K_2	0.05	0.006	0.04	0.015
K_3	1.1	0.2	1	0.4
N_3	3.3	5	3.2	3.7
H	1.8	1.35	1.6	1.45
E_a (J/mol)	41,570	20,785	54,040	34,087

Based on the estimated hydration degree of individual clinker phases (α_{C_3S} , α_{C_2S} , α_{C_3A} , and α_{C_4AF}), the overall hydration degree of cement paste (α_c) for a given time step can be calculated as outlined in Eq. (6.8).

$$\alpha_c = \frac{\alpha_{C_3S} \cdot W_{C_3S} + \alpha_{C_2S} \cdot W_{C_2S} + \alpha_{C_3A} \cdot W_{C_3A} + \alpha_{C_4AF} \cdot W_{C_4AF}}{W_{C_3S} + W_{C_2S} + W_{C_3A} + W_{C_4AF}} \quad (6.8)$$

where, W_{C_3S} , W_{C_2S} , W_{C_3A} , and W_{C_4AF} represent the mass fractions of the individual clinker phases.

Upon mixing cement with water, K, Na, and S ions are released into the pore solution because of the dissolution of soluble alkali sulphates, and less soluble minerals, such as gypsum and calcite, partially dissolve until an equilibrium with the pore solution is attained. In this context, gradually dissolving clinker phases were assumed to continuously release Ca, Si, Al, Fe, and hydroxide ions in proportion to the degree of reaction of the individual phases. Meanwhile, minor components in the cement matrix like Na₂O, K₂O, and MgO release Na, K, Mg, and O ions into the pore solution as a function of the total hydration degree (α_c) for a specific time. Furthermore, the degree of nano-silica was determined based on the pozzolanic reaction between portlandite and nano-silica, as proposed in a previous study (Bentz et al., 1998) and depicted in Eq. (6.9). It is evident that the reaction degree of nano-silica primarily depended on the availability of CH, which is a by-product of the hydration of the C₃S and C₂S phases, at every time step—stoichiometric calculations based on Eq. (6.9) revealed that 0.74 g of nano-silica reacts with 1 g of portlandite during the pozzolanic reaction. Additionally, the formation of portlandite due to hydration decreased as the replacement ratio of nano-silica increased. Considering these factors, the proposed equation (Eq. (6.10)) accurately describes the degree of nano-silica.



$$\alpha_s(t) = \frac{\mu (W_{C_3S} \times 0.49 \times \alpha_{C_3S}(t) + W_{C_2S} \times 0.22 \times \alpha_{C_2S}(t)) \times 0.74}{W_s/W_c} \quad (6.10)$$

Here, α_s is the degree of pozzolanic reaction, and μ (a constant) is the ratio of reacted silica to the total amount of nano-silica added. The value was taken as 0.05 by calibrating the cement paste's experimental results (Waller, 1994) at a particular degree of hydration.

W_{C_3S} and W_{C_2S} are the weight ratio of the C₃S and C₂S phases in the cement.

$\alpha_{C_3S}(t)$ and $\alpha_{C_2S}(t)$ are the reaction degrees of the C_3S and C_2S phases, respectively.

W_s and W_c are the total weight of nano-silica and cement, respectively, in the mix.

The aforementioned (hydration and thermodynamic) models were coupled and simulated to predict the solid assemblage of the hydration products and dissolution of clinker minerals over hydration time, as shown in **Figure 6.1**. A small-time step was used, particularly during the early stages of hydration, to capture the rapid changes accurately. The time step was gradually adjusted as the hydration progressed to stabilise the simulation.

6.3 Computation of the volume fractions of phases present in a nano-modified cement paste

6.3.1 Computation of volume fractions of phases in plain cement paste

In this study, the total weight of the C–S–H matrix, as predicted by the coupled model mentioned above, was further categorised into two distinct components, namely low- and high-density C–S–H, for the accurate prediction of hydrate assemblages using the correlation in Eq. (6.11), as suggested by Tennis and Jennings (Tennis and Jennings, 2000). This categorisation follows the research conducted by Constantinides and Ulm (Constantinides and Ulm, 2004), who observed the development of C–S–H primarily on the surface of the cement particles during the early stages of the hydration process. However, as time progressed, the cement particles became partially or fully covered by a layer of C–S–H, and further growth of C–S–H occurred within the confined spaces due to the diffusion of clinker minerals such as C_3S and C_2S .

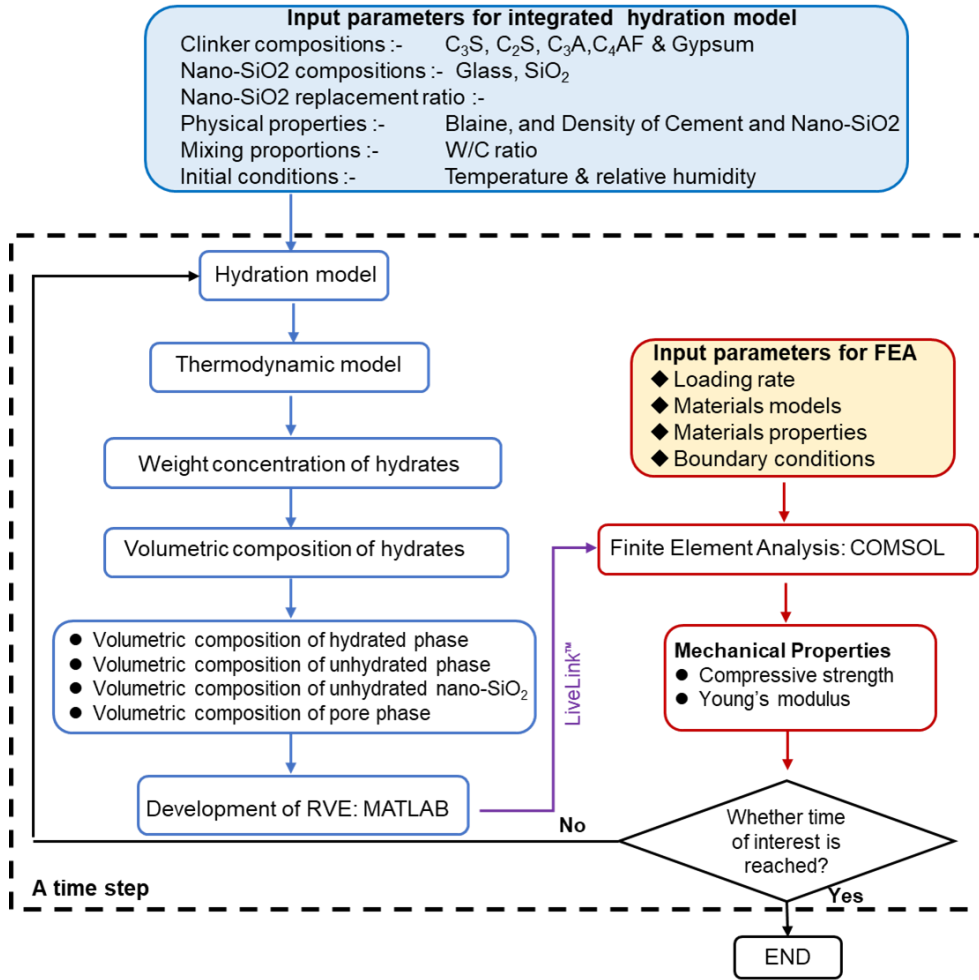


Figure 6.1: Schematic illustration of the proposed model.

Consequently, the outer layer of C–S–H formed on the surface exhibited a lower density than the inner C–S–H, which grew within confined spaces. The average densities of the high-density and low-density C-S-H were obtained from the literature. Without the incorporation of nano-silica, the densities were 2000 and 1700 kg/m³, respectively (Tennis and Jennings, 2000). With the incorporation of nano-silica, the densities changed to 1800 and 1500 kg/m³, respectively, owing to the transformation of C-S-H from a jennite-like structure to a tobermorite structure (Richardson, 2004).

$$M_r = 3.017 (w/c)\alpha - 1.347\alpha + 0.538 \quad (6.11)$$

In addition, it is essential to consider the molar volume differences between the hydration products and clinker minerals. This difference leads to a phenomenon known as chemical shrinkage, where the total volume of the hydration products is less than the total volume of the clinker minerals; this phenomenon contributes to self-desiccation and autogenous contraction in cementitious systems (Idiart et al., 2012; Ishida and Maekawa, 2013). Previous studies have often overlooked or assumed constant percentages of reacted cement; however, this can have implications in accurately predicting capillary porosity. The total chemical shrinkage was calculated by multiplying the weight proportion of each phase by its corresponding shrinkage coefficient (Dale P. Bentz et al., 2005).

The volumes of the hydration products were determined based on their respective molar volumes. Subsequently, the capillary porosity of the cement matrix was estimated using an equilibrium approach by calculating the difference between the initial and final volumes of the hydration products. This calculation considers chemical shrinkage and unreacted clinker minerals, as shown in Eq. (6.12). The evaluation of the chemical shrinkage involved multiplying the reacted clinker phases with their respective shrinkage coefficients, which were 0.0704 for C_3S , 0.0724 for C_2S , 0.171 for C_3A (when converting to ettringite), 0.115 for C_3A (when converting to monosulfoaluminate), 0.117 for C_4AF (when converting to ettringite), and 0.086 for C_4AF (when converting to monosulfoaluminate) (Bentz et al., 2005).

$$V_{cap} = V_i - (V_{UC} + V_{HP} + V_{CS}) \quad (6.12)$$

where V_{cap} is the volume of the capillary pore space, V_{CS} is the chemical shrinkage, V_i is the initial volume of the matrix, V_{UC} is the unreacted clinker volume, and V_{HP} is the volume of the hydration products.

6.3.2 Prediction of volume fraction of main phases of nano-silica modified cement paste with hydration time

Following the discussion in Section 6.3.1, the volume fractions of the phases, namely hydrated, unhydrated, unreacted nano-silica, chemical shrinkage, and capillary pores, were estimated as functions of the hydration age. The predictions are shown in **Figure 6.2**. The most significant increase in the volume fractions of the hydrates, particularly C-S-H, was observed with the substitution of 2% nano-silica (**Figure 6.2(a)**), regardless of the hydration age. **Figure 6.2(b)** shows a gradual reduction in the unhydrated phases in all pastes (CO, CO + NS2, and CO + NS4) as hydration progressed. Notably, there is a linear relationship between the volume fractions of the unhydrated phases in the mixtures. These results indicate that the hydration of clinker minerals remained independent of the nano-silica reactivity; instead, it was solely governed by the initial cement content present in each specific mixture. The changes in the volume fractions of the pore phases with hydration age are illustrated in **Figure 6.2(c)**, as discussed in Section 6.3.1. The findings reveal a steady reduction in the pores within the cement paste containing nano-silica, compared to those without nano-silica, at all stages of hydration. This phenomenon was attributed to the denser microstructure resulting from incorporating nano-silica.

The ultra-fine nano-silica particles acted as a filler material, contributing to decreased porosity within the cement paste. **Figure 6.2(d)** illustrates the relationship between the unreacted nano-silica volume fraction and the different pastes' hydration age. Unreacted nano-silica increased proportionally to the initial nano-silica content in the cement paste. However, within a specific cement paste, the unreacted nano-silica content diminished as hydration progressed, owing to the increasing contribution of nano-silica to the pozzolanic reactions over time. Considering the overall reactivity of nano-silica in the cement paste, the optimal replacement ratio was determined to be 2%.

6.4 Development of representative volume elements for paste

Simulating the actual microstructure of cement paste using the current advanced computing technologies presents significant challenges in terms of computational time. This is primarily due to nanoscale gel pores, typically ranging from 0.5 to 10 nm in size (Powers and Brownnyard, 1946). Incorporating these nanoscale phases into a microscale model introduces computationally demanding complexity. Nevertheless, researchers have successfully employed simplified microstructural models to analyse the mechanical properties of cement pastes (Wu et al., 2021; Zhang and Jivkov, 2014). However, owing to the significant computational requirements for simulating a numerically generated three-dimensional (3D) cement specimen, the 3D model was successfully converted into an equivalent two-dimensional (2D) plane element using probabilistic and statistical approaches (Chen et al., 2018; Wriggers and Moftah, 2006). Although this 2D representation ignores out-of-plane factors, several earlier studies (Pal and Ramaswamy, 2023; Rupasinghe, 2015; X. Wang et al., 2015) have shown that using a comparable 2D model has a minor impact on homogenised mechanical responses compared to a full 3D model.

Hence, we developed a 2D representative volume element in MATLAB based on the predicted volume fractions in Section 6.3. To preserve the heterogeneity of the cement paste, the matrix material was assumed to represent the hydrated phase, while the unhydrated cement, unreacted nano-silica, and pore phases were randomly dispersed (Pal and Ramaswamy, 2023; Rupasinghe et al., 2017b). The volume fraction of the unhydrated phase within the representative volume element was determined by adding the volumes of the major clinker phases (C_3S , C_2S , C_3A , and C_4AF) at each time step, as described in Section 6.3.1. Conversely, the pore phase was calculated by combining the capillary pore volume and chemical shrinkage at each time step. Moreover, the unhydrated cement, unreacted nano-silica particles, and pores were represented by independent circular particles and circular cavities, following approaches found in the literature (Kim and Abu Al-Rub, 2011; Pal and Ramaswamy, 2023; Skaryński and Tejchman, 2010). The “take-

and-place” method was utilised to ensure the particles' random distribution and non-overlapping arrangement(Chen et al., 2018; Wriggers and Moftah, 2006). To maintain consistency with the actual hydration process and microstructural development, the sizes of the particles representing the unhydrated phase were determined as a function of the degree of hydration by maintaining the area/volume ratio at any hydration time, as described by Eqs. (6.13).

$$R_t = R_i(1 - \alpha_c)^{1/3} \quad (6.13)$$

where R_t , R_i , and α_c are the radii of a particle at time t , the initial radii of the particle, and the degree of cement hydration, respectively.

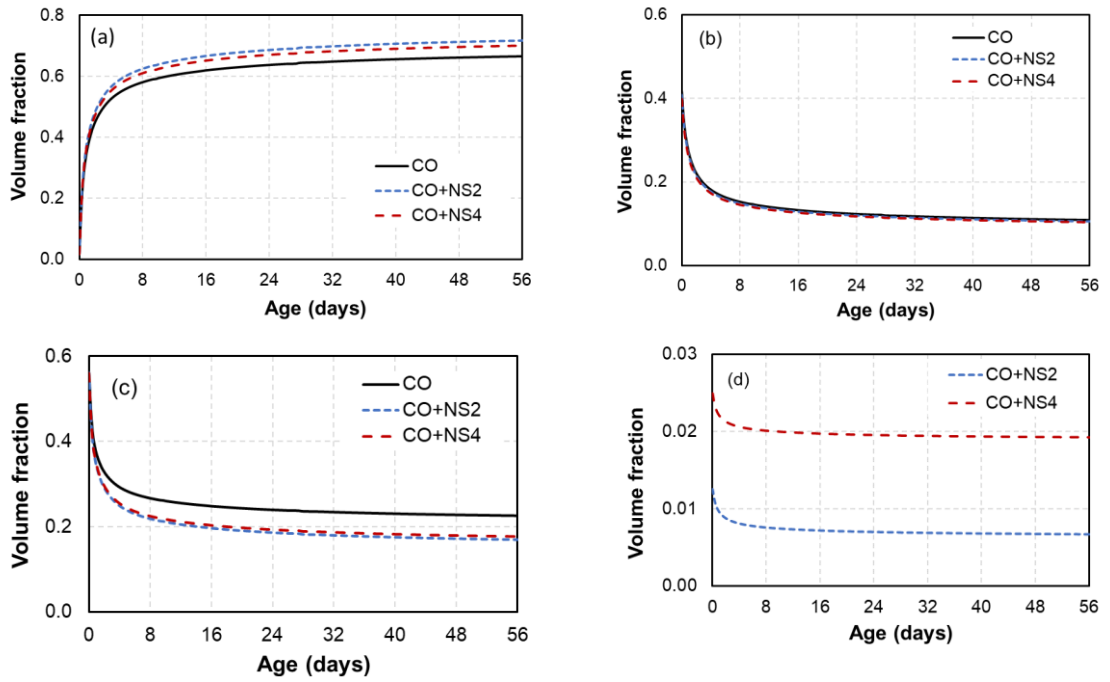


Figure 6.2: Volume fraction of (a) hydrated phase, (b) unhydrated phase, (c) pore phase, and (d) unreacted nano-silica of the cement pastes.

The clinker particles and pores in cement paste exhibit a wide range of sizes, from nanometres to several micrometres. However, including the actual particle distribution in

the numerical analysis introduces computational complexity. The grain sizes of cement particles typically fall within the range of 7–200 μm (Zhang H, 2011), and 50 % of the cement particles pass through a size of 15 μm (Haecker et al., 2005). Subsequently, the initial size of the anhydrous particles was set at 15 μm . In addition, capillary pores in cement paste have been reported to range in size from 10 nm to 100 μm , with a peak distribution between 4–6 μm (Maekawa et al., 2008). Accordingly, two pore sizes (6 and 4 μm) were considered, each contributing 50% to the total pore volume, unlike other studies that considered mono-sized pores (Pal and Ramaswamy, 2023; Rupasinghe et al., 2017b).

Moreover, previous studies have proposed various approaches to represent significantly more minor inclusions, such as unreacted nano-silica particles, compared to the size of the RVE. Maekawa et al. (Maekawa et al., 2008) suggested using the equivalent radius calculated from the geometric mean to account for the different orders of magnitude of the pore radii in concrete modelling. Rupasinghe et al. (Rupasinghe et al., 2017b) employed lumping techniques to represent nanoparticles smaller than 10 nm at the micro-level by aggregating smaller individual particles. These particles were approximately 10^4 times smaller than the 100 μm -sized RVE. Therefore, this study adopted mono-size particles, whose size was set to 4 μm , to represent unreacted nano-silica particles in cement paste. Similar approaches that consider the pores within a given RVE at the concrete mesoscale can be found in (X. F. Wang et al., 2015).

To ensure numerical accuracy and computational efficiency when predicting material properties using a sequential homogenisation approach in a multiscale model (Bentz, 1999), selecting an appropriate size for the RVE is crucial. Previous studies have indicated that reliable predictions of the mechanical characteristics of cement paste can be achieved using RVE sizes ranging from 100 μm to 200 μm (Cappelli et al., 2019). Therefore, a representative volume element size of 100 μm was chosen for modelling cement paste in this study. **Figure 6.3** illustrates the geometry of the RVE developed

based on the selected values for unhydrated cement particles, pores, and the 100 μm RVE size, corresponding to seven-day aged cement pastes with a water-cement ratio of 0.4.

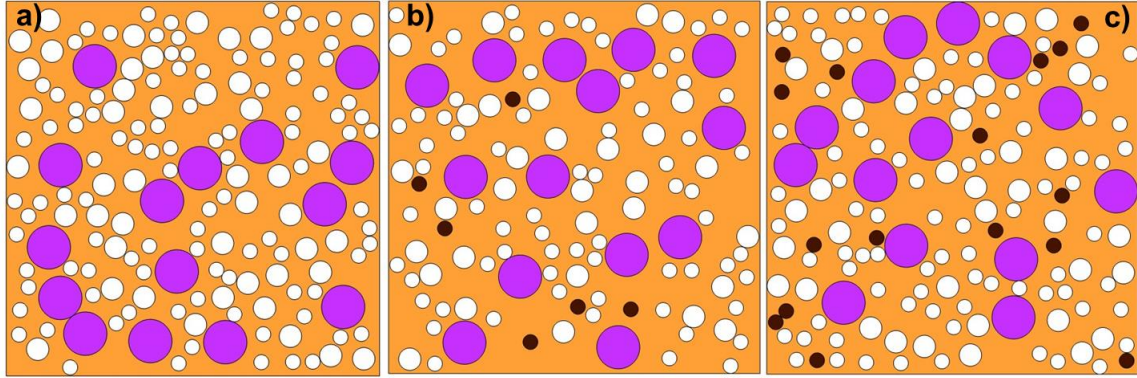


Figure 6.3: Geometry of the RVE of seven-day aged cement pastes: (a) CO, (b) CO+NS2, and (c) CO+NS4 (Orange, magenta, black, and white colours represent the hydrated phase, unhydrated cement particles, unreacted nano-silica particles, and pores, respectively).

6.5 Numerical investigation of the RVE

6.5.1 Materials modelling, loading conditions, and boundary constraints.

The finite element analysis of the RVE for cement pastes, developed in Section 3.3, was performed using the structural mechanics module in COMSOL Multiphysics 6.0 (BV and OY, 1998). As shown in **Figure 6.3**, the RVE generated in MATLAB is transferred to COMSOL using the LiveLink of the MATLAB tool (COMSOL Multiphysics, 2018). To determine the homogenised mechanical properties of the cement paste, the material behaviour of each phase was defined using COMSOL. In a previous study by Rupasinghe et al. (Rupasinghe et al., 2017b), hydrated products and unhydrated clinkers were modelled as linearly elastic perfectly plastic materials, and it was demonstrated that these simplifications had a negligible influence on the homogenised elastic modulus and strength. However, considering the nonlinear behaviour of cementitious materials, this

study employs the Bresler–Pister yield criterion proposed by Bresler and Pister (B. Bresler and K.S. Pister, 1958). The Bresler–Pister yield criterion is a constitutive model explicitly developed to assess the strength of concrete subjected to multiaxial stress. This yield criterion represents an extension of the well-known Drucker–Prager criterion to account for the brittle behaviour of concrete. The Bresler–Pister yield criterion is expressed in stress invariants, as shown in Eq. (6.14). Although this material is commonly utilised to simulate concrete components, to our knowledge, its use in multiscale methodologies for nanocomposites of cement paste has not been documented.

$$F_y = \sqrt{J_2} + k_1 I_1^2 + k_2 I_1 + k_3 \quad (6.14)$$

Here, k_1 , k_2 , and k_3 are the function of the uniaxial compressive strength (σ_{cs}), uniaxial tensile strength (σ_{ts}), and biaxial compressive strength (σ_{bc}), and their detailed description can be found in (BV and OY, 1998).

In contrast, the unhydrated clinkers exhibited a much higher strength than the hydrated products. For instance, the tensile strength of unhydrated cement reported in several studies was 683 MPa (Hlobil et al., 2016; Zhang and Jivkov, 2014), whereas those of the hydrated products were 58–92 MPa. These values were obtained through inverse analysis of the experimental results and nanoindentation techniques (Nemecek, 2018). Therefore, to account for the higher stiffness and strength, this study modelled unhydrated clinkers as linearly elastic materials (Hlobil et al., 2016; Nguyen et al., 2012). Similarly, the unreacted nano-silica particles were modelled as linear elastic materials.

To simulate the uniaxial compressive test, the bottom surface of the RVE was immobilised to restrict movement along the y-direction, as illustrated in **Figure 6.4**. A prescribed displacement was applied to the top surface in the negative y-direction to simulate compressive loading. Furthermore, the bottom-left corner of the RVE was restrained horizontally to prevent rigid-body motion in the horizontal direction. Additionally, periodic boundary conditions were implemented on opposite vertical surfaces to simulate infinite repetition within a limited computational domain.

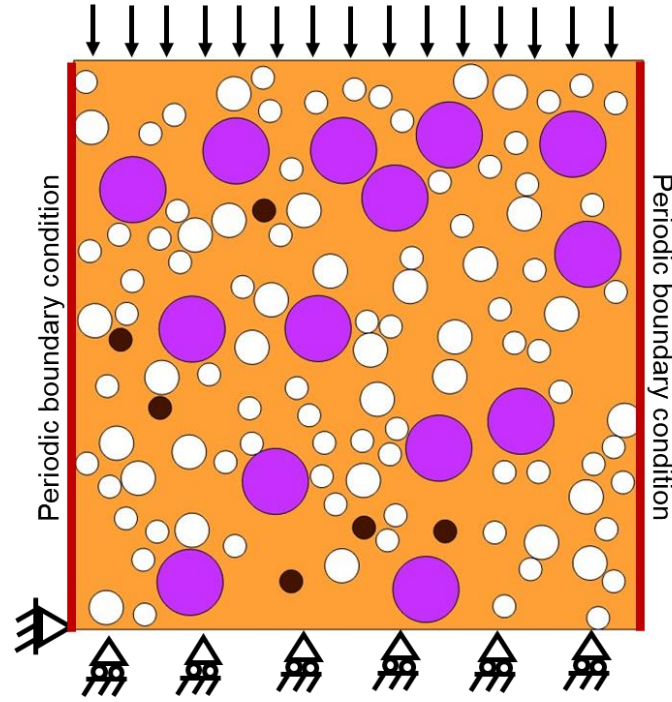


Figure 6.4: Boundary conditions applied on the RVE.

6.5.2 Input parameters for material models

The Bresler–Pister yield criterion adopted to model the mechanical behaviour of the hydrated phase requires specific input parameters, such as Young’s modulus, Poisson’s ratio, density, tensile strength, compressive strength, and biaxial compressive strength. In this study, a Poisson’s ratio of 0.24 was assigned to the hydrated phase (Velez et al., 2001), while the remaining input parameters were allowed to vary with hydration time to capture the evolving properties of the cement matrix as the microstructure developed. Unlike previous studies (J. J. Kim et al., 2010b; Rupasinghe et al., 2017b), the contributions of hydrates, such as C-S-H, ettringite, monosulfate, and portlandite, in strengthening of the hydrated phase were also considered. Consequently, the effective parameters of the hydrated phase were calculated using Eqs. (6.15), as outlined in a previous study (Rupasinghe et al., 2017a). The intrinsic mechanical properties of the individual phases are summarised in **Table 6.2**.

$$X_t^m = \sum (VF)_t^m \times Y_t^m \quad (6.15)$$

where, X represents the effective properties, such as the compressive strength, Young's modulus, and density of the hydrated phase at a particular hydration time.

VF is the volume fraction of the m^{th} phase (where m corresponds to C-S-H (LD and HD), portlandite, ettringite, or monosulfate) in the hydrated phase at a particular time.

Y represents intrinsic properties, such as compressive strength, Young's modulus, and density of the m^{th} phase (C-S-H, ettringite, monosulfate, or portlandite) at a particular hydration time.

Furthermore, in this study, the effective compressive strength of the hydrated phase was attributed solely to the compressive strength of the C-S-H phase. This is because experimental data for other phases were unavailable. Furthermore, previous studies, such as Taylor's (Taylor, 1997), indicated that the C-S-H matrix predominantly contributes to the overall strength of the hydrated matrix. In addition, owing to the lack of experimental results for the tensile and biaxial strengths of the hydrated phase, assumptions were made based on the Griffith model (Griffith, 1924), which describes the failure and damage mechanics of cement-based materials. Consequently, the tensile strength of the hydrated phase was assumed to be 1/8 times the compressive strength of the C-S-H matrix, and the biaxial strength was 1.2 times the strength of the C-S-H matrix.

Table 6.2: Mechanical properties of hydrates

Phases/properties	Young's modulus (GPa)	Compressive strength (MPa)	Density (kg/m³)	Ref.
C-S-H (LD)	21.7	528	1700/1400*	(Hlobil et al., 2016)
C-S-H (HD)	29.4	856	2000/1700*	(Hlobil et al., 2016)
Portlandite	38	-	2240	(Haecker et al., 2005)
Ettringite	22.4	-	1800	(Li et al., 2004)
Monosulfate	38	-	1990	(Haecker et al., 2005)

*When nano-silica is incorporated

The input parameters for the unhydrated phase were Young's modulus, Poisson's ratio, and density. The density of the unhydrated phase was based on the actual density of the clinker, which was used as input for the coupled model (Section 3.1). The Young's modulus and Poisson's ratio were assumed to be constant at 137 GPa and 0.3, respectively. These values were selected because the material properties of the clinker remained constant during hydration. Additionally, these values are consistent with the findings reported in the literature (Rupasinghe et al., 2017b; Velez et al., 2001). Similarly, Young's modulus, Poisson's ratio, and density of unreacted nano-silica were assumed to be 70 GPa, 0.21, and 2200 kg/m³, respectively. These values selected based on similar studies (J. J. Kim et al., 2010c) reasonably represent the material properties. Furthermore, circular voids were incorporated into the pore phase within the hydrated phase.

6.5.3 Finite element analysis and homogenised mechanical properties

The RVEs were meshed using triangular plane elements. Capillary pores were not meshed but instead regarded as cavities embedded within the hydrated phase. The homogenised microscopic stress was determined by averaging the stress tensor (σ_y) and field across the RVE domain, as shown in Eq. (6.16). Similarly, the homogenised microscopic strain (Wriggers and Moftah, 2006) was computed by averaging the strain tensor (ε_y) over the RVE domain (Eq. (6.16)).

$$\bar{\sigma} : \bar{\varepsilon} = \frac{1}{|A|} \int_R \sigma_y : \varepsilon_y dy \quad (6.16)$$

Subsequently, a stress-strain curve was generated, and important homogenised material properties, including the compressive strength and Young's modulus, were determined. The maximum stress value on the curve was taken as the material's compressive strength, whereas the stress-strain curve's initial slope was Young's modulus.

6.6 Verification of the proposed model

6.6.1 Verification of the proposed hydration model

As discussed in section 4.3.1.2, **Figure 6.5** provides a graphical representation of the hydration reactions within individual clinker minerals (C_3S , C_2S , C_3A , and C_4AF) and the overall degree of cement hydration, as determined by the XRD/Rietveld analysis. Although the hydration degree of C_3A remained unchanged, the presence of nano-silica significantly affected the hydration degrees of C_3S , C_2S , and C_4AF . This effect can be attributed to the apparent pozzolanic reactivity and nucleation effect caused by nano-silica. However, these alterations in the degree of hydration did not affect the overall degree of cement hydration (**Figure 6.5(e)**). Furthermore, a comparison of the predicted hydration reactions of the clinker minerals (using the coupled hydration and thermodynamic model outlined in Section 3.1) with the experimental values over the hydration age is presented

in **Figure 6.5**. This comparison illustrates the remarkable reliability of the coupled models in accurately reproducing the realistic evolution of the clinker mineral reactions over the hydration age.

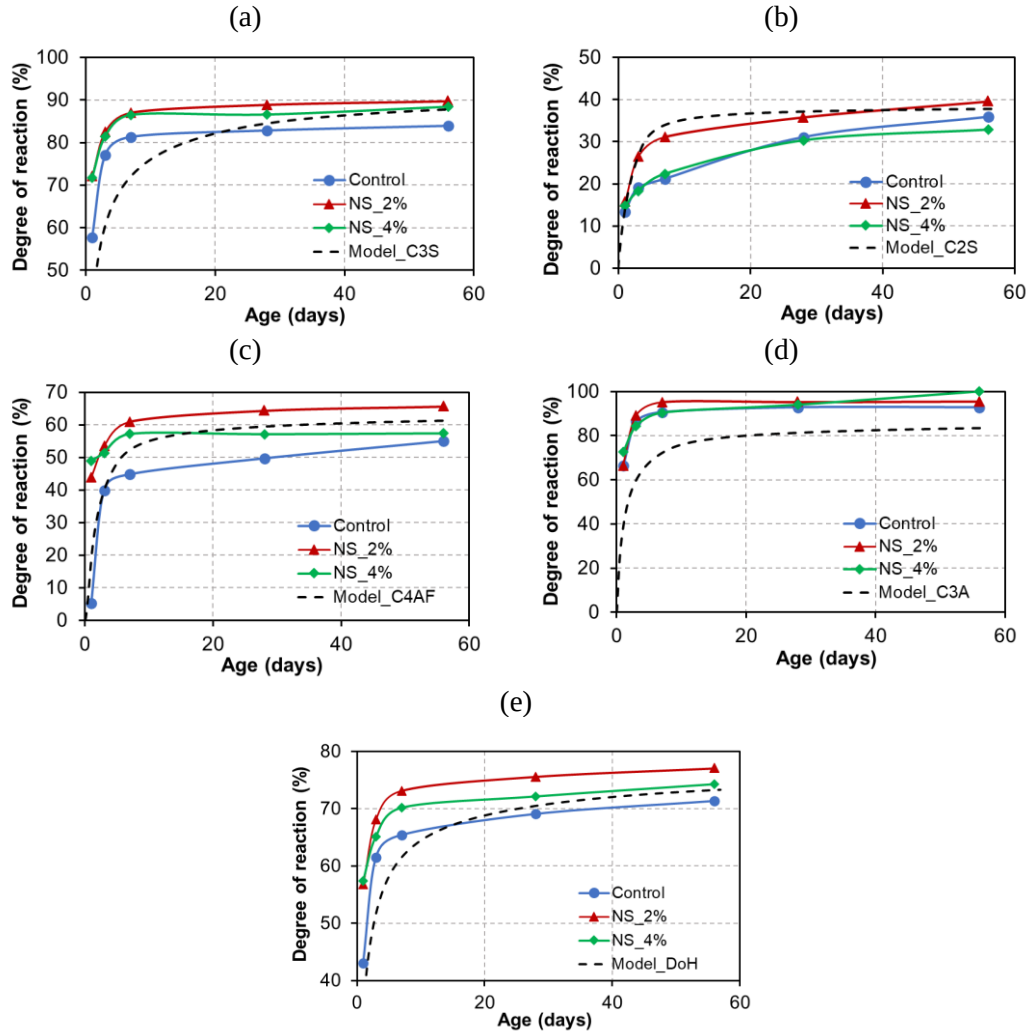


Figure 6.5: Reaction degree of clinker minerals in the cement pastes: (a) C_3S , (b) C_2S , (c) C_3A , and (d) C_4AF . (e) Overall hydration degree of cement pastes.

6.6.2 Predictability of the proposed Finite element model

As outlined in Section 3.4, the numerical microstructure (RVE) generated for the seven-day aged cement paste without nano-silica incorporation was examined using various mesh sizes. The predicted compressive strengths are shown in **Figure 6.6**. The simulations revealed that the compressive strength of the cement paste exhibited limited sensitivity to changes in the mesh size (**Figure 6.6**). Nevertheless, reducing the mesh size led to decreased variability in the predicted compressive strengths, consistent with theoretical expectations (Kanit et al., 2003). Therefore, unless otherwise stated, a fine mesh was selected for all the analyses in this study for the sake of result consistency.

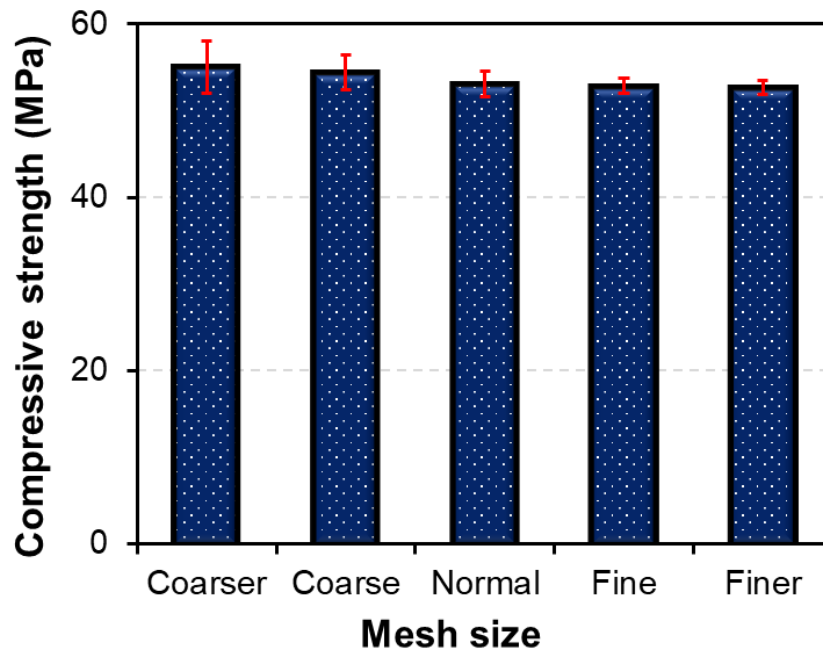


Figure 6.6: Results of the mesh convergency study of the control paste at day seven.

Because the homogenisation of materials with randomly distributed inclusions affects localised deformation and leads to inaccurate computation of mechanical properties, stress-strain responses were simulated for five distinct configurations of unhydrated particles and pores within the hydrated paste. **Figure 6.7** depicts the stress-strain responses of these random configurations with the mean stress-strain response, revealing

standard deviations of 1.6 MPa and 0.4 GPa for homogenised compressive strength and Young's modulus, respectively. These values align with existing literature (Pelissou et al., 200), suggesting that approximately five random samples are generally sufficient to determine the mean mechanical properties.

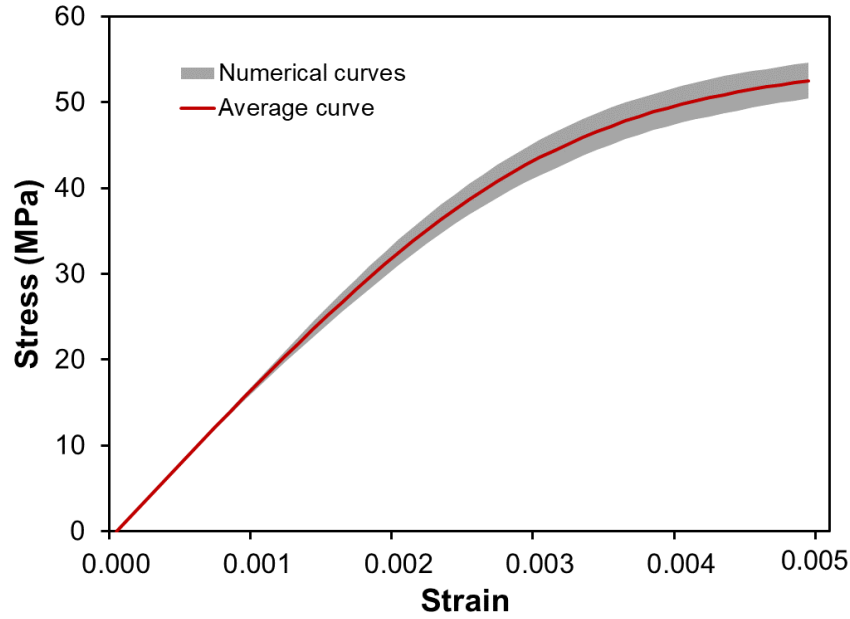


Figure 6.7: Stress-strain behaviour of a random RVE, corresponding to the control paste at day seven.

Figure 6.8 illustrates the computed stress-strain curves for the cement paste with (2 and 4 %) and without nano-silica after seven days of ageing. Furthermore, the stress distributions depicting the plastic potential at the strain values of 0.002 and 0.004 for each RVE are shown in **Figure 6.9**. A comparison of the microstructures with and without nano-silica at 0.002 strain (**Figure 6.9(a–c)**) reveals that the cement paste without nano-silica exhibits higher plastic potential values across the microstructure, indicative of ductile behaviour (Han and Chen, 1985). Conversely, incorporating nano-silica reinforced the microstructure and reduced the plastic potential. As a result, nano-silica-

reinforced cement pastes demonstrated a higher Young's modulus and strength (**Figure 6.8**) than the control cement paste, which was more prone to deformation under stress.

Similarly, when examining the microstructure of the pastes at a strain of 0.004, the cement pastes with nano-silica exhibited increased pore closure (depicted by a larger red area) compared to the control paste due to compressive stress. This enhanced pore closure increases the effective load transfer area between the microstructural elements, thereby reducing the stress concentration areas and enhancing the strength of the material (**Figure 6.8**) (Higaeg et al., 2019). Additionally, the increased strength was accompanied by a more significant ultimate deformation (**Figure 6.9(e-f)**); nano-silica further influenced the nonlinear behaviour by augmenting the nonlinear deformation capacity of the material. Thus, it can be concluded that the developed RVE and microscale finite element analysis can realistically predict the influence of nano-silica in cement pastes, elucidating its role in enhancing both mechanical strength and nonlinear behaviour.

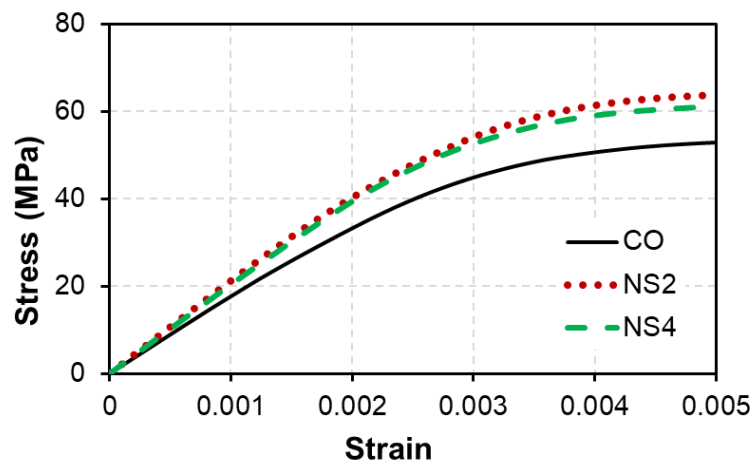


Figure 6.8: Stress-strain response of the control paste (CO) aged for seven days and pastes containing nano-silica (NS2 and NS4)

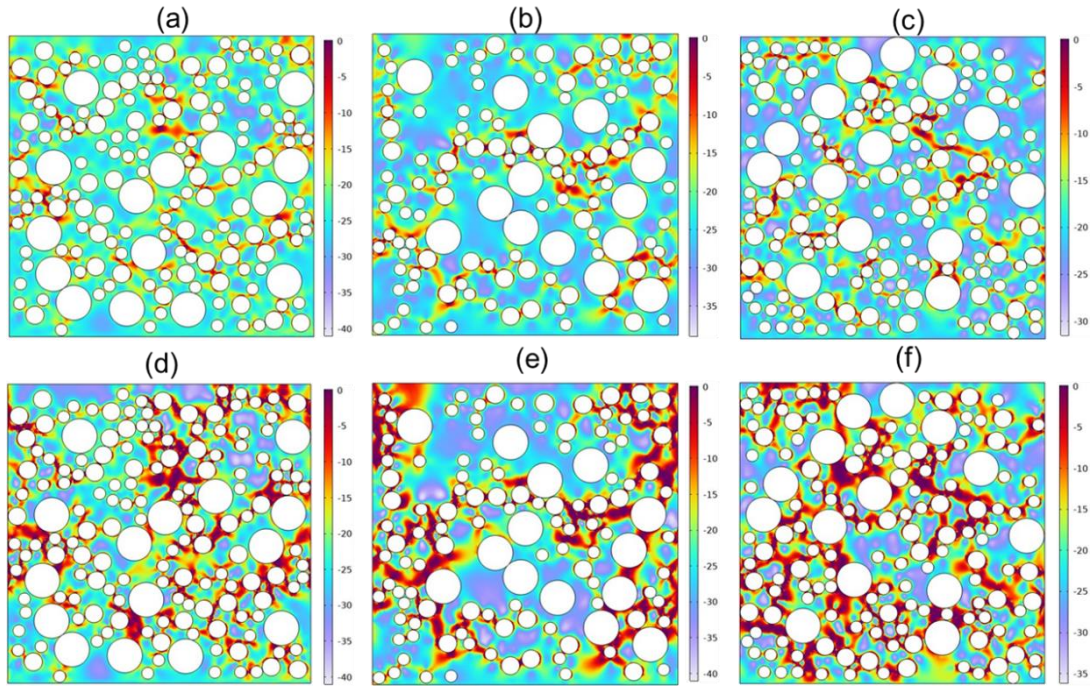


Figure 6.9: Stress distribution (plastic potential) of seven-day aged pastes: (a) control, (b) 2 % nano-silica containing, and (c) 4 % nano-silica containing pastes at strain values of 0.002 and (d) control, (e) 2 % nano-silica containing, and (f) 4 % nano-silica containing pastes at strain values of 0.004.

As the experimental compression tests in this study focused solely on capturing the ultimate compressive strength, the entire stress-strain response was comprehensively compared with those in other studies (Dede and Ayvaz, 2010; Nithurshan et al., 2023) that reported similar compressive behaviours. The compressive strengths of all cement pastes across different ages are shown in **Figure 6.10**. Notably, a significant improvement in strength compared to the control paste was observed with increasing concentrations of nano-silica substitution. This effect, particularly prominent during the early stages of hydration, was attributed to nucleation and pozzolanic influences. This effect resulted in the significant presence of hydrated phases (C-S-H), the primary contributors to strength development in cement pastes (Praveen Kumar and Dey, 2023). However, when substituted with 4 % nano-silica, the compressive strength decreased compared to 2 %

substitution. This outcome can be attributed to the agglomeration of nano-silica particles (Section 4.2), which impedes the hydration process and forms hydration products such as C-S-H. Furthermore, the model slightly underestimated the compressive strength for all samples at the age of one day (**Figure 6.10**). This can be attributed to the inferior mechanical properties of the cement matrix due to incomplete hydration and higher volume fraction of the pore phase, which collectively lead to a weaker matrix that is less capable of withstanding higher loads.

Nonetheless, the experimental findings indicate that substituting 2 % nano-silica increases the compressive strength by 35.2, 21.2, and 17.2 % on days one, three, and seven, respectively. In contrast, 4 % nano-silica substitution resulted in a compressive strength increase of 17.8, 7.6, and 15.9 % on days one, three, and seven, respectively. This trend aligns closely with the predictions of the proposed numerical model. The variation in Young's modulus with hydration age is depicted in **Figure 6.11**. The predicted values were not compared with experimental results since only the ultimate compressive strength was captured during the experimental tests. Nevertheless, **Figure 6.11** illustrates that substituting nano-silica into cement paste increases Young's modulus, indicating improved stiffness and resistance to deformation. This enhancement is attributed to the stronger interparticle bonding and cohesion facilitated by nano-silica (Senff et al., 2009; Snehal et al., 2020), which bridges the gaps between the cement particles. Furthermore, the filling of nanoscale voids and porosity reduction contributed to a denser microstructure (Stefanidou and Papayianni, 2012), ultimately enhancing the material's rigidity.

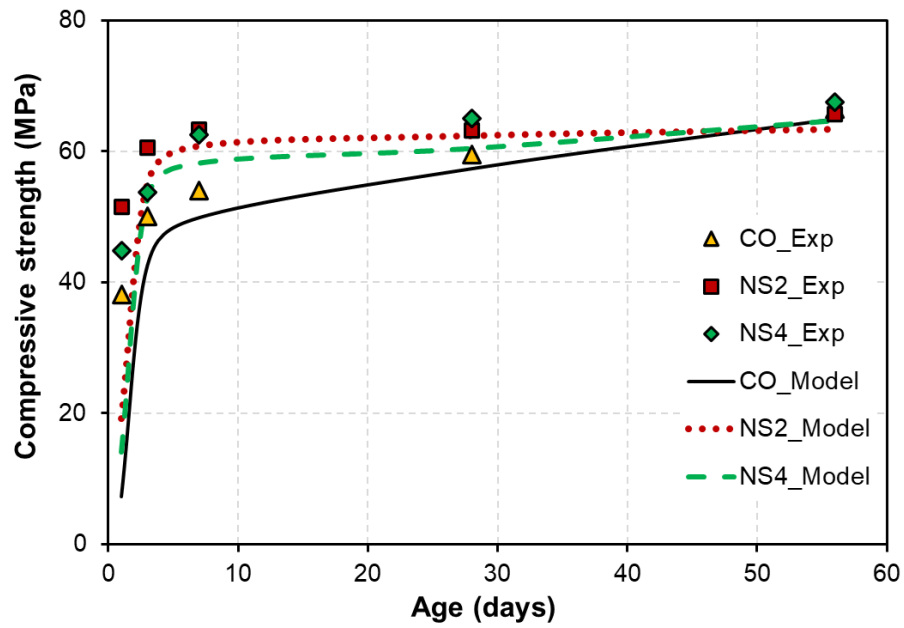


Figure 6.10: Comparison of compressive strength values from experimental and numerical models.

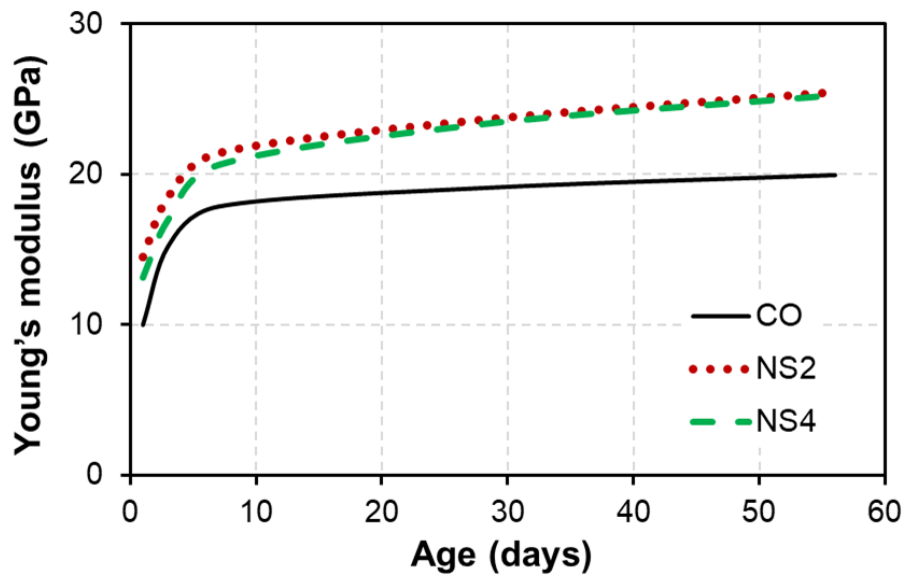


Figure 6.11: Predicted Young's modulus of the cement pastes with respect to hydration age.

6.7 Conclusions

This study introduced a coupled hydration and thermodynamic model to optimise nano-silica replacement in nano-silica reinforced cement paste and proposed a numerical approach to predict its nonlinear behaviour. Furthermore, the predicted results were verified using experimental results. The following conclusions were drawn based on both numerical and experimental results.

1. A coupled hydration and thermodynamic model were proposed to predict the volume fractions of the phases, such as hydrates, unhydrated clinker, pores, and unreacted nano-silica, in cement pastes with and without including nano-silica over varying hydration times. This model was implemented using the PHREEQC-MATLAB interface. Subsequently, the predicted results were validated against the experimental data.
2. Replacing cement with nano-silica in cement pastes significantly enhanced the mechanical properties of the nano-silica-reinforced cement pastes. This improvement stems from the synergistic effects of nucleation and pozzolanic reactions. Through numerical simulations and experimental observations, the optimal replacement level was determined to be 2 % by the weight of the cement content.
3. A cement paste RVE was developed in MATLAB based on the predicted phase volume fraction while accounting for the hydration of clinker particles and agglomeration of nano-silica particles.
4. Finite element analysis was conducted on the developed RVE using COMSOL Multiphysics software by incorporating suitable boundary conditions. This analysis predicted the nonlinear behaviour of pastes with and without nano-silica. Introducing nano-silica significantly improved the strength and deformation capacity of the paste under compression.
5. The mechanical properties, such as the compressive strength and Young's modulus, of the pastes with and without nano-silica, were predicted, and the values were consistent with the experimental values.

6. Refining the proposed models to accurately depict the dispersion and agglomeration of nano-silica in numerical simulations offered a more intricate and comprehensive understanding of the material behaviour. This enhancement enabled a more precise assessment of the impact of nano-silica on the mechanical properties of cement paste, leading to further insights and advancements in material science.

CHAPTER 7

EXTENSION OF THE PROPOSED MODEL TO PREDICT THE MECHANICAL PROPERTIES OF PLAIN MORTAR

7.1 Introduction

Concrete is a multi-scale material with properties ranging from the nanoscale to the macro-scale. The previous chapter introduced a model to predict the mechanical properties of cement paste, focusing on the micro-scale. In this chapter, we extend this model to predict the properties of mortar, which operates at the mesoscale, as shown in **Figure 7.1**. In modelling cement paste, the RVE included a higher number of phases: the hydrated phase, unhydrated cement phase, capillary pore phase, and unreacted nano-silica phase. This detailed approach allowed for a comprehensive understanding of the microstructural interactions within the cement paste.

The RVE is simplified into three phases for mortar: aggregates, cement paste, and ITZ. Voids are not included in this RVE, reflecting the composite nature of mortar at the mesoscale. Including aggregates and ITZ is crucial, as they significantly influence mortar's mechanical properties and durability. By extending the proposed model to mortar, we bridge the gap between the micro-scale properties of cement paste and the meso-scale behaviour of mortar. This transition is essential for developing a more holistic understanding of nano-modified concrete and its performance. The refined model provides insights into how the modifications at the micro-scale influence the overall properties of mortar, paving the way for improved predictive capabilities and more effective material design.

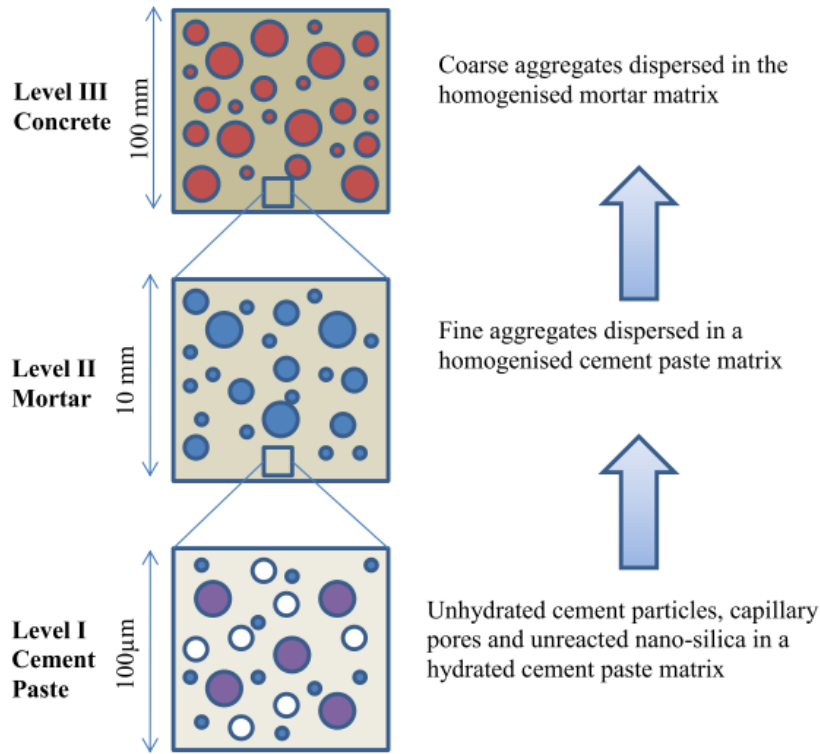


Figure 7.1: Multiscale modelling approach for nano-modified Cement Systems

7.2 Generation of RVE for mortar

In creating the RVE for mortar, we adopted the same procedure described in Section 6.4, applying it to a two-dimensional scale. The RVE is defined as a 10 mm × 10 mm square. The matrix material is the cement paste, and the aggregates are represented as circular particles. The fine aggregate volume fraction of the mortar used in the experiments is 30% (Siventhirarajah, 2022). Therefore, the total area fraction of the aggregates in the RVE is set to 30%. The fine aggregate particle sizes are 0.7 mm and 1 mm, and their proportions in the RVE are determined based on Fuller's formula (Eq. 7.1), which is widely recognized for achieving optimal density and strength in the modelling of mortar and concrete (Schlangen, 2022, 1993; Van Mier et al., 2002; Wittmann et al., 1993).

$$P(d_i) = (d_i/d_{max})^n \quad (7.1)$$

Where $P(d_i)$ is the cumulative percentage passing a sieve with an aperture diameter d_i , d_{max} is the maximum size of aggregate particles, and n is the exponent of the equation (e.g., $n = 2$).

Using Fuller's formula, the volume fraction of each aggregate size $V(d_i)$ can be calculated using Eq. (7.2):

$$V(d_i) = P(d_i) * V_{agg} * V \quad (7.2)$$

Where $V(d_i)$ is the volume fraction of each aggregate size, V_{agg} is the volume fraction of aggregate, and V is the total volume of the RVE.

The total number of aggregates of each size ($N(d_i)$) can then be calculated using Eq. 7.3:

$$N(d_i) = \frac{V(d_i)}{\pi(d_i/2)^2} \quad (7.3)$$

A MATLAB code was developed to randomly place the aggregates within the RVE, from larger to smaller sizes, ensuring no overlap between the aggregates. A Cartesian coordinate system x_i is used in the mortar RVE. When a particle is placed into the mortar RVE, its position is defined by the coordinate x of a reference point O, which is taken to be the centre of the particle. Assuming a uniform probability distribution for the location of O throughout the RVE, the coordinates of O can be obtained as (Eq. 7.4):

$$x = x_{min} + \lambda \cdot (x_{max} - x_{min}) \quad (7.4)$$

Where x is the position vector of O, x_{min} and x_{max} are the minimum and maximum coordinates of the RVE, and λ are three independent random numbers uniformly distributed between 0 and 1.

Two conditions must be satisfied to place an aggregate particle in a free position within the RVE. First, the entire particle must be entirely within the boundary of the RVE. Second, there must be no overlap with previously placed particles. Unlike most studies, each particle must be surrounded by an Interfacial Transition Zone (ITZ) with a minimum thickness of 50 μm . This implies a minimum distance between a particle's edge and the concrete specimen's boundary and a minimum gap width between adjacent particles. Schlangen and van Mier (Schlangen, 2022) proposed a value of $0.1(d_a + d_b/2)$, where d_a and d_b are the sizes of two particles for the minimum gap width between adjacent particles. The RVE developed using the proposed method of 28-day aged mortar with 30% fine aggregates is depicted in **Figure 7.2**.

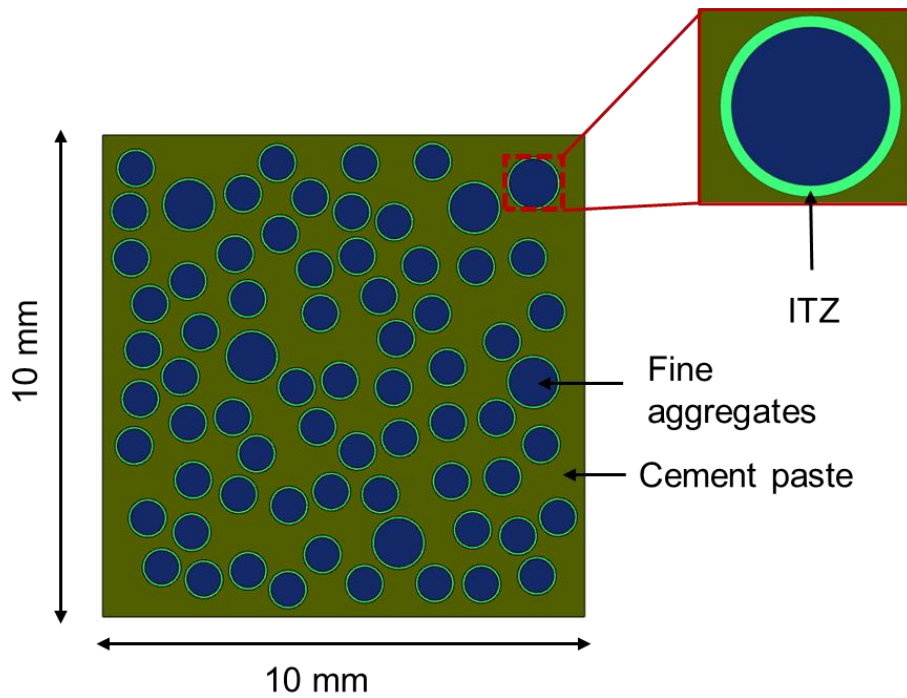


Figure 7.2: The developed Mortar RVE with fine aggregates and ITZs.

7.3 Material Properties of the Phases

Over the past few years, the numerical simulation of damage and fracture processes in mortar and concrete has significantly improved. Understanding the fracture behaviour of concrete under various external loads is crucial for developing more efficient concrete materials for engineering applications. It is widely recognized that mortar and concrete deformation involves highly complex progressive failures characterized by microcracks initiation, propagation, and coalescence due to its heterogeneous nature (Lemaitre, 2001; Lemaitre and Sermage, 1997). Historically, classical mathematical models based on elasticity, plasticity, and viscoelasticity formulations have been used to describe the nonlinearity of concrete. In the 1970s, models based on nonlinear fracture mechanics and continuum damage mechanics were developed to simulate crack propagation and the degradation of material stiffness in concrete. However, these classical models treat concrete as a homogenized material, neglecting its heterogeneity. Such homogenization fails to capture the entire fracture process, from the initiation and propagation of microcracks to the formation of macrocracks. Furthermore, these models do not account for the randomness of concrete's microstructural properties, which is essential for a comprehensive understanding of the fracture process (Wriggers and Moftah, 2006).

Various numerical models have been proposed to address these limitations and simulate the fracture process in concrete at the mesoscale. For instance, Bazant et al. (Bazant et al., 1991) introduced a random particle model for the fracture of brittle aggregate composite materials. This model uses a softening stress-strain relationship for the matrix material, corresponding to a prescribed microscopic interparticle fracture energy. In the lattice models developed by Schlangen and Garboczi (Schlangen and Garboczi, 1997) and Schlangen and van Mier (Schlangen, 2022), tensile strengths are assigned to lattice elements to simulate the fracture mechanism in heterogeneous materials like concrete. Lilliu and van Mier (Lilliu and van Mier, 2003) extended the lattice model for three-dimensional analyses. Eckardt et al. (Schrader et al., 2009) used the smeared crack

concept to describe the fracture behaviour of aggregates and the matrix, observing reasonable crack patterns during their simulations.

Continuum damage mechanics has been extensively applied to model the progressive degradation of materials caused by microcracking. It has been established that the damage mechanics approach can accurately represent the strain-softening response of concrete. These continuum models assume that local damage in the material can be averaged and represented as damage variables related to the tangential stiffness tensor. Researchers such as Krajcinovic(Krajcinovic, 1979), Mazars and Pijaudier-Cabot(Mazars and Pijaudier-Cabot, 1996) have used a scalar damage variable to model isotropic damage based on experimental stress-strain curves of concrete under uniaxial tension. Further details on continuum damage models can be found in works by Mazars, Pijaudier-Cabot, and Peerlings(Mazars and Pijaudier-Cabot, 1996; Peerlings, 1999). In this work, the scalar damage model of Mazars is used to model the mechanical behaviour of concrete due to its simplicity.

7.3.1 Mazars damage model

In this study, the cement paste phase is modelled using the Mazars damage material model integrated into COMSOL Multiphysics. According to continuum damage constitutive theory, the nonlinear stress-strain relationship of a material can be characterized by its damage and degradation. This relationship can be expressed in Eq. (7.5) (Mazars, 1986):

$$\sigma = (1 - D)E_0\varepsilon \quad (7.5)$$

where, D is a scalar damage variable that ranges from 0 (indicating an undamaged state) to 1 (indicating a fully damaged material). The damage variable should be updated according to the strain or stress state of the material.

In the Mazars damage model, the damage variable D depends on the elastic equivalent strain and the damage internal variable κ . The elastic equivalent strain ε_{eq} is defined in Eq. (7.6):

$$\varepsilon_{eq} = \sqrt{\sum_{i=1}^3 \langle \varepsilon_i \rangle^2} \quad (7.6)$$

where $\langle . \rangle$ is the Macauley bracket and ε_i are the principal strains. The loading function of damage is given in Eq. (7.7).

$$f = \varepsilon_{eq} - \kappa \quad (7.7)$$

Where κ is the threshold for damage growth. Initially, its value is κ_0 , which can be related to the peak stress f_t of the material under uniaxial tension.

$$\kappa_0 = \frac{f_t}{E} \quad (7.8)$$

During the loading process, κ assumes the maximum value of the equivalent strain attained at any point in the loading history. This is governed by the Kuhn-Tucker conditions: $f \leq 0, \dot{\kappa} \leq 0, \dot{\kappa} \cdot f = 0$.

In the Mazars damage model, the damage variable is expressed as a linear combination of damage generated under compression and damage generated under tension, as shown in Eq. (7.9).

$$D = \alpha_t D_t + \alpha_c D_c \quad (7.9)$$

Tensile and compressive damage variables can be written as in Eq. (7.10) and Eq. (7.11), respectively:

$$D_t = 1 - \frac{\kappa_0(1-A_t)}{\kappa} - \frac{A_t}{\exp[B_t(\kappa - \kappa_0)]} \quad (7.10)$$

$$D_c = 1 - \frac{\kappa_0(1-A_c)}{\kappa} - \frac{A_c}{\exp[B_c(\kappa-\kappa_0)]} \quad (7.11)$$

Where, A_t , B_t , A_c and B_c are parameters utilized to govern the evolution of damage and must be determined based on experimental data.

The parameters α_t and α_c in Eq. (7.9) quantifying the influence of D_t and D_c on the total damage variable D are shown in Eq. (7.12) and Eq. (7.13).

$$\alpha_t = \sum_i \frac{\varepsilon_{ti} \langle \varepsilon_i \rangle}{\varepsilon_{eq}^2} \quad (7.12)$$

$$\alpha_c = \sum_i \frac{\varepsilon_{ci} \langle \varepsilon_i \rangle}{\varepsilon_{eq}^2} \quad (7.13)$$

In uniaxial tension, $\alpha_t = 1$ and $\alpha_c = 0$, whereas in uniaxial compression, $\alpha_t = 0$ and $\alpha_c = 1$. In a general state, $\alpha_t + \alpha_c = 1$.

The strain-softening behaviour is significantly influenced by the inherent mesh dependency of the model, which can lead to unintended energy dissipation during the strain-softening process. To mitigate the impact of meshing on simulation outcomes, the equivalent strain ε_{eq} is approximately homogenized using an implicit gradient enhancement scheme (Eq. 7.14) (Peerlings et al., 2002).

$$\tilde{\varepsilon} - c \nabla^2 \tilde{\varepsilon} = \varepsilon_{eq} \quad (7.14)$$

where $\tilde{\varepsilon}$ is effective equivalent strain; ∇^2 is the Laplace operator; c is the homogenised gradient coefficient. For two dimensional calculations, $c = r^2/2$, where $r = \sqrt{A}$ is homogenization radius, and A represents element area.

It should be noted that since an experimental stress-strain curve was not accessible, the material parameters, such as A_t , B_t , A_c and B_c for the Mazars damage model assigned to cement paste and ITZ were derived by examining literature from comparable

studies (Kim and Abu Al-Rub, 2011; Wriggers and Moftah, 2006; Yu et al., 2022). The strength parameters, such as compressive strength and elastic moduli of the cement paste, were determined using Level I of the multiscale approach.

Furthermore, the strength parameters for the Interfacial Transition Zone (ITZ) were established by reducing the compressive strength and elastic moduli by 15% and 5%, respectively, from the original values of the cement paste (Bao et al., 2021). This adjustment accounts for the weakened nature of the ITZ, which serves as a transitional zone between the cement paste and aggregates. This weakness arises from the constraining influence of aggregates, which limits the packing of hydration products.

7.3.2 Linear elastic model

In similar literature and simulations, fine aggregates are typically modelled as a linear elastic material (with properties $E = 80,000$ GPa and $\nu = 0.2$). This choice is justified by the relatively brittle behaviour of aggregates, along with their higher elastic modulus and yield strength compared to the paste phase.

7.4 Results and discussions

7.4.1 Mesh convergency study.

The mesh convergence study on the RVE is essential for ensuring the accuracy and reliability of the numerical simulations. In this study, the RVE, representing the mortar with a 30 % aggregate volume at 28 days aged, was meshed using various element sizes, ranging from very coarse (1.3 mm) to very fine (0.37 mm), and subjected to the same loading conditions discussed previously. The stress-strain behaviour of the mortar RVE, obtained with different mesh sizes, is illustrated in **Figure 7.3**. The results of the mesh convergence study indicate that a finer mesh is preferable for analysing the mortar RVE. This conclusion is drawn based on the convergence of results across different mesh sizes and the computational efficiency of the analysis. A finer mesh (0.53 mm) allows for

capturing the complex behaviour of the material and provides more accurate predictions of mechanical properties. Additionally, it ensures that the numerical solution is less sensitive to changes in mesh density, thereby enhancing the reliability of the simulation results.

Figure 7.4 depicts the RVE meshed using a fine element size, demonstrating the level of detail achieved in capturing the internal structure and heterogeneity of the mortar. A fine mesh enables the simulation to accurately represent the intricate interactions between the mortar constituents, including the aggregates and cement paste.

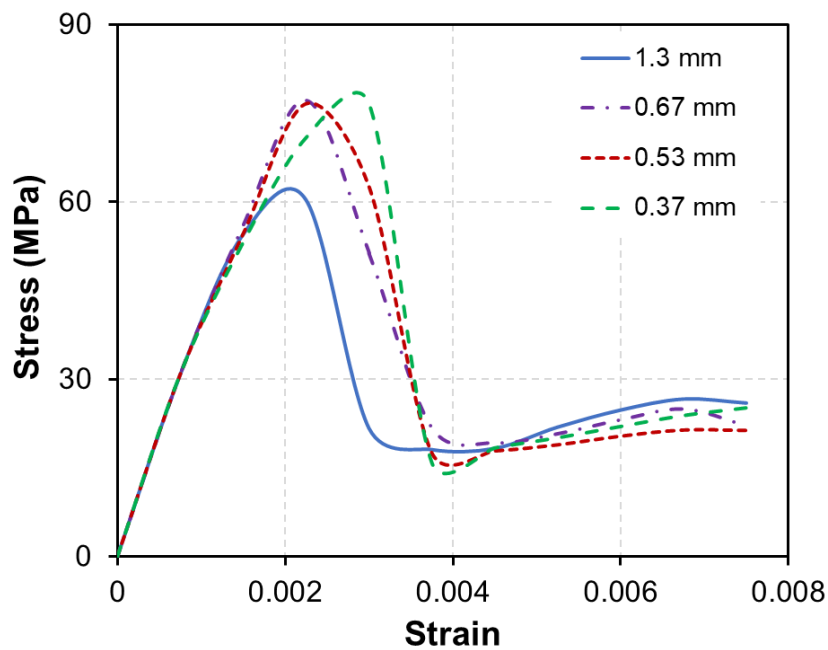


Figure 7.3: Variation of stress-strain behaviour of mortar RVE with different mesh size

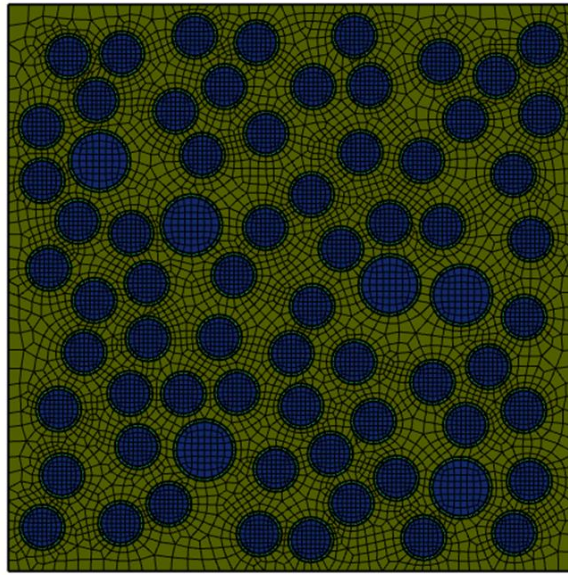


Figure 7.4: Mortar RVE meshed with fine mesh size.

7.4.2 The importance of incorporating the ITZ

Many studies have disregarded the distinct properties of the ITZ, often treating it as part of the homogeneous aggregates. In contrast, this study explicitly accounted for the ITZ in the analysis of the RVE. The stress-strain behaviour of the mortar was examined with and without the ITZ's consideration, as illustrated in **Figure 7.5**. When the ITZ was not considered, the mortar exhibited brittle behaviour after reaching maximum stress, which does not accurately reflect real-world conditions. However, with the inclusion of the ITZ, the model accurately predicted the softening behaviour of the mortar after reaching maximum stress or initial cracking. Additionally, without considering the ITZ, the model overestimated the strength by assuming complete bonding between the aggregates and cement paste, which is unrealistic.

In contrast, incorporating the ITZ into the model led to predictions of compressive strength that closely aligned with experimental results (**Figure 7.6**). Therefore, the

proposed model, which accounts for the ITZ, provides a more realistic framework for predicting the mechanical properties of cement paste.

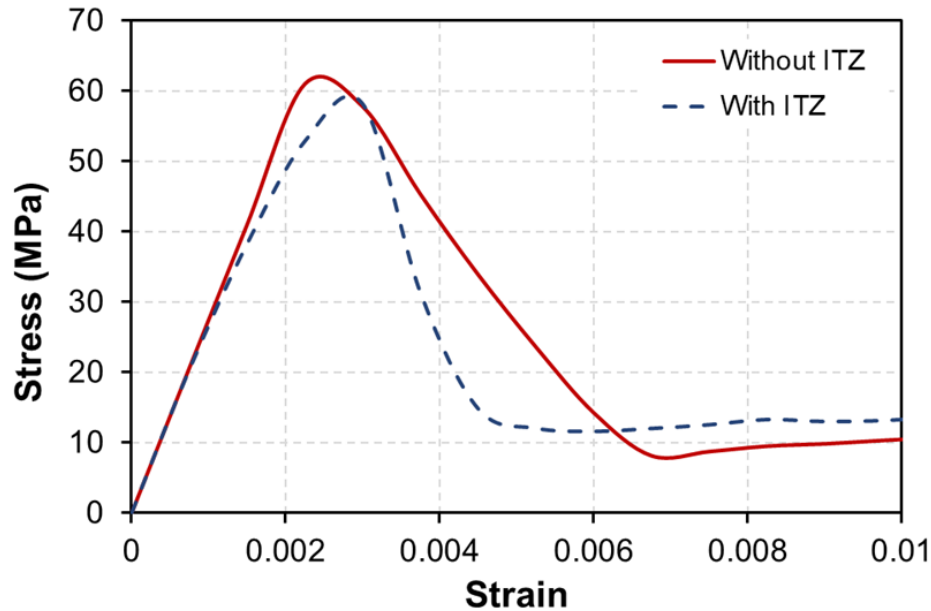


Figure 7.5: Stress-strain curve with and without considering ITZ

7.4.3 Effect of ITZ thickness

Experimental studies have demonstrated that the thickness of the ITZ varies depending on the mixture proportions and types of aggregates used, typically ranging from about 10 to 50 μm . To determine the most suitable ITZ thickness, the mortar RVE was developed with three different ITZ thicknesses (13, 30, and 50 μm). The stress-strain curves obtained with these varying ITZ thicknesses are illustrated in **Figure 7.7**. It was observed that very small ITZ thicknesses (15 and 30 μm) failed to adequately capture the stress concentrations at the interfaces between the aggregate and the matrix. However, an ITZ thickness of 50 micrometres more accurately predicted the stress-strain behaviour of mortar, aligning closely with experimental results.

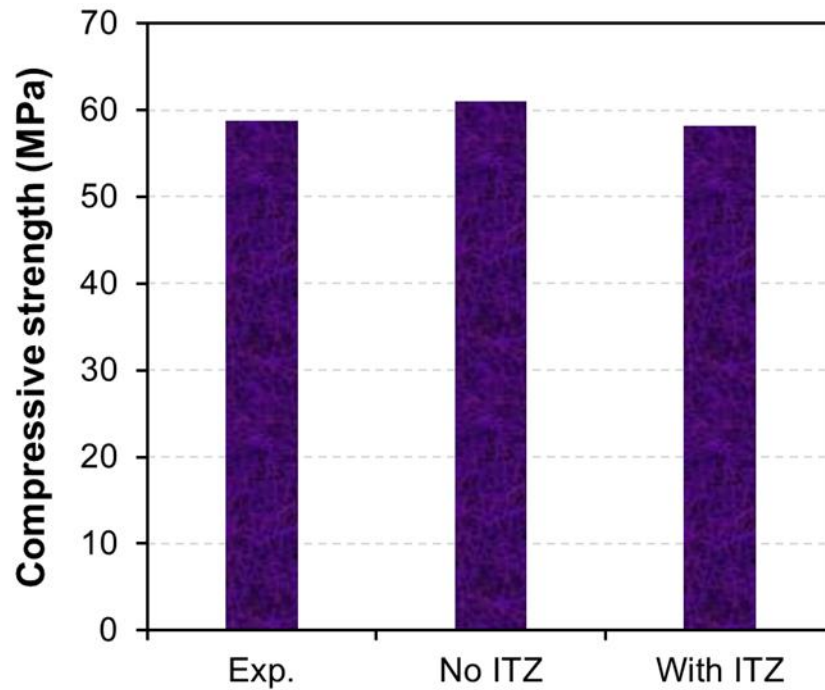


Figure 7.6: Comparison of predicted results (with and without ITZ) with experimental results

This discrepancy may be attributed to the need for the chosen ITZ thickness to be compatible with the finite element mesh size used in the simulation. When the ITZ thickness is smaller (e.g. 15 and 30 μm) than the mesh size, numerical inaccuracies can arise, resulting in underestimating stress concentrations. Moreover, minimal ITZ thicknesses may oversimplify the transition region between the aggregate and the surrounding cement paste, overlooking crucial material heterogeneities such as variations in composition, porosity, and mechanical properties. Additionally, localized stress concentrations at the interfaces between the aggregate and the cement paste can extend beyond the thickness of the ITZ, especially under loading conditions that induce significant strain gradients near the interface. These interface effects underscore the importance of selecting an appropriate ITZ thickness that can effectively capture the complexities of the interfacial behaviour within the mortar microstructure.

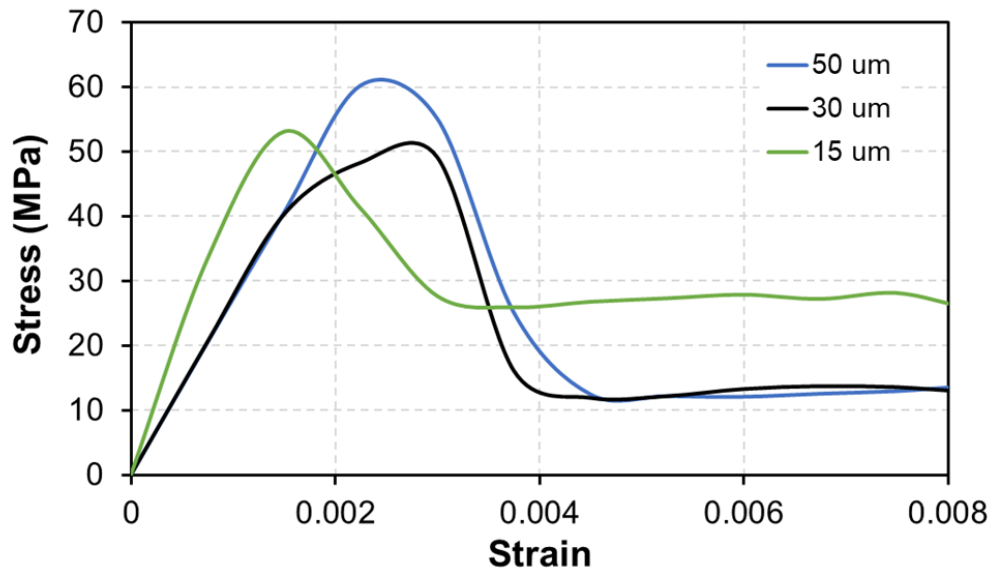


Figure 7.7: Stress-strain curve predicted with varying ITZ thickness.

7.4.4 Effect of multiple sizes of aggregates

Many studies have often utilized single-size aggregates in their modelling procedures to simplify the process, yet this approach may not accurately reflect the actual packing density of the RVE. To address this limitation, our study incorporated two different sizes of aggregates, with their proportions determined from Fuller's curve. The stress-strain behaviour of the RVEs containing two aggregate sizes was compared with that of RVEs containing a single aggregate size, as illustrated in **Figure 7.8**. While both types of RVEs predicted similar strengths, there were notable differences in their behaviour. The RVE with a single aggregate size tended to overestimate the strain at maximum stress due to the lower packing density of the aggregates, which delayed stress propagation. Conversely, the RVE with multiple aggregate sizes exhibited denser aggregate packing, allowing for comparatively quicker crack propagation and, thus, lower stress at maximum stress. This study underscores the significance of considering multiple sizes of aggregates when modelling mortar or concrete, as it can significantly influence the predicted mechanical behaviour and ultimately enhance the accuracy of simulation results.

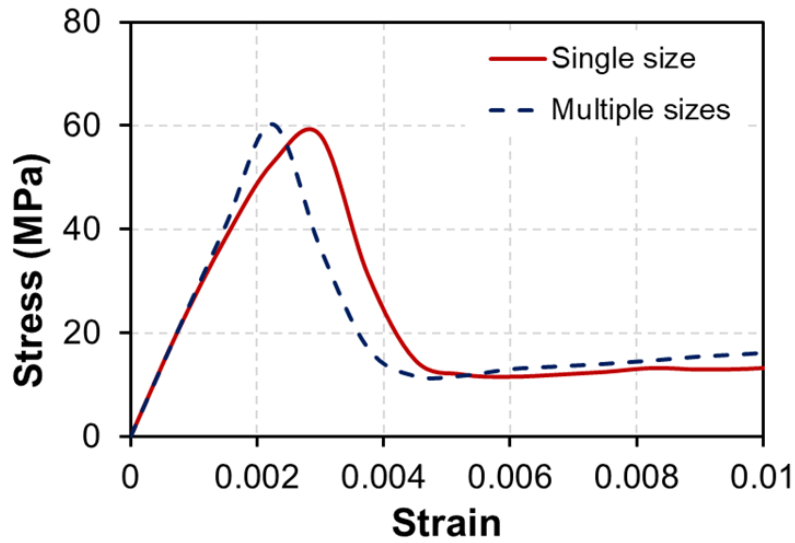


Figure 7.8: Stress-strain behaviour with single and multiple-sized aggregates

7.4.5 Effect of aggregate configuration

To assess the impact of random aggregate distribution on the predictive capability of our proposed model regarding stress-strain behaviour, aggregates were positioned within the RVE using four distinct configurations and analysed under identical conditions. The resulting stress-strain behaviour is illustrated in **Figure 7.9**. The proposed model consistently predicted the same strength across all configurations. However, a slight deviation was observed in the softening region, which was predominantly influenced by stress concentration due to the initiation and propagation of microcracks within the mortar resulting from the arrangement of the aggregates. This underscores the robustness of the model in predicting the mechanical properties of mortar despite variations in aggregate distribution within the RVE.

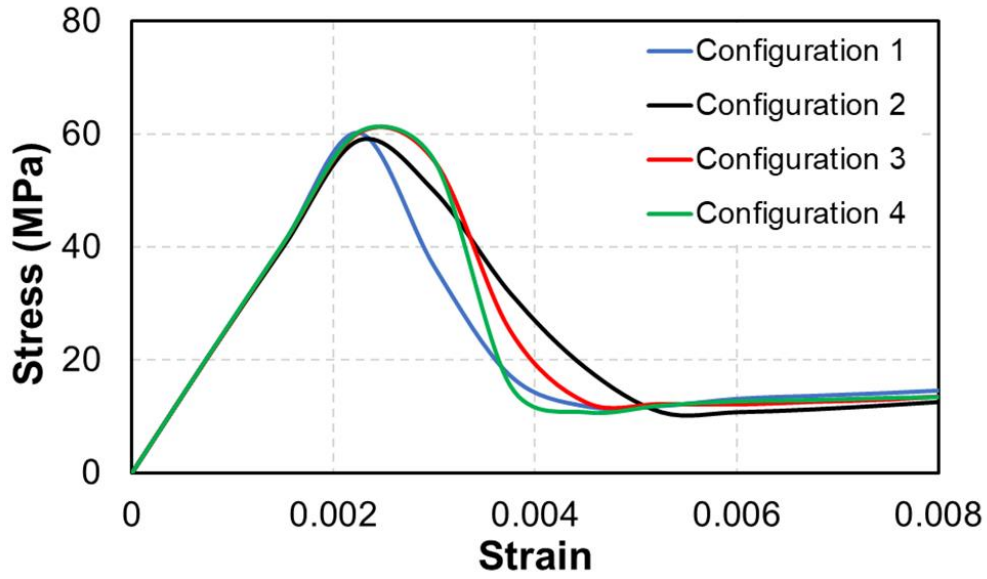


Figure 7.9: Stress-strain curve for different aggregate configurations.

7.4.6 Effect of aggregate shape

The shape of aggregates in mortar varies widely based on their nature and production methods, ranging from rounded and angular to irregular, flaky, elongated, and crushed. However, fine aggregates are typically circular or elliptical. To capture this variability, we developed Mortar RVEs with circular and elliptical-shaped aggregates randomly distributed within the RVE. When positioning the elliptical aggregates, we considered arbitrary major and minor axis values and their inclination relative to the horizontal plane to achieve a realistic random distribution. In both RVEs, the aggregate volume remained constant, and the ITZ was considered for both aggregates. The derived stress-strain behaviour is depicted in **Figure 7.10**. The proposed model underestimates the stress-strain behaviour of the RVE with elliptical-shaped aggregates. This discrepancy may be attributed to stress concentrations occurring at the tips of the elliptical aggregates (**Figure 7.11**), leading to strain localization and reducing their load-carrying capacity. However, the proposed model predicts the stress-strain behaviour of mortar fairly well with circular aggregates.

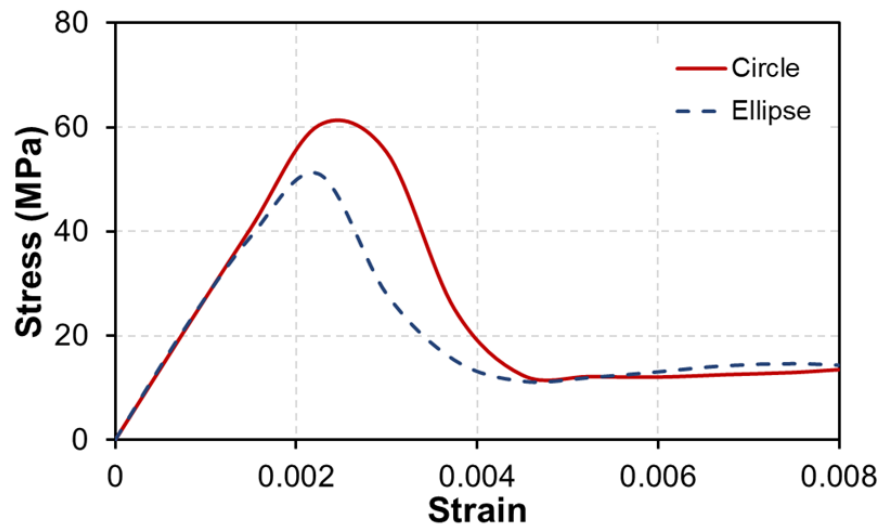


Figure 7.10: Stress-strain behaviour with different aggregate shapes

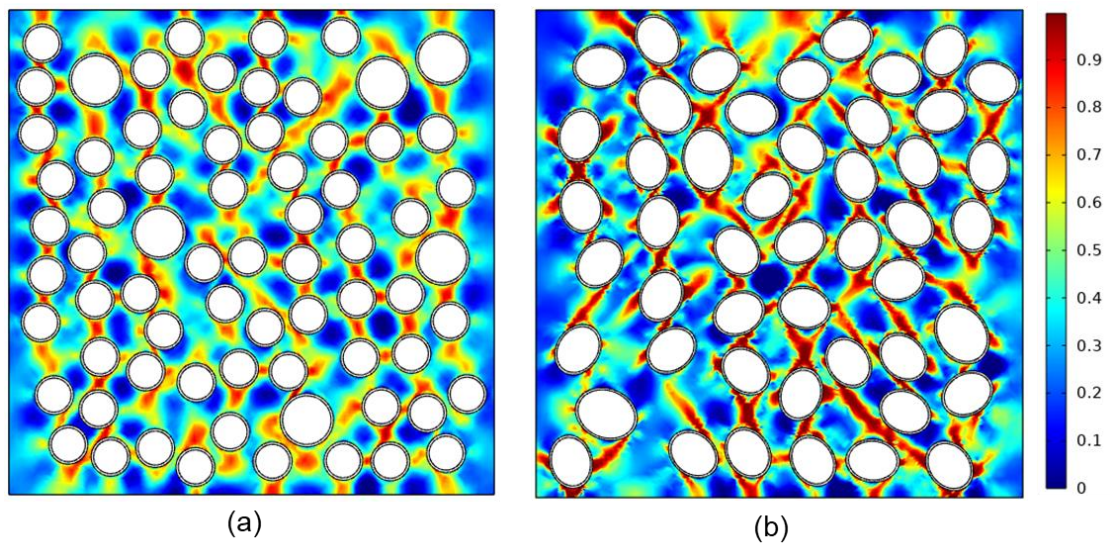


Figure 7.11: Stress distribution (plastic potential) with circular and elliptical aggregates

7.5 Conclusions

The successful extension of the multi-stage model from cement paste to mortar, including the ITZ, marks a significant advancement in predictive modelling for concrete materials. The model's robustness was thoroughly examined through sensitivity analyses encompassing various parameters such as aggregate size, ITZ thickness, aggregate shape, and Randomly Varying Element (RVE) configurations. It reliably predicted the mechanical properties of mortar, particularly when considering multi-sized circular aggregates and the presence of ITZ. However, calibration of Mazar's material parameters against experimental results at different mortar ages is necessary to enhance the model's accuracy further. This iterative process ensures that the model accurately captures the dynamic evolution of mechanical properties over time.

Overall, the developed multi-stage model, incorporating the complexities of ITZ, has demonstrated its efficacy in predicting the mechanical behaviour of mortar. Its successful validation against experimental results underscores its potential as a valuable tool in advancing our understanding and design capabilities in concrete materials engineering.

CHAPTER 8

CONCLUSIONS AND FUTURE WORKS

8.1 Introduction

This dissertation analyses the performance enhancement of nano additives in cementitious materials. The objectives of the research are to address the contradictory findings related to nano additives, such as nano silica and GO, in cementitious materials and to develop a new model capable of determining the optimum quantity of nano additives and predicting the nonlinear behaviour resulting from their impact on microstructure evolution with fewer assumptions. From the perspective of Material Engineering, significant effort has been dedicated to understanding the microstructural, mechanical, and durability responses of cementitious materials. Various factors have been considered, including different types of cement (clinker composition), water-to-cement ratio (w/c), aggregate content, hydration processes, and exposure periods.

The research work comprises several major components. First, an overview of experimental studies on nano-modified cement-based materials using nano silica and GO is provided, focusing on cement hydration, microstructure development, and mechanical properties evolution (Chapter 2). Second, a review of the available techniques to simulate cement hydration, predict microstructure development, and compute the mechanical behaviour of cement-based materials is presented (Chapter 3). Third, the research experimentally explores the effects of nano-silica on cement hydration and mechanical properties (Chapter 4). Fourth, it investigates the effects of GO on cement hydration and the formation of C-S-H (Chapter 5). Fifth, a new model is developed to predict the mechanical properties of nano silica-modified cement paste based on hydration products and matrix porosity (Chapter 6). Finally, the proposed cement paste model is extended to predict the mechanical properties of mortar.

8.2 Effect of nano-silica on the clinker hydration, microstructural development and mechanical properties evolution.

In this part of the study, cement paste was prepared by replacing the cement with 2 % and 4 % by weight of nano silica. A control cement paste was also prepared to quantify the effects of nano-silica on cement hydration and the enhancement of mechanical properties. TGA, XRD, and SEM were employed to characterize the microstructural changes. The conclusions of this experimental program are as follows:

1. TGA analysis confirmed that nano-silica promotes cement hydration in the initial stages.
2. Nano silica replacement levels beyond 2 % show no significant difference in the amount of portlandite.
3. At early ages (1 and 3 days), the pozzolanic reactivity of nano silica is predominantly due to the nucleation effect.
4. After 7 days, a significant reduction in portlandite is observed up to a 4 % replacement level due to the pozzolanic reaction.
5. Rietveld analysis of XRD curves reveals that incorporating nano silica slightly affects the hydration degree of C_3S , C_2S , and C_4AF , while it does not affect the hydration of C_3A . However, the overall hydration degree of clinker is not significantly affected.
6. Visual observation of SEM images indicates that replacing cement with nano silica results in a denser microstructure at specific ages, with more compact C-S-H observed.
7. EDS analysis revealed that replacing cement with nano silica forms tobermorite C-S-H, while ordinary cement produces jennite C-S-H.
8. The compressive strength increased maximally with a 2 % replacement level up to 7 days, compared to the control sample and the 4 % replacement level.
9. Overall, the optimum cement replacement level with nano silica is around 2 % for maximum strength increase.

8.3 Chemical and microstructural analysis of graphene oxide incorporated cement paste and synthesised C-S-H

This study prepared two cement pastes, one incorporating GO at 0.06 wt.% and the other without GO. The as-received GO was characterized using FTIR and XRD before preparing the cement paste. The compatibility of GO with the pore solution was determined using a Zeta potential analyser. The effects of GO on clinker hydration and microstructural development were characterized using TGA, XRD, SEM, and ^1H NMR. Additionally, C-S-H was synthesized with and without GO to study microstructural changes at the nanoscale, characterized using ^{29}Si NMR along with other techniques. The conclusions from these experiments are as follows:

1. The characterization of GO confirmed the presence of active oxygen-containing functional groups.
2. Zeta potential results indicate that GO particles show a stronger affinity for calcium ions.
3. TGA results showed a continuous increase in portlandite in GO composites compared to the control up to 28 days, attributed to the nucleation effect of GO and further hydration promoted by the release of adsorbed water.
4. Rietveld analysis of XRD diffraction curves is consistent with TGA results, confirming the formation of more amorphous C-S-H.
5. SEM analysis reveals that with the addition of GO, micropores are sealed with amorphous C-S-H, and the C-S-H density is increased.
6. TGA, XRD, and FTIR analyses of synthesized C-S-H confirm that incorporating GO promotes the formation of more ordered C-S-H crystals.
7. SEM images indicate that larger pores in pure C-S-H are sealed with finer nano-foils with folding structures.
8. ^{29}Si NMR results show that incorporating GO promotes C-S-H's polymerisation.
9. ^1H NMR suggests that adding GO decreases gel pores, increases interlayer water, and facilitates the formation of more ordered C-S-H crystals.

8.4 Developing a multiscale model for predicting the mechanical properties of nano-silica-modified cement paste

In this part of the study, a multiscale model has been developed to predict the mechanical properties of nano silica-modified cement paste, such as compressive strength and Young's modulus, based on microstructure development during the hydration process. The research followed a systematic approach: firstly, the reaction degree of nano silica was analytically integrated into an existing cement hydration and thermodynamic model. This integration allowed for the systematic output of the integrated hydration model's volume fractions of hydrates, unhydrates, shrinkage, and pores. Using these volume fractions, the mechanical properties were predicted through a numerical approach and validated against experimental results. The conclusions drawn from this modelling approach and the model predictions are as follows:

1. The reaction degree of nano silica was successfully integrated into the coupled cement hydration and thermodynamic models.
2. The integrated model accurately reproduces the actual reaction degree of clinker minerals with nano silica replacement.
3. The integrated model systematically computed volume fractions of hydrates, unhydrates, shrinkage, and pores.
4. Based on these volume fractions, a representative volume element (RVE) was successfully developed for cement paste at the microscale (100 μm) using MATLAB.
5. The developed RVE was successfully transferred to the finite element software COMSOL Multiphysics.
6. Actual loading conditions were simulated, and the numerical analysis resulted in the nonlinear behaviour of the hardened cement pastes with curing age, validated by experimental results.
7. The proposed model also predicts that the optimum nano silica replacement level is 2 %.

Overall, the proposed multiscale model effectively captures the complex interactions between nano silica and cement hydration, providing a reliable tool for predicting the mechanical properties of nano silica-modified cement paste. This model can significantly aid in optimizing nano silica content for enhanced performance in cementitious materials.

8.5 Extending the proposed cement paste model to predict the mechanical properties of mortar

In this chapter, the mechanical properties of mortar were reliably predicted by modifying the developed multiscale model initially designed for cement paste. Mortars and concretes were treated as three-phase composites, with the ITZ for fine aggregate accurately considered in the RVE. The ITZ properties were assumed to be lower than the cement pastes. The proposed model for mortar was validated against experimental results, and sensitivity analysis was conducted considering various ITZ thicknesses, multiple aggregate sizes, aggregate placement in the RVE, and aggregate shape. The conclusions from this modelling approach and the model predictions are as follows:

1. The ITZ was successfully introduced into the mortar RVE, and reliable material properties were assigned.
2. The proposed model emphasizes the importance of considering the ITZ in predictive models for mortar and concrete.
3. Aggregates were modelled using a linear material model, while the cement paste and the ITZ were modelled using the Mazars damage model, with parameters extracted from the literature.
4. The proposed model accurately predicts the compressive strength of mortar made with 30 % aggregate content.
5. Sensitivity analysis suggests that the most feasible ITZ thickness is 50 μm and that considering multiple aggregate sizes leads to more reliable predictions.
6. The random placement of aggregates in the RVE did not influence the strength prediction capacity of the proposed model.

7. Including aggregates as circular inclusions provides more accurate results than using elliptical-shaped aggregates.

Overall, this chapter demonstrates that the modified multiscale model effectively captures the mechanical behaviour of mortar, highlighting the critical role of the ITZ and the need for precise modelling of aggregate characteristics. This model provides a robust tool for predicting the mechanical properties of mortar and can be extended to more complex concrete systems for enhanced performance prediction.

8.6 Recommendations for future research

This section provides recommendations for future research to enhance and optimize the findings of this study. Future research should explore several types of nano-silica, particularly colloidal forms with different concentrations, to broadly generalize the enhancements provided by nano-silica in cement paste, as this study only investigated one type. Determining the optimal replacement level of nano silica for mortar and concrete is necessary. The results can be used for model validation for nano-modified mortar and concrete, expanding beyond this study's limited scope of cement paste.

Nanoindentation methods should be used to evaluate the mechanical properties of cement paste, mortar, and the ITZ. Incorporating these measured values into the proposed model will increase its robustness and predictability. Effective mixing procedures must be developed to disperse GO in cementitious materials to achieve repeatability. The effects of GO in mortar and concrete should also be studied to integrate these findings into the predictive model, extending the scope beyond the cement paste covered in this study.

Conducting nanoindentation tests on GO composites will help establish a correlation between GO dosage and the mechanical properties of HD C-S-H. This data can be used to extend the proposed model to predict the mechanical properties of GO-reinforced cement paste. Furthermore, methods to incorporate unreacted nanoparticles into the numerical RVE for reliable prediction should be explored.

Finally, it is essential to investigate other significant aspects, such as durability, ductility, and rheological properties of nano-silica and GO/cement systems. This would improve the overall understanding of these innovative materials and increase their applicability in the construction sector, complementing the primary focus on strength characteristics in this research.

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