

JANUARY 2025

M.Sc. in Civil Engineering

KAYAHAN ERİTEN

REPUBLIC OF TÜRKİYE

GAZİANTEP UNIVERSITY

GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES

**INVESTIGATION OF USING CARBON NANOTUBES IN
CEMENTITIOUS GROUTS**

M.Sc. THESIS

IN

CIVIL ENGINEERING

BY

KAYAHAN ERİTEN

JANUARY 2025

**INVESTIGATION OF USING CARBON NANOTUBES IN
CEMENTITIOUS GROUTS**

**M.Sc. Thesis
in
Civil Engineering
Gaziantep University**

**Supervisor
Prof. Dr. Hamza GÜLLÜ**

**by
Kayahan ERİTEN
January 2025**



©2025[Gaziantep University]

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Kayahan ERİTEN

ABSTRACT

INVESTIGATION OF USING CARBON NANOTUBES IN CEMENTITIOUS GROUTS

ERİTEN, Kayahan
M.Sc. in Civil Engineering
Supervisor: Prof. Dr. Hamza GÜLLÜ
January 2025
85 pages

Grouting is an essential technique in geotechnical engineering, enhancing soil and rock properties for structural stability. This study investigates carbon nanotube (CNT) enhanced cementitious grouts, focusing on their rheological behavior, fresh properties, curing, and mechanical performance. Rheological models, including Cross and Herschel-Bulkley, were evaluated, with the Cross model being more suitable for low water-to-binder (w/b) ratios and high CNT additions, and Herschel-Bulkley better suited for high w/b ratios with low CNT content. CNT addition led to shear-thinning behavior, reduced workability, and increased yield stress. Ultrasonic pulse velocity (UPV) and unconfined compressive strength (UCS) tests confirmed sufficient strength for grouting applications despite a decrease in peak axial strength with CNT addition. Electrical resistivity progressively increased with curing time. Digital Image Correlation (DIC) effectively monitored crack detection and its development. CNT addition enhanced stability and ductility, extended the uncracked phase, and increased strain at the first surface crack. It also shifted the failure modes from axial splitting to more complex modes, attributed to increased ductility. These findings emphasize the potential of CNTs to optimize cementitious grouts.

Key Words: Nanotube, Grouting, Rheology, Soil Improvement, CNT, Cementitious, DIC

ÖZET

KARBON NANOTÜPLERİN ÇİMENTO BAZLI ENJEKSİYONLARDA KULLANIMININ ARAŞTIRILMASI

ERİTEN, Kayahan
Yüksek Lisans Tezi, İnşaat Mühendisliği
Danışman: Prof. Dr. Hamza GÜLLÜ
Ocak 2025
85 sayfa

Enjeksiyon, zemin ve kaya özelliklerini iyileştirerek yapısal stabiliteyi artıran geoteknik mühendisliğinde önemli bir tekniktir. Bu çalışma, karbon nanotüp (CNT) katkılı çimento enjeksiyonlarının reolojik davranışını, taze özelliklerini, kürlleme süresini ve mekanik performansını incelemektedir. Cross ve Herschel-Bulkley gibi reolojik modeller değerlendirilmiş, Cross modelinin düşük su/bağlayıcı (w/b) oranlarında ve yüksek CNT ilavelerinde, Herschel-Bulkley modelinin ise yüksek w/b oranlarında ve düşük CNT içeriklerinde daha uygun olduğu belirlenmiştir. CNT ilavesi, groutların kesme incelmesi davranışını tetiklemiş, işlenebilirliği azaltmış ve akma gerilmesini artırmıştır. Ultrasonik darbe hızı (UPV) ve serbest basınç dayanımı (UCS) testleri, CNT ilavesine bağlı eksenel dayanım düşüşlerine rağmen, geliştirilmiş enjeksiyonların zemin uygulamaları için yeterli dayanımı sağladığını doğrulamıştır. Elektriksel direnç, kürlleme süresiyle birlikte artmıştır. Dijital Görüntü Korelasyonu (DIC), çatlakların tespiti ve gelişiminin etkili bir şekilde izlenmesini sağlamıştır. CNT eklemesi, stabiliteyi ve sünekliği artırmış, çatlamadan önceki fazı uzatmış ve ilk yüzey çatlağının görüldüğü birim kısalmayı artırmıştır. Ayrıca, artan süneklikten dolayı göçeme modları eksenel ayrılmadan daha karmaşık modlara kaymıştır. Bu bulgular, CNT'lerin çimento enjeksiyonlarını optimize etme potansiyelini vurgulamaktadır.

Anahtar Kelimeler: Nanotüp, Enjeksiyon, Reoloji, Zemin İyileştirme, CNT, Çimento bazlı, DIC



“Dedicated to my family”

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Prof. Dr. Hamza GÜLLÜ for his guidance and support throughout the study. I am thankful for his encouragement and motivation.

I would like to express my love and gratitude to my family for their support, always best wishes.



TABLE OF CONTENTS

	Page
ABSTRACT	i
ÖZET.....	ii
DEDICATION	iii
ACKNOWLEDGEMENTS.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	viii
LIST OF FIGURES	ix
LIST OF SYMBOLS	xi
LIST OF ABBREVIATIONS.....	xii
CHAPTER 1 INTRODUCTION.....	1
1.1 General.....	1
1.2 Purpose of the Study.....	3
1.3 Organization of the Study.....	4
CHAPTER 2 LITERATURE REVIEW	6
2.1 Grouting.....	6
2.1.1 Early Days of Grouting.....	6
2.1.2 Grouting, Grouting Types, and Their Applicability.....	6
2.1.3 Grouting Materials.....	9
2.1.4 Grouting Application Process	10
2.1.5 Rheological Behavior of Cement-based Suspension Grouts	11
2.2 Carbon Nanotubes	13
2.2.1 Discovery of Carbon Nanotubes and Pioneer Studies.....	13
2.2.2 Single-walled Carbon Nanotubes, Their Structure and Chirality	14
2.2.3 Beam-like Behavior of Carbon Nanotubes	17
2.2.4 Continuum Models	18

2.2.5 Mechanical, Chemical, Electronic and Thermal Properties of Carbon Nanotubes.....	19
2.3 Cementitious Grouts Enhanced with CNTs.....	20
2.3.1 Studies on Mechanical Properties	20
2.3.2 Studies on Electrical and Thermal Properties	21
2.3.3 Studies on Hydraulic Properties and Performance in Dynamic Water Conditions	22
2.3.4 Studies on Functionalized Carbon Nanotubes and Coating.....	24
CHAPTER 3 EXPERIMENTAL STUDY	27
3.1 Materials	27
3.2 Sample Preparation and Testing Program	28
3.3 Rheological Testing.....	31
3.4 Mini-slump Testing	35
3.5 UPV Testing.....	36
3.6 Electrical Resistivity Testing	37
3.7 UCS Testing.....	38
CHAPTER 4 RESULTS AND DISCUSSION	40
4.1 Rheological Results	40
4.1.1 Rheological Model Comparison.....	40
4.1.2 Rheological Curves and Behavior	48
4.2 Mini-slump Results and Yield Stress	54
4.3 Strength Performances.....	56
4.4 Development of Strength with Curing Age and Early Strength	59
4.4.1 UPV Results	59
4.4.2 Electrical Resistivity Results.....	62
4.5 Results Obtained Using Video Recording During UCS Testing	64
4.5.1 Crack Initiation and Propagation.....	64
4.5.2 DIC Analysis	65
4.5.3 Failure Planes	70
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS	72
REFERENCES	75

CURRICULUM VITAE	85
-------------------------------	-----------



LIST OF TABLES

	Page
Table 2.1 Characteristics of grout materials.....	10
Table 3.1 Chemical and physical properties of ordinary Portland cement(OPC)	28
Table 3.2 Structural properties of SWCNTs.....	28
Table 3.3 Mixture proportions and mixing process	31
Table 3.4 Sonic velocity classes for hard and soft rocks.....	36
Table 4.1 Statistical metrics (SM) of rheological model performances.....	43
Table 4.2 AIC of rheological model performances.....	44
Table 4.3 Summary of rheological models comparison.....	47
Table 4.4 Herschel Bulkley model parameters and flow type.....	51
Table 4.5 Cross model parameters	52
Table 4.6 Yield stresses based on mini-slump.....	55
Table 4.7 UPV results and UCS counterparts	60
Table 4.8 Electrical resistivity results during the curing period.....	62

LIST OF FIGURES

	Page
Figure 2.1 Types of grouting. From Han (2015)	8
Figure 2.2 Range of applicability of soil grouting techniques	9
Figure 2.3 Schematic diagram of typical grouting setup	11
Figure 2.4 Thixotropy and shear rate in cracks	12
Figure 2.5 Thixotropic comparison of grouts based on w/c.....	13
Figure 2.6 Schematic illustration of carbon nanotubes with different chirality	15
Figure 2.7 Schematics of the length scales in the atomic lattice structure.....	16
Figure 2.8 Types of deformation of the beam-like lattices of carbon nanotubes	18
Figure 2.9 Schematics of microscopic mechanism and SEM picture.....	24
Figure 2.10 Hydrophilization and interaction mechanism	25
Figure 3.1 Experimental study workflow.....	27
Figure 3.2 High-resolution TEM images of produced Tuball at different scales.....	29
Figure 3.3 The stirrer and container proportions.....	30
Figure 3.4 The labeling system of grout mixtures	31
Figure 3.5 Rheometer, proRheo R180	32
Figure 3.6 Rheological test procedures.....	33
Figure 3.7 Mini-slump test apparatus and measuring	35
Figure 3.8 UPV testing equipment and samples.....	37
Figure 3.9 Electrical resistivity test setup	38
Figure 3.10 UCS test setup.....	39
Figure 4.1 Flow curves of shear stress versus shear rate	41
Figure 4.2 Shear stress – viscosity versus shear rate for G33	46
Figure 4.3 Rheological curves and measurements.....	48
Figure 4.4 Flow behaviors.....	50
Figure 4.5 Yield stress dependency of factors.....	53
Figure 4.6 Minislump spread patterns and diameters of grout mixtures	54
Figure 4.7 UCS test curves a) seating/bedding correction and calculations	57

Figure 4.8 UCS test results versus CNT addition ratio.....	58
Figure 4.9 28 days results of UPV and UCS.....	61
Figure 4.10 UPV-UCS correlation.....	61
Figure 4.11 The average electrical resistivity results during the curing period	63
Figure 4.12 UPV-Electrical resistivity correlation.	63
Figure 4.13 Axial strain and crack propagation of G23.....	64
Figure 4.14 Strain at first crack comparison	65
Figure 4.15 DIC analysis of G23 before the first crack.....	67
Figure 4.16 DIC analysis of G23 at first crack.....	68
Figure 4.17 DIC analysis of G23 at peak axial strength	69
Figure 4.18 DIC analysis of G23 at failure	70
Figure 4.19 Failure planes of grout samples	71

LIST OF SYMBOLS

τ	Shear stress
τ_0	Yield stress
γ	Shear rate
M	Torque
R_e	Bob radius
R_i	Cup radius
ω	Angular velocity
μ	Viscosity
c	Curvature term
λ	Time constant for zero shear rate viscosity models
n	Flow behaviour index
a	Widthth of transition region
K	Consistency index
ρ	Electrical resistivity
w/b	Water binder ratio
R^2	Coefficient of determination

LIST OF ABBREVIATIONS

ACI	Akaike Information Criterion
CNTs	Carbon Nanotubes
DIC	Digital Image Correlation
ER	Electrical Resistivity
MWCNTs	Multi-Walled Carbon Nanotubes
OPC	Ordinary Portland cement
RMSE	Root Mean Square Error
SEM	Scanning Electron Microscope
SWCNTs	Single-Walled Carbon Nanotubes
UCS	Unconfined Compressive Strength
UPV	Ultrasonic Pulse Velocity

CHAPTER 1

INTRODUCTION

1.1 General

Grouting, a physical and chemical ground modification technique, is pivotal in enhancing the mechanical behavior of soils and ensuring the structural integrity of technical projects with its applicability to many geotechnical and structural cases. The grouting process involves injecting fluidized materials under pressure into voids within the ground or between the ground and adjacent structures to create stronger, denser, and less permeable soil or rock formations (Hausmann, 1990). The selection of suitable grout material is vital because of its effect on grout's mobility, penetrability, cohesion, bleed potential, setting time, and solubility (Han, 2015). Even though chemical grouts offer a broader range of properties and can be suitable for specific applications where cementitious grouts may not perform as effectively, cementitious grouts, primarily composed of Portland cement, are widely preferred due to their abundant raw material availability, high strength, being non-toxic, offering excellent consolidation performance, and ease of preparation (Coduto et al., n.d.; da Rocha Gomes et al., 2023). Improving cementitious grouts with admixtures and fibers is sensible to improve the above-mentioned traits and decrease the disadvantages of cement-based materials (e.g., low tensional strength compared to compressive strength, cracking due to chemical shrinkage during hardening).

Nanomaterials get attention in the geotechnical engineering field because soil scientists and engineers can be considered the original nanotechnologists, as they work with clay particles—ultra-fine materials that require advanced scientific techniques such as X-ray analysis or scanning electron microscopy for detailed investigation (Thomas et al., 2022). Carbon nanofilaments (nanotubes and nanofibers), with their exceptional mechanical and chemical properties, offer significant potential to address these challenges. The axial Young's modulus of single-walled carbon nanotubes (SWCNTs) reaches the terapascal (TPa) scale, while their tensile strength often exceeds gigapascal (GPa) levels (Khang et al., 2008;

Salvetat et al., 1999; Treacy et al., 2000; M. F. Yu et al., 2000). In addition to their remarkable mechanical properties, SWCNTs possess unique electronic and chemical characteristics (Gogotsi, 2006), making them among the most promising nanomaterials for enhancing materials and composites, e.g., cement-based materials.

Accurately predicting workability, injectability, and pumpability in such enhanced grouts requires suitable rheological models. These models, such as Bingham, Modified Bingham, Herschel-Bulkley, Cross, and Carreau-Yasuda, describe the flow behavior of grout under different shear conditions (i.e., shear rates), offering insights into its performance during mixing, transportation, and injection. This study evaluates the performance of these models for carbon nanotube-enhanced cementitious grouts using 20 mix designs with varying water-to-binder ratios and CNT contents. Rheological measurements were analyzed using statistical metrics and the Akaike Information Criterion (AIC) to balance model accuracy and complexity. The findings aim to guide the selection of optimal models for different water-binder and CNT addition ratios and to assess grout's applicability for different grout applications in geotechnical engineering. In addition to rheological analysis, mini-slump tests were conducted to quickly evaluate the grouts' workability (e.g., initial flow and spreadability), which is critical for ensuring proper placement and injection.

Ultrasonic pulse velocity (UPV) measurements were performed during curing to monitor the hardness progress of mixtures in the hydration process of cement-CNTs matrix and hardness comparison of CNTs addition ratio effectiveness for varying water-binder ratios. The results are comparable with peak axial strength results. Simultaneously, electrical resistivity measurements are carried out, which is generally used for quality control and durability assessment of cement-based materials, to track the electrical resistivity change of grouts with varying CNTs addition ratios and the change during the curing process for each grout mix.

Unconfined compressive strength (UCS) tests were carried out with strain records to assess the mechanical performance of the hardened grout (i.e., peak axial strength, strain at failure, and elastic modulus). Moreover, with camera records taken during the UCS test, the grout specimens' crack propagation was analyzed using digital image correlation (DIC). This simultaneous measuring system of UCS testing (strength, strain, and video recordings to be used for DIC that is used for tracking

crack initiation and growth), contributes to understanding the failure mechanisms of the hardened grout. These wide ranges of tests allow one to evaluate the enhanced grout's performance and provide a robust foundation for optimizing its application in diverse geotechnical engineering scenarios.

1.2 Purpose of the Study

This study aims to evaluate and optimize the performance of carbon nanotube-enhanced cementitious grouts for geotechnical engineering applications by analyzing their rheological and mechanical characteristics. The specific objectives of the study are as follows:

- To analyze the flow behavior of carbon nanotube-enhanced grouts under varying shear conditions using rheological models, including Bingham, Modified Bingham, Herschel-Bulkley, Cross, and Carreau-Yasuda, and to determine the most suitable models for varying water-binder and CNT addition ratios through statistical metrics and the Akaike Information Criterion (AIC) to be able to predict workability, injectability, and pumpability.
- To assess the workability of the grout mixtures through rheological model parameters and mini-slump spread diameters, which provide a quick and effective evaluation of initial flow and spreadability, essential for proper placement and injection in practical applications.
- Monitor the development of internal structure and stiffness during the curing process by conducting ultrasonic pulse velocity (UPV) and electrical resistivity measurements, providing insights into the uniformity and evolution of the grout matrix over time. Furthermore, electrical resistivity results give insight into CNT addition's effect on the electrical conductivity of grout.
- To evaluate the mechanical performance of the hardened grout specimens through unconfined compressive strength tests (UCS).
- To analyze crack initiation and propagation in grout specimens using digital image correlation (DIC), a non-contact method that tracks crack growth with high precision, contributing valuable data on the failure mechanisms of the material.

- To integrate findings from rheological and mechanical analyses, offering a comprehensive evaluation of carbon nanotube-enhanced grouts and providing recommendations for their optimal design and application in geotechnical engineering scenarios.

1.3 Organization of the Study

This thesis is organized into five chapters to present the work systematically. The chapters are outlined as follows:

Chapter One: This chapter introduces the study, discussing the importance of grouting in geotechnical engineering and the potential of carbon nanotube-enhanced cementitious grouts. Summarizes the tests done in the study and assess traits of grouts via these experiments. It also highlights the study's objectives and the significance of using advanced materials and techniques to improve grout performance.

Chapter Two: A comprehensive literature review covering groutings' history, types, materials, and rheological behavior, as well as cementitious grout properties and applications. Then, carbon nanotube structure, types, geometric traits, mechanical behavior, strength, chemical, and conductive properties are compiled and reviewed. Carbon nanotube cementitious matrix interactions and previous works on carbon nanotube-enhanced cementitious grouts reviewed.

Chapter Three: Details the materials, sample preparation of carbon nanotube-enhanced cementitious grout mixtures with varying water-to-binder ratios and CNT contents, and experimental methodology, which describes the procedures for rheological measurements, mini-slump tests, ultrasonic pulse velocity (UPV) measurements, unconfined compressive strength (UCS) tests, electrical resistivity measurements, and crack propagation analysis using digital image correlation (DIC).

Chapter Four: The experimental study results, analysis based on results, and comparison of results with literature presented in this chapter.

Chapter Five: Summarizes the study's significant findings and provides recommendations for designing and applying carbon nanotube-enhanced

cementitious grouts in geotechnical engineering practices. Suggestions for future research are also included to guide further exploration in this field.



CHAPTER 2

LITERATURE REVIEW

2.1 Grouting

2.1.1 Early Days of Grouting

Grouting has nearly 200 years of history, which starts with French civil engineer Charles Berigny, who is credited with inventing the injection for foundation repair (Littlejohn, 2003). In 1802, while managing the harbor of Dieppe, he faced issues with soil erosion under shallow foundations at highly permeable gravels below the scouring sluice of the harbor. To address this, he developed a grouting method to stabilize the structures technique, which he named "procédé injection." Berigny injected plastic clay into holes drilled through the sluice foundation using a "blow pump" he invented, which consisted of a wooden cylinder and piston. The technique was successful in restoring the sluice. In 1809, Berigny applied the method again to prevent erosion in a new sluice foundation, using a suspension of pozzolana. This marked the first application of grouting in foundation engineering. The method evolved, with clay and pozzola being replaced by Portland cement. This material was first introduced in England in 1838 by Marc Isambard Brunel for the construction of the Thames Tunnel and in France in 1839 by Collin to seal cracks in the structure of the Grosbois Dam (Littlejohn, 2003; Nonveiller, 2013).

2.1.2 Grouting, Grouting Types, and Their Applicability

The grouting technique involves injecting fluidized materials under pressure into voids, fissures, crevices, or cavities within soil or rock formations or between the ground and adjacent structures to create stronger, denser, and less permeable formations. The process typically begins with drilling boreholes into the target formation, followed by grout injection under pressure until the voids are filled and the conditions specified in the design are satisfied (Hausmann, 1990; Houlsby, 1990). The technique serves numerous purposes, such as controlling seepage and reducing permeability beneath hydrotechnical structures, preventing soil erosion and uplift, and improving the strength or reducing foundation materials' deformability

through consolidation grouting. Additionally, grouting is employed to connect structural elements, secure reinforcing cables and rock anchors, stabilize leaning structures, and fill gaps between rock and tunnel linings through contact grouting. It also plays a critical role in rehabilitating historical masonry, constructing underwater concrete using preplaced gravel, and various other specialized applications. This versatile technique ensures technical and structural projects' safety, stability, and durability across multiple fields.

Grouting is commonly classified into five types: (1) permeation grouting, (2) compaction grouting, (3) hydrofracture grouting, (4) compensation grouting, and (5) jet grouting, as illustrated in Figure 2.1. Permeation grouting involves filling soil voids with grout; void or cavity filling is a specific form of this method. Compaction grouting is used to compact loose soils by injecting a stiff, low-mobility grout to displace soil particles. Hydrofracture grouting requires injecting stiff grout under high pressure to fracture the soil and force grout into the cracks. Compensation grouting aims to restore ground lost during construction activities such as excavation or tunneling. Jet grouting uses grout, sometimes combined with water or air, to erode soil at various depths, then mixes the soil with grout to create hardened columns or walls (Han, 2015).

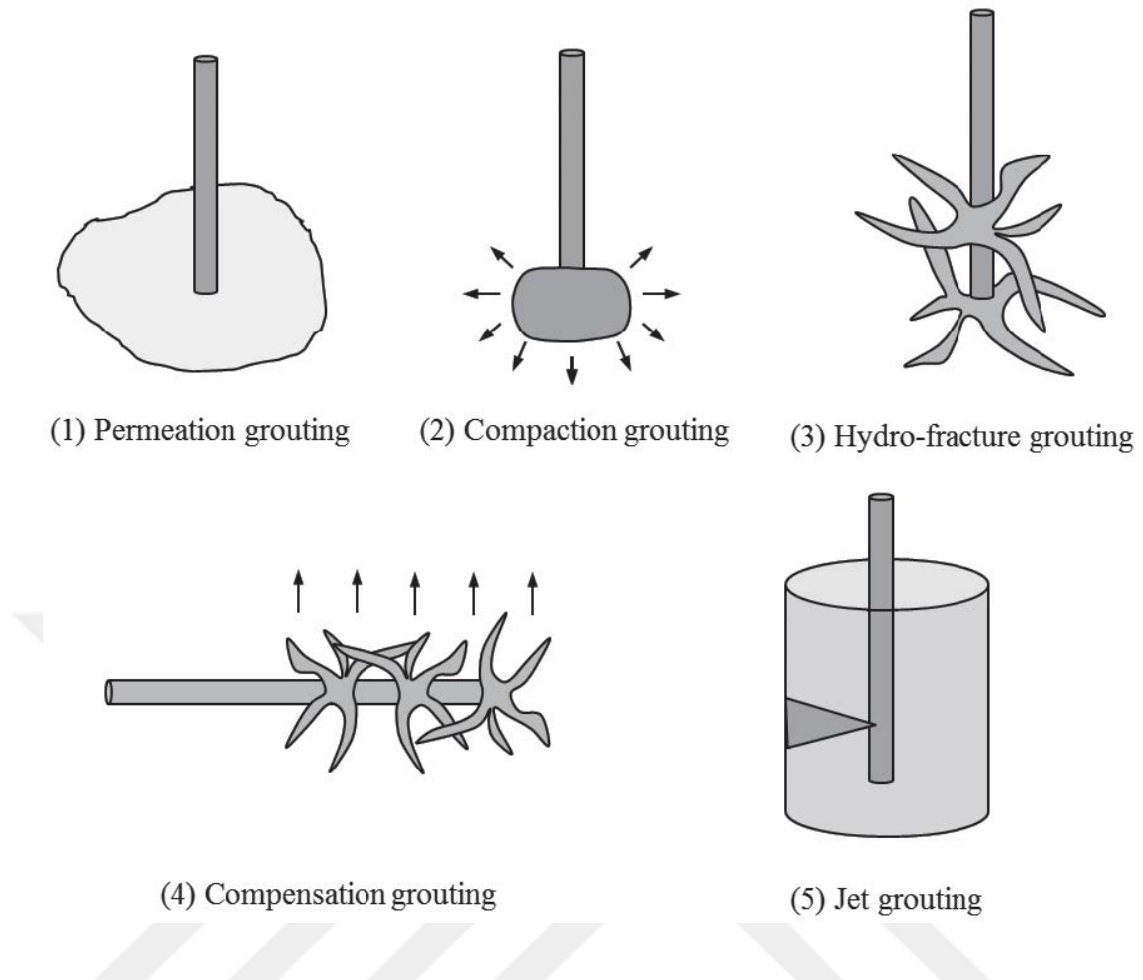


Figure 2.1 Types of grouting. From Han (2015)

The choice of the proper grouting technique largely depends on the type of soil being treated. While various soil grouting methods can be applied to most soil types, each technique is generally restricted to certain soils, with jet grouting being the exception due to its adaptability to all soil types, as shown in Figure 2.2. Permeation grouting is ideal for cohesionless soils, such as gravel and sand. It includes cement slurry and chemical grouting, with cement slurry being more effective for gravel and chemical grouting better suited for sand. Compaction grouting is primarily used for sand but can also be applied to silt and clay, provided that excess pore water pressure can be released. Hydrofracture grouting works well with sand, silt, and clay and is often employed for compensation grouting. Permeation, compaction, and hydrofracture grouting can also be applied to decomposed and fissured rock (J. Han, 2015; Schaefer et al., 2016).

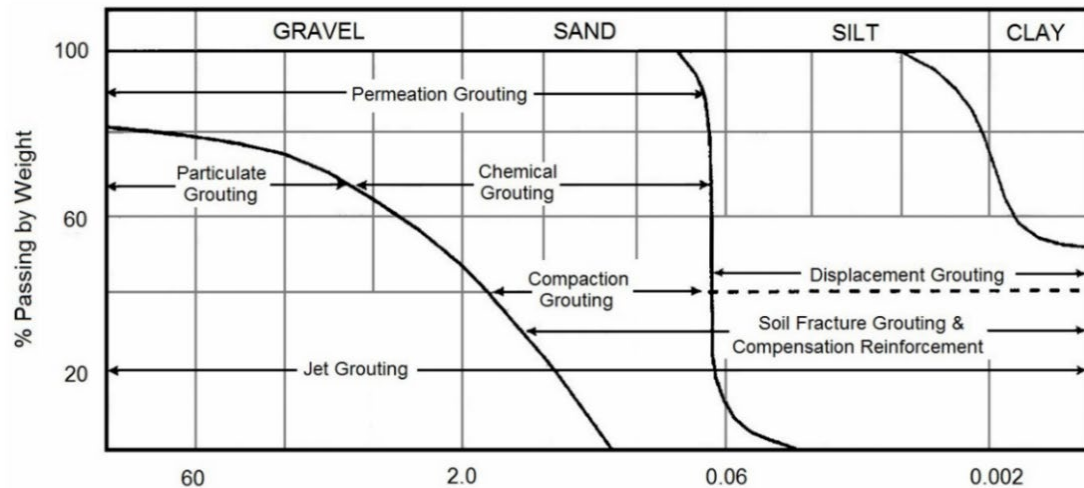


Figure 2.2 Range of applicability of soil grouting techniques. From Schaefer et al. (2016)

2.1.3 Grouting Materials

Grouting materials can be categorized into four types based on their rheological performance and cost, in ascending order: 1) Particulate grouts, including suspension and cementitious types, exhibit Binghamian behavior. 2) Colloidal solutions are evolutive Newtonian fluids whose viscosity increases over time. 3) Pure solutions are non-evolutive Newtonian fluids, where viscosity remains constant until the setting occurs within an adjustable timeframe. 4) Miscellaneous materials (Bruce et al., 1997; Schaefer et al., 2016).

Particulate grout, typically a mixture of water and particulate materials like cement, fly ash, clay, or sand, relies on its water-to-solid ratio to determine stability, fluidity, rheology, strength, and durability. Depending on the composition, these mixtures can be stable (i.e., minimal bleeding) or unstable, with stable, thixotropic grouts exhibiting increased cohesion and plastic viscosity over time, particularly under pressure (Schaefer et al., 2016). Portland cement is the most widely used grout material, with Type-I being the standard choice for most applications. Type-II offers moderate sulfate resistance and lower heat of hydration. At the same time, Type-III is suited for emergency repairs due to its rapid strength development and fine particle size for grouting fine cracks. Type-IV generates minimal heat during hydration and develops strength slowly, making it ideal for situations where heat is a concern. Type-V is used in environments with high sulfate levels, and air-entraining Portland

cement is preferred for exposure to severe freezing and thawing conditions (Patel, 2019b).

Colloidal and pure solutions are generally categorized as chemical solutions. Colloidal solutions consist of mixtures of sodium silicate and reagents that form gels as their viscosity changes over time. Pure solutions, typically resins, are organic substances dissolved in water or non-aqueous solvents, capable of forming gels with specific mechanical properties under normal temperature conditions in a confined environment. The exceptional rheological characteristics and low viscosities of certain resin grouts allow them to infiltrate fine soils such as silty sands ($k = 10.16 \times 10^{-5}$ cm/second). Miscellaneous materials, primarily made of organic compounds or resins, encompass a variety of less common grout materials used sparingly and mainly in specialized industries, such as hot bitumen applications (Schaefer et al., 2016). Table 2.1 presents common grout materials and their comparative characteristics, such as viscosity, water-to-binder ratio, toxicity, strength, and approximate cost.

Table 2.1 Characteristics of grout materials. From Han (2015)

Description	Viscosity (cP) (w/b)	Toxicity	Strength	Relative Cost
Particulate grout				
Type I cement	High (50 cPs) (2:1)	Low	High	Low
Type III cement	Medium (15 cPs) (2:1)	Low	High	Low
Ultra-fine cement	Low (8 cPs) (2:1)	Low	High	Medium
Colloidal solution				
Silicates	Low (>6 cPs)	Low	Medium	Low
Solution grout				
Lignosulfites	Medium (>8 cPs)	High	Low	Medium
Polyurethane	High (>400 cPs)	High	High	High
Acrylamides	Low (1.2 cPs)	High	Low	Medium
Acrylates	Low (1.5 cPs)	Low	Low	Medium

2.1.4 Grouting Application Process

The schematic in Figure 2.3 illustrates a typical grouting setup based on jet grouting, outlining key components and their roles in the process. Grout material, such as cement or bentonite, is mixed with water in a mixer to achieve uniform consistency

and then transferred to an agitator that prevents settling by continuously stirring the mixture. The grout is pumped through circulation lines to the injection point, which is introduced into drilled holes using a packer system that seals the hole and ensures proper injection. The setup may include single-, double-, or triple-tube jet grouting systems depending on site conditions and grouting requirements. High-pressure air and water can be added to improve grout penetration and column quality. The control fitting and pressure gauges regulate flow and pressure, ensuring efficient and precise grout placement (Patel, 2019a).

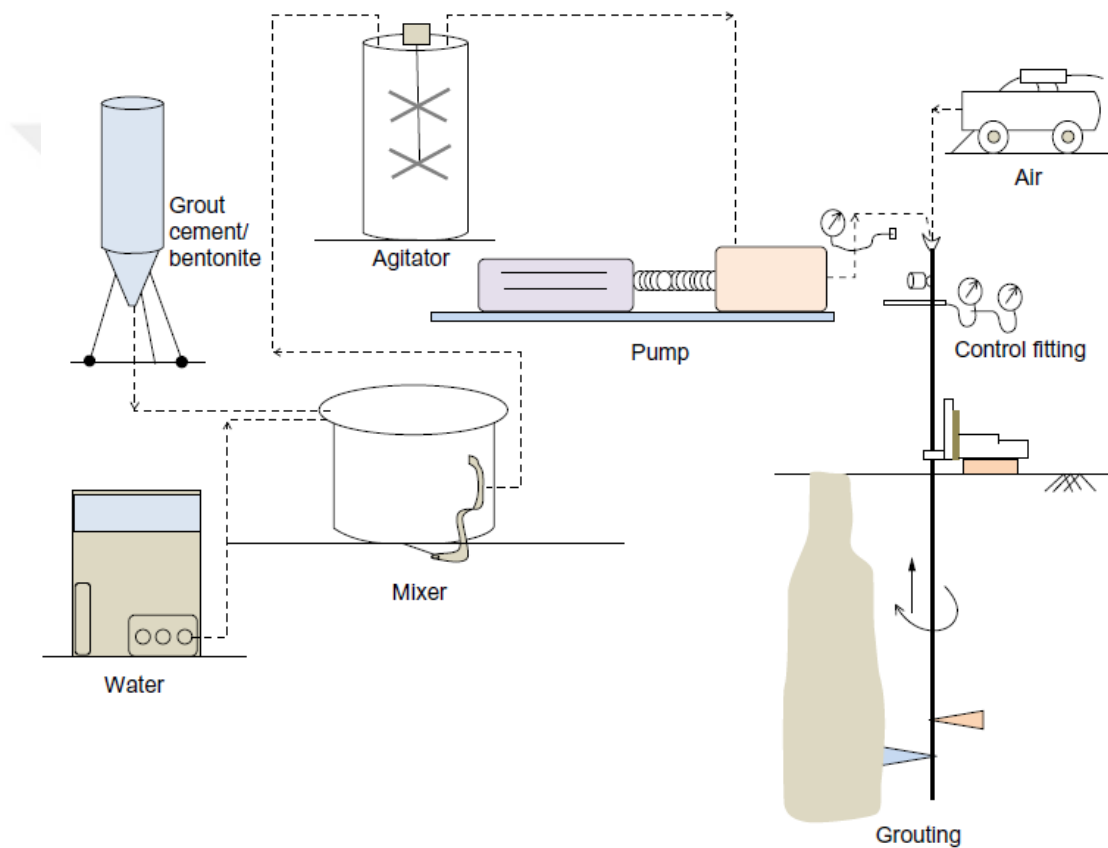


Figure 2.3 Schematic diagram of typical grouting setup. From Patel (2019a)

2.1.5 Rheological Behavior of Cement-based Suspension Grouts

Cement-based suspension grouts behave as Bingham fluids, requiring a minimum pressure, known as the yield point, to initiate flow by overcoming internal cohesive forces. This yield point defines the threshold stress needed to mobilize grout within fractures, distinguishing it from Newtonian fluids like water, which flow linearly with shear stress (Figure 2.4). Beyond this threshold, grout flow is governed by viscosity, dictating the pressure necessary to sustain or accelerate movement. Shear

rate, or shear strain, representing the velocity gradient across the cracks, directly influences flow behavior—higher shear rates typically reduce internal resistance, facilitating flow. Thixotropy introduces further complexity by causing grout to thicken and form a gel-like structure when static, resuming flow only after sufficient pressure rebuilds to surpass the yield point. This is an important trait when the grouting process stops for a reason at the field. This time-dependent property stabilizes grout within cracks, preventing washout by groundwater and enabling controlled injection in sensitive environments (Houlsby, 1990; Owen, 2017)

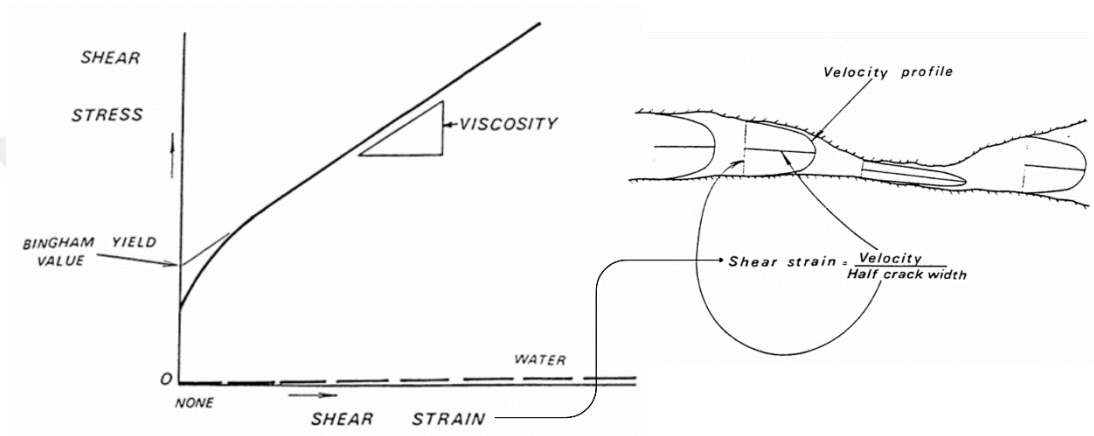


Figure 2.4 Thixotropy and shear rate in cracks. Modified from Houlsby (1990)

Thixotropy becomes more pronounced as the water-to-cement (w/c) ratio decreases (Figure 2.5), with thicker mixes (e.g., 1:1 or lower by volume) exhibiting more vigorous gel formation and greater resistance to flow interruptions, while thinner mixes (e.g., 3:1) show minimal thixotropic stiffening. However, thixotropic stiffening can impede flow in narrow fractures, requiring higher pressures to restart, whereas thinner grouts maintain continuous flow with less resistance. The interplay between yield point, viscosity, shear rate, and pressure gradients controls grout propagation, influencing fracture distribution and performance (Houlsby, 1990; Owen, 2017).

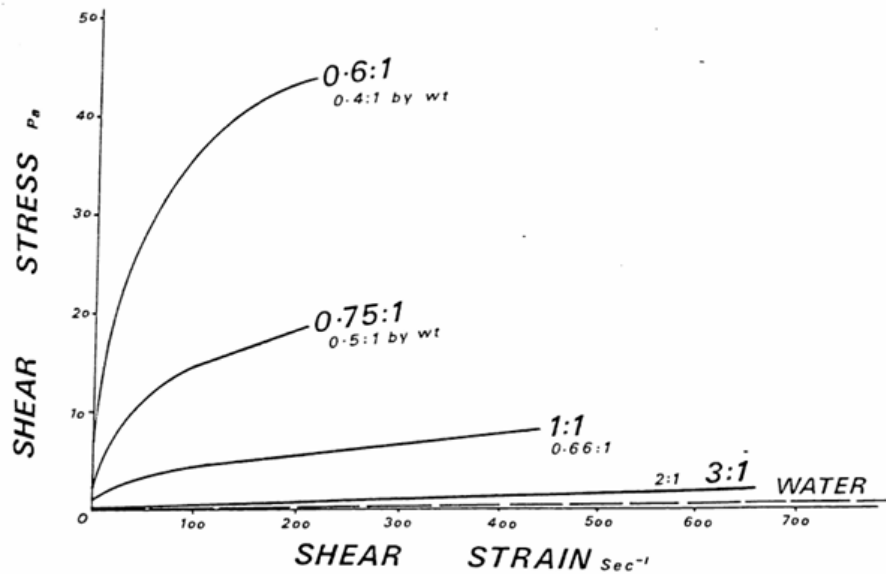


Figure 2.5 Thixotropic comparison of grouts based on w/c. From Houlsby (1990)

2.2 Carbon Nanotubes

2.2.1 Discovery of Carbon Nanotubes and Pioneer Studies

In 1991, Iijima announced his discovery of needle-shaped carbon nanotubes (CNTs) through an arc-discharge evaporation method at NEC Corporation (Iijima, 1991). Soon after, Iijima and Ichihashi (1993), along with Bethune et al. (1993), independently reported the growth of single-walled CNTs (SWCNTs), marking the beginning of a new era in nanoscience and nanotechnology (Liew et al., 2017). In 1993/94, R.S. Ruoff and J. Tersoff's team conducted the first theoretical modeling of carbon nanotubes and their crystal structures. By 1996, M.M.J. Treacy, T.W. Ebbesen, and J.M. Gibson carried out the first experiments on carbon nanotubes using atomic force microscopy (AFM). That same year, by using a shell-based model, B.I. Yakobson, C.J. Brabec, and J. Bernholc performed molecular dynamics simulations to analyze carbon nanotubes' axial buckling and twisting behavior. In 1997, C.M. Lieber and his team extended experimental testing to vibrating carbon nanotubes, conducting tests similar to AFM experiments at Harvard. By 1998, extensive testing, modeling, and analysis of single-wall carbon nanotubes had been undertaken by numerous researchers (e.g., Ajayan, Brenner, Dai, Halicioglu, Lordi, Ru, Ruoff, Sinnott, Schadler, Wagner, and White). In 2001, V.M. Harik introduced a classification system that categorized carbon nanotubes into four distinct classes: thin

and thick lattice shells, long high-aspect-ratio nanotubes, and beam-like carbon nanotube crystals with very small radii. (V. Harik, 2014).

2.2.2 Single-walled Carbon Nanotubes, Their Structure and Chirality

A single-walled carbon nanotube (SWCNT) can be conceptualized as mapping the two-dimensional hexagonal graphene lattice onto a cylinder's surface, creating a seamless tubular structure. To fulfill the necessary boundary conditions surrounding the cylinder, one of the Bravais lattice vectors of the graphene sheet must coincide with the cylinder's circumference. Each lattice vector in the two-dimensional graphene lattice indicates a distinct method for rolling the sheet into a tube based on the alignment. Since the diameter and chirality of nanotubes significantly influence their properties, a vector $c_h = na_1 + ma_2$ is introduced to describe geometric structure and chirality. Here, a_1 and a_2 are the graphene lattice vectors and n and m are integers (Figure 2.6.a).

A SWCNT formed with a vector c_h has its axial direction perpendicular to this lattice vector. The classification of SWNTs depends on the vector's indices (n, m) . Nanotubes created by rolling a graphene sheet along a direction corresponding to the lattice indices $(n, 0)$ or (n, m) known as zigzag SWCNTs or armchair SWCNTs where $n = m$, respectively. In contrast, nanotubes rolled in directions transitioning from $(n, 0)$ to (n, m) with a 30-degree rotation are classified as chiral (n, m) SWCNTs, where $n \neq m \neq 0$. Figure 2.6.b-d provides schematic illustrations of these types of SWCNTs, respectively with examples of SWCNTs that depict armchair, zigzag, and chiral nanotubes are $(5,5)$, $(9,0)$, and $(8,2)$. The orientation of carbon rings within the atomic structure of single-walled carbon nanotubes significantly influences their physical properties. Armchair SWCNTs' metallic properties, like electrical conductivity, are connected to their atomic lattice. On the other hand, SWCNTs' zigzag atomic arrangement is linked to brittle material characteristics and semiconducting behavior. Additionally, the elastic properties of SWCNTs, including stiffness and strength, are affected by the specific orientation of their atomic lattice (V. Harik, 2018c). Carbon nanotubes (CNTs) are further categorized based on the number of graphene sheets. The CNTs composed of a single graphene sheet are called SWCNTs, while those with multiple graphene sheets are classified as multi-walled carbon nanotubes (MWCNTs) (Qiu & Yang, 2017).

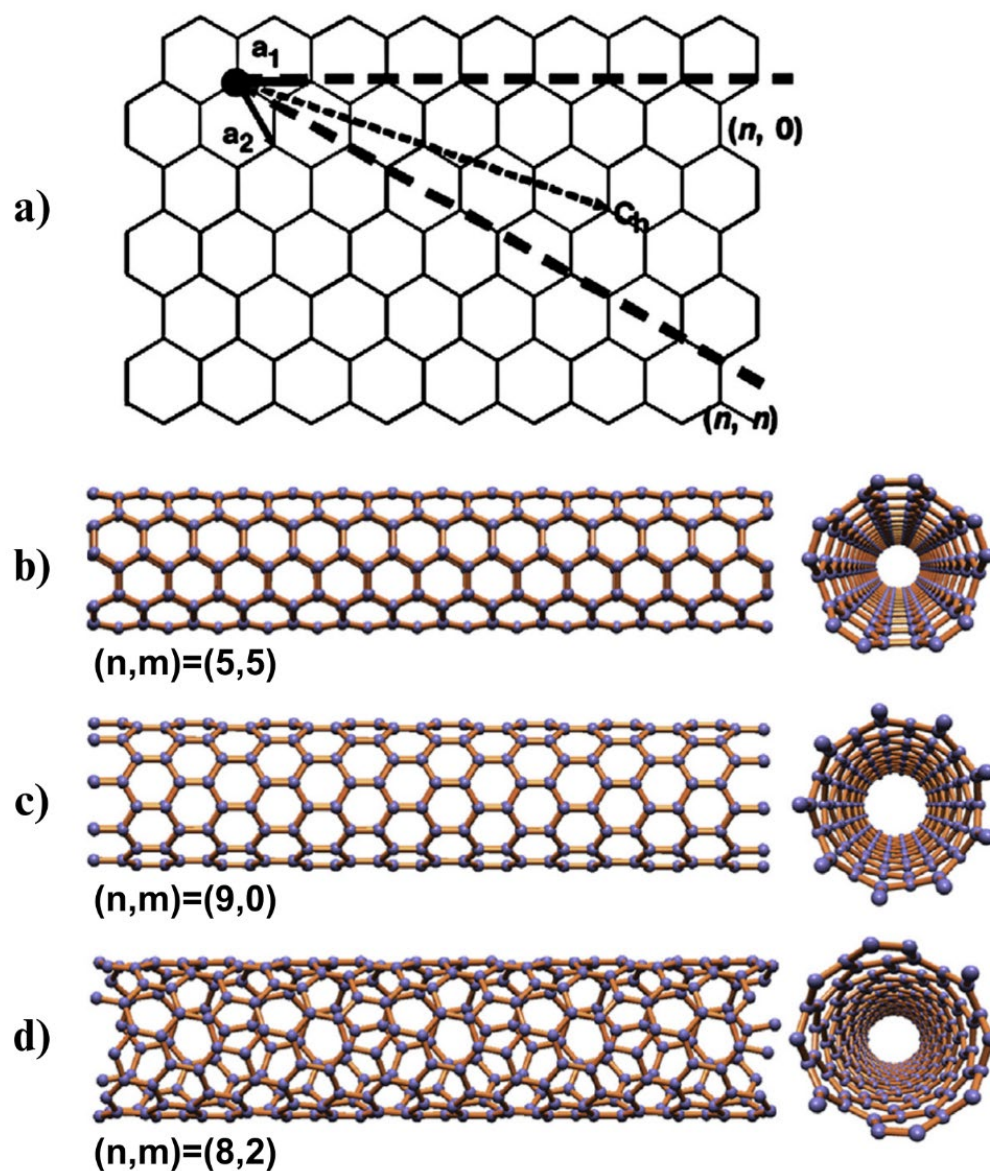


Figure 2.6 Schematic illustration of carbon nanotubes with different chirality: a) schematic of a two-dimensional graphene sheet illustrating lattice vectors and the roll-up vector, b) armchair (5,5) single-walled carbon nanotube (SWNT), c) zigzag (9,0) SWNT, and d) chiral (8,2) SWNT. Modified from Qiu & Yang (2017)

The atomic structure of carbon nanotubes (e.g., diameter, length, thickness) influences their deformation behavior and structural properties. Key parameters include the covalent bond length (l_{C-C}), with typical values of 1.41-1.42 Å, the size of carbon rings (a), with typical value of 2.46 Å, the radius (R_{NT}), ~ 0.2 – 2 nm for SWCNTs and ~ 35 – 80 nm for MWCNTs or diameter of the lattice (d_{NT}), ~ 1 nm, and the length (L_{NT}), which ranges from nanometers to several centimeters (Figure 2.7). The approximate lattice thickness of SWCNTs (h_{NT}) is also a key geometric parameter, which varies depending on the number of layers of MWCNT. These structural parameters can change under different conditions, such as tensile or compressive loading, affecting bond lengths, ring sizes, and lattice thickness.

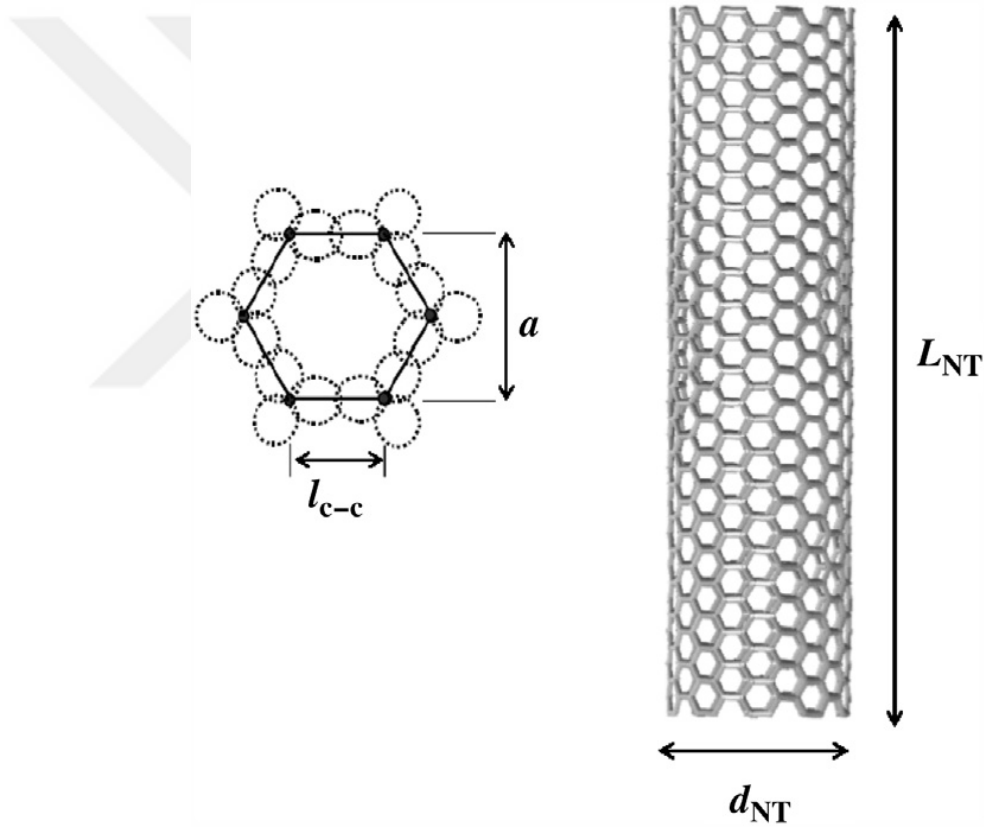


Figure 2.7 Schematics of the length scales in the atomic lattice structure of a carbon nanotube showing carbon ring with the length of the C-C bond (l_{C-C}), the size of carbon ring (a), carbon nanotube diameter (d_{NT}), and the length (L_{NT}), which represent four length scales. From Harik (2018a)

2.2.3 Beam-like Behavior of Carbon Nanotubes

Carbon nanotubes can exhibit nanoscale beam-like behavior if their aspect ratio (L_{NT}/d_{NT}) is high or when they acquire polygonal cross-sections resembling hollow nanobeams or thin rods.—the thickness of their shells, whether single or multiple, significantly influences their mechanical response. The longitudinal and circumferential dimensions of these nanoscale lattice beams also impact the mechanical behavior of lattice cells, with larger dimensions yielding smoother two-dimensional responses. For carbon nanotubes to demonstrate beam-like behavior, their aspect ratio must satisfy $L_{NT}/d_{NT} < 1/10$ or $L_{NT}/d_{NT} \ll 1$. The diameter (d_{NT}) typically ranges from 0.2 to 2–3 nm for single-walled carbon nanotubes (SWCNTs) and 35 to 85 nm for multi-walled carbon nanotubes (MWCNTs), while their length (L_{NT}) must exceed 2 nm for SWCNTs or 20–30 nm for MWCNTs. This criterion is commonly met, meaning most SWCNTs behave as nanoscale hollow beams or fibers. Consequently, analyzing their buckling, bending, and deflection requires applying the principles of nanoscale beam theory and mechanics (Harik, 2018b).

Carbon nanotubes (CNTs) exhibit unique deformation responses under various loading conditions, including axial, radial, and bending forces (see Figure 2.8). The distribution of these forces involves both local and global lattice deformations, with nanoscale behavior influenced by the chirality of SWCNTs and the structure of MWCNTs. Poisson's ratio ($\nu = -\epsilon_r/\epsilon_x$) can be defined using axial strain ($\epsilon_x = \Delta L_{NT}/L_{NT}$), radial strain ($\epsilon_r = \delta r/R_{NT}$), or circumferential strain ($2\pi\delta r/a_c N_c$) of the lattices depending on how the Poisson ratio is defined. N_c represents the number of carbon rings along the circumference of an SWCNT lattice, while a_c denotes the circumferential size of a carbon ring. The lateral deformation of a carbon ring can be calculated as $\Delta a_c = 2\pi\delta r/a_c N_c^2$. Deformation mechanisms, particularly in SWCNTs, highlight phenomena like structural circumferential carbon ring buckling (SCCRB) and dynamic circumferential carbon ring buckling. SCCRb occurs when the normalized circumference satisfies $2\pi R_{NT}/a = \sqrt{n^2 + m^2 + nm} \approx 2\pi$, or the normalized radius $R_{NT}/a \leq 1$ (the ring size, $a = 2.46 \text{ \AA}$). These deformations, studied through changes in radius $\delta r/R_{NT}$ and carbon ring corrugation, provide insights into nanoscale mechanics and the unique structural behaviors of CNTs under axial tension and radial deformation.

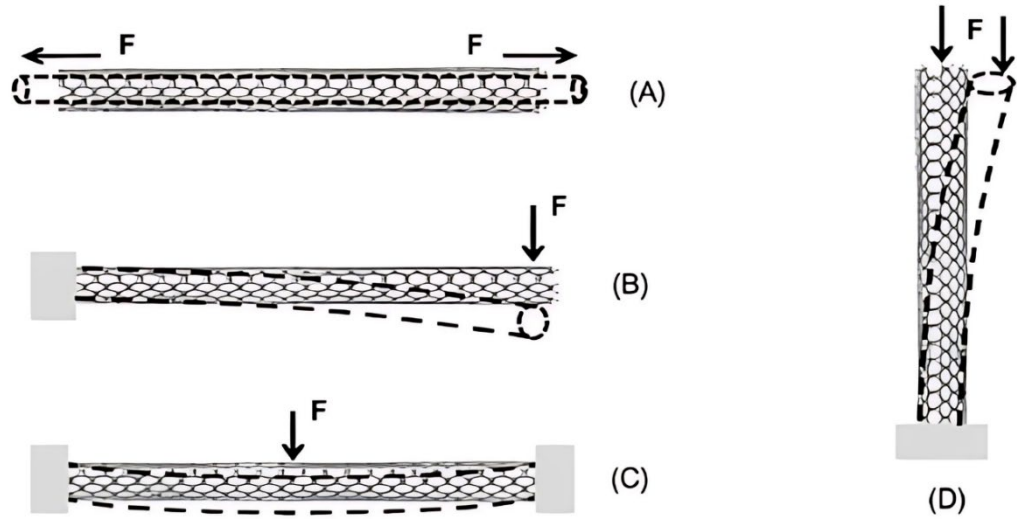


Figure 2.8 Types of deformation of the beam-like lattices of carbon nanotubes: a) axial tension, b) bending of a cantilever beam, c) the middle point bending of a long beam, d) and the axial buckling of the high aspect ratio lattice beam. From Harik, (2018b)

2.2.4 Continuum Models

Continuum models have been extensively employed to describe the mechanical behavior of carbon nanotubes, particularly high aspect ratio SWCNTs, where experimental studies (Treacy et al., 1996; Wong et al., 1997) showed that hollow cylinder models provide reasonable estimates for Young's modulus during vibration tests. These studies demonstrated carbon nanotubes' beam-like behavior and their material properties' dependency on cylindrical system size (Govindjee & Sackman, 1999). The applicability of continuum concepts to atomic lattice structures has limitations and must account for geometric parameters and length-scale effects. The Euler beam theory, governed by the equation $EI (\partial^2 w / \partial x^2) + Pw = 0$, effectively describes small elastic strains in SWCNTs with radii smaller than 2 nm but requires exceptionally high aspect ratios for larger radii (Timošenko & Gere, 1961). Critical buckling strain predictions, such as $\varepsilon_{cr} \approx (\pi^2/2)(d_{NT}/L_{NT})^2$ depend on nanoscale dimensions and aspect ratios. Adjustments to buckling strain formulas are necessary for thin SWCNT shells to incorporate thickness-to-radius ratios. While continuum models serve as useful approximations, their assumptions must be carefully validated against atomic lattice structures, considering SWCNTs' unique hyperelastic properties and material maps (Harik, 2001, 2002).

2.2.5 Mechanical, Chemical, Electronic and Thermal Properties of Carbon Nanotubes

Theoretical and experimental studies have extensively explored the mechanical properties of carbon nanotubes (CNTs), emphasizing their exceptional strength and stiffness under various conditions. Theoretical investigations have focused on strain energy, elasticity, and responses to deformation, with strain energy following a c/d_t^2 dependence (where d_t is the diameter), consistent across empirical, tight-binding, and ab initio calculations. Young's modulus for SWCNTs is largely independent of diameter or chirality for $d_t > 0.6$ nm, averaging around 1 TPa (Lifshitz et al., 1986; Hernández et al., 1998, 1999)

Experimental efforts have validated these findings, with Treacy et al. (1996) measuring Young's modulus of multiwall nanotubes (MWCNTs) at 1.8 TPa via thermal oscillation and Krishnan et al. (1998) finding a mean of 1.25 TPa for SWCNTs. Atomic force microscopy (AFM) bending studies reported values ranging from 0.8 to 1.28 TPa (Salvetat et al., 1999; Wong et al., 1997), with defects and synthesis methods influencing results. Tensile tests revealed strengths of 11–63 GPa and moduli up to 1.47 TPa (Yu et al., 2000a, 2000b), while hydrostatic pressure experiments showed structural changes impacting mechanical properties (Venkateswaran et al., 1999).

Exceptional chemical, electronic, and thermal properties of carbon nanotubes making them promising materials for diverse applications. Chemically, CNTs are highly stable due to their sp^2 -hybridized carbon bonds, yet functionalization through covalent or non-covalent methods can tailor their properties for specific uses such as drug delivery and sensors (Balasubramanian & Burghard, 2005; Dresselhaus et al., 2001). Electronically, their behavior depends on chirality and diameter, allowing them to be either metallic or semiconducting, as predicted by tight-binding calculations (Saito et al., 1992) and later validated experimentally (Odom et al., 1998). This unique tunability has enabled their integration into nanoelectronic devices like transistors and sensors. Thermally, CNTs have outstanding conductivity, with room-temperature values exceeding 3000 W/m·K in individual nanotubes, attributed to efficient phonon transport along their one-dimensional structure (Berber et al., 2000). However, defects and inter-tube interactions in bundles can reduce conductivity (Pop et al., 2006). These properties collectively highlight CNTs'

potential in fields ranging from nanoelectronics to composite materials and thermal management systems.

2.3 Cementitious Grouts Enhanced with CNTs

2.3.1 Studies on Mechanical Properties

CNTs have been added to a hydraulic injection grout for the first time by Restuccia et al. (2018). The samples were prepared by adding MWCNTs in the range of 0.025 to 0.8% by the grout weight. The test results indicate that these additions enhanced flexural and compressive strengths by 73% and 35%, respectively, compared to plain mortar, and increased fracture energy by 80%, with a CNT level of up to 0.12 wt% of the binder. The results can be elucidated by a decrease in porosity, demonstrated by mercury intrusion porosimetry, alongside a crack bridging mechanism and the likely emergence of nucleation sites for hydration products, as revealed via scanning electron microscopy.

Li et al. (2023) studied the dynamic mechanical behavior of cement-based grouting materials containing carbon nanotubes (CNTs) and ultrafine fly ash (UFFA), which is vital due to frequently occurring dynamic impact loading in underground engineering. The enhanced grouts exhibit superior peak stress (up to 31.86% average change, with the highest value of 59.33 MPa), dynamic elastic modulus (up to 23.63% average change, with the highest value of 30.53 GPa), and dissipative energy (up to 24.47% average change, with the highest value of $4.66\text{e}5 \text{ J.m}^{-3}$) to plain cementitious grout. The highest values for all mechanical properties were obtained with samples prepared with ultrasonication as the dispersion method of CNTs into the solution. Moreover, the nephogram and fractal dimensions further suggest an ultrasonic treatment performance over magnetic stirring. Also, the performance of enhanced grouts gets even better when samples are subjected to strong external dynamic impact loading.

Qu et al. (2024) investigated changes in the pore structure of carbon nanotube-added grouts under impact conditions as a follow-up to Li et al. (2023), which showed a performance increase in the rock matrix. It is found that the peak dynamic stress of the carbon nanotube (CNT) group increased by 4.76–21.54%, while porosity reduced by 57.26% compared to plain cement-based grouts. Moreover, the CNT group exhibits stronger impact resistance than the Non-CNT group. After dynamic impact,

the Non-CNTs group's cement proportion increased by 12.09%, while the CNTs group's proportion increased by 6.75%. The CNTs groups' cement proportion increased by 79.11%, while the Non-CNTs group's aggregates decreased by 18.04%

Han et al. (2023) explored the impact of fly ash and CNTs on the properties of cement-based grouting materials. They found that the use of fly ash to replace part of the cement in the grouting sample to reduce the cost of material would cause deterioration of the pore structure of hardened slurry, which will reduce the mechanical and impermeability of the hardened slurry for a high w/b ratio even though the replacement will increase the workability of fresh grout. Adding 0.08 wt% of CNTs can increase mechanical and impermeability to the previous level (i.e., plain cement grout) with improved workability gained by fly ash addition. Finally, 20 wt% fly ash and 0.08 wt% CNTs were suitable with unchanged mechanical properties, a 5% increase in workability, and a 6% improvement in impermeability.

Jiao et al. (2024) reviewed the application of CNTs in cementitious grouts by mainly focusing on dispersion methods, microstructure, hydration, and early shrinkage performance. A few highlights from the study are that CNTs addition up to 0.6% (wt) increases strength properties due to the bridging and filling effect, with the best results being gained between 0.4% and 0.6%. Moreover, pore diameters over 200 nm were refined to 50-100 nm, reducing porosity. Moreover, CNT's addition delays crack development and inhibits early shrinkage.

2.3.2 Studies on Electrical and Thermal Properties

Lee et al. (2019) used CNT addition of 1% and 2% by the weight of grout to detect voids in concrete with SWCNTs and MWCNTs; results showed that SWCNTs grouts were more suitable to identify voids in concrete through electrical resistance analysis. They also performed tests to assess the thermal properties of CNT-added cement grouts; it was found that the electrical and thermal properties of CNT cement grout depend on CNT type, concentration, and filling rate. 0.1 wt% and 0.2 wt% SWCNT specimens showed 66% (2.16 k Ω to 3.59 k Ω) and 108% (0.74 k Ω to 1.54 k Ω) increase in resistance, respectively. Moreover, SWCNT specimens showed more variation, especially with 0.1 wt% filled samples reaching 78.9°C and partially filled ones at 58.3°C. Unlikely, MWCNT grouts offer uniform heating and stable resistance.

Lee et al. (2020) investigated MWCNTs enhanced cementitious grout void detection and filling rates electrical, thermal, and magnetic properties. The results of the thermal image tests indicate that 1.0 wt % MWCNT cement grout is optimal for void detection by showing maximum temperature change but did not exhibit notable electric resistance change. Moreover, FE-SEM results showed dispersion and thread-like network formation of MWCNT within the cement matrix's calcium silicate hydrates (C-S-H).

2.3.3 Studies on Hydraulic Properties and Performance in Dynamic Water Conditions

Gao et al. (2020) conducted water permeability tests of granites with single fractures grouted by different carbon nanomaterial-based cement composites. The impact on the pore structure and interface between the sealed material (i.e., granite) was investigated. The equivalent permeability decreased by 31.8-81.0% under varying confining pressures compared to the plain cement grouting. The equivalent permeability has an inversely proportional relation with confining pressure. The graphene oxide (GO)/multi-walled carbon nanotube (MWCNT)-based ordinary Portland cement (OPC) grouted sample exhibits the most significant enhancement, increasing permeability resistance by 240.3–315.0%. and mercury intrusion porosimetry (MIP) results showed that in average decrease of 33.8%, 40.7% and 22.9% in total intruded volume, average pore diameter and porosity compared with plain OPC sample, respectively. Moreover, the SEM images confirmed that carbon nanomaterials enhance pore structure with bridging micro-sized cracks and interfacial adhesion. Also, at boundaries (grouting-granite), flow resistance improved.

Liu et al. (2020) investigated nanomaterial-enhanced cement-based grouts for the dynamic water grouting process in rock fracture with rough surfaces with a physical setup to mimic the dynamic water grouting process in natural conditions. Diffusion distance, maximal fluid pressure, residual grouts percentage, and sealing efficiency were evaluated for the performance of enhanced grouts. CNT composite grout presented the best performance of residual grout percentage and highest maximal fluid pressure compared to other nanoparticles (e.g., 0.04% CNT added grouts' pressure reached 19.35 kPa compared to 7.98 kPa for plain grout). Nevertheless, the

sealing efficiency of CNT-added grouts was found to be the lowest compared to other nanomaterial-added ones due to their high viscosity and low diffusion rate.

As a follow-up study, Liu et al., 2021 investigated the performance of silica fume-added CNTs enhanced cementitious grouts in inclined fracture grouting with flowing water via viscosity, maximal fluid pressure, and sealing efficiency. It was found that incorporating CNTs increased viscosity up to 0.5%, but more addition decreased results. Silica fume addition of up to 10% increased the maximal fluid pressure of CNT-enhanced grouts. Moreover, the sealing efficiency of grouts increased with the increase of CNT content due to its improving the early strength and with an inclination angle of up to 5 degrees, which can increase the diffusion rate of grouts and offset the negative effect of high viscosity. However, after 5 degrees, grout will be washed out from fracture earlier, which causes a decrease in sealing efficiency. Furthermore, SEM results show that CNTs are prone to agglomerate into clumps, but the addition of silica fume can increase the dispersion of CNTs (Figure 2.9).

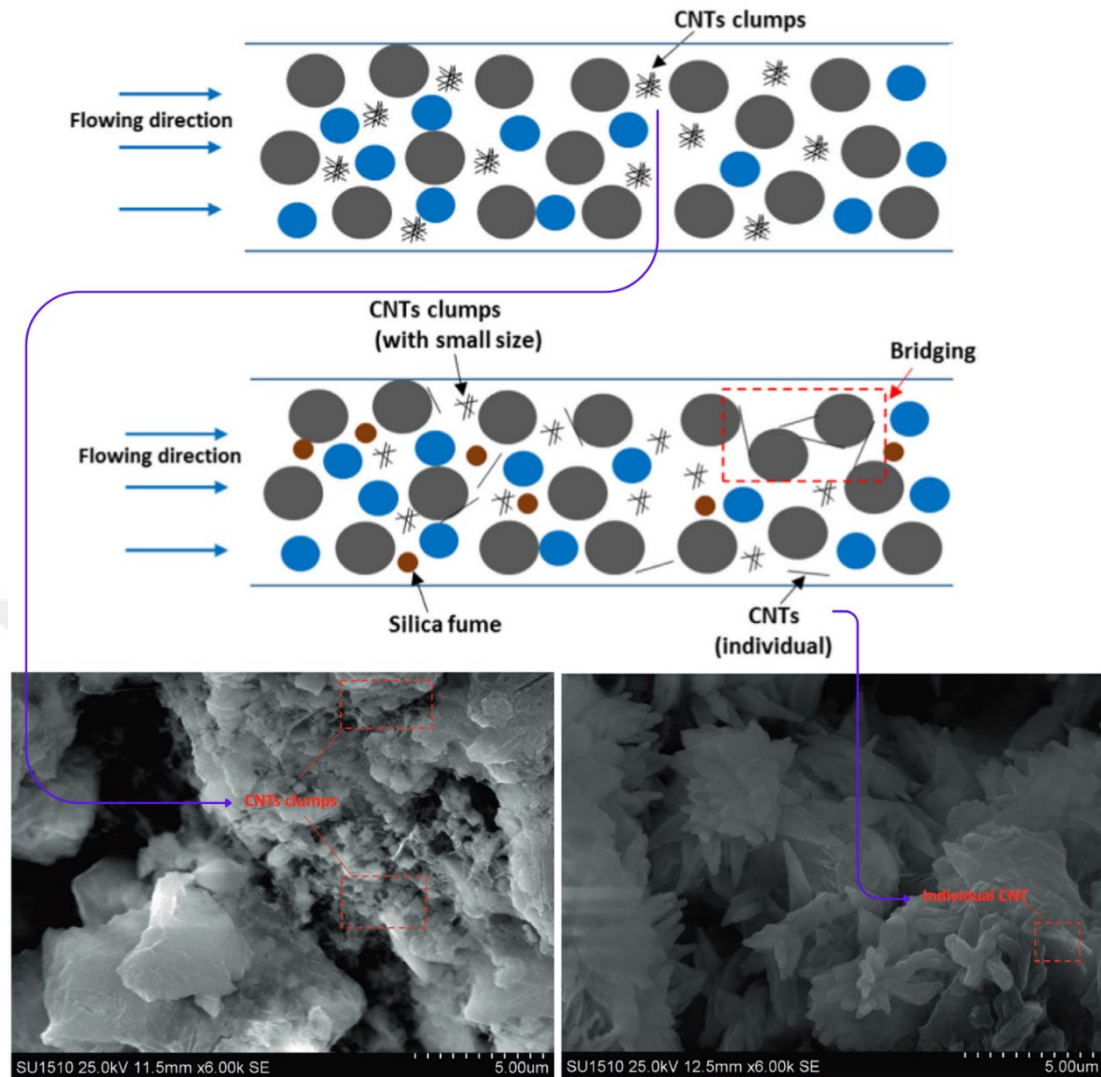


Figure 2.9 Schematics of microscopic mechanism and SEM picture of CNT added cement-based grouts with/without silica fume. Adapted from Liu et al. (2021)

2.3.4 Studies on Functionalized Carbon Nanotubes and Coating

Yang et al. (2022) manufactured functionalized CNT fiber (CNT-COOH and CNT-OH) with chemical processes, which show superior flexibility, dispersibility, tensile strength, and electric conductivity compared to non-functionalized CNTs with the benefit of chemical bonds between cement hydration products (e.g., C-S-H, AFt, and AH_3) and functionalized CNT fibers. The functionalization process, known as hydrophilization, is shown in Figure 2.10.a. It can be summarized as the oxidation of raw CNT fibers with HNO_3 , followed by $\text{HNO}_3/\text{H}_2\text{SO}_4$ and H_2O_2 treatment in sequence, yielding CNT-COOH fibers. Glycerol was attached to the resulting CNT

fibers through an esterification reaction, forming CNT-OH fibers. As shown in Fig. 10.b, raw CNT fibers have limited interaction with cement hydration products, but CNT-OH can generate hydrogen bonds with them, which creates stronger interfacial bonding; for CNT-COOH fiber, the extra ionic bonds formed create a much stronger connection to the cement matrix. Due to this effect, for w/c of 0.8 and 0.5% CNT-COOH addition, the sample showed flexural strength (4.8 MPa), compressive strength (27 MPa), and tensile strength (1.6 MPa) increased by %50, 30%, and 50%, respectively, respect to the plain sample after 28-day curing. Furthermore, this interconnected network architecture of the CNT-COOH cement matrix is expected to improve electrical conductivity and heat transfer.

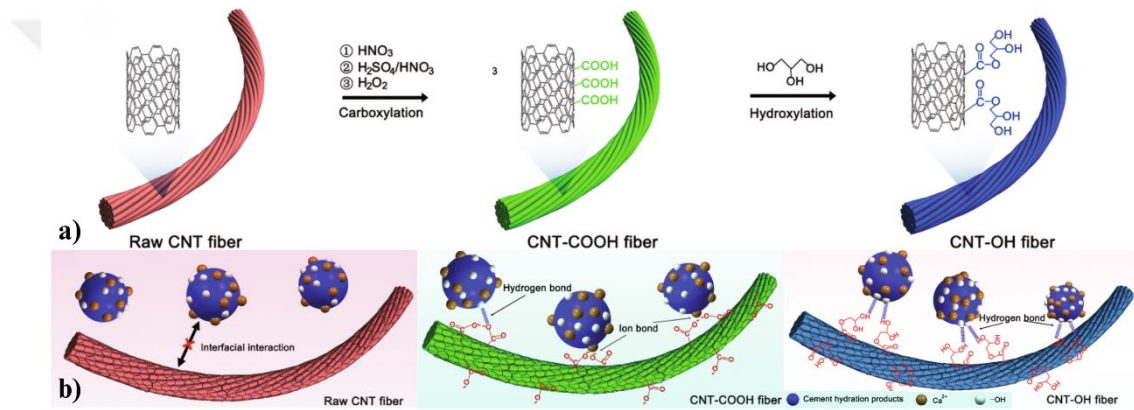


Figure 2.10 Hydrophilization and interaction mechanism of functionalized CNT fibers a)Schematic illustration for manufacturing procedure of CNT-COOH and CNT-OH fibers b) Interfacial interaction mechanism between cement hydration products and raw CNT fiber, CNT-COOH fiber, and CNT-OH fiber. Adapted from Yang et al. (2022)

Chen et al. (2023) created a method to coat CNTs on the surfaces of fly ash particles with amino-functionalized functional groups to improve the dispersion of CNTs in the cementitious matrix for high-performance grouts. The experimental results showed that 0.023 wt% CNTs and 14.3 wt% fly ash can increase compressive strength, tensile strength, and workability to 1.142, 1.258, and 1.28 (i.e., spread diameter increased from 138.8 mm to 156.6 mm) times, respectively. When the results were compared with Han. et al. (2023) (no coating process) improved interaction between hydration products and CNTs due to the coating process improving strength properties.

Han et al. (2024) introduced a similar method to Chen et al. (2023) by using amino-functionalized carbon nanotubes coated on fly ash to enhance the dispersion and performance of cementitious composites. This study focuses explicitly on workability and early strength qualities. The research indicated that substituting 14.3 wt% of cement with fly ash and adding 0.023 wt% CNTs enhanced fluidity by 21.6%, increased the 7-day consolidation strength by 7.9%, and decreased porosity by 11.9%. The 7-day compressive strength improved by 15.1–33.6%, while Young's modulus increased by 70%. The CNTs with a substantial specific surface area on the fly ash surface provide sites for cement hydration reactions, expedite cement hydration, and generate dense hydration products recognized for their bridging function in the literature. Carbon nanotubes (CNTs) were demonstrated to diminish micro-damage during loading, enhance structural integrity, and augment resistance to loading, as validated by acoustic emission and electron microscopy analyses.

Liu et al. (2024) examined the impact of various factors on the properties and sealing efficiency of foam-CNT composite grouts. They found that increasing the water-cement ratio and additive content reduced compressive strength, while CNT content enhanced the strength. The optimal grout composition was 1.3 w/c, 3% additive, 30% foam, and 1.0% CNT, with a correlation coefficient of 0.955. Foam content initially increased and decreased the flowing water resistance, while CNTs improved it. Moreover, the sealing efficiency ranged from 50% to 100%. The study also highlighted that foam reduced grout self-weight and that the sealing efficiency in vertical, inclined fractures decreased compared to horizontal fractures, emphasizing the importance of grout composition and fracture angle in improving sealing efficiency.

CHAPTER 3

EXPERIMENTAL STUDY

Figure 3.1 shows the workflow of the experimental study, outlining the steps from material preparation to testing and analysis. Detailed explanations of each step are provided in the following subsections.

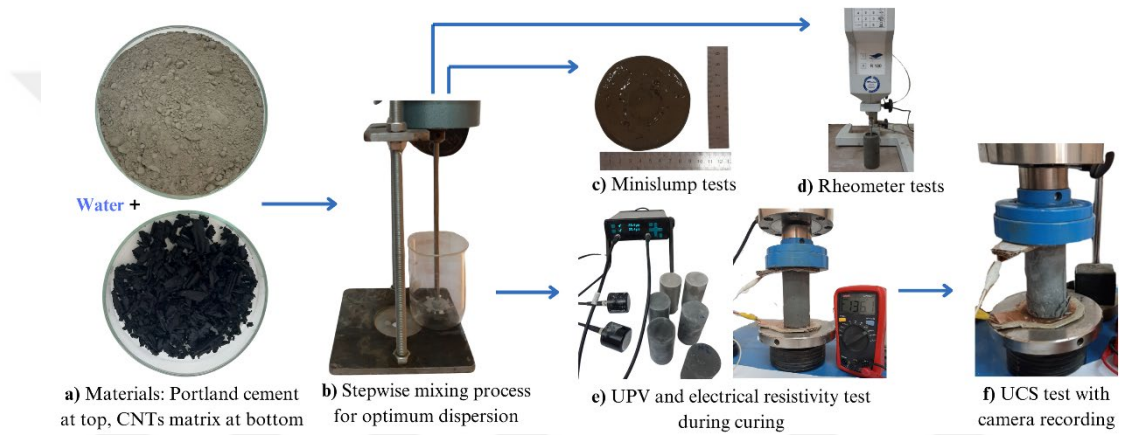


Figure 3.1 Experimental study workflow

3.1 Materials

The materials used in the binder composition of the grout mixtures, Portland cement (PC) and single-walled carbon nanotubes (SWCNTs), have been illustrated in Figure 3.1.a. The cement was an ordinary Portland cement (OPC), comparable to ASTM C150/C150M-24 type CEM I-42.5R; the chemical and physical properties of the cement are given in Table 3.1. The carbon nanotubes are single-walled graphene nanotubes (SWCNTs) synthesized using the catalytic CVD method, which decomposes hydrocarbons on a catalytic metal surface (Predtechenskiy et al., 2022). The SWCNTs are at a 10% concentration matrix for water-based acrylic, water-based polyurethane, and phenolic resole (solvent-based and water-based) systems within concentrate carriers of alkylene glycol derivatives and styryl biphenyl derivatives, manufactured by OCSiAl. SWCNTs appear fiber-like due to their high aspect ratio under transmission electron microscopy (TEM), as shown in Figure 3.2

for varying magnification levels. The structural properties of SWCNTs provided by the manufacturer are presented in Table 3.2.

Table 3.1 Chemical and physical properties of ordinary Portland cement(OPC)

Properties	Value
Specific gravity	3.15
Specific Surface (m ² /kg)	326
% retained on 45-μm	<15
Mean particle size (μm)	15-20
CaO (%)	62.12
SiO ₂ (%)	19.69
Al ₂ O ₃ (%)	5.16
Fe ₂ O ₃ (%)	2.88
MgO (%)	1.17
SO ₃ (%)	2.63
K ₂ O (%)	0.88
Na ₂ O (%)	0.17
Loss on ignition (%)	2.99

Table 3.2 Structural properties of SWCNTs

Specification	Unit of Measure	Value	Method of Evaluation
Appearance	-	Black powder	Visual inspection
SWCNT content	wt. %	99 ± 05	OCSIAI internal method: ash residue
SWCNT length	um	>5	AFM
Specific surface area	m ² /g	800 - 1600	Bet method ISO 92772010 (E)
SWCNT outer mean diameter	nm	1.6 ± 0.4	Optical absorption: ISO/TS 10868:2017 (E)
G/D ratio	unit	>40	Raman (532 nm): NIST SP 960-19
Metal impurities (in dry matter)	ppm	<350/<8000/ <20/<350/<20	OCSIAI IM: ICP-AES
Cr/Fe/Cu/Ni/Zn			
Moisture	wt. %	<5	OCSIA IM: infrared thermogravimetry

3.2 Sample Preparation and Testing Program

An overhead mechanical stirrer with an optimized impeller blade configuration capable of achieving a peripheral speed of 7–15 m/s was utilized to ensure adequate mixing. The process was conducted in a flat-bottomed cylindrical mixing container dimensioned to match the stirrer's specifications for enhanced dispersion efficiency and uniformity (Figure 3.3).

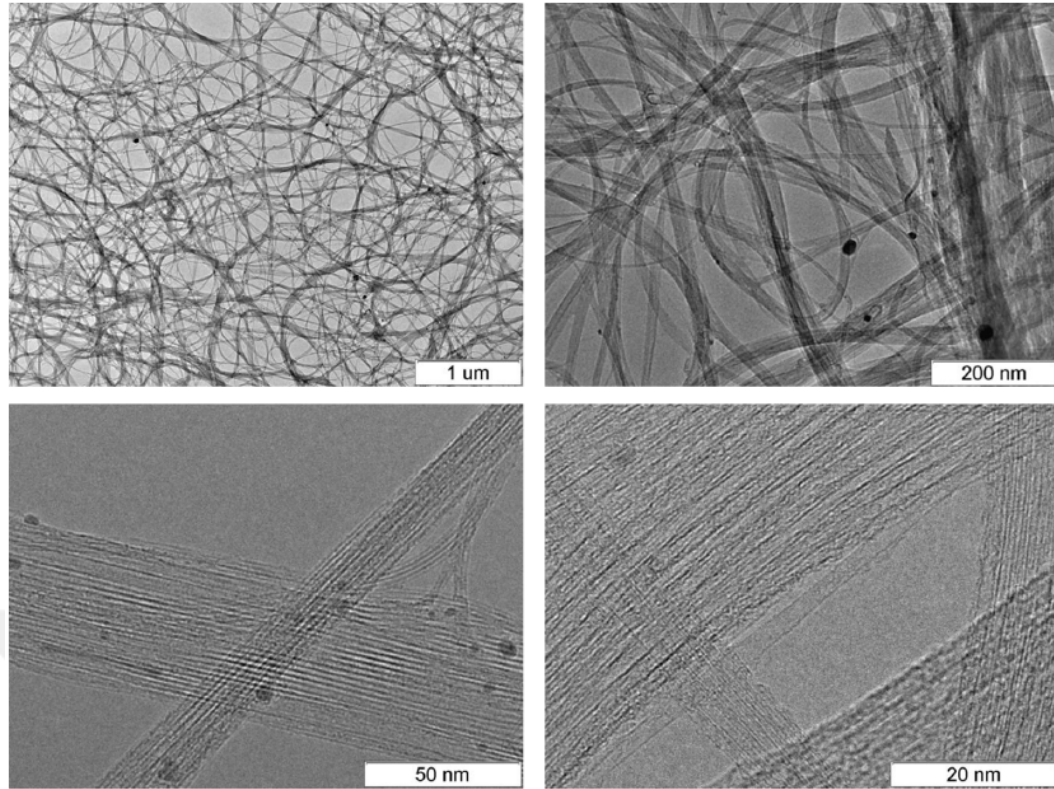


Figure 3.2 High-resolution TEM images of produced Tuball at different scales. From Predtechenskiy et al. (2022)

The mixing procedure adhered to the two-step protocol, ensuring proper interaction between the stirrer and the container to maximize the efficiency of the mixing process. In Step 1, the initial mix ratio of CNTs matrix to solution (water and cement) was set at 1:49, the total amount of calculated CNTs matrix for mixture used with a corresponding solution of water-to-cement (w/c) ratio of 1. The mixture was stirred for 20 minutes at a peripheral speed of 10 m/s. In Step 2, the remaining cement and water were added to the container and stirred for an additional 5 minutes at the same speed as in Step 1. For control mixtures (no CNTs), water and cement are stirred for 25 minutes in one step. During the preparation of the grout mixtures and subsequent testing, laboratory conditions were controlled, maintaining a relative humidity of 50-65% and a temperature of $24 \pm 2^{\circ}\text{C}$. The weight-based material proportions of the steps and the testing program are detailed in Table 3.3. It includes the binder proportions (Portland cement and CNTs matrix), water-to-binder ratios, and the amounts of binder and water used in the cement-based grout mixtures, covering 20 different mix designs.

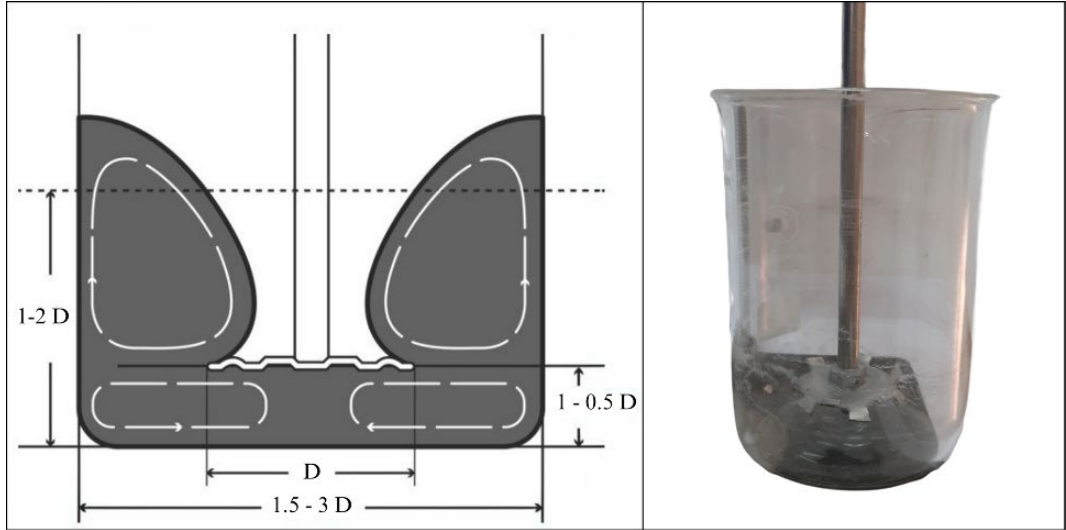


Figure 3.3 The stirrer and container proportions

The water-to-binder (w/b) ratios of 0.5, 0.75, 1, 1.25, and 1.5 were chosen to align with the specific grouting application, such as sealing, compaction, penetration, or injection grout. CNTs, even at low dosages, are highly effective in enhancing the properties of the cementitious matrix, with numerous studies highlighting significant improvements in material performance achieved with minimal CNT concentrations (Chen et al., 2023; G. Li et al., 2023; Y. Liu et al., 2021; Restuccia et al., 2018). Based on these findings, CNT dosages ranging from 0.05% to 0.30% by weight of the solution were chosen, balancing performance and economic considerations. Accordingly, three CNT dosages—0.05%, 0.10%, and 0.30%—were selected for this study, with the first mixtures for each w/b ratio containing only Portland cement, designated as the control grout for comparison.

The naming convention follows a structured format where the second decimal digit '0' in labels such as G10, G20, G30, G40, and G50 indicates that these mixtures contain no carbon nanotubes (CNTs). So, the second digit represents the percentage of CNTs added by weight of the solution, with '0' indicating no CNTs and '3' representing the highest CNT addition at 0.3%. On the other hand, the first digit, ranging from 1 to 5, corresponds to the water-to-binder (w/b) ratio, increasing incrementally from 0.5 to 1.5. This systematic approach ensures clarity in identifying mixture compositions based on their labeling (Figure 3.4).



Figure 3.4 The labeling system of grout mixtures

Table 3.3 Mixture proportions and mixing process

Grout ID	Ratios		Weights			Mixing process			
	w/b	CNT/s (%)	water (gr)	cement (gr)	CNT** (gr)	Step 1*		Step 2	
						W (gr)	C (gr)	W (gr)	C (gr)
G10	0.50	0.00	129.51	258.83	0.00	0.00	0.00	129.51	258.83
G11	0.50	0.05	127.05	252.00	1.90	46.67	46.67	80.38	205.33
G12	0.50	0.10	124.67	245.42	3.74	91.59	91.59	33.08	153.83
G13	0.50	0.30	122.39	233.58	11.01	122.39	233.58	0.00	0.00
G20	0.75	0.00	154.41	205.95	0.00	0.00	0.00	154.41	205.95
G21	0.75	0.05	151.68	200.53	1.77	43.36	43.36	108.32	157.17
G22	0.75	0.10	149.04	195.30	3.48	85.22	85.22	63.83	110.09
G23	0.75	0.30	146.50	185.13	10.26	146.50	185.13	0.00	0.00
G30	1.00	0.00	168.07	168.07	0.00	0.00	0.00	168.07	168.07
G31	1.00	0.05	165.29	163.64	1.65	40.50	40.50	124.79	123.14
G32	1.00	0.10	162.60	159.35	3.25	79.67	79.67	82.93	79.67
G33	1.00	0.30	160.00	150.40	9.60	160.00	150.40	0.00	0.00
G40	1.25	0.00	174.96	140.00	0.00	0.00	0.00	174.96	140.00
G41	1.25	0.05	172.25	136.28	1.55	37.98	37.98	134.26	98.29
G42	1.25	0.10	170.92	133.69	3.08	75.38	75.38	95.54	58.31
G43	1.25	0.30	169.62	126.56	9.16	169.62	126.56	0.00	0.00
G50	1.50	0.00	181.82	121.21	0.00	0.00	0.00	181.82	121.21
G51	1.50	0.05	180.45	118.80	1.50	36.84	36.84	143.61	81.95
G52	1.50	0.10	179.10	116.42	2.99	73.13	73.13	105.97	43.28
G53	1.50	0.30	177.78	109.63	8.89	177.78	109.63	0.00	0.00

* CNT Matrix added in Step 1 ** %10 concentrate of CNT

3.3 Rheological Testing

The rheological properties of the grout mixtures were measured with a coaxial rotating cylinder rheometer (proRheo R180 Instrument, Germany, shown in Figure 3.5), which operates on the Searle method. In this setup, the bob rotates while the cup remains stationary, following the Searle principle developed by G.F.C. Searle in 1912 (Barnes et al., 1989). ISO 3219-1 and DIN 53019-1 standards outline the design of concentric cylinder (CC) systems, emphasizing the importance of a narrow, circular gap between the surfaces to ensure a consistent shear rate across the gap. Adherence to these standards is essential when employing the narrow gap configuration. For instance, ISO 3219 specifies that the ratio between the radii of the cup and the bob must not exceed 1.085. For large-gap cylinder measuring systems

that do not meet these standards, alternative formulas are applied for shear stress (τ_i) and shear rate ($\dot{\gamma}_i$) (Mezger, 2021):

$$\tau_i = \frac{M}{2\pi LR_i^2} \quad (3.1)$$

$$\dot{\gamma}_i = \left[\frac{2R_e^2}{(R_e^2 - R_i^2)} \right] \omega \quad (3.2)$$

where, M denotes the torque, L is the length of the cylindrical section of the bob, R_i is the bob radius, R_e is the cup radius and ω represents the angular velocity.



Figure 3.5 Rheometer, proRheo R180

Two bob sizes (bob I and bob II) were used in testing, with diameters of 30 mm and 24 mm and lengths of 45 mm and 36 mm, respectively. Shear stress measurements were recorded at various shear rates: for $w/b = 1.0$, $w/b = 1.25$, and $w/b = 1.50$, bob I used at shear rates of 4.61 s^{-1} , 55.42 s^{-1} , 106.22 s^{-1} , 157.02 s^{-1} , 207.81 s^{-1} , 258.61 s^{-1} , 309.41 s^{-1} , 360.21 s^{-1} , 411.00 s^{-1} , and 461.81 s^{-1} while for $w/b = 0.5$ and $w/b = 0.75$, the bob II used at shear rates of 3.03 s^{-1} , 36.41 s^{-1} , 69.79 s^{-1} , 103.18 s^{-1} , 136.56 s^{-1} , 169.94 s^{-1} , 203.32 s^{-1} , 236.71 s^{-1} , 270.09 s^{-1} , and 303.47 s^{-1} . Tests were conducted in

10 ascending and 10 descending steps, each lasting 15 seconds, with a 30-second rest period between transitions. No pre-shearing was applied to any samples before the rheological measurements. The test procedure is illustrated in Figure 3.6.

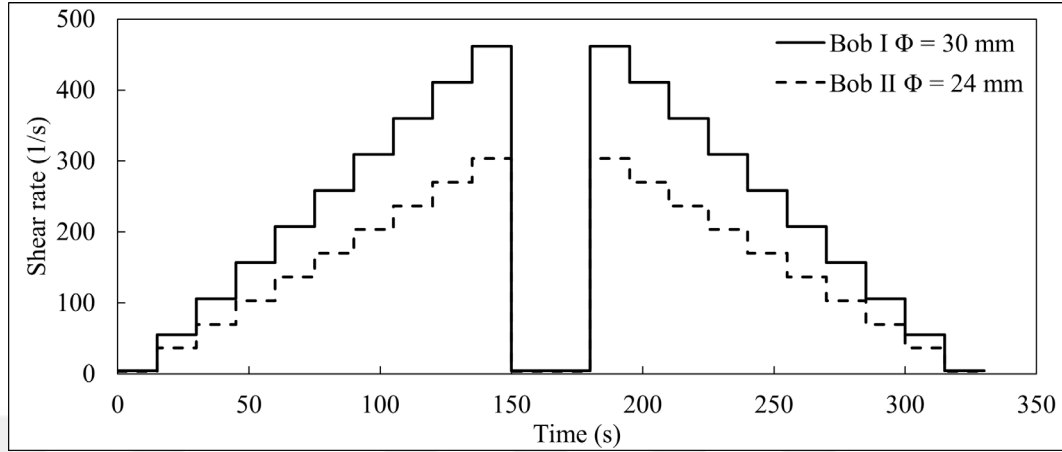


Figure 3.6 Rheological test procedures

The flow behavior of fresh grout is effectively described by flow curves that relate yield stress, shear rate, and plastic viscosity. The Bingham model characterizes yield stress (τ_0) as the minimum force needed to initiate flow, governed by particle interactions and bonds in cementitious materials, and plastic viscosity (μ) as the linear relationship between shear stress and shear rate, influenced by Brownian forces, cement hydration, and viscous interactions. To determine the most suitable rheological model for CNT-enhanced cementitious grouts, five commonly used models—Bingham, Modified Bingham, Herschel-Bulkley, Cross, and Carreau-Yassua—were evaluated, as these are some of the most used models for describing non-Newtonian fluids such as grouts and cementitious suspensions (Güllü, 2016; C. Liu et al., 2024; Nazar et al., 2020).

The modified Bingham model addresses limitations of the Bingham model, such as its assumption of constant viscosity limits its applicability to more complex, shear-dependent behaviors, by introducing a curvature term (c), allowing for a nonlinear response at higher shear rates and better capturing shear-thinning and shear-thickening behaviors typical of non-Newtonian fluids like cementitious grouts. The Herschel-Bulkley model further generalizes the approach by incorporating a power-law term with a flow behavior index (n) to characterize shear-thinning ($n < 1$) or

shear-thickening ($n>1$) behaviors; when $n=1$, it drops to the Bingham model and the consistency index (K) becomes viscosity.

The Cross and Carreau-Yasuda models are empirical rheological models that describe non-Newtonian fluids with complex flow behaviors. The Cross model characterizes fluids as power-law fluids over a range of shear rates but transitions to a region of constant viscosity at both low and high shear rates. Conversely, and beyond that, the Carreau-Yasuda model provides a more gradual transition between power-law and constant viscosity regions, offering a better fit for fluids exhibiting complex shear-thinning or shear-thickening behaviors. The formulas for these models are:

$$\tau_B = \tau_0 + \mu\dot{\gamma} \quad (3.3)$$

$$\tau_{MB} = \tau_0 + \mu\dot{\gamma} + c\dot{\gamma}^2 \quad (3.4)$$

$$\tau_{HB} = \tau_0 + K\dot{\gamma}^n \quad (3.5)$$

$$\tau_C = \tau_0 + \frac{\tau_\infty - \tau_0}{(1 + (\lambda\dot{\gamma})^n)} \quad (3.6)$$

$$\tau_{CY} = \tau_0 + \frac{\tau_\infty - \tau_0}{(1 + ((\lambda\dot{\gamma})^a)^{\frac{n-1}{a}})} \quad (3.7)$$

where τ_B , τ_{MB} , τ_{HB} , τ_C , τ_{CY} represents the shear stress (Pa) for Bingham, modified Bingham, Herschel-Bulkley, Cross and Carreau-Yasuda models, respectively. τ_0 is the shear stress at zero shear rate (Pa) representing the stress at rest, μ is the viscosity (Pa.s) and $\dot{\gamma}$ is the shear rate (1/s). c is the curvature term, K is the consistency index, and n is the flow behavior index indicating shear thickening and shear-thinning behavior. τ_∞ is the shear stress at infinite shear rate (Pa) representing the asymptotic value at very high shear rates, λ is the time constant (s) related to the relaxation time, and a is the width of the transition region between Newtonian and power-law behavior.

Flow curves were generated with rheological models, displaying apparent viscosity and shear stress as functions of shear rate, with data collected for both the ascending

and descending phases. However, only the descending data were analyzed for this study, as they were more stable for model fitting.

3.4 Mini-slump Testing

The mini-slump test is a practical and cost-effective method for evaluating the yield stress of cementitious grouts, providing valuable insights into their rheology and workability. During the test, the material flows under its self-weight until the stress at every point within the sample equals or falls below the yield stress, causing the flow to stop (Schowalter & Christensen, 1998). Analytical and numerical studies have demonstrated that this stoppage condition reflects the material's transition from a flowing to a stable state, making it a key parameter in evaluating workability, corresponding to yield stress. (Murata, 1984; Pashias et al., n.d.; Roussel & Coussot, 2005; Saak et al., 2004).

In this study, the mini-slump test employed a scaled-down version of the Abrams cone with a top diameter of 19 mm, a bottom diameter of 38 mm, and a height of 57 mm (Figure 3.7). The freshly mixed grouts were promptly poured into the cone, which was then lifted as slowly as possible to reduce inertial impact. After the stoppage of the spread, a digital photo was captured from directly above the sample. Then, the final spread diameter was calculated as the average of two measurements taken in perpendicular directions (Güllü et al., 2023, 2024).

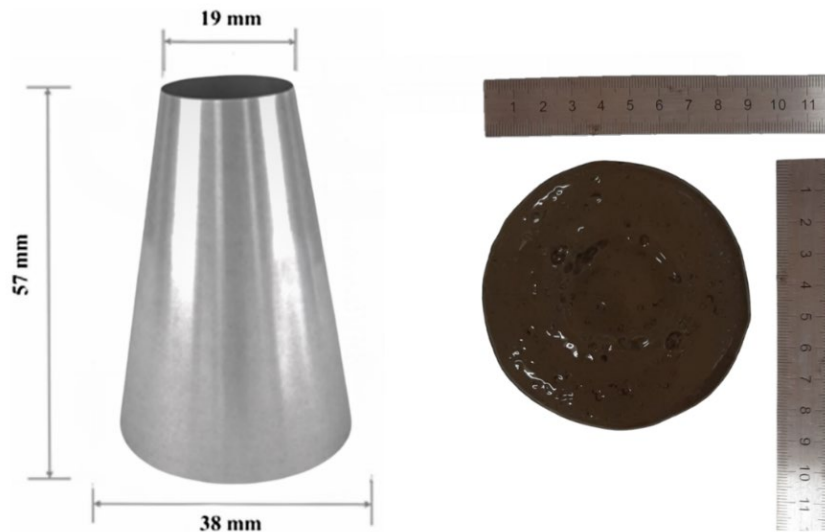


Figure 3.7 Mini-slump test apparatus and measuring

3.5 UPV Testing

The ultrasonic pulse velocity (UPV) test, as defined by ASTM C597–09, is a non-destructive method used to evaluate the quality, uniformity, and structural integrity of materials such as concrete. This test measures the velocity of longitudinal stress wave pulses traveling through the material, which is influenced by its elastic modulus, density, and Poisson’s ratio. The relationship is expressed as:

$$V = \sqrt{\frac{E(1 - \mu)}{\rho(1 + \mu)(1 - 2\mu)}} \quad (3.8)$$

where V is the pulse velocity, E is the dynamic modulus of elasticity, μ is the dynamic Poisson’s ratio, and ρ is the material density. The pulse velocity V is directly calculated using the formula $V = L/T$, where L is the distance between transducers and T is the transit time. Higher pulse velocities typically indicate denser and more uniform materials, whereas lower velocities may suggest the presence of defects, cracks, or voids.

The UPV test is handy for assessing material uniformity, identifying internal flaws, and monitoring changes in structural conditions over time. It can also estimate the stiffness and strength of materials through empirical relationships between pulse velocity and mechanical properties, such as UCS results. Anon, 1979 offers a classification for the strength quality of hardened material based on sonic velocity (Table 3.4).

Table 3.4 Sonic velocity classes for hard and soft rocks (Annon,1979)

Class	UPV (m/s)	Definition
1	<2500	Very low
2	2500–3500	Low
3	3500–4000	Moderate
4	4000–5000	High
5	>5000	Very high

This study utilized a PROCEQ apparatus with transducers ranging from 24 kHz to 500 kHz for UPV measurements on cylindrical grout samples (Figure 3.8). Tests were carried out during the curing process, and the hardening of the specimens was

monitored using ultrasonic pulse velocity (UPV) tests at intervals of 7, 14, and 28 days.



Figure 3.8 UPV testing equipment and samples

3.6 Electrical Resistivity Testing

Electrical resistivity (ER) characterizes a cementitious material's ability to impede the flow of electric current when subjected to a voltage. The two-point uniaxial method is the prevalent method used to measure electrical resistance. Alternative approaches, such as the Wenner probe and the C1760-12 ASTM methods, have been developed to measure electrical resistance. The two-point uniaxial method entails applying a voltage difference across a specimen, which can assume various geometries such as cylinders, cubes, or prisms. By employing a multimeter to measure the resulting current, the resistance value can be determined using Ohm's law. The calculation of electrical resistivity (ρ) is expressed by

$$\rho = VA/IL \text{ (}\Omega\text{m)} \quad (3.9)$$

here, V represents the applied voltage difference, A is the cross-sectional area of the specimen, L is the length of the specimen, and I signifies the current.

In this study, the electrical resistance of grouts was measured using the two-point uniaxial method; cylindrical specimens featuring a diameter of 5 cm and a length of 10 cm were meticulously fabricated, two copper plates were positioned on the specimen surfaces, and a contact pressure of 2 kPa was applied to the specimen. The resistance was subsequently computed based on the measured current generated by the applied voltage between the two plates. The visual representation of the experimental setup is given in Figure 3.9.



Figure 3.9 Electrical resistivity test setup

3.7 UCS Testing

The strength tests on grout mixtures cured for 28 days were carried out according to ASTM C 942-15. The freshly mixed grouts were poured into standard PVC molds with dimensions of 50 mm in diameter and 100 mm in height, then sealed with plastic membranes to create cylindrical specimens. Care was taken to prevent any leakage from the molds. After 24 hours, the specimens were demolded and

transferred to a moist chamber, where they were cured at 23 ± 3 °C and 100% relative humidity to test their 28-day strength. Following the final UPV and ER tests on day 28, the unconfined compressive strength (UCS) was determined by applying uniaxial loading at a rate of 0.25 mm/min while recording strain deformations. Simultaneously, crack propagation was recorded using two cameras placed in the front and back of the test sample to capture the initiation and growth of fractures in real time (Figure 3.10).



Figure 3.10 UCS test setup

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Rheological Results

4.1.1 Rheological Model Comparison

Figure 4.1 presents the shear stress-shear rate graphs of grout mixtures for various water-to-binder (w/b) ratios (0.50, 0.75, 1.00, 1.25, and 1.50) and CNT concentrations (0%, 0.05%, 0.10%, and 0.30%). From left to right, the CNT addition percentage increases, and from top to bottom, the w/b ratio increases. Measurements for G12 and G13 (w/b = 0.5 and CNTs = 0.10%, CNTs = 0.30%, respectively) could not be obtained due to the torque limits of the rheometer used in the rheological test.

Statistical measures, such as the Root Mean Square Error (RMSE) and the Coefficient of Determination (R^2), are essential tools for evaluating and comparing the performance of regression models, providing insights into their accuracy and goodness of fit. The RMSE is a widely used metric that quantifies the average magnitude of prediction errors by measuring the differences between predicted and observed values. Lower RMSE values indicate a better fit of the model to the data, signifying more minor prediction errors. Unlike the Mean Absolute Error (MAE), which treats all errors equally, RMSE places greater emphasis on more significant errors, making it particularly suitable for situations where significant deviations are undesirable—such as selecting the optimal rheological model for the shear stress–shear rate relationship in cementitious grouts. Moreover, RMSE is expressed in the same units as the dependent variable (i.e., shear stress), providing a straightforward and interpretable measure of prediction accuracy. In contrast, the Coefficient of Determination (R^2) is a statistical metric that evaluates the proportion of variance in the dependent variable explained by the independent variable(s) in a regression model. R^2 offers insight into the model's goodness-of-fit, indicating how well the independent variables account for the variability in the dependent variable. R^2 ranges from 0 to 1, with higher values representing better model performance. Since the sample size and number of predictors are consistent across all datasets (10

observations and one predictor, respectively), the use of adjusted R^2 (R^2_{adj}) was deemed unnecessary as there is no variation in the number of predictors or observations. The comparison of rheological models by statistical measures (RMSE and R^2) is given in Table 4.1.

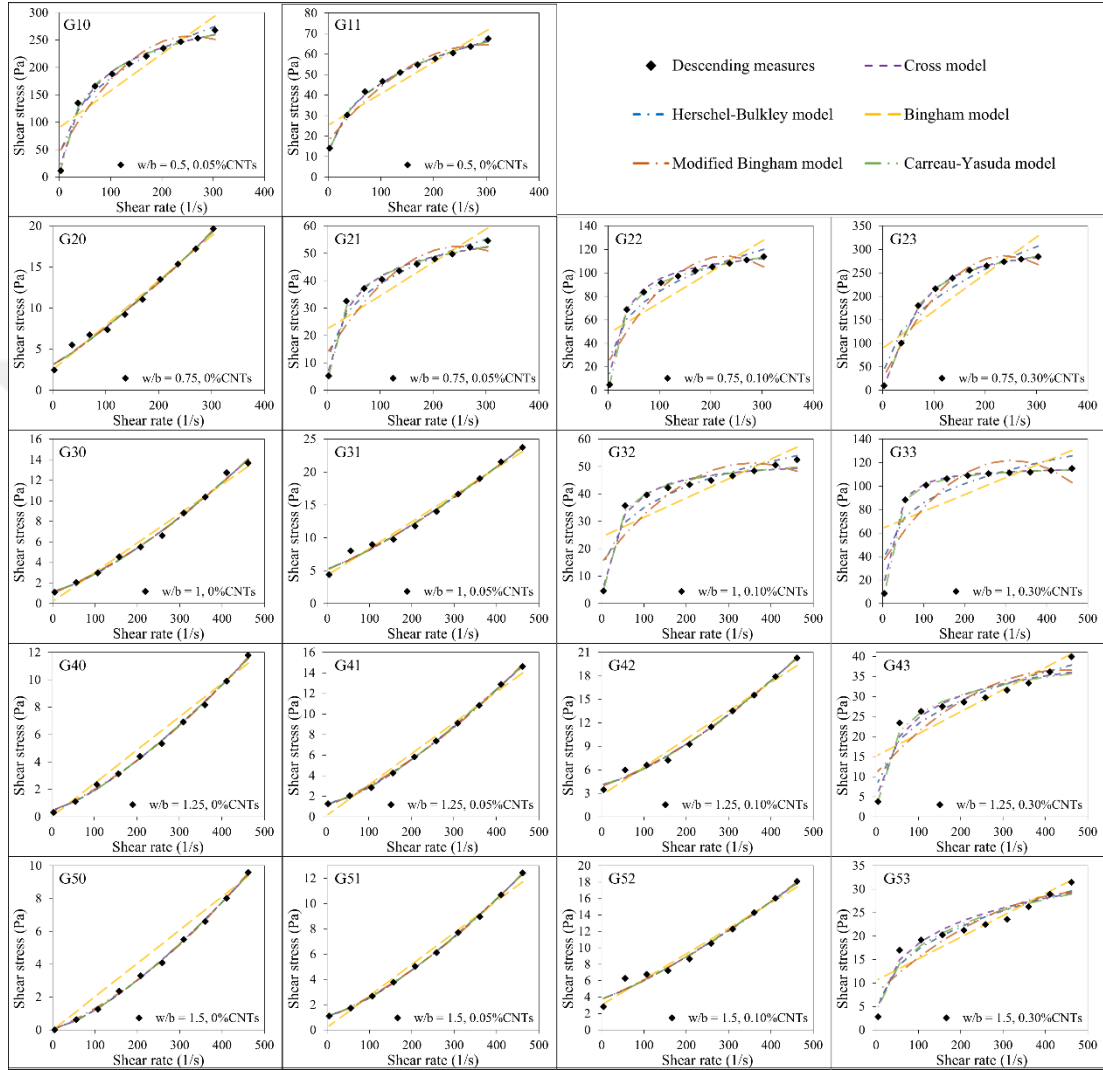


Figure 4.1 Flow curves of shear stress versus shear rate

It should be noted that RMSE and R^2 assess models' performance based on prediction accuracy and goodness-of-fit, respectively; they do not account for model complexity or the risk of overfitting. To address this limitation, the Akaike Information Criterion (AIC) is a widely used statistical measure that evaluates model performance while balancing goodness-of-fit with the number of parameters in the model. By penalizing excessive complexity, AIC helps identify models that achieve an optimal trade-off between accuracy and simplicity (Akaike, 1973, 1974; Hurvich & Tsai, 1989).

Models with lower AIC values are considered to have better overall performance, as they minimize both prediction error and overfitting. AIC differences ($\Delta AIC = AIC_i - AIC_{min}$) are a quick comparison and ranking of candidate models. The model's performance is deemed substantial to Δ_i values between 0 and 2, considerably less for values between 5 and 7, and essentially none for values greater than 10 (Burnham & Anderson, 2004). The comparison of rheological model performances by AIC differences is presented in Table 4.2. The formulas for RMSE, R^2 , and, AIC are as follows:

$$RMSE = \left(\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \right)^{0.5} \quad (4.1)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (4.2)$$

$$AIC \text{ (or } AIC_c) = \begin{cases} n \ln \left(\frac{RSS}{n} \right) + 2k, & \text{when } \frac{n}{k} \geq 40 \\ n \ln \left(\frac{RSS}{n} \right) + 2k + \frac{2k(k+1)}{n-k-1}, & \text{when } \frac{n}{k} < 40 \end{cases} \quad (4.3)$$

where y is the observed value for the i -th data point, $\hat{y}$ is the predicted value for the i -th data point, $\bar{y}$ is the mean of all observed values, RSS is the residual sum of squares, n is the total number of observations and k is the number of independent variables.

Table 4.1 Statistical metrics (SM) of rheological model performances

Grout ID	SM	C	HB	B	MB	CY	Performance Comparison
G10	RMSE	1.051	1.049	5.766	3.104	1.113	HB > C > CY > MB > B
	R ²	0.996	0.996	0.877	0.964	0.995	
G11	RMSE	8.946	15.811	36.335	23.583	6.842	CY > C > HB > MB > B
	R ²	0.986	0.957	0.772	0.904	0.992	
G20	RMSE	0.656	0.607	0.642	0.555	0.719	MB > HB > B > C > CY
	R ²	0.986	0.988	0.987	0.990	0.983	
G21	RMSE	2.114	3.561	7.702	5.650	1.640	CY > C > HB > MB > B
	R ²	0.978	0.938	0.709	0.843	0.987	
G22	RMSE	4.995	10.618	19.911	13.269	0.439	CY > C > HB > MB > B
	R ²	0.976	0.893	0.625	0.834	1.000	
G23	RMSE	2.692	23.321	44.555	17.376	0.910	CY > C > MB > HB > B
	R ²	0.999	0.933	0.756	0.963	1.000	
G30	RMSE	0.374	0.346	0.600	0.349	0.410	HB > MB > C > CY > B
	R ²	0.9928	0.9939	0.9816	0.9938	0.9914	
G31	RMSE	0.790	0.732	0.830	0.672	0.866	MB > HB > C > B > CY
	R ²	0.984	0.987	0.983	0.989	0.981	
G32	RMSE	2.431	4.976	8.810	6.960	2.102	CY > C > HB > MB > B
	R ²	0.969	0.868	0.587	0.742	0.976	
G33	RMSE	4.362	15.863	24.895	17.844	0.669	CY > C > HB > MB > B
	R ²	0.982	0.758	0.404	0.694	1.000	
G40	RMSE	0.237	0.219	0.604	0.162	0.260	MB > HB > C > CY > B
	R ²	0.996	0.997	0.975	0.998	0.995	
G41	RMSE	0.099	0.117	0.598	0.190	0.108	C > CY > HB > MB > B
	R ²	1.000	0.999	0.984	0.998	0.999	
G42	RMSE	0.567	0.525	0.833	0.479	0.622	MB > HB > C > CY > B
	R ²	0.990	0.991	0.978	0.993	0.988	
G43	RMSE	2.800	2.988	5.175	4.698	2.729	CY > C > HB > MB > B
	R ²	0.918	0.907	0.721	0.770	0.922	
G50	RMSE	0.148	0.137	0.803	0.116	0.163	MB > HB > C > CY > B
	R ²	0.998	0.998	0.938	0.999	0.997	
G51	RMSE	0.106	0.098	0.478	0.095	0.116	MB > HB > C > CY > B
	R ²	0.999	0.999	0.985	0.999	0.999	
G52	RMSE	0.809	0.749	0.775	0.692	0.886	MB > HB > B > C > CY
	R ²	0.972	0.976	0.974	0.979	0.966	
G53	RMSE	2.443	2.171	3.572	3.373	2.511	HB > C > CY > MB > B
	R ²	0.904	0.924	0.794	0.816	0.898	

The evaluation of rheological model performance using RMSE and R² revealed consistent rankings, though these rankings should not be viewed as a linear hierarchy. For G23 grout, the RMSE increased by 195% from the Carreau-Yasuda (CY) model to the Cross (C) model and by 608% from the Cross to the Modified Bingham (MB) model. Correspondingly, R² decreased by 0.1% and 3.6%, respectively. Some models, such as CY-C and MB-HB, showed closely aligned performance. Based on the best RMSE and R² values, the CY and C models were considered the most accurate in explaining shear stress-shear rate relationships. In factoring in model complexity, simpler models like Bingham gained prominence

despite poorer statistical performance. ΔAIC assessments introduced a gradual ranking, broadly aligning with the statistical findings but highlighting a preference for simpler models due to the penalty for increased complexity. This demonstrates that simpler models are favored in AIC-based evaluations.

Table 4.2 AIC of rheological model performances

Grout ID	Models	RSS	N	Parameters	AIC	ΔAIC	Performance Comparison
G10	HB	7.70	10	3	13.39	-	HB > C > MB = CY = B
	C	6.63	10	4	20.89	7.51	
	MB	67.46	10	3	35.09	21.70	
	CY	6.19	10	5	35.21	21.82	
	B	265.95	10	2	42.81	29.42	
G11	C	480.22	10	4	63.72	-	C > HB = CY > MB = B
	HB	1749.81	10	3	67.65	3.93	
	CY	234.07	10	5	71.53	7.81	
	MB	3892.94	10	3	75.64	11.93	
	B	10561.65	10	2	79.62	15.91	
G20	B	3.30	10	2	-1.09	-	B = MB > HB = C = CY
	MB	2.16	10	3	0.66	1.75	
	HB	2.58	10	3	2.44	3.53	
	C	2.58	10	4	11.45	12.53	
	CY	2.58	10	5	26.46	27.55	
G21	C	26.81	10	4	34.86	-	C > HB = CY > MB = B
	HB	88.78	10	3	37.84	2.97	
	CY	13.45	10	5	42.96	8.10	
	MB	223.45	10	3	47.07	12.20	
	B	474.55	10	2	48.60	13.73	
G22	CY	0.97	10	5	16.62	-	CY > C = HB = MB = B
	C	149.70	10	4	52.06	35.44	
	HB	789.25	10	3	59.69	43.07	
	MB	1232.40	10	3	64.14	47.52	
	B	3171.73	10	2	67.59	50.98	
G23	CY	4.14	10	5	31.18	-	CY > C > MB = HB = B
	C	43.48	10	4	39.70	8.52	
	MB	2113.46	10	3	69.53	38.35	
	HB	3807.13	10	3	75.42	44.24	
	B	15881.15	10	2	83.70	52.52	
G30	HB	0.84	10	3	-8.77	-	HB = MB > B = C > CY
	MB	0.85	10	3	-8.60	0.17	
	B	2.88	10	2	-2.45	6.32	
	C	0.84	10	4	0.23	9.00	
	CY	0.84	10	5	15.24	24.01	
G31	B	5.51	10	2	4.04	-	B = MB > HB = C = CY
	MB	3.16	10	3	4.48	0.44	
	HB	3.75	10	3	6.19	2.15	
	C	3.75	10	4	15.19	11.15	
	CY	3.75	10	5	30.19	26.16	

Table 4.2 (cont.) AIC of rheological model performances

Grout ID	Models	RSS	N	Parameters	AIC	Δ AIC	Performance Comparison
G32	C	35.45	10	4	37.65	-	C > HB > CY = MB = B
	HB	173.29	10	3	44.52	6.87	
	CY	22.10	10	5	47.93	10.27	
	MB	339.04	10	3	51.24	13.58	
	B	620.90	10	2	51.29	13.63	
G33	CY	2.24	10	5	25.03	-	CY > C = HB = MB = B
	C	114.18	10	4	49.35	24.32	
	HB	1761.45	10	3	67.71	42.68	
	MB	2228.91	10	3	70.07	45.04	
	B	4957.94	10	2	72.06	47.03	
G40	MB	0.18	10	3	-23.97	-	MB > HB = C = B = CY
	HB	0.34	10	3	-17.95	6.02	
	C	0.34	10	4	-8.94	15.03	
	B	2.92	10	2	-2.32	21.64	
	CY	0.34	10	5	6.15	30.11	
G41	HB	0.10	10	3	-30.44	-	HB > C = MB > CY = B
	C	0.06	10	4	-26.44	4.00	
	MB	0.25	10	3	-20.76	9.68	
	CY	0.06	10	5	-11.43	19.01	
	B	2.86	10	2	-2.52	27.92	
G42	MB	1.61	10	3	-2.27	-	MB = HB > B > C = CY
	HB	1.93	10	3	-0.47	1.80	
	B	5.55	10	2	4.10	6.37	
	C	1.93	10	4	8.53	10.80	
	CY	1.94	10	5	23.58	25.85	
G43	HB	62.51	10	3	34.33	-	HB > C = B = MB > CY
	C	47.04	10	4	40.48	6.16	
	B	214.26	10	2	40.65	6.32	
	MB	154.50	10	3	43.38	9.05	
	CY	37.25	"	5	53.15	18.82	
G50	MB	0.09	10	3	-30.57	-	MB > HB > C = CY = B
	HB	0.13	10	3	-27.32	3.26	
	C	0.13	10	4	-18.31	12.26	
	CY	0.13	10	5	-3.19	27.38	
	B	5.16	10	2	3.38	33.96	
G51	MB	0.06	10	3	-34.57	-	MB = HB > C > CY = B
	HB	0.07	10	3	-34.00	0.57	
	C	0.07	10	4	-24.98	9.59	
	CY	0.07	10	5	-9.93	24.64	
	B	1.83	10	2	-7.01	27.56	
G52	B	4.80	10	2	2.67	-	B > MB = HB > C = CY
	MB	3.35	10	3	5.08	2.41	
	HB	3.92	10	3	6.64	3.97	
	C	3.93	10	4	15.65	12.98	
	CY	3.93	10	5	30.65	27.98	
G53	HB	32.99	10	3	27.94	-	HB > B = MB = C > CY
	B	102.07	10	2	33.23	5.29	
	MB	79.66	10	3	36.75	8.81	
	C	35.80	10	4	37.75	9.82	
	CY	31.54	10	5	51.49	23.55	

The statistical metrics and AIC comparisons were based on models calibrated using data up to a shear rate of 500 s^{-1} . However, the parameters derived from these models must also remain valid for higher shear rates to ensure broader applicability. Models that do not follow power-law principles, such as Bingham and Modified Bingham, tend to produce unrealistic results at elevated shear rates. As shown for G33 in Figure 4.2, for shear rates of up to 1000 s^{-1} , the outcomes deviated significantly from previous works and general cementitious grout behavior (Dehghani & Aslani, 2022; Güllü et al., 2023; Güllü & Agha, 2021).

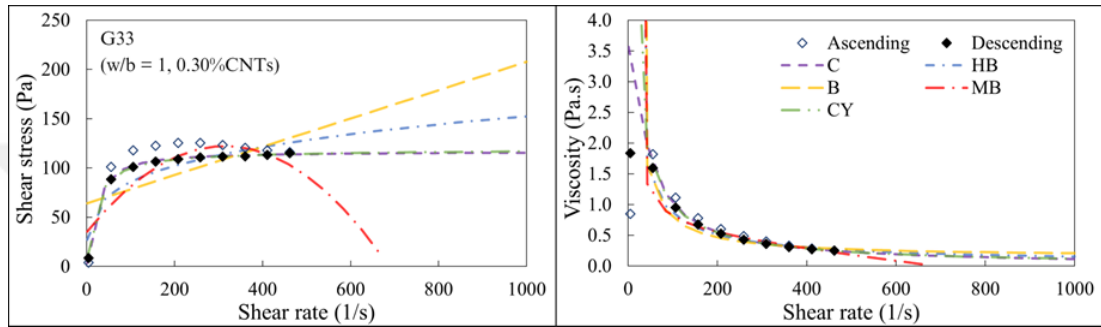


Figure 4.2 Shear stress – viscosity versus shear rate for G33

Considering statistical metrics (SM), AIC values, and performance at high shear rates, recommended models for various water-to-binder (w/b) ratios and CNT additions are summarized in Table 4.3. For grouts with high w/b ratios and low CNT additions, the Herschel-Bulkley model exhibited superior performance in prediction accuracy, fitting quality, simplicity, and compatibility with higher shear rates, including those beyond the scope of this study. Conversely, for low w/b ratios and high CNT additions, the Cross model was identified as the most effective, excelling across the same criteria.

Table 4.3 Summary of rheological models comparison

CNTs w/b	0%	0.05%	0.10%	0.30%
0.5	SM: HB, C AIC: HB Autors: HB	SM: C, CY AIC: C Autors: C	Autors:C	Autors:C
0.75	SM: HB, MB AIC: MB, B Autors: HB	SM: C, CY AIC: C Autors: C	SM: C, CY AIC: CY Autors: C	SM: C, CY AIC: CY Autors: C
1	SM: HB, MB AIC: HB, MB Autors: HB	SM: HB, MB AIC: MB, B Autors: HB	SM: C, CY AIC: C Autors: C	SM: C, CY AIC: CY Autors: C
1.25	SM: HB, MB AIC: MB Autors: HB	SM: C, CY AIC: HB Autors: HB	SM: HB, MB AIC: HB, MB Autors: HB	SM: C, CY AIC: HB Autors: C
1.5	SM: HB, MB AIC: MB Autors: HB	SM: HB, MB AIC: HB, MB Autors: HB	SM: HB, MB AIC: B Autors: HB	SM: C, CY AIC: HB Autors: C

Based on the findings, the RMSE and R^2 values consistently ranked the rheological models' predictive accuracy, demonstrating reliability in statistical evaluations, with complex models like the Carreau-Yasuda (CY) model excelling at low w/b ratios and high CNT additions due to the insensitivity of these metrics to overfitting. In contrast, simpler models such as the Bingham model, despite poorer performance in statistical metrics, gained prominence in ΔAIC -based evaluations, highlighting the need to balance model complexity and accuracy for practical applications. However, models that deviate from power-law principles, such as the Bingham and Modified Bingham models, often produce unrealistic results at higher shear rates, limiting their broader applicability. Considering all performance evaluations, the Herschel-Bulkley model is recommended for high w/b ratios and low CNT additions due to its superior predictive accuracy, simplicity, and compatibility with elevated shear rates. In contrast, the Cross model is the most effective for low w/b ratios and high CNT additions, excelling in the same criteria.

4.1.2 Rheological Curves and Behavior

Figure 4.3 presents the shear stress-shear rate and apparent viscosity-shear rate graphs of grout mixtures for ascending and descending measure with curves for Cross and Herschel-Bulkley models, which are found to best rheological models for varying w/b and CNTs additions in 4.1.1.

When shear stress – shear rate measures, Cross and Herschel-Bulkley model curves are interpreted, except form w/b =0.5 (see, Fig.23.a), all w/b ratios of the control mixtures (no CNT) show shear thickening behavior in investigated shear rate range (up to 500 s^{-1}) as compatible with previous works in literature (da Rocha Gomes et al., 2023; Dehghani & Aslani, 2022; Güllü, 2016; Güllü et al., 2023; C. Liu et al., 2024; Nazar et al., 2020). However, with the addition of CNTs, the behavior shifts through shear thinning behavior (i.e., apparent viscosity decreases with shear rate increase). The rheological behavior shift becomes more dramatic for higher w/b ratio levels. Moreover, the correlation between the shear thinning effect and the best rheological ranking of Cross is evident (see Table 4.3).

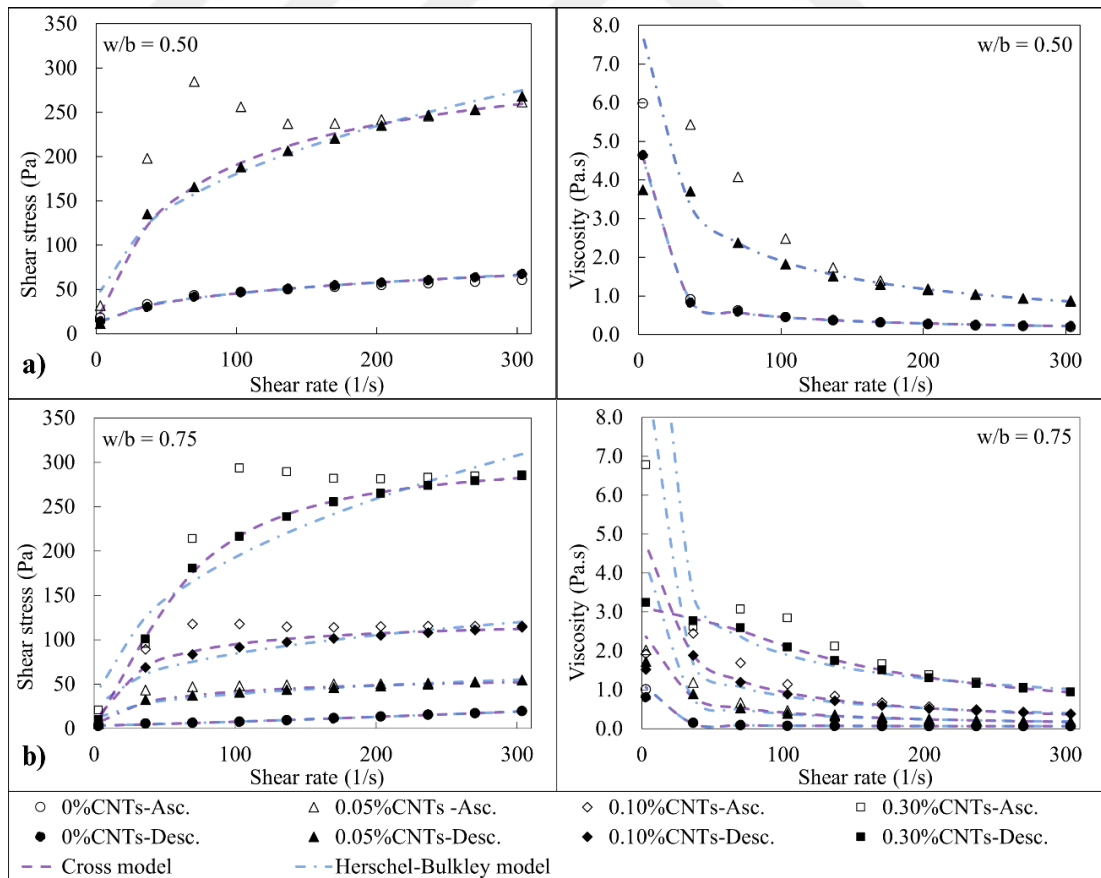


Figure 4.3 Rheological curves and measurements

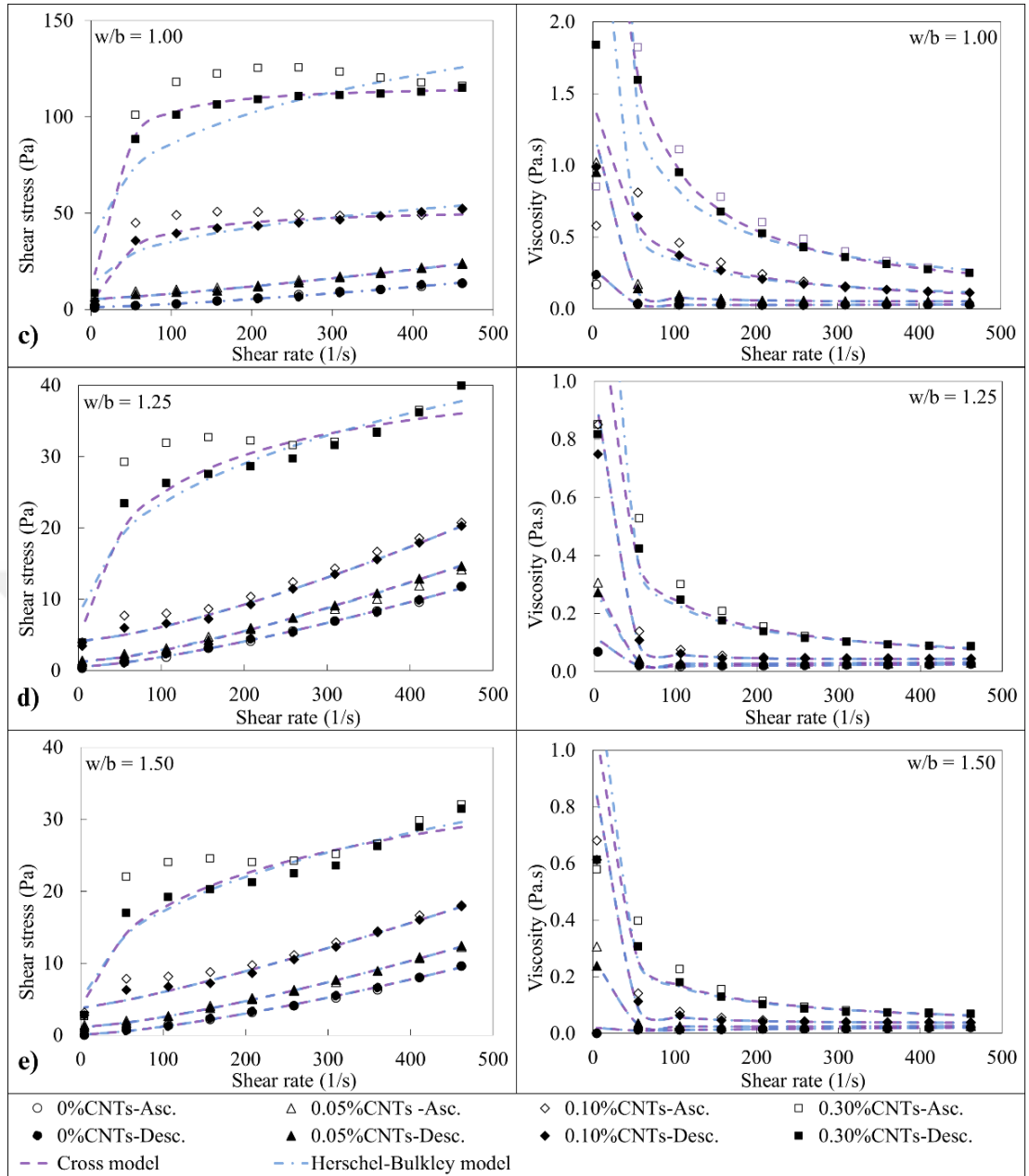


Figure 4.3 (cont.) Rheological curves and measurements

As shown in Figure 4.4, different fluid flow behaviors can be categorized based on the relationship between shear stress and shear rate and the presence of yield stress. Newtonian fluids (Figure 4.4.II) exhibit a linear relationship between shear stress and shear rate, with a constant viscosity regardless of flow conditions (e.g., water). In contrast, non-Newtonian fluids show a more complex response: shear-thinning fluids, also known as pseudo-plastic, display decreasing viscosity with increasing shear rate due to structural alignment or disentanglement, as seen in materials like paints or polymer solutions (Figure 4.4.III) while shear-thickening, or dilatant, fluids

exhibit increasing viscosity with shear rate, often due to particle interactions or jamming effects, which are common in suspensions (Figure 4.4.I). On the other hand, yield stress fluids require minimum stress, i.e., yield stress, to initiate flow. The fluid with constant viscosity regardless of shear rate is known as Bingham plastic (Figure 4.4.V). Furthermore, yield stress fluids can exhibit shear-thinning (Figure 4.4.VI) or shear-thickening (Figure 4.4.IV) behaviors.

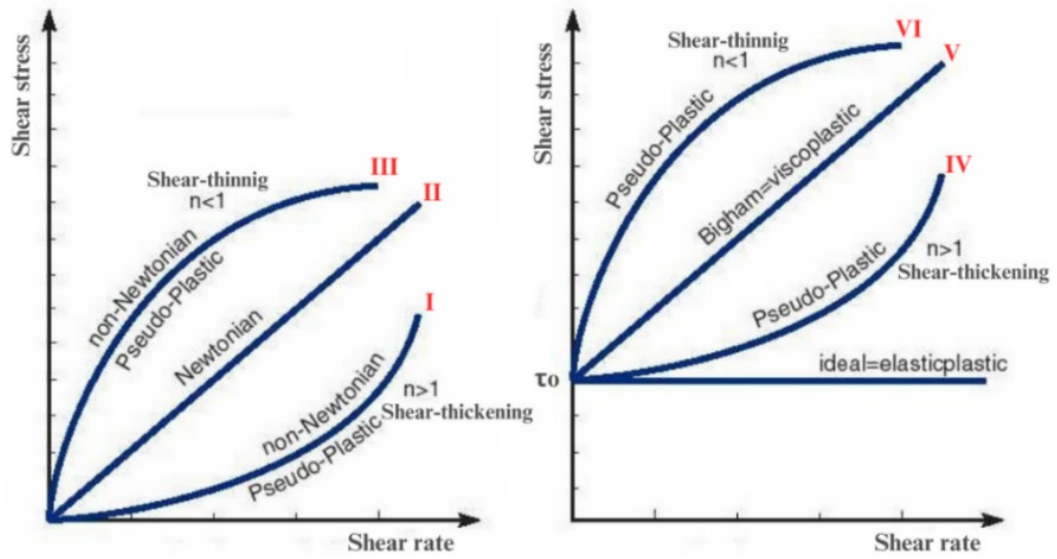


Figure 4.4 Flow behaviors

To discriminate yield stress fluids and quantify shear-thinning or shear-thickening behavior, which is observed in rheological curves (Figure 4.3), Herschel-Bulkley models parameters (τ_0, K, n) are evaluated as given in Table 4.4. Not only that, the Cross model parameters are presented in Table 4.5 for further discussion.

The findings from the Herschel-Bulkley model parameters provide insights into the rheological properties of the grout mixtures. Mixtures with $\tau_0 = 0$ (e.g., G11, G21, G53) exhibit shear-thinning behavior ($n < 1$). In contrast, grout mixtures with $\tau_0 > 0$, such as G20, G30, and G52, show shear-thickening behavior ($n > 1$), where viscosity increases under stress. Furthermore, the power law index (n) of the Herschel-Bulkley model and the dimensionless rate constant (m) of the Cross model classify grout samples as shear-thinning or shear-thickening in a compatible manner (see Table 4.4 and Table 4.5).

Table 4.4 Herschel Bulkley model parameters and flow type

ID	Herschel-Bulkley model parameters			Flow type (Representative curve in Fig. 24)
	τ_0 (Pa)	K	n	
G10	0.336	9.141	0.348	$\tau_0 > 0, n < 1$ pseudo-plastic shear-thinning (VI)
G11	0.000	31.507	0.380	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G20	3.140	0.022	1.157	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G21	0.000	9.072	0.317	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G22	0.000	19.547	0.318	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G23	0.000	27.301	0.425	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G30	1.175	0.004	1.330	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G31	5.292	0.011	1.220	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G32	0.000	9.580	0.282	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G33	0.000	27.291	0.250	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G40	0.482	0.003	1.343	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G41	1.186	0.004	1.359	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G42	4.105	0.004	1.368	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G43	0.000	5.468	0.315	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)
G50	0.075	0.002	1.385	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G51	1.110	0.003	1.352	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G52	3.815	0.009	1.214	$\tau_0 > 0, n > 1$ pseudo-plastic shear-thickening (IV)
G53	0.000	3.359	0.355	$\tau_0 = 0, n < 1$ Non-newtonian shear-thinning (III)

Even though plastic viscosity could not be obtained with the Herschel-Bulkley model, the consistency index (K) denotes grout's resistance to flow under shear, with elevated values signifying thicker, more resistive flow (e.g., G11) and diminished values indicating a more fluid-like behavior (e.g., G33). The rheological properties are essential for assessing the grout's appropriateness for various purposes—shear-thinning combinations facilitate efficient pumping and injection, such as permeation grouting applications (Houlsby, 1990; Nonveiller, 2013), whereas shear-thickening mixtures are preferable for applications requiring flow resistance such as compaction grouting or sealing grouts (Bruce et al., 1997; Y. Liu et al., 2021, 2024).

Table 4.5 Cross model parameters

ID	μ_0 (Pa.s)	μ_∞ (Pa.s)	t	m
G10	7.71	145.89	0.00	0.60
G11	0.00	345.99	0.01	0.81
G20	3.14	101414.05	0.00	1.16
G21	0.00	64.92	0.02	0.76
G22	0.00	125.40	0.03	0.91
G23	6.38	303.82	0.02	1.55
G30	1.17	47571.96	0.00	1.33
G31	5.29	172739.41	0.00	1.22
G32	0.00	53.10	0.03	1.00
G33	0.00	116.61	0.05	1.17
G40	0.48	69475.32	0.00	1.34
G41	1.29	84.25	0.00	1.53
G42	4.10	55778.84	0.00	1.37
G43	0.00	49.39	0.01	0.65
G50	0.07	43596.72	0.00	1.38
G51	1.11	26563.92	0.00	1.35
G52	3.82	7035.66	0.00	1.22
G53	0.00	56.53	0.00	0.51

The Cross model parameters (Table 4.5) allow the assessment of low w/b and high CNT-added grouts like concentrated polymer solutions and melts, which can be represented for flow behavior with zero-shear (μ_0) and infinite-shear viscosity (μ_∞). The highest μ_0 value was found for plain grout with a w/b ratio of 0.5 as 7.71 Pa.s, then the addition of 0.05% CNTs dropped initial viscosity to zero (Chen et al., 2023; Y. Liu et al., 2021). Except from w/b = 0.75 grouts, the lowest μ_0 results were obtained at 0.30% CNT-added grouts, expected to stem from CNT agglomeration due to the abundance of material in the solution. The shear-thickening grout mixtures showed unrealistically high infinite-shear viscosity (μ_∞), which, as previously stated, can be modeled best with the Herschel-Bulkley (HB) model.

HB model's yield stress dependency to w/b and CNT% investigated i) CNT addition ratio changes for varying w/b ratios (Figure 4.5.a) and ii) for w/b ratio increase for varying CNT addition ratios (Figure 4.5.b). The highest yield stress value (5.292 Pa) was obtained for G31 (w/b =1 and 0.05%CNT) while 0.03%CNT grouts (G23, G33, G43, and G53) have zero yield stress regardless of w/b ratio (Figure 4.5.a). By comparing the maximum yield stress shifting through higher w/b ratios for other CNT-addition levels, positive yield stress values are expected to be seen for w/b

levels higher than 1.5. Even though the highest yield stress was obtained from 0.05% CNT grout, 0.10% grout shows the second (4.105 Pa) and third (3.815 Pa) highest values.

Upon examining Figure 4.5.b, $w/b = 1.25$ and $w/b = 1.5$, grouts show a similar trend, which peaks at 0.10% CNT addition with a gradual increase from plain grout and then drops to zero at 0.30% CNT dosage. $w/b = 1$ showed an exaggerated version of higher w/b ratio grouts with lesser CNT addition to reach peak value. Contrarily, low w/b ratios showed a decreasing trend of yield stress for increasing CNT addition. The results emphasize the critical balance between CNT concentration and water content in optimizing rheological properties.

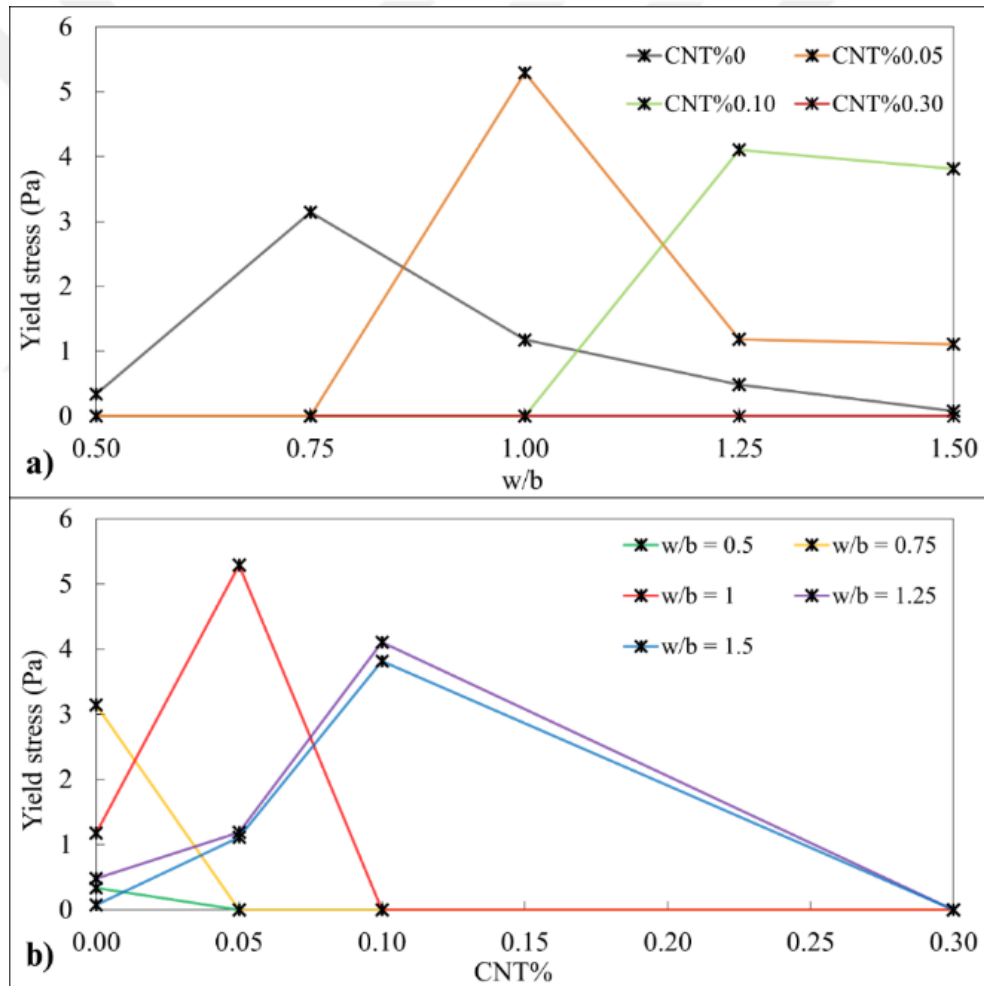


Figure 4.5 Yield stress dependency of factors a) yield stress versus w/b ratio b) yield stress versus CNTs addition rates

4.2 Mini-slump Results and Yield Stress

Figure 4.6 presents the mini-slump spread patterns and the average spread diameters of the mixtures.

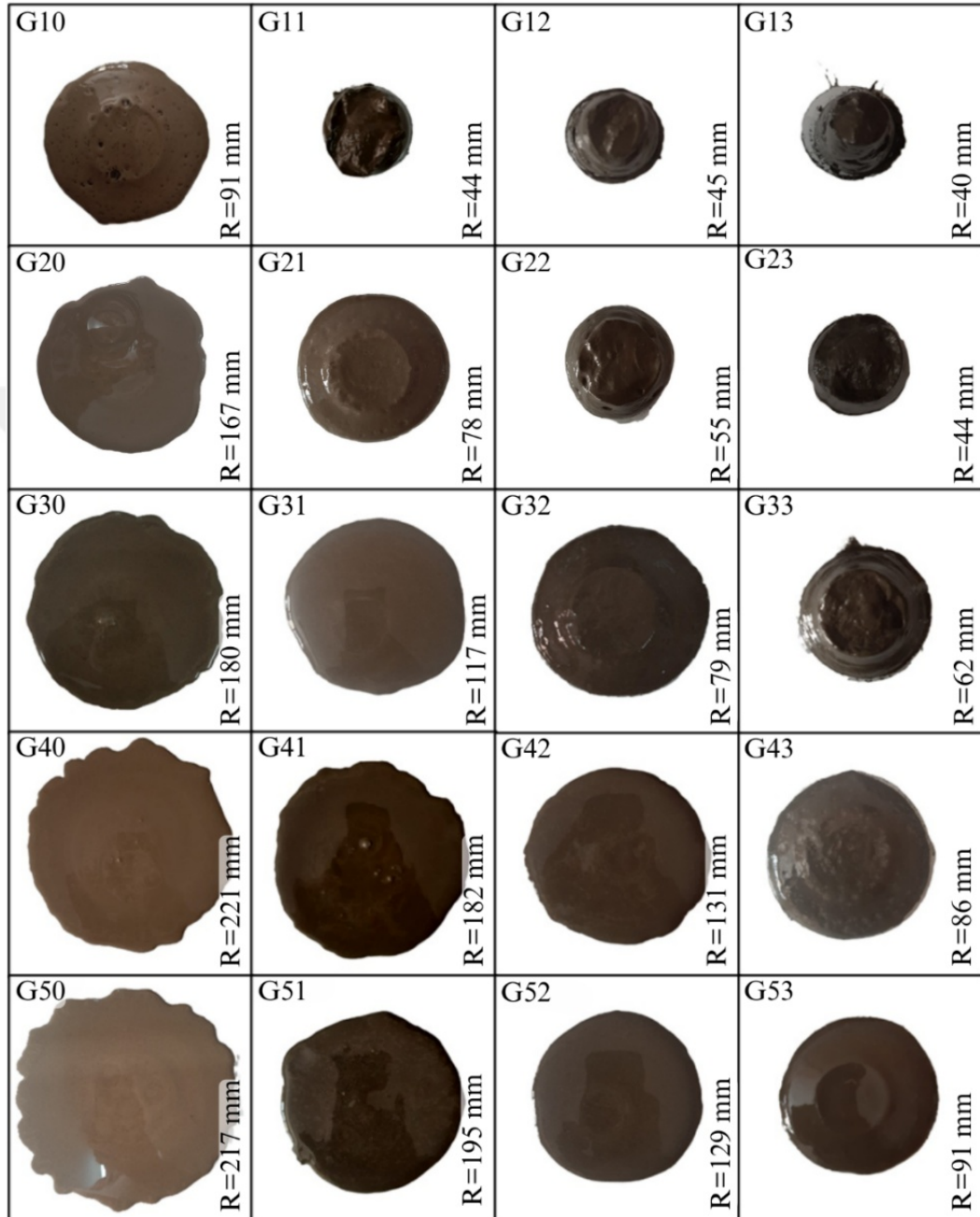


Figure 4.6 Minislump spread patterns and diameters of grout mixtures

The comparison of the spread thickness (H) and spread diameters (R) reveals that certain mixtures - those with CNTs/s = 0.05%, 0.10%, and 0.30% at w/b = 0.5; CNTs/s = 0.10% and 0.30% at w/b = 0.75; and CNTs/s = 0.30% at w/b = 1- spread diameter are smaller than spread thickness, which means they do not conform to a

pure shear flow regime ($H \gg R$) (Roussel & Coussot, 2005). The yield stress (τ_o) of grout mixtures demonstrating pure shear flow was calculated using Equation 4.4 (Pierre et al., 2013; Tan et al., 2017), which relates the yield stress to the grout's density (ρ), the volume of the mini-slump cone (Ω), and the mini-slump spread diameter (R):

$$\tau_o = \frac{225\rho g\Omega^2}{128\pi^2 R^5} \quad (4.4)$$

where g denotes the acceleration due to gravity (9.81 m/s^2). The density of each grout mixture was determined based on its composition and the densities of its individual components. Yield stress results are calculated with mini-slump results shown in Table 4.6.

Table 4.6 Yield stresses based on mini-slump

ID	R (mm)	ρ (gr/cm ³)	Minislump τ_o (Pa)
G10	91	1.835	0.73
G11	44	1.824	-
G12	45	1.814	-
G13	40	1.773	-
G20	167	1.64	0.031
G21	78	1.631	1.404
G22	55	1.623	-
G23	44	1.59	-
G30	180	1.518	0.02
G31	117	1.511	0.171
G32	79	1.504	1.214
G33	62	1.476	-
G40	221	1.436	0.007
G41	182	1.429	0.018
G42	131	1.423	0.092
G43	86	1.398	0.738
G50	217	1.376	0.007
G51	195	1.37	0.012
G52	129	1.364	0.095
G53	91	1.341	0.534

The highest yield stress results for G21 at 1.404 Pa between the grouts conformed to a pure shear flow regime because of high CNT addition and low w/b ratio. Table 4.6 shows a gradual increase in yield stress with an increasing CNT-addition ratio and decreasing w/b ratio. The complicated trends of yield stress results obtained by the rheometer test were not seen here. The flow stop mechanism is different from the

rheometer testing system; even at low shear rates, it is expected that the interaction forces between cement particles and carbon nanotubes (e.g., van der Waals forces) affect minislump flow characteristics (instead of CNT alignment and orientation which is dominant in rheometer results) which are positively correlated with the CNT-addition rate and negatively correlated with the w/b ratio, which is already known from the literature.

4.3 Strength Performances

UCS test results of all grout mixtures are corrected for seating/bedding errors, as shown for G50 in Figure 4.7.a. The strain at failure values, where the maximum UCS is retained, and elastic modulus are calculated based on corrected strains. Except from w/b = 0.75 grouts (Figure 4.7.c), the addition of CNTs has a negative effect on the peak axial strength of the grouts indeed to the extent that for high w/b ratios (i.e., 1, 1.25, and 1.5), the gap between plain grout and CNT-added grouts gets more prominent (Figure 4.7.d-f). On the other hand, stress-strain curves are flattened compared to the control group grouts (no CNT), which shows a switch to ductile behavior with the addition of CNTs. Contrary to relatively regular patterns of relatively high w/b grouts, the grouts of w/b=0.5 and 0.75 exhibit complicated patterns (Figure 4.7.b and 4.7.c).

Peak axial strength changes concerning the CNT addition percentage (Figure 4.8.a) show a general trend for relatively high w/b ratios (i.e., 1, 1.25, and 1.50) that increase in CNT dosage causes a decrease up to 0.10%, then stays mainly stable. In addition, w/b=0.5 grout samples show a similar trend with a slight strength increase after 0.10% CNT addition level. The peak axial strength values range between 22.39 MPa (G11) and 4.32 (G53) for CNT-added grouts. Even though CNT addition decreased the peak axial strength, the final results are still enough for soil grouting application through any grouting techniques (i.e., > 0.4 MPa) (Güllü et al., 2023).

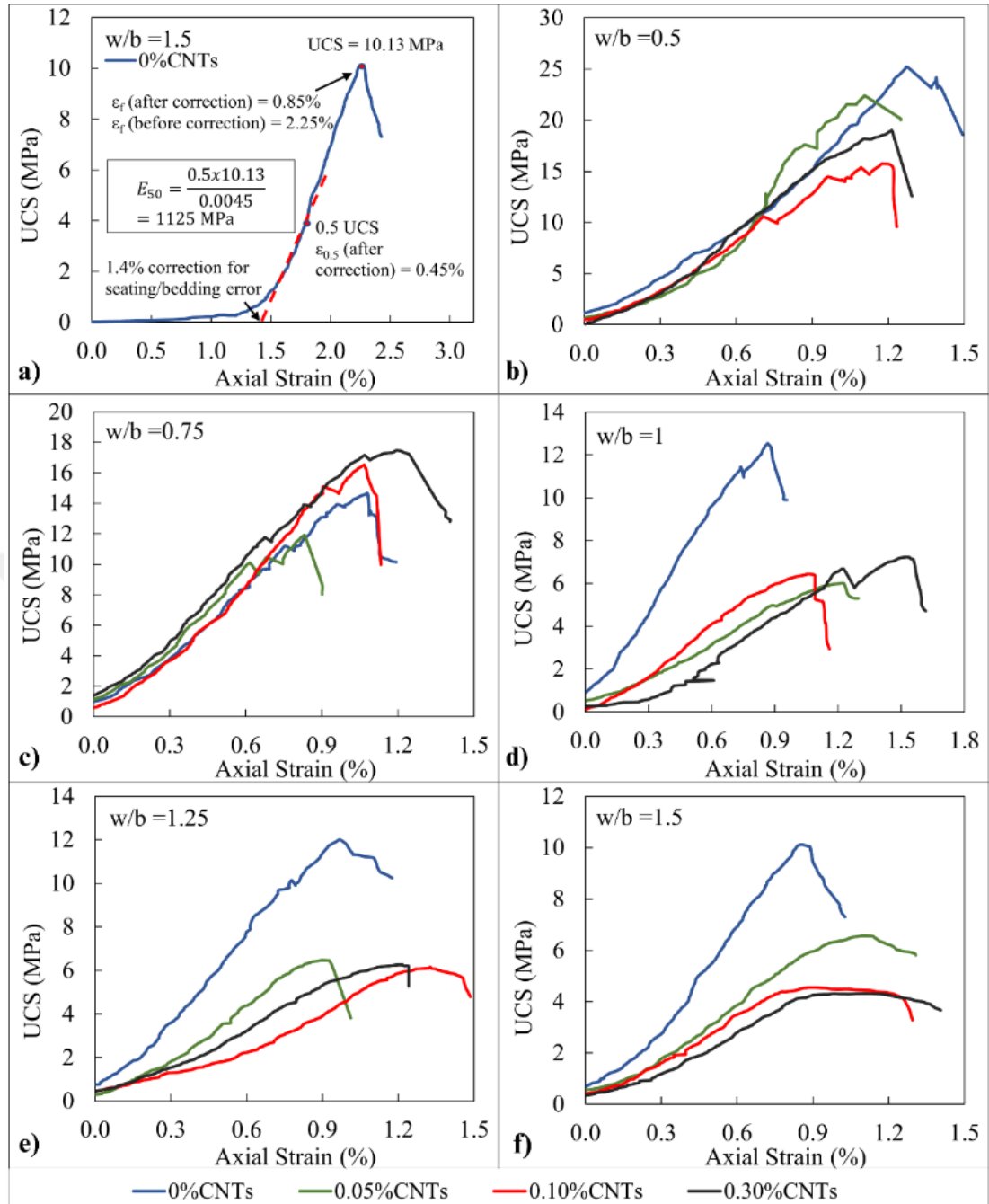


Figure 4.7 UCS test curves a) seating/bedding correction and calculations b-f) UCS versus axial strain graphs for varying w/b ratios

The elastic modulus, representing the stiffness of the grout, shows mainly two patterns based on w/b ratios. Low w/b ratio grouts' elastic modulus (i.e., 0.5 and 0.75) decreases after 0.05% CNT addition level but rebounds after 0.10 CNT% dosage. While w/b = 0.5 has the highest elastic modulus at 0% CNT level (plain cement) as 1620.87 MPa, w/b = 0.75 peaked at the highest CNT addition (i.e., 0.30%) as 1645.93 MPa. Relatively high w/b ratio grouts (i.e., 1, 1.25, and 1.5)

showed a dramatic decrease by adding 0.05% CNTs, then elastic modulus results fluctuate in a small range seamless to each other. Due to the importance of ductility, the lower elastic modulus is preferable for grout materials; therefore, 0.10% addition of CNT for low w/b ratios (which results in 1341.68 MPa and 1416.33 MPa for w/b =0.5 and w/b=0.75, respectively) and 0.30% dosage of CNTs for high w/b ratio grouts (i.e., w/b = 1, 1.25 and 1.50) with a measured elastic modulus of 463.32 MPa, 538.41 MPa, and 432.08 MPa in increasing order of w/b ratio are found to preferable dosages.

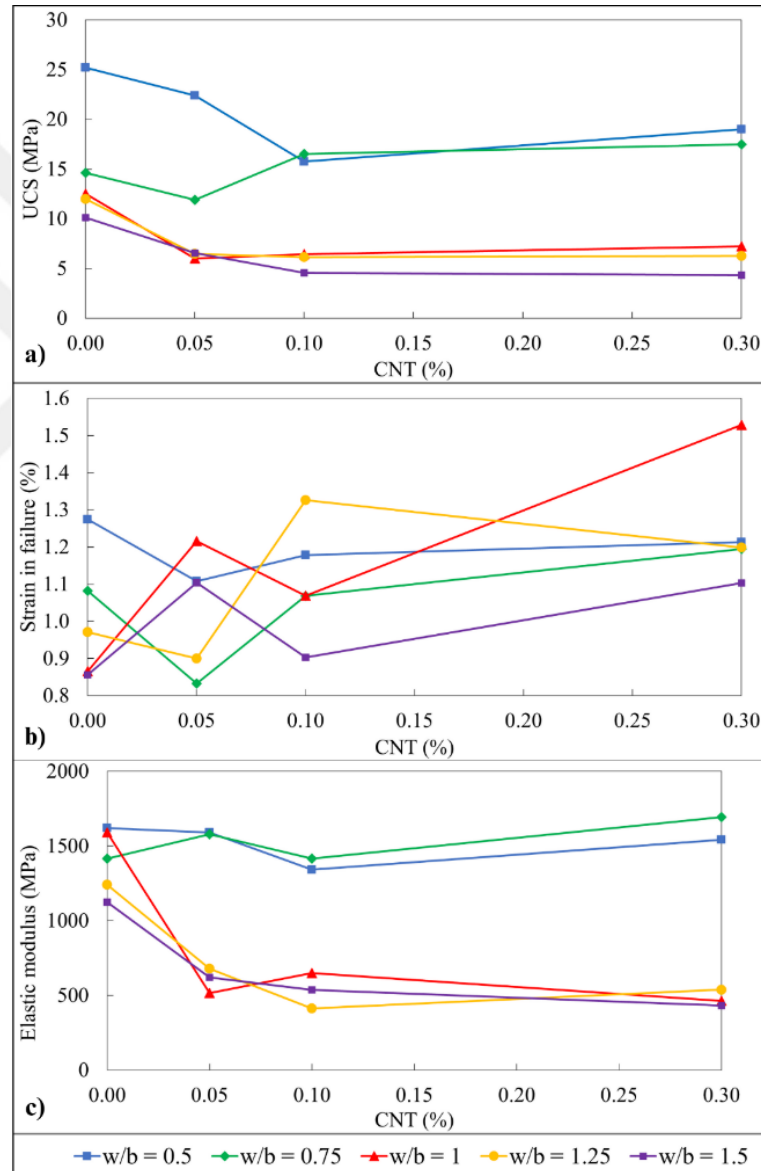


Figure 4.8 UCS test results versus CNT addition ratio a) peak axial strength b) strain at failure c) elastic modulus

4.4 Development of Strength with Curing Age and Early Strength

4.4.1 UPV Results

Table 4.7 shows 7, 14, and 28 days results of UPV which are enable to investigate influence of w/b ratio and CNT addition on grout densification (i.e., hardness), change throughout curing period. Similar to UCS results, adding CNTs decreases grouts' UPV. The highest result for G10 (w/b=0.5 and no CNTs) was 3471 m/s, while the lowest value measured on G53 (w/b=1.5 and 0.30% CNT dosage) was 1991m/s. According to Annon (1979), the strength quality of hardened material based on sonic velocity can be classified as below 2500 m/s, which is very low, and 2500-3500 m/s, which is low for soft and hard rocks. If hardened grout mixtures are subjected to this criterion, CNT-added grouts with a w/b ratio of 1 or higher are classified as very low, while other grouts and plain cement grouts are categorized as low. It should be noted that this criterion is for rocks, which are much denser materials compared to binder-based materials, e.g., cementitious grouts.

Even though CNTs have a decreasing effect on UPV results, the change compared to plain cement grouts becomes more dramatic with increasing w/b ratios. For 28-day results, a 0.30% addition of CNT caused a decrease of 2.85% at w/b =0.5 ratios (i.e., G10 to G13), while the same amount of dosage resulted in a diminishing of 24.78% at w/b = 1.5 ratios (i.e., G50 to G53). However, when the exact comparisons were made for 7-day results, the decrease ratio became more dramatic for w/b = 0.5 as 3.18% unlikely that the decrease lessens for w/b = 1.5 as 22.95%. It is understood that at low w/b ratios due to interaction between hydration products of cement (e.g., C-S-H, CH) and carbon nanotubes, the decreasing effect is seen early because of the faster hydration process, then grout gains strength because of the curing process. On the other hand, slower progress of the hydration process postpones the effect to a further period.

Table 4.7 UPV results and UCS counterparts

ID	w/b	CNTs (%)	UPV (m/s)			UCS (MPa)		
			7 day	14 day	28 day	7 day*	14 day*	28 day
G10	0.50	0.00	3269	3311	3471	18.73	19.26	25.21
G11	0.50	0.05	3201	3248	3447	17.86	18.46	22.39
G12	0.50	0.10	3114	3061	3321	16.76	16.08	15.76
G13	0.50	0.30	3165	3201	3372	17.40	17.86	19.01
G20	0.75	0.00	2754	2754	2977	12.18	12.18	14.64
G21	0.75	0.05	2624	2769	2903	10.53	12.38	11.90
G22	0.75	0.10	2556	2706	2831	9.67	11.58	16.52
G23	0.75	0.30	2758	2774	2935	12.24	12.44	17.49
G30	1.00	0.00	2692	2791	2935	11.40	12.65	12.53
G31	1.00	0.05	2190	2143	2338	5.027	4.43	6.01
G32	1.00	0.10	2438	2163	2302	8.17	4.68	6.43
G33	1.00	0.30	2265	2327	2435	5.97	6.76	7.22
G40	1.25	0.00	2452	2624	2778	8.35	10.53	12.00
G41	1.25	0.05	2284	2479	2647	6.22	8.69	6.47
G42	1.25	0.10	1996	2077	2228	2.56	3.59	6.16
G43	1.25	0.30	1957	1991	2123	2.06	2.49	6.26
G50	1.50	0.00	2370	2432	2647	7.31	8.10	10.13
G51	1.50	0.05	1899	2103	2278	1.33	3.92	6.56
G52	1.50	0.10	2162	2151	2304	4.67	4.53	4.56
G53	1.50	0.30	1826	1957	1991	0.40	2.06	4.32

* Estimated by 28 days UPV-UCS correlation

The influence of w/b and CNT dosage on UPV results are visualized for 28-day results in Figure 4.9.a. A gradual decrease of UPV results can be observed with increasing CNT addition, while UCS results of 28 days react more aggressively to the exact amounts of CNTs shown in Fig 29.b. Even though changes are not at the same rates, a correlation between them can be used to obtain early strength of enhanced grout (i.e., asymptotic UCS results of 7 and 14 days).

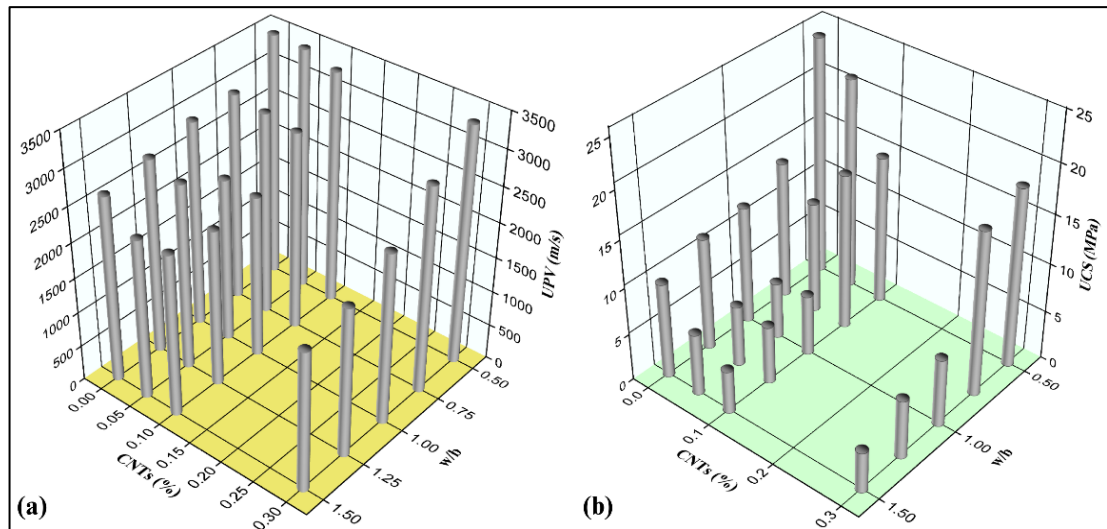


Figure 4.9 28 days results of a) UPV b) UCS

Figure 4.10 shows a linear regression of UPV-UCS results for 28 days. The R^2 value of 0.8725 indicates a reasonably strong (≥ 0.8) linear relationship (Smith, 1986). The trend line equation of $y = 0.0127x - 22.786$ was used to estimate grout mixtures' 7- and 14-day UCS values (Table 4.7). The minimum UCS result found for G53 (w/b = 1.5 and CNT dose of 0.30%) after 7 days of curing is 0.4 MPa, which remains at the threshold for the requisite bearing strength of construction foundations during ground improvements (i.e., >0.4 MPa).

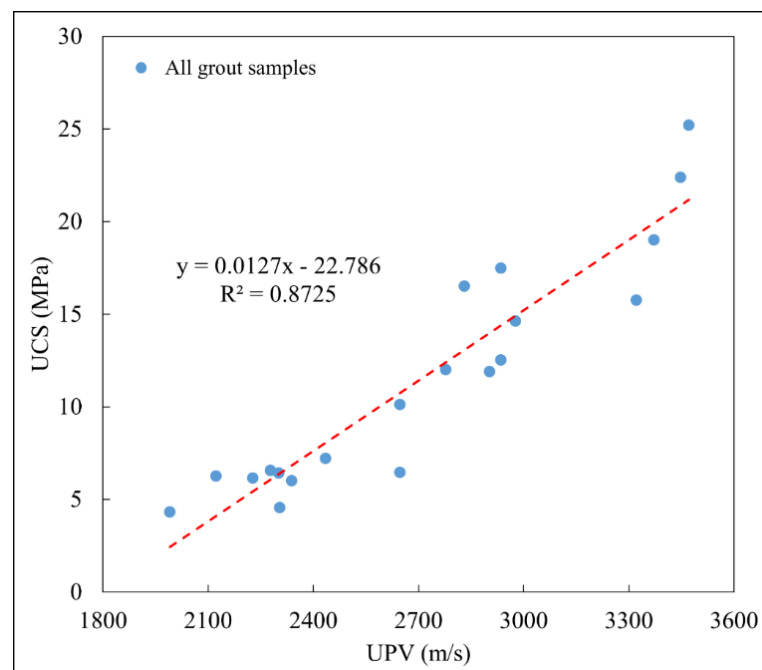


Figure 4.10 UPV-UCS correlation

4.4.2 Electrical Resistivity Results

The electrical resistivity results are presented in Table 4.8. CNT addition increased the resistivity of enhanced grouts by 2.68% on average after 28 days of curing compared to plain grout. Also, the resistivity increase of 7-day measures shows an average increase of 1.44%, which shows that the effect became more evident with curing time. The highest resistivity result of 28 days found for G13 was 9.29 k Ω m, while the lowest result of enhanced grouts measured for G33 was 8.65 k Ω m. It is worth emphasizing that even though G33 has the second lowest 28-day resistivity (8.72 k Ω m), it also shows the highest increase in resistance from 7 days to 28 days at 6.47%. It is relatively high compared to the average increase of all enhanced grouts, 1.99%.

Table 4.8 Electrical resistivity results during the curing period

Grout ID	w/b	CNT%	Resistivity, ρ (k Ω m)		
			7 days	14 days	28 days
G10	0.5	0	8.02	8.00	8.02
G11	0.5	0.05	8.67	8.60	9.09
G12	0.5	0.1	8.93	8.93	9.06
G13	0.5	0.3	9.14	9.24	9.29
G20	0.75	0	8.73	8.79	8.96
G21	0.75	0.05	8.99	9.14	9.05
G22	0.75	0.1	8.76	8.93	9.01
G23	0.75	0.3	8.83	8.96	9.03
G30	1	0	8.89	8.91	8.93
G31	1	0.05	8.96	8.95	9.08
G32	1	0.1	8.19	8.24	8.72
G33	1	0.3	8.56	8.55	8.65
G40	1.25	0	9.04	9.11	9.17
G41	1.25	0.05	9.03	9.10	9.16
G42	1.25	0.1	8.84	8.81	8.89
G43	1.25	0.3	9.00	9.06	9.19
G50	1.5	0	9.04	9.09	8.98
G51	1.5	0.05	8.95	9.08	9.12
G52	1.5	0.1	8.85	8.97	8.91
G53	1.5	0.3	9.08	9.10	9.13

Figure 4.11 illustrates the evolution of electrical resistivity over curing time by average values of grouts of the same w/b ratio and average values of grouts with the same CNT dosage. The average values for w/b = 0.5 and w/b =1 show a similar trend, even though individual grout behavior is distinctly different. Moreover, w/b

=1.25 shows a nearly linear increase of electrical resistivity while $w/b = 0.75$ and $w/b = 1.5$ surged and declined at 14 days (Figure 4.11.a). Conversely, CNT dosage shows a relatively straightforward increase during the curing period. While CNT addition of 0.05% and 0.30% shows similar trends and values during the process, CNT dosage of 0.10% grouts follows them with nearly 2 k Ω m lower results (Figure 4.11.b).

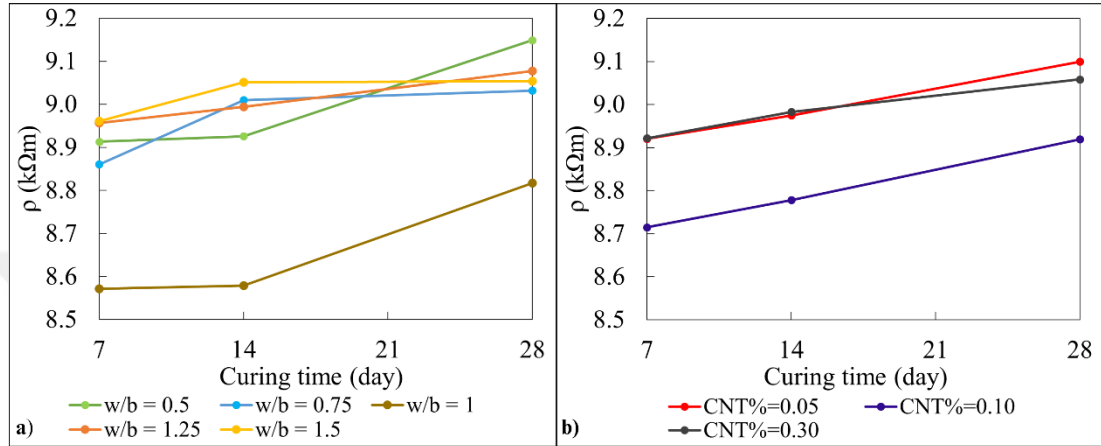


Figure 4.11 The average electrical resistivity results during the curing period a) for w/b b) for CNT%

Figure 4.12 shows the relationship between ultrasonic pulse velocity (UPV) and electrical resistivity throughout curing time (7, 14, and 28 days). The trendline shows a weak negative correlation with an R^2 value of 0.0385. Even though UPV and electric resistivity shed light on early strength and curing period densification, a correlation was not found.

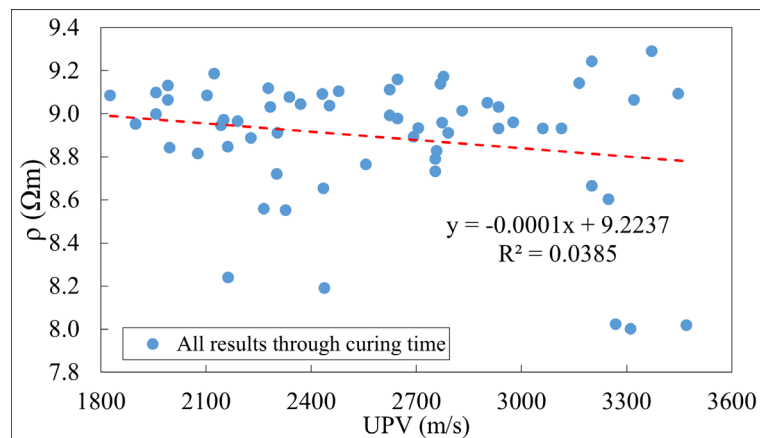


Figure 4.12 UPV-Electrical resistivity correlation.

4.5 Results Obtained Using Video Recording During UCS Testing

4.5.1 Crack Initiation and Propagation

Surface crack initiation and propagation were examined based on strain levels, as shown for G23 in Figure 4.13. With cameras placed at the front and back of the tested sample, the first surface crack initiation and cracks grow until peak axial strain is observed. The results of $w/b = 0.75$ and $w/b = 1.5$ grouts were evaluated as representatives of low w/b and high w/b level grouts, respectively (Figure 4.14).

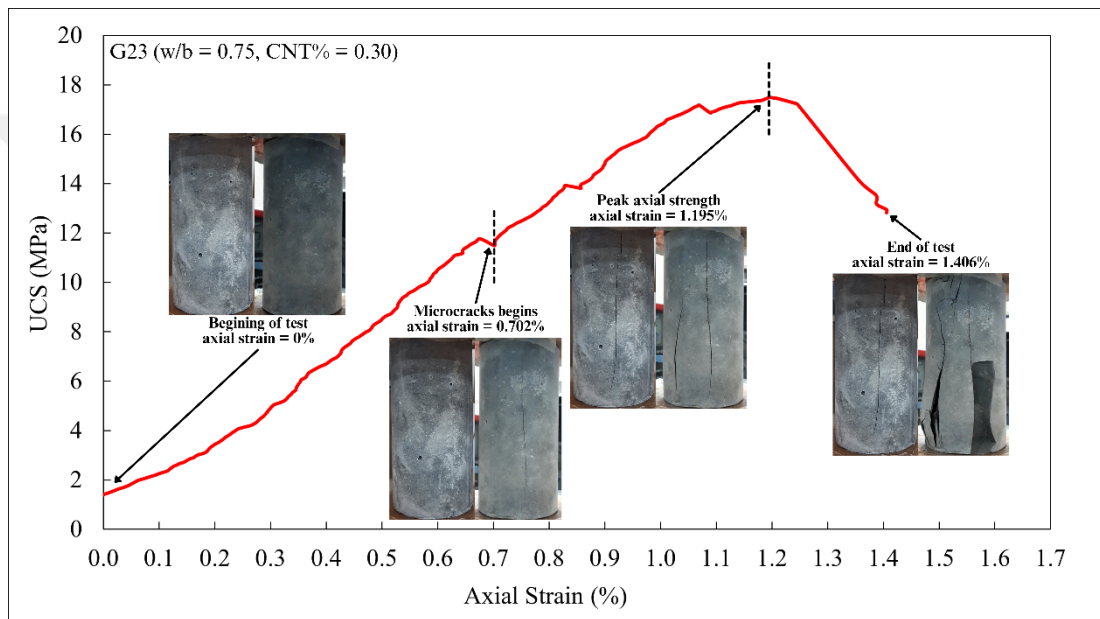


Figure 4.13 Axial strain and crack propagation of G23

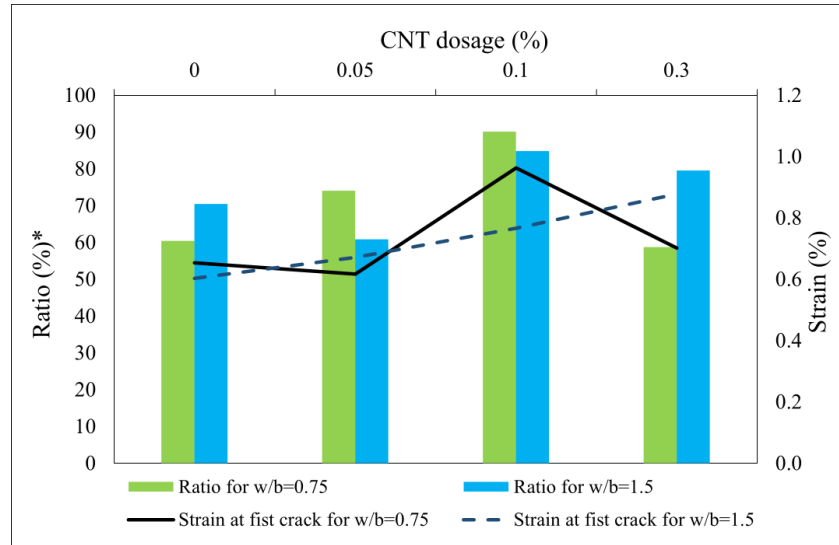


Figure 4.14 Strain at first crack comparison

The strain level of the first surface crack increases linearly with the addition of CNTs for $w/b = 0.75$ while $w/b = 1.5$ grouts show a fluctuated pattern which peaks at 0.10% CNT-addition. Moreover, 0.10% CNT dosage yields a higher strain level at the first surface crack to peak axial strain ratios for both w/b levels. It is understood that the addition of 0.10% CNTs by the weight of the solution prolonged the uncracked phase compared to the pristine sample, which is an increase from 60.48% to 90.12% for $w/b = 0.75$ and from 70.49% to 84.86 for $w/b = 1.5$.

4.5.2 DIC Analysis

Digital Image Correlation (DIC) is a modern, non-contact optical measurement technique widely used for evaluating material deformation. By capturing high-resolution digital images of a specimen's surface before and after deformation, DIC identifies pixel displacements to compute full-field displacement and strain maps (Hu et al., 2024; W. Li et al., 2020). This technique offers significant advantages over traditional methods like strain gauges, as it provides comprehensive strain distribution without requiring multiple point measurements (Kumar et al., 2019). The accuracy of DIC depends on factors such as image resolution, speckle pattern quality, and algorithm parameters. Open-source software Ncorr, developed by Blaber et al., 2015, is often used to process the captured images and analyze surface strain fields, which can be used from small-scale samples to significant structural elements and can accurately monitor strain and crack progression.

In this study, video recordings captured from both the front and back of specimen G23 ($w/b = 0.57$, CNT dosage = 0.30%) were analyzed using Ncorr software within the MATLAB environment. The strain and displacement variations relative to the reference image (i.e., the initial stage of the test) were evaluated at key stages of the test: just before surface cracking (Figure 4.15), at the onset of the first surface crack (Figure 4.16), at peak axial strength (Figure 4.17), and failure (Figure 4.18). The analysis provided strain field maps (ϵ_{xx} , ϵ_{yy} , and ϵ_{xy}) and displacement maps (U-displacement and V-displacement), which offer detailed insights into the specimen's behavior at each stage.

Figure 4.15.a shows the specimen's frame at a strain level of 0.676%, corresponding to the stage just before the first surface crack (observed at a strain level of 0.702%, as shown in Figure 4.16.a). Although the vertical displacements (Figure 4.15.f) and lateral displacements (Figure 4.15.e) demonstrate the deformation of the specimen under loading, the subsequent crack on the back of the specimen is not visible in the ϵ_{xx} strain field (Figure 4.15.c). This indicates that the crack location cannot be directly observed from the strain field due to the brittle nature of the material. However, cracks can be detected and their propagation tracked using DIC strain fields, where crack orientation depends on the loading direction and the material's failure patterns. For brittle cementitious grout, cracks typically form parallel to the loading direction, and ϵ_{xx} strain fields make it possible to monitor the development of these cracks (see Figure 4.15.c, 4.16.c, 4.17.c, and 4.18.c).

In Figure 4.18 (a-f), the lack of color observed in the crushed areas of the specimen's back view can be attributed to high local deformation or cracking. In these regions, significant strain and crack formation cause the speckle pattern to distort excessively, which makes it difficult for Ncorr to accurately match the pixel patterns between the reference and deformed images. This results in the software being unable to compute valid strain or displacement values for these areas. Similar issues have been reported in previous studies, where large deformations or crack propagation hindered accurate DIC analysis (Blaber et al., 2015).

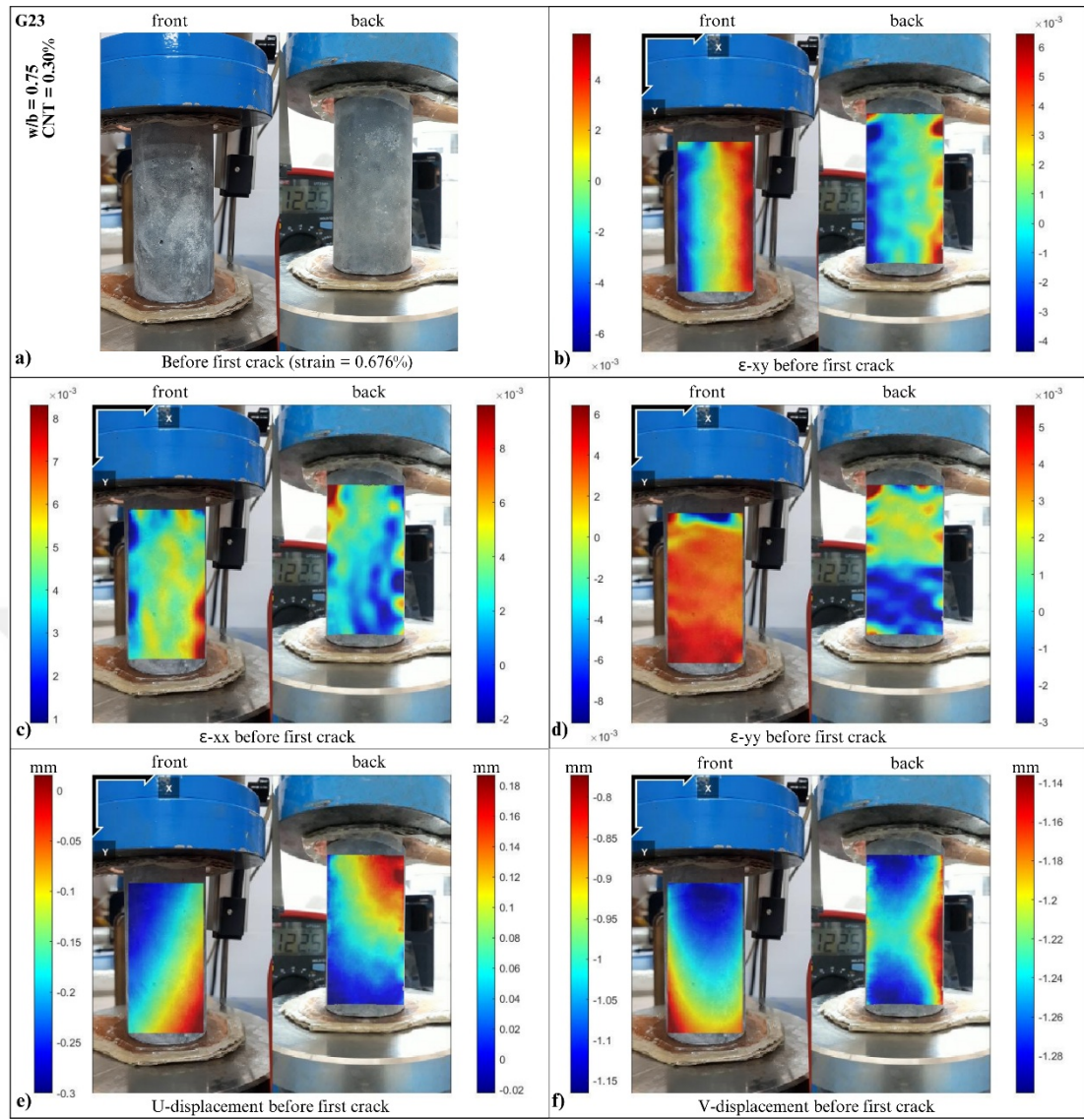


Figure 4.15 DIC analysis of G23 before the first crack

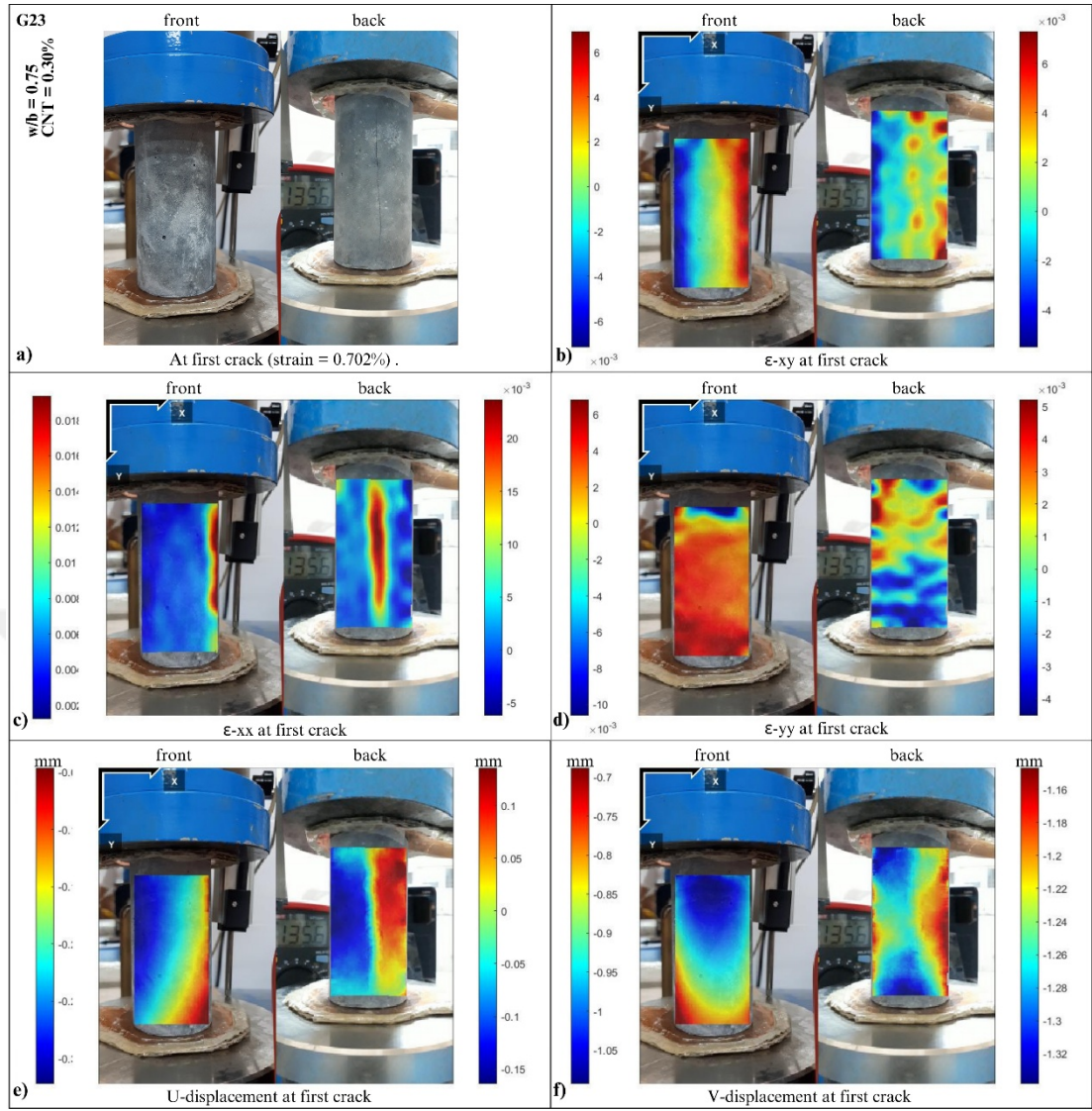


Figure 4.16 DIC analysis of G23 at first crack

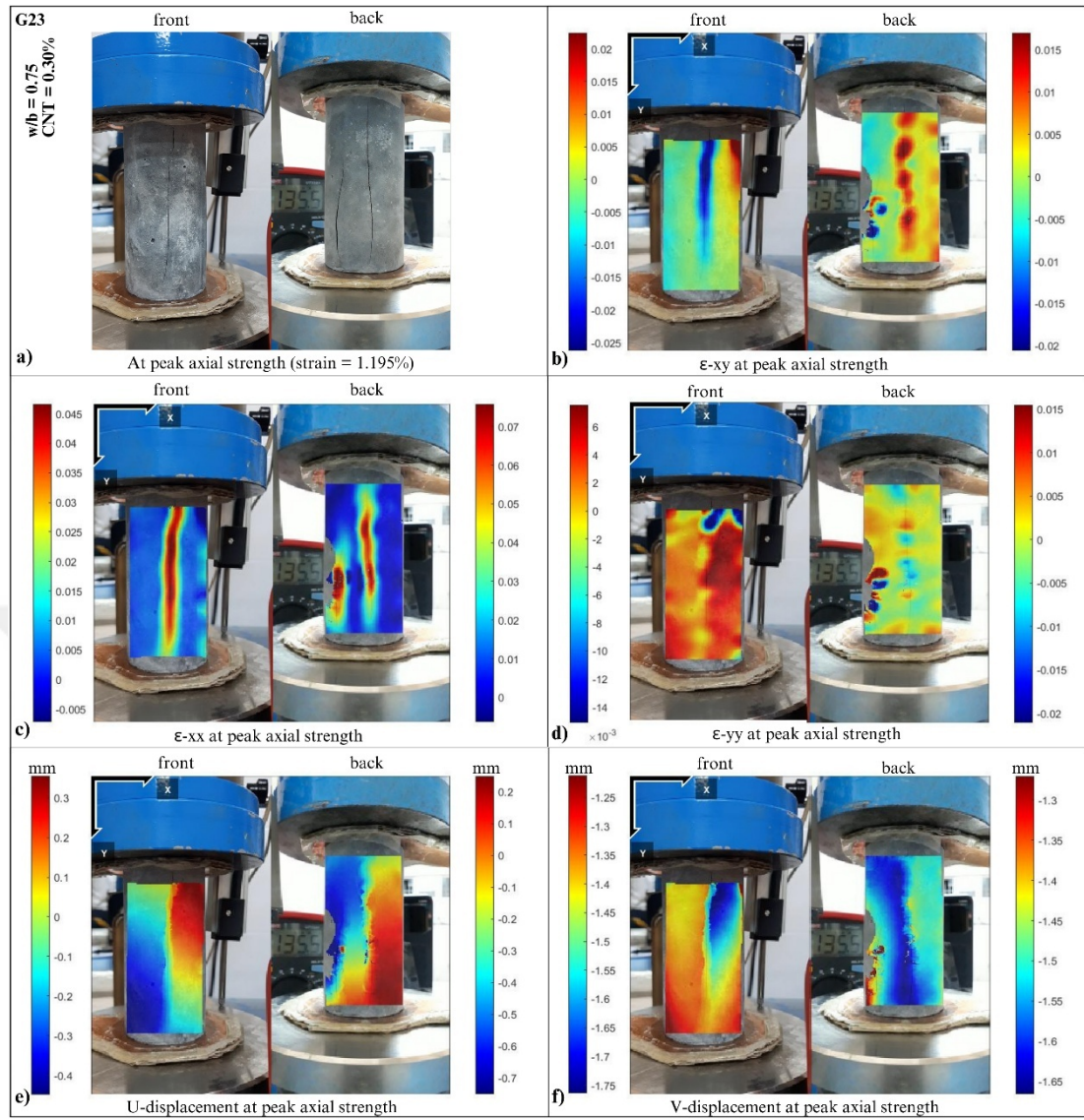


Figure 4.17 DIC analysis of G23 at peak axial strength

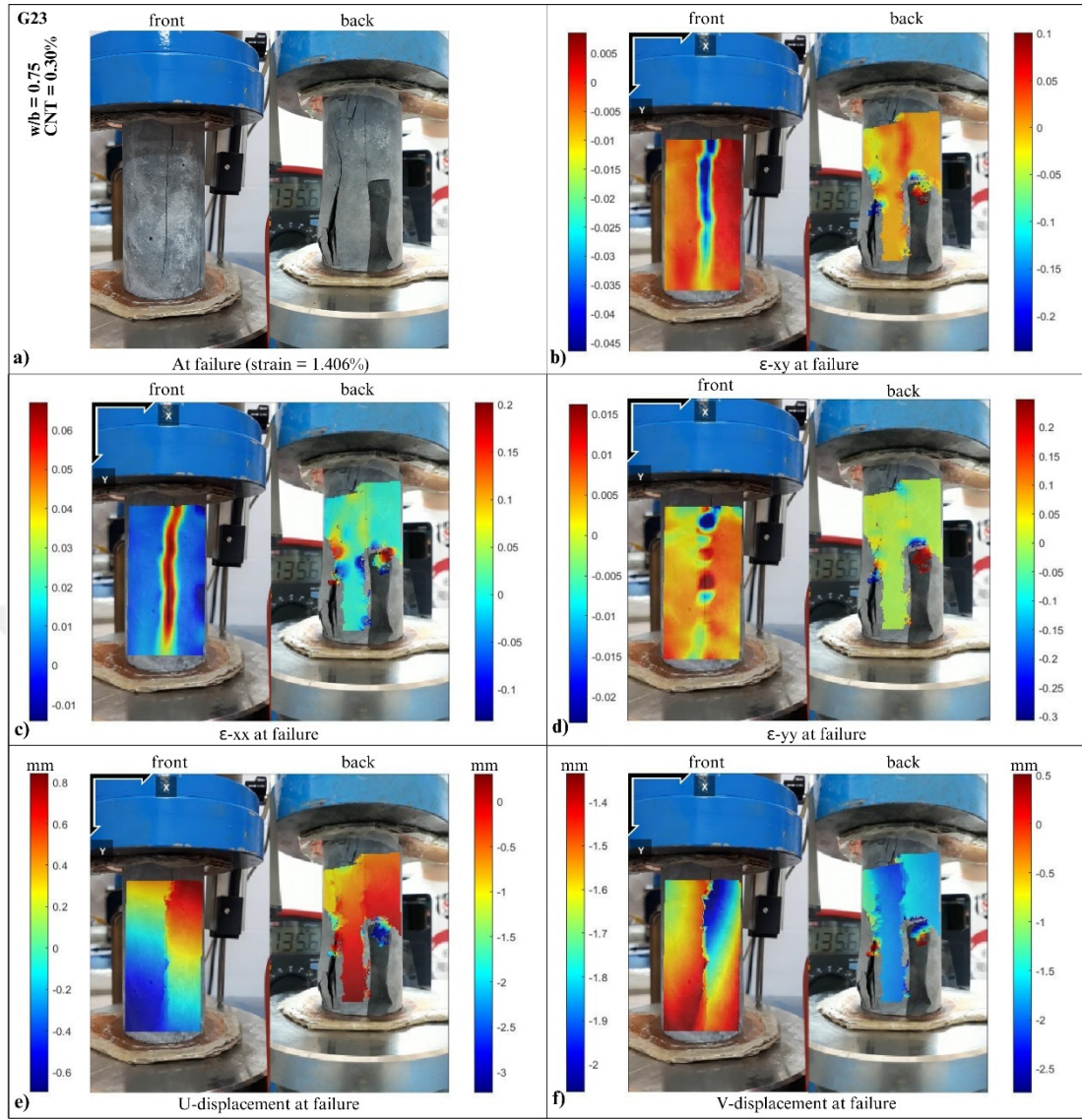


Figure 4.18 DIC analysis of G23 at failure

4.5.3 Failure Planes

The failure patterns of the grouts for all water-to-binder (w/b) ratios and carbon nanotube (CNT) dosage levels are shown in Figure 4.19. While the addition of CNTs generally decreases the failure load, it has a relatively minor impact on the overall configuration of the failure plane. Various failure mechanisms were observed, including axial splitting, single-plane shearing, double shearing, multiple fracturing, Y-shaped fracturing, extended foliation, and surface crushing (Canakci et al., 2019; Celik & Canakci, 2020; Güllü et al., 2023). These patterns typically occurred similarly and were characterized by axial splitting cracks, fractures, and some planar foliations. Such behaviors are expected due to the brittle nature of cementitious materials (Celik & Canakci, 2020).

The failure modes in control samples (without CNT addition) ranged from axial splitting to single-plane shearing. However, with CNT addition, the predominant failure mode shifted to axial splitting, and other complex failure modes, such as double shearing, multiple fracturing, Y-shaped fracturing, extended foliation, and surface crushing, were observed more frequently (e.g., Y-shaped fracture in G53). Additionally, as the CNT dosage increased, the number of failure planes increased (e.g., from G13 to G10 and G23 to G20). Specimens with higher CNT dosages demonstrated improved stability during unconfined compressive strength (UCS) tests, resisting complete collapse even after failure, likely due to the ductile behavior introduced by the nanotube addition.

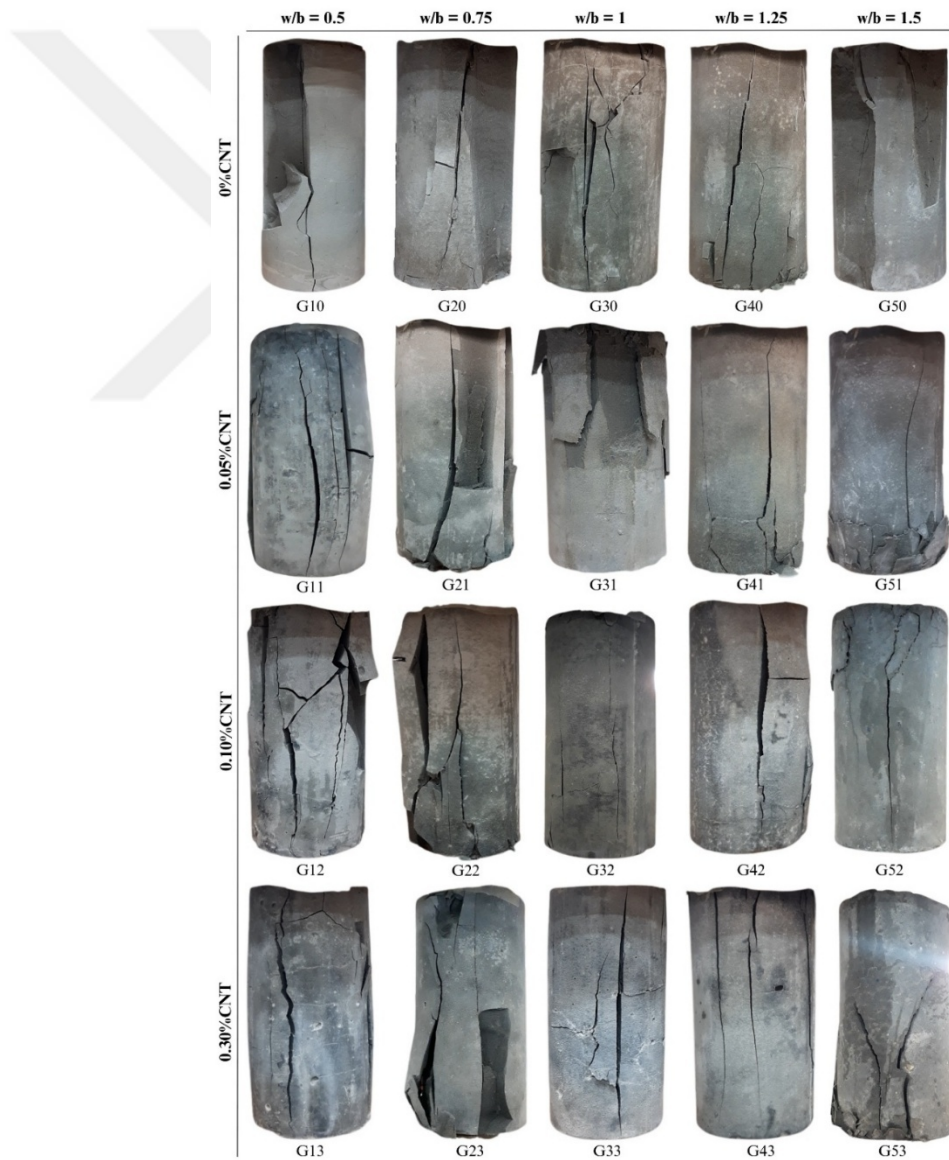


Figure 4.19 Failure planes of grout samples

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In this study, rheological, fresh properties, early strength, curing period, and mechanical and crack propagation characteristics of carbon nanotube-enhanced cementitious grouts are investigated thoroughly. This multifaceted investigation is hoped to contribute to the understanding and advancement of nano-modified grout performance and application in geotechnical applications. The following conclusions were made according to the test results of the current study.

- Based on the rheological model comparison for various water-binder ratios and carbon nanotube addition percentages, the Cross model has been found to be the most suitable model for low w/b ratios and high CNT additions due to carbon nanofibers structural alignment and debuting with flow as a similar phenomenon seen in polymer solutions. At the same time, Herschel-Bulkley became the best for high w/b ratios and low CNT additions for predictive accuracy, simplicity, and compatibility with elevated shear rates.
- Compared to plain cement-based grouts of varying water-binder ratios, the addition of CNTs shifts the flow behavior of grouts through shear thinning, and the transition of behavior becomes more evident at high w/b ratios, which can play an important role due to a decrease in the needed energy to accelerate the grout flow in geotechnical applications.
- The peak yield stress values were found to be obtained at higher w/b levels with increasing CNT dosage such that the grouts with 0.30% CNTs addition showed non-Newtonian shear thinning characteristics with zero yield value at all w/b ratio levels. The yield stress levels acquired with CNT addition can benefit pump grouts with less application effort.
- Mini-slump test results showed a gradual decrease in spread diameter with increasing CNT dosages, leading to a corresponding increase in yield stress results based on the mini-slump test. Although the mini-slump test provides a quick assessment of grout workability, its flow-stop mechanism differs from

response to shear forces based on the principle of rheometer testing. In mini-slump tests, van der Waals forces between cement particles and carbon nanotubes influence the stop mechanism; in contrast with rheometer results, CNT alignment and orientation dominate yield stress results. Due to the higher shear rates in rheometer testing, which better reflect the high flow speeds of grout during application, rheometer results should be prioritized over mini-slump measurement.

- The addition of CNTs has a negative effect on the peak axial strength of the grouts, which stands out more at high w/b ratios. However, stress-strain curves flatten failure strain shifts forward and decrease elastic modulus, which signifies a switch to a ductile behavior desired for grouts to be used for ground improvement applications where material deformations are not important. Moreover, even though CNT addition decreased the UCS results, grout performances are still enough for soil grouting application through any grouting techniques (i.e., > 0.4 MPa), even for the lowest value of 4.32 MPa.
- UPV results showed a similar adverse effect of CNT dosage on the grout mixture's hardness to UCS, and the trend becomes more evident for high w/b ratios. In the curing period densification aspect, the decrease in hardness compared to plain cement-based grout becomes higher for low w/b ratios, while for high w/b ratios, the decrease softens. Moreover, UPV-based early strength results showed that after 7 days of curing, even the grout mixture with the lowest UCS remains at the threshold for needed bearing strength of construction foundations during ground improvements.
- CNT addition increased the resistivity of enhanced grouts by 2.68% on average after 28 days of curing compared to plain concrete. Also, the resistivity increase of 7-day measures shows an average increase of 1.44%, which shows that the effect became more evident with curing time. However, when the samples are examined individually, it is observed that the addition of CNTs causes different effects at different w/b ratios. The percentage changes are also relatively small, except for the 0.5 w/b ratio. Therefore, the electrical resistivity results should be carefully considered.
- The incorporation of carbon nanotubes (CNTs) into cementitious grouts significantly improved their stability and ductility. Video recordings from

unconfined compressive strength (UCS) tests revealed that CNTs extended the uncracked phase and increased the strain at the initiation of the first surface crack, particularly at a 0.10% CNT dosage. The failure modes were notably altered, with a shift toward axial splitting and an increased frequency of complex failure mechanisms, including double shearing and Y-shaped fracturing.

- The use of Digital Image Correlation (DIC) provided valuable insights into the deformation and cracking behavior of cementitious grouts. While DIC strain fields cannot predict cracks before their occurrence due to the brittle nature of cementitious materials, once cracks initiate, DIC effectively detects and tracks their propagation.

Based on the findings and limitations of this study, the following recommendations are proposed to enhance future research and applications.

- Further investigations are needed for the rheological properties of carbon nanotube-enhanced cementitious grouts at higher shear rates for a more comprehensive understanding of the application of permeability grouts.
- In addition to the strength tests conducted in this study, investigating the tensile strength properties can provide a more comprehensive understanding of the material's mechanical characteristics.
- Coating or functionalization of CNTs for better dispersion and a more cohesive structure matrix with cement hydration products and the examination of structure using SEM during the curing period.

REFERENCES

- Akaike, H. (1973). Information theory and an extension of the maximum likelihood principle. *Trees - Structure and Function*, 29(6), 655–662. https://doi.org/10.1007/978-1-4612-0919-5_38
- Akaike, H. (1974). A new look at the statistical model identification. *IEEE Transactions on Automatic Control*, 19(6), 716–723. <https://doi.org/10.1109/TAC.1974.1100705>
- Anon, O. H. (1979). Classification of rocks and soils for engineering geological mapping. Part 1: Rock and soil materials. *Bulletin of the International Association of Engineering Geology*, 19, 364–437. <https://doi.org/10.1007/BF02600503>
- ASTM C942. (2015). Standard test method for compressive strength of G. Retrieved December 23, 2024, from <https://www.intertekinform.com/en-gb/standards/>
- ASTM International. (2024). ASTM C150/C150M-24—Standard specification for Portland cement. Retrieved from <https://webstore.ansi.org/standards/astm/astmc150c150m24>
- Balasubramanian, K., & Burghard, M. (2005). Chemically functionalized carbon nanotubes. *Small*, 1(2), 180–192. <https://doi.org/10.1002/sml.200400118>
- Barnes, H. A., Hutton, J. F., & Walters, K. (1989). *An introduction to rheology*. Rheology Series. Elsevier.
- Berber, S., Kwon, Y.-K., & Tománek, D. (2000). Unusually high thermal conductivity of carbon nanotubes. *Physical Review Letters*, 84(20), 4613–4616. <https://doi.org/10.1103/PhysRevLett.84.4613>
- Bethune, D. S., Klang, C. H., De Vries, M. S., Gorman, G., Savoy, R., Vazquez, J., & Beyers, R. (1993). Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature*, 363(6430), 605–607. <https://doi.org/10.1038/363605a0>
- Blaber, J., Adair, B., & Antoniou, A. (2015). Ncorr: Open-source 2D digital image correlation MATLAB software. *Experimental Mechanics*, 55(6), 1105–1122. <https://doi.org/10.1007/s11340-015-0009-1>

- Bruce, D. A., Littlejohn, G. S., & Naudts, A. (1997). Grouting materials for ground treatment: A practitioner's guide. In *Grouting: Compaction, Remediation, and Testing* (pp. 306–334). ASCE.
- Burnham, K. P., & Anderson, D. R. (Eds.). (2004). *Model selection and multimodel inference*. Springer. <https://doi.org/10.1007/b97636>
- C09 Committee. (n.d.). *Test method for pulse velocity through concrete*. ASTM International. <https://doi.org/10.1520/C0597-09>
- Canakci, H., Güllü, H., & Alhashemy, A. (2019). Performances of using geopolymers made with various stabilizers for deep mixing. *Materials*, 12(16), Article 62542. <https://doi.org/10.3390/ma12162542>
- Celik, F., & Canakci, H. (2020). Examination of the mechanical properties and failure pattern of soilcrete mixtures modified with rice husk ash. *European Journal of Environmental and Civil Engineering*, 24(8), 1245–1260. <https://doi.org/10.1080/19648189.2018.1458656>
- Chen, W., Liu, Y., Wu, J., Lu, S., Han, G., Wei, X., & Gao, Y. (2023). Enhancing cementitious grouting performance through carbon nanotube-coated fly ash incorporation. *Construction and Building Materials*, 409, 133907. <https://doi.org/10.1016/j.conbuildmat.2023.133907>
- Coduto, D. P., Kitch, W. A., & Yeung, M. R. (n.d.). *Foundation design principles and practices* (3rd ed.). Pearson Education.
- da Rocha Gomes, S., Ferrara, L., Sánchez, L., & Moreno, M. S. (2023). A comprehensive review of cementitious grouts: Composition, properties, requirements and advanced performance. *Construction and Building Materials*, 375, 130991. <https://doi.org/10.1016/J.CONBUILDMAT.2023.130991>
- Dehghani, A., & Aslani, F. (2022). Nano-modification of the rheological properties of cementitious composites. In *Recent Advances in Nano-Tailored Multi-Functional Cementitious Composites* (pp. 209–249). <https://doi.org/10.1016/B978-0-323-85229-6.00002-0>
- DIN 53019-1:2008-09. (2008, September). *Viskosimetrie - Messung von Viskositäten und Fließkurven mit Rotationsviskosimetern - Teil 1: Grundlagen und Messgeometrie*. DIN Media GmbH. <https://doi.org/10.31030/1439277>

- Dresselhaus, M. S., Dresselhaus, G., & Avouris, P. (Eds.). (2001). *Carbon Nanotubes* (Vol. 80). Springer Berlin Heidelberg. <https://doi.org/10.1007/3-540-39947-X>
- Lifshitz, E. M., Kosevich, A. M., & Pitaevskii, L. P. (1986). *Theory of Elasticity*. Elsevier. <https://doi.org/10.1016/C2009-0-25521-8>
- Gao, Y., Liu, R., Jing, H., Chen, W., & Yin, Q. (2020). Hydraulic properties of single fractures grouted by different types of carbon nanomaterial-based cement composites. *Bulletin of Engineering Geology and the Environment*, 79(5), 2411–2421. <https://doi.org/10.1007/s10064-019-01707-8>
- Gogotsi, Y. (2006). *Nanomaterials Handbook*. CRC/Taylor & Francis.
- Govindjee, S., & Sackman, J. L. (1999). On the use of continuum mechanics to estimate the properties of nanotubes. *Solid State Communications*, 110(4), 227–230. [https://doi.org/10.1016/S0038-1098\(98\)00626-7](https://doi.org/10.1016/S0038-1098(98)00626-7)
- Güllü, H. (2016). Comparison of rheological models for jet grout cement mixtures with various stabilizers. *Construction and Building Materials*, 127, 220–236. <https://doi.org/10.1016/J.CONBUILDMAT.2016.09.129>
- Güllü, H., & Ali Agha, A. (2021). The rheological, fresh, and strength effects of cold-bonded geopolymer made with metakaolin and slag for grouting. *Construction and Building Materials*, 274. <https://doi.org/10.1016/j.conbuildmat.2020.122091>
- Güllü, H., Yetim, M. E., & Bacak Güllü, E. (2024). On the rheological, fresh, and strength effects of using nano-silica added geopolymer grout for grouting columns. *European Journal of Environmental and Civil Engineering*, 28(5), 1183–1207. <https://doi.org/10.1080/19648189.2023.2245867>
- Güllü, H., Yetim, M. E., & Güllü, E. B. (2023). Effect of using nano-silica on the rheological, fresh, and strength characteristics of cement-based grout for grouting columns. *Journal of Building Engineering*, 76, 107100. <https://doi.org/10.1016/J.JOBE.2023.107100>
- Han, G., Dai, S., Zhang, J., Gao, Y., & Liu, Y. (2024). Study on the workability and early mechanical properties of carbon nanotube-coated fly ash modified cement-based grouting materials. *Construction and Building Materials*, 439, 137327. <https://doi.org/10.1016/j.conbuildmat.2024.137327>

- Han, G., Xiang, J., Jing, H., Wei, X., Gao, Y., & Chen, W. (2023). Carbon nanotubes assisted fly ash for cement reduction on the premise of ensuring the stability of the grouting materials. *Construction and Building Materials*, 368, 130476. <https://doi.org/10.1016/j.conbuildmat.2023.130476>
- Han, J. (2015). *Principles and practice of ground improvement* (p. 435).
- Harik, V. (2014). New trends in nanoscale mechanics of carbon nanotubes: Editor's notes. In V. Harik (Ed.), *Trends in Nanoscale Mechanics* (pp. 3–18). Springer Netherlands. https://doi.org/10.1007/978-94-017-9263-9_1
- Harik, V. (2018a). Classification of carbon nanotubes. In *Mechanics of Carbon Nanotubes* (pp. 73–105). Elsevier. <https://doi.org/10.1016/B978-0-12-811071-3.00004-4>
- Harik, V. (2018b). Mechanics of the high aspect ratio carbon nanotubes. In *Mechanics of Carbon Nanotubes* (pp. 107–134). Elsevier. <https://doi.org/10.1016/B978-0-12-811071-3.00005-6>
- Harik, V. (2018c). Nanotechnology of carbon nanotubes. In *Mechanics of Carbon Nanotubes* (pp. 1–24). Elsevier. <https://doi.org/10.1016/B978-0-12-811071-3.00001-9>
- Harik, V. M. (2001). Ranges of applicability for the continuum beam model in the mechanics of carbon nanotubes and nanorods. *Solid State Communications*, 120(7), 331–335. [https://doi.org/10.1016/S0038-1098\(01\)00383-0](https://doi.org/10.1016/S0038-1098(01)00383-0)
- Harik, V. M. (2002). Mechanics of carbon nanotubes: Applicability of the continuum-beam models. *Computational Materials Science*, 24(3), 328–342. [https://doi.org/10.1016/S0927-0256\(01\)00255-5](https://doi.org/10.1016/S0927-0256(01)00255-5)
- Hausmann, M. R. (1990). *Engineering principles of ground modification*. McGraw-Hill.
- Hernández, E., Goze, C., Bernier, P., & Rubio, A. (1998). Elastic properties of C and B x C y N z composite nanotubes. *Physical Review Letters*, 80(20), 4502–4505. <https://doi.org/10.1103/PhysRevLett.80.4502>
- Hernández, E., Goze, C., Bernier, P., & Rubio, A. (1999). Elastic properties of single-wall nanotubes. *Applied Physics A: Materials Science & Processing*, 68(3), 287–292. <https://doi.org/10.1007/s003390050890>
- Houlsby, A. C. (1990). *Construction and design of cement grouting: A guide to grouting in rock foundations*. Wiley.

- Hu, Q., Chen, G., Sun, X., Li, Y., & Liu, G. (2024). Effect of grouting on damage and fracture characteristics of fractured rocks under mode I loading. *Construction and Building Materials*, 418, 135376. <https://doi.org/10.1016/j.conbuildmat.2024.135376>
- Hurvich, C. M., & Tsai, C. L. (1989). Regression and time series model selection in small samples. *Biometrika*, 76(2), 297–307. <https://doi.org/10.1093/BIOMET/76.2.297>
- Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354(6348), 56–58. <https://doi.org/10.1038/354056a0>
- Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature*, 363(6430), 603–605. <https://doi.org/10.1038/363603a0>
- ISO 3219-1:2021—Rheology—Part 1: Vocabulary and symbols for rotational and oscillatory rheometry. (n.d.). Retrieved November 3, 2024, from <https://www.iso.org/standard/76032.html>
- Jiao, H.-C., Li, Y.-F., & Yuan, J. (2024). Research progress on use of carbon nanotubes in cementitious grouting materials. *Journal of Sustainable Cement-Based Materials*, 13(7), 1090–1106. <https://doi.org/10.1080/21650373.2024.2348132>
- Khang, D. Y., Xiao, J., Kocabas, C., MacLaren, S., Banks, T., Jiang, H., ... & Rogers, J. A. (2008). Molecular scale buckling mechanics in individual aligned single-wall carbon nanotubes on elastomeric substrates. *Nano letters*, 8(1), 124-130.
- Krishnan, A., Dujardin, E., Ebbesen, T. W., Yianilos, P. N., & Treacy, M. M. J. (1998). Young's modulus of single-walled nanotubes. *Physical Review B*, 58(20), 14013–14019. <https://doi.org/10.1103/PhysRevB.58.14013>
- Kumar, S. L., Aravind, H. B., & Hossiney, N. (2019). Digital image correlation (DIC) for measuring strain in brick masonry specimen using Ncorr open source 2D MATLAB program. *Results in Engineering*, 4, 100061. <https://doi.org/10.1016/j.rineng.2019.100061>
- Lee, H., Kang, D., Kim, J., Choi, K., & Chung, W. (2019). Void detection of cementitious grout composite using single-walled and multi-walled carbon nanotubes. *Cement and Concrete Composites*, 95, 237–246. <https://doi.org/10.1016/J.CEMCONCOMP.2018.10.003>

- Lee, H., Park, S., Park, S., & Chung, W. (2020). Enhanced detection systems of filling rates using carbon nanotube cement grout. <https://doi.org/10.3390/nano10010010>
- Li, G., Shi, X., Gao, Y., Ning, J., Chen, W., Wei, X., Wang, J., & Yang, S. (2023). Reinforcing effects of carbon nanotubes on cement-based grouting materials under dynamic impact loading. <https://doi.org/10.1016/j.conbuildmat.2023.131083>
- Li, W., Huang, Y., Jiang, Y., Shi, T., & Xing, F. (2020). Application of DIC technology to shear crack measurement of concrete beam. In R. Kountchev, S. Patnaik, J. Shi, & M. N. Favorskaya (Eds.), *Advances in 3D Image and Graphics Representation, Analysis, Computing and Information Technology* (pp. 339–346). Springer. https://doi.org/10.1007/978-981-15-3867-4_39
- Liew, K. M., Yan, J.-W., & Zhang, L.-W. (2017). Introduction. In *Mechanical Behaviors of Carbon Nanotubes* (pp. 1–22). Elsevier. <https://doi.org/10.1016/B978-0-323-43137-8.00001-9>
- Littlejohn, S. (2003). The development of practice in permeation and compensation grouting: A historical review (1802–2002): Part 1 permeation grouting. *Grouting and Ground Treatment*, 50–99. [https://doi.org/10.1061/40663\(2003\)3](https://doi.org/10.1061/40663(2003)3)
- Liu, C., Li, Y., Bezuijen, A., Cachim, P., & Mei, G. (2024). Rheological characteristics and model applicability of shield tunnel backfilling grouts with supplementary cementitious materials. *Tunnelling and Underground Space Technology*, 154, 106121. <https://doi.org/10.1016/J.TUST.2024.106121>
- Liu, Y. hui, Yang, P., Ku, T., & Gao, S. wen. (2020). Effect of different nanoparticles on the grouting performance of cement-based grouts in dynamic water condition. *Construction and Building Materials*, 248, 118663. <https://doi.org/10.1016/J.CONBUILDMAT.2020.118663>
- Liu, Y., Lv, F., Ouyang, Z., & Wang, T. (2024). Experimental investigation on the grouting performance of foam-CNT composite grouts in vertical inclined fractures under flowing condition. *Lithosphere*, 2024(1). Scopus. https://doi.org/10.2113/2024/LITHOSPHERE_2023_341
- Liu, Y., Zhang, L., Yang, P., & Wei, X. (2021). Experimental investigation on sealing efficiency of CNT composite grouts in inclined fractures with flowing

- water. *Construction and Building Materials*, 270, 121494.
<https://doi.org/10.1016/J.CONBUILDMAT.2020.121494>
- Mezger, T. G. (2021). *The Rheology Handbook*.
- Murata, J. (1984). Flow and deformation of fresh concrete. *Matériaux et Constructions*, 17(2), 117–129. <https://doi.org/10.1007/BF02473663>
- Nazar, S., Yang, J., Thomas, B. S., Azim, I., & Ur Rehman, S. K. (2020). Rheological properties of cementitious composites with and without nano-materials: A comprehensive review. *Journal of Cleaner Production*, 272, 122701. <https://doi.org/10.1016/J.JCLEPRO.2020.122701>
- Nonveiller, E. (2013). *Grouting theory and practice*. Elsevier.
<https://books.google.com/books?hl=tr&lr=&id=ulItFyb-UEGoC&oi=fnd&pg=PP1&dq=Grouting+Theory+and+Practice&ots=Hy6n7LMHIH&sig=QvHvPdV3SrJ4IMLWA68J5PByk5o>
- Odom, T. W., Huang, J.-L., Kim, P., & Lieber, C. M. (1998). Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature*, 391(6662), 62–64. <https://doi.org/10.1038/34145>
- Owen, P. (2017). Engineering and Design GROUTING TECHNOLOGY, EM 1110-2-3506.
- Pashias, N., Boger, D., Summers, J., *rheology*, D. G.-J. of, & 1996, undefined. (n.d.). A fifty cent rheometer for yield stress measurement. *Pubs.Aip.Org*. Retrieved November 22, 2024, from <https://pubs.aip.org/sor/jor/article-abstract/40/6/1179/239177>
- Patel, A. (2019a). 5—Grouting. In A. Patel (Ed.), *Geotechnical Investigations and Improvement of Ground Conditions* (pp. 37–48). Woodhead Publishing. <https://doi.org/10.1016/B978-0-12-817048-9.00005-6>
- Patel, A. (2019b). Grouting. In *Geotechnical Investigations and Improvement of Ground Conditions* (pp. 37–48). Elsevier. <https://doi.org/10.1016/B978-0-12-817048-9.00005-6>
- Pierre, A., Lanos, C., & Estellé, P. (2013). Extension of spread-slump formulae for yield stress evaluation. *Applied Rheology*, 23(6). <https://doi.org/10.3933/APPLRHEOL-23-63849/MACHINEREADABLECITATION/RIS>

- Pop, E., Mann, D., Wang, Q., Goodson, K., & Dai, H. (2006). Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Letters*, 6(1), 96–100. <https://doi.org/10.1021/nl052145f>
- Predtechenskiy, M. R., Khasin, A. A., Bezrodny, A. E., Bobrenok, O. F., Dubov, D. Y., Muradyan, V. E., Saik, V. O., & Smirnov, S. N. (2022). New perspectives in SWCNT applications: Tuball SWCNTs. Part 1. Tuball by itself—All you need to know about it. *Carbon Trends*, 8, 100175. <https://doi.org/10.1016/J.CARTRE.2022.100175>
- Qiu, H., & Yang, J. (2017). Chapter 2—Structure and properties of carbon nanotubes. In H. Peng, Q. Li, & T. Chen (Eds.), *Industrial Applications of Carbon Nanotubes* (pp. 47–69). Elsevier. <https://doi.org/10.1016/B978-0-323-41481-4.00002-2>
- Qu, X., Shi, X., Li, X., Ning, J., Li, G., Chen, W., & Zhang, Z. (2024). Enhancement behaviours of carbon nanotubes reinforced cement-based grouting materials under dynamic loading. *Case Studies in Construction Materials*, 21. Scopus. <https://doi.org/10.1016/j.cscm.2024.e03965>
- Restuccia, L., Lopez, A., Ferro, G. A., Liberatore, D., & Tulliani, J. M. (2018). An investigation of the beneficial effects of adding carbon nanotubes to standard injection grout. *Fatigue & Fracture of Engineering Materials & Structures*, 41(1), 119–128. <https://doi.org/10.1111/FFE.12663>
- Roussel, N., & Coussot, P. (2005). “Fifty-cent rheometer” for yield stress measurements: From slump to spreading flow. *Journal of Rheology*, 49(3), 705–718. <https://doi.org/10.1122/1.1879041>
- Saak, A. W., Jennings, H. M., & Shah, S. P. (2004). A generalized approach for the determination of yield stress by slump and slump flow. *Cement and Concrete Research*, 34(3), 363–371. <https://doi.org/10.1016/j.cemconres.2003.08.005>
- Saito, R., Fujita, M., Dresselhaus, G., & Dresselhaus, M. S. (1992). Electronic structure of graphene tubules based on C 60. *Physical Review B*, 46(3), 1804–1811. <https://doi.org/10.1103/PhysRevB.46.1804>
- Salvetat, J. P., Briggs, G. A. D., Bonard, J. M., Bacsá, R. R., Kulik, A. J., Stöckli, T., Burnham, N. A., & Forró, L. (1999). Elastic and shear moduli of single-walled carbon nanotube ropes. *Physical Review Letters*, 82(5), 944–947. <https://doi.org/10.1103/PhysRevLett.82.944>

- Schaefer, V. R., Berg, R., Collin, J. G., Christopher, B. R., DiMaggio, J. A., Filz, G. M., Bruce, D. A., Ayala, D., & Shelsta, H. (2016). *Ground modification methods: Reference manual*. National Highway Institute.
- Schowalter, W. R., & Christensen, G. (1998). Toward a rationalization of the slump test for fresh concrete: Comparisons of calculations and experiments. *Journal of Rheology*, 42(4), 865–870. <https://doi.org/10.1122/1.550905>
- Smith, G. N. (1986). *Probability and statistics in civil engineering*. Collins Professional and Technical Books, 244.
- Standard Test Method for Bulk Electrical Conductivity of Hardened Concrete (Withdrawn 2021). (n.d.). Retrieved December 23, 2024, from <https://www.astm.org/c1760-12.html>
- Tan, Z., Bernal, S. A., & Provis, J. L. (2017). Reproducible mini-slump test procedure for measuring the yield stress of cementitious pastes. *Materials and Structures/Materiaux et Constructions*, 50(6), 1–12. <https://doi.org/10.1617/S11527-017-1103-X/TABLES/4>
- Thomas, S., Chandrakaran, S., & Sankar, N. (2022). Nanocomposites are state-of-the-art in the field of ground improvement- a review. *Materials Today: Proceedings*. <https://doi.org/10.1016/J.MATPR.2022.03.454>
- Timošenko, S. P., & Gere, J. M. (Eds.). (2009). *Theory of elastic stability* (2nd ed., Dover ed). Dover Publications.
- Treacy, M. M. J., Ebbesen, T. W., & Gibson, J. M. (1996). Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature*, 381(6584), 678–680. <https://doi.org/10.1038/381678a0>
- Treacy, M. M. J., Krishnan, A., & Yianilos, P. N. (2000). Inferring physical parameters from images of vibrating carbon nanotubes. *Microscopy and Microanalysis*, 6(4), 317–323. <https://doi.org/10.1007/S100050010037>
- Venkateswaran, U. D., Rao, A. M., Richter, E., Menon, M., Rinzler, A., Smalley, R. E., & Eklund, P. C. (1999). Probing the single-wall carbon nanotube bundle: Raman scattering under high pressure. *Physical Review B*, 59(16), 10928–10934. <https://doi.org/10.1103/PhysRevB.59.10928>
- Wong, E. W., Sheehan, P. E., & Lieber, C. M. (1997). Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes. *Science*, 277(5334), 1971–1975. Scopus. <https://doi.org/10.1126/science.277.5334.1971>

- Yang, Z., Yang, J., Shuai, B., Niu, Y., Yong, Z., Wu, K., Zhang, C., Qiao, X., & Zhang, Y. (2022). Superflexible yet robust functionalized carbon nanotube fiber reinforced sulphoaluminate cement-based grouting materials with excellent mechanical, electrical and thermal properties. *Construction and Building Materials*, 328, 126999. <https://doi.org/10.1016/J.CONBUILDMAT.2022.126999>
- Yu, M. F., Files, B. S., Arepalli, S., & Ruoff, R. S. (2000). Tensile loading of ropes of single-wall carbon nanotubes and their mechanical properties. *Physical Review Letters*, 84(24), 5552–5555. <https://doi.org/10.1103/PhysRevLett.84.5552>
- Yu, M.-F., Lourie, O., Dyer, M. J., Moloni, K., Kelly, T. F., & Ruoff, R. S. (2000). Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science*, 287(5453), 637–640. <https://doi.org/10.1126/science.287.5453.637>

CURRICULUM VITAE

Kayahan ERİTEN

Education

BSc. – Civil Engineering – Gaziantep University / Türkiye – 2017

BA - Cappadocia University – Tourist Guidance / Türkiye – 2025

MSc. – Geotechnics / Civil Engineering – Gaziantep University/ Türkiye – 2025

Work Experience

Gaziantep University / Türkiye – Research Assistant – since 2021

Bilgi2000 Engineering and Construction Co. Ltd. / Türkiye – Civil Geotechnical Engineer - 2020

Mak-Grup Construction Co. Ltd. / Türkiye – Civil Site Engineer – 2018

Zin D Property Development Inc. / Türkiye – Civil Engineering Intern – 2017

Languages

English: Full professional proficiency

Russian: Elementary proficiency